UNDERSTANDING THE EFFECTS OF ELECTROLYTE pH AND SPECTATOR IONS ON ELECTROCATALYSIS

A Dissertation in Chemical Engineering

by

Ian T. McCrum

© 2017 Ian T. McCrum

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

August 2017
The dissertation of Ian T. McCrum was reviewed and approved* by the following:

Michael J. Janik  
Professor and Chair of the Brennan Clean Energy Early Career Professorship  
Dissertation Co-advisor  
Chair of Committee

Michael A. Hickner  
Associate Professor of Materials Science and Engineering, Chemical Engineering  
Dissertation Co-advisor

Robert M. Rioux  
Professor of Chemical Engineering

Chao-Yang Wang  
Professor and Diefenderfer Chair, Mechanical and Nuclear Engineering,  
Chemical Engineering

Phillip E. Savage  
Professor of Chemical Engineering  
Head of the Department of Chemical Engineering

*Signatures are on file in the Graduate School
Recent experimental evidence suggests that the rate and mechanisms of many
electrocatalytic reactions depend on electrolyte pH and the identity of the alkali metal cation
present in an alkaline electrolyte. In particular, the rate of the hydrogen oxidation reaction,
important in hydrogen fuel cells, is 2-3 orders of magnitude slower in an alkaline electrolyte than
in an acid electrolyte, even on the most active platinum catalyst. While it is well known that many
anions effect the rates of electrocatalytic reactions, through their specific adsorption and blocking
of active sites on the electrode surface, the mechanism by which alkali metal cations exert their
effects is unknown. Both experiment and density functional theory modeling of the electrode-
electrolyte interface are used in this dissertation to better understand how pH and alkali metal
cations effect electrocatalytic reactions.

Density functional theory calculations show that alkali metal cation specific adsorption is
favorable at low potentials to many electrode surfaces, including platinum, in an alkaline
electrolyte. Once on the surface, these alkali metal cations show only a small interaction with
adsorbed hydrogen, but a significant weakening of adsorbed hydroxide. These results explain an
experimentally observed anomalous shift in the low potential features of cyclic voltammograms
measured on Pt(110), Pt(100), and stepped Pt surfaces with increasing pH, which correlate with
the pH dependence of the rate of the hydrogen oxidation reaction. The rate of the hydrogen
oxidation reaction is experimentally measured in alkaline electrolytes, and is found to depend on
the alkali metal cation present, following the trend Li > Na > K > Cs. The density functional
theory calculated trend in the effect of these cations on hydroxide adsorption matches the trend in
rate, supporting that adsorbed hydroxide may be an intermediate in the hydrogen oxidation
reaction. To design highly active hydrogen oxidation/evolution catalysts, both hydrogen
adsorption strength and hydroxide adsorption strength must be considered.
# TABLE OF CONTENTS

List of Figures .......................................................................................................................... viii

List of Tables ............................................................................................................................... xxiv

Acknowledgements ...................................................................................................................... xxx

Chapter 1 Introduction .................................................................................................................. 1

1.1. Motivation .............................................................................................................................. 1
1.2. Background ........................................................................................................................... 4
  1.2.1. pH and Alkali Cation Effects on Electrocatalysis ......................................................... 4
  1.2.2. pH and Alkali Cation Effects on the Thermodynamics of Hydrogen/Hydroxide Adsorption ................................................................. 7
1.3. Hypothesis and Research Objectives .................................................................................. 10
1.4. Computational Methods ...................................................................................................... 12
  1.4.1. Density Functional Theory .......................................................................................... 13
  1.4.2. Ab Initio Thermodynamics ........................................................................................... 16
  1.4.3. Solvation Near the Electrode Surface .......................................................................... 18
  1.4.4. Near Surface Electric Field ......................................................................................... 20
1.5 Experimental Methods ......................................................................................................... 21
1.6. Summary of Chapters ......................................................................................................... 24
1.7. References ........................................................................................................................... 30

Chapter 2 Alkali Cation Specific Adsorption onto fcc(111) Transition Metal Electrodes ......35

Abstract ....................................................................................................................................... 35
2.1. Introduction ........................................................................................................................... 35
2.2. Methods ............................................................................................................................... 39
  2.2.1. Calculating Cation Adsorption Equilibrium Potential ................................................. 40
  2.2.2. Surface Solvation .......................................................................................................... 43
2.3. Results and Discussion ......................................................................................................... 45
  2.3.1. Surface Solvation .......................................................................................................... 48
2.4. Summary and Conclusion .................................................................................................... 54
2.5. Acknowledgements ............................................................................................................. 55
2.6. References ........................................................................................................................... 55
2.7 Supplementary Information .................................................................................................... 58

Chapter 3 Electrochemical Specific Adsorption of Halides on Cu 111, 100, and 211: A Density Functional Theory Study ................................................................. 63

Abstract ....................................................................................................................................... 63
3.1. Introduction ........................................................................................................................... 64
3.2. Methods ............................................................................................................................... 68
  3.2.1 Computational Methods ............................................................................................... 68
  3.2.2. Specific Adsorption Equilibrium Potentials ................................................................. 69
  3.2.3. Surface Solvation .......................................................................................................... 72
  3.2.4. Bulk CuX & CuX₂ Formation ....................................................................................... 73
Chapter 4 pH and Alkali Cation Effects on the Pt Cyclic Voltammogram Explained
Using Density Functional Theory ........................................ 108

Abstract ................................................................................. 108
4.1. Introduction ......................................................................... 109
4.2. Methods ............................................................................. 114
  4.2.1. Computational Details ...................................................... 114
  4.2.2. Calculating Equilibrium Adsorption Potentials .................. 115
  4.2.3. Surface Solvation and Adsorbed Water .............................. 118
  4.2.4. Quantifying Adsorbate-Adsorbate Interactions ................. 121
  4.2.5. Computational Cyclic Voltammograms .............................. 122
4.3. Results ................................................................................ 124
  4.3.1. Hydrogen Adsorption ...................................................... 124
  4.3.2. Hydroxide and Solvated Hydroxide Adsorption ................. 127
  4.3.3. Potassium Cation Adsorption .......................................... 133
  4.3.4. Hydrogen and Potassium Co-adsorption ........................... 136
  4.3.5. Hydroxide-Water-Potassium Co-adsorption ....................... 138
4.4. Conclusions .......................................................................... 145
4.5. Acknowledgements .............................................................. 146
4.6. References ........................................................................... 146
4.7 Supplementary Information ................................................... 153
  4.7.1. Simulating Cyclic Voltammograms ................................... 159

Chapter 5 First Principles Simulations of Cyclic Voltammograms on Stepped Pt(553) and Pt(533) Electrode Surfaces ................................................... 166

Abstract ................................................................................. 166
5.1. Introduction .......................................................................... 167
5.2. Results and Discussion ......................................................... 171
  5.2.1. H* Adsorption on Steps and Terraces of Pt(553) and Pt(533) ........................................ 171
  5.2.2. OH* Adsorption and OH*+H2O* Co-adsorption on Steps of Pt(553) and Pt(533) ........ 174
  5.2.3. Simulated Cyclic Voltammograms for Pt(553) and Pt(533) ........................................ 175
  5.2.4. Effect of Specifically Adsorbed Cation on Hydroxide and Water Adsorption ............. 180
5.3. Conclusions ......................................................................... 183
5.4. Computational Details .......................................................... 184
  5.4.1. Computational Methods .................................................... 184
  5.4.2. Calculating Equilibrium Adsorption Potentials .................. 185
Chapter 10 Conclusions and Recommendations for Future Research

10.1. Summary .................................................................................................................. 335
10.2. Conclusions and Evaluation of Hypotheses ......................................................... 339
10.3. Recommendations for Future Investigations ......................................................... 342
    10.3.1. Density Functional Theory Modeling of HOR/HER Mechanisms .......... 343
    10.3.2. Experimental Measurements of the HOR/HER Rate .............................. 345
    10.3.3. Preliminary Results: Comparing Experimentally Measured Rates of the
            HOR/HER with DFT Calculated Hydroxide Adsorption Strength Across
            Transition Metal Surfaces ........................................................................... 347
10.4. References ............................................................................................................... 350
LIST OF FIGURES

Figure 1-1. Schematic of the double layer structure near a negatively charged electrode surface in an aqueous electrolyte solution (with the bulk electrolyte above the surface; not shown). The inner Helmholtz plane is comprised of water molecules and ions adsorbed on the electrode surface, the outer Helmholtz plane a high concentration of charge to counter the charge on the electrode surface, and the diffuse layer, containing anions and cations which continue to screen the charge at the electrode surface until the disordered arrangement of anions and cations in the bulk electrolyte is reached. For a metal electrode, the negative charge is distributed across the surface. ........................................................................................................3

Figure 1-2. Cyclic voltammograms measured on Pt(111) in an acidic (0.1 M HClO₄) and basic (0.1 M NaOH) electrolyte at a scan rate of 50 mV/s. Figure adapted from Garcia et al., Ref. 50, with permission from the PCCP Owner Societies. .................................8

Figure 2-1. Free energy of adsorption for H⁺, K⁺, and Ba²⁺ onto a Pt(111) electrode as a function of electrode potential. Adsorption free energies are reported with (equation 7) and without (equation 2) dipole corrections. Without dipole correction: red- K⁺, green- Ba²⁺; with dipole correction: light blue- K⁺, orange- Ba²⁺; purple-H⁺ with and without dipole correction. .........................................................................47

Figure 2-2. Equilibrium adsorption potential for H⁺ adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using three references for the energy of the surface-water system before cation addition: gas phase reference (red square), fixed water reference (purple x), relaxed water reference (blue triangle). A flat line is included to show the value calculated with the fully solvated DR Method (green line). ........................................50

Figure 2-3. Equilibrium adsorption potential for Na⁺ adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using three references for the energy of the surface-water system before cation addition: gas phase reference (red square), fixed water reference (purple x), relaxed water reference (blue triangle). A flat line is included to show the value calculated with the fully solvated DR Method (green line). ........................................50

Figure 2-4. Equilibrium adsorption potential for Ba²⁺ adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using three references for the energy of the surface-water system before cation addition: gas phase reference (red square), fixed water reference (purple x), relaxed water reference (blue triangle). A flat line is included to show the value calculated with the fully solvated DR Method (green line). ........................................51

Figure 2-5. Solvated surface structures on Pt(111) in 3x3 unit cell. a) Pt(111) with 6 H₂O molecules. b) Pt(111) + H with 6 H₂O molecules. c) Pt(111) + Na with 6 H₂O
molecules. d) Pt(111) + Ba with 6 H$_2$O molecules. e) Pt(111) + Na with 23 H$_2$O molecules used in the double reference method.

Figure S2-1. Relaxed solvated Pt(111) surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O

Figure S2-2. Relaxed solvated Pt(111)+H surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O

Figure S2-3. Relaxed solvated Pt(111)+Na surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O

Figure S2-4. Relaxed solvated Pt(111)+Ba surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O

Figure 3-1. The specific adsorption reaction equation, in which an aqueous phase halide anion directly binds to the electrode surface, releasing an electron into the electrode/external circuit.

Figure 3-2. Parity plot between DFT calculated diatomic halogen dissolution potentials and experimental dissolution potentials. (Solid red line gives y=x.)

Figure 3-3. Equilibrium adsorption potentials for F$^-$, Cl$^-$, Br$^-$, and I$^-$ adsorption at θ = 1/9 ML onto Cu (111) (green), Cu (211) (beige), and Cu (100) (blue) calculated using the experimental anion solvation energy method. The surface adsorbed state was not solvated.

Figure 3-4. Surface-halide dipole moment (along surface normal direction) on F$^-$, Cl$^-$, Br$^-$, and I$^-$ adsorption at θ = 1/9 ML onto Cu (111) (green), Cu (211) (beige), and Cu (100) (blue).

Figure 3-5. Solvated structures of F adsorbed to the three Cu surface facets: a) F + 4 H$_2$O on Cu (211) b) F + 6 H$_2$O on Cu (111) c) F + 5 H$_2$O on Cu (100). Cu (orange, large species) and F (blue) are shown in space filling representation with water (O-red, H-white) shown in ball and stick representation. Dashedlines represent hydrogen bonds.

Figure 3-6. Equilibrium adsorption potentials for fluoride (blue) and iodide (red) calculated using the solvation energy method for adsorption to bare and solvated copper surfaces. Cross hatched bars are the potentials calculated without surface solvation, solid bars include converged surface solvation.

Figure 3-7. Favorability of bulk CuCl formation, bulk CuCl$_2$ formation, and chloride adsorption onto Cu(111) as a function of potential. Dotted lines represent chloride specific adsorption (light yellow 1/9 ML, dark red 1ML) and solid lines represent bulk copper chloride formation (purple CuCl, blue CuCl$_2$). The vertical dashed lines separate regions of the most favorable surface or bulk state as a function of potential, as indicated by the labels within the four regions below the ΔG=0 line.
Figure S3-1. Equilibrium adsorption potential for $F^-$, $Cl^-$, $Br^-$, and $I^-$ onto Cu (111) (green), Cu (211) (beige), and Cu (100) (blue) calculated using the diatomic gas phase energy method. .................................................................90

Figure S3-2. Calculated Bader charge of specifically adsorbed $F^-$, $Cl^-$, $Br^-$, and $I^-$ on Cu (111) (green), Cu (211) (beige), and Cu (100) (blue). .................................................................90

Figure S3-3. Equilibrium adsorption potential for fluoride adsorption (blue diamond) and iodide adsorption (red square) on to Cu (211) as a function of the number of explicit water molecules solvating the surface-adsorbate bond. ....................................................91

Figure S3-4. Equilibrium adsorption potential for fluoride adsorption (blue diamond) and iodide adsorption (red square) on to Cu (111) as a function of the number of explicit water molecules solvating the surface-adsorbate bond. ....................................................91

Figure S3-5. Equilibrium adsorption potential for fluoride adsorption (blue diamond) and iodide adsorption (red square) on to Cu (100) as a function of the number of explicit water molecules solvating the surface-adsorbate bond. ....................................................92

Figure S3-6. Bulk formation and surface adsorption free energy vs. potential diagram for $Br^-$ adsorption at 1/9 ML (yellow circle), 2/9 ML (yellow square), 1/3 ML (orange triangle), 1/2 ML (yellow diamond), and 1 ML (orange circle) onto Cu (111) and bulk CuBr (purple line) and CuBr$_2$ (blue line) formation. Vertical line (black, dashed) indicates potential where CuBr$_2$ becomes more favorable than CuBr (potential dependence of bulk formation not shown). ....................................................92

Figure S3-7. Bulk formation and surface adsorption free energy vs. potential diagram for $I^-$ adsorption at 1/9 ML (yellow circle), 2/9 ML (yellow square), 1/3 ML (orange triangle), and 1/2 ML (orange circle) onto Cu (111) and bulk CuI formation (purple square). ....................................................93

Figure S3-8. Bulk formation and surface adsorption free energy vs. potential diagram for $Cl^-$ adsorption at 1/9 ML (yellow circle), 1/4 ML (yellow square), 1/2 ML (orange triangle), and 1 ML (orange circle) onto Cu (100) and bulk CuCl (purple line) and CuCl$_2$ (blue line) formation. Vertical line (black, dashed) indicates potential where CuCl$_2$ formation becomes more favorable than CuCl (potential dependence of bulk formation not shown). ....................................................93

Figure S3-9. Bulk formation and surface adsorption free energy vs. potential diagram for $Br^-$ adsorption at 1/9 ML (yellow circle), 1/4 ML (yellow square), 1/2 ML (orange triangle), and 1 ML (orange circle) onto Cu (100) and bulk CuBr (purple line) and CuBr$_2$ (blue line) formation. Vertical line indicates potential where bulk formation of CuBr$_2$ becomes more favorable than CuBr (potential dependence of bulk formation not shown). ....................................................94

Figure S3-10. Bulk formation and surface adsorption free energy vs. potential diagram for $I^-$ adsorption at 1/9 ML (yellow circle), 1/4 ML (yellow square), 1/2 ML (orange triangle), and 1 ML (orange circle) onto Cu (100) and bulk CuI (purple line) formation. ....................................................94
Figure S3-11. Cu (100)-F (a) and solvated structures for Cu (100)-F 1 H2O (b), Cu (100)-F 2 H2O (c), Cu (100)-F 3 H2O (d), Cu (100)-F 4 H2O (e), and Cu (100)-F 5 H2O (f)....99

Figure S3-12. Cu (100)-I (a) and solvated structures for Cu (100)-I 1 H2O (b), Cu (100)-I 2 H2O (c), Cu (100)-I 3 H2O (d), and Cu (100)-I 4 H2O (e). ..............................................99

Figure S3-13. Cu (100)-I (a) and solvated structures for Cu (100)-I 1 H2O (b), Cu (100)-I 2 H2O (c), Cu (100)-I 3 H2O (d), and Cu (100)-I 4 H2O (e). ..............................................100

Figure S3-14. Cu (111)-F (a) and solvated structures for Cu (111)-F 1 H2O (b), Cu (111)-F 2 H2O (c), Cu (111)-F 3 H2O (d), Cu (111)-F 4 H2O (e), Cu (111)-F 5 H2O (f), and Cu (111)-F 6 H2O (g). ..............................................100

Figure S3-15. Cu (111)-I (a) and solvated structures for Cu (111)-I 1 H2O (b), Cu (111)-I 2 H2O (c), Cu (111)-I 3 H2O (d), and Cu (111)-I 4 H2O (e). ..............................................101

Figure S3-16. Cu (211)-F (a) and solvated structures for Cu (211)-F 1 H2O (b), Cu (211)-F 2 H2O (c), Cu (211)-F 3 H2O (d), and Cu (211)-F 4 H2O (e). ..............................................102

Figure S3-17. Cu (211)-I (a) and solvated structures for Cu (211)-I 1 H2O (b), Cu (211)-I 2 H2O (c), Cu (211)-I 3 H2O (d), and Cu (211)-I 4 H2O (e). ..............................................103

Figure S3-18. Cu (211) solvated bare surfaces for Cu (211) 1 H2O (a), Cu (211) 2 H2O (b), Cu (211) 3 H2O (c), and Cu (211) 4 H2O (d) ........................................................104

Figure S3-19. Cu (111) solvated bare surfaces for Cu (111) 1 H2O (a), Cu (111) 2 H2O (b), Cu (111) 3 H2O (c), Cu (111) 4 H2O (d), Cu (111) 5 H2O (e), and Cu (111) 6 H2O (f) ........................................................105

Figure S3-20. Cu (100) solvated bare surfaces for Cu (100) 1 H2O (a), Cu (100) 2 H2O (b), Cu (100) 3 H2O (c), Cu (100) 4 H2O (d), and Cu (100) 5 H2O (e) ........................................................106

Figure S3-21. Equilibrium adsorption potential (V_{NHE}) vs. halide coverage on Cu(111) calculated using diatomic gas phase energy method (coverage of 1 ML given in Table S3-19) ........................................................................................................106

Figure S3-22. Equilibrium adsorption potential (V_{NHE}) vs. halide coverage on Cu(100) calculated using diatomic gas phase energy method (coverage of 1 ML for F* and I* given in Table S3-20) ........................................................................................................107

Figure 4-1. Equilibrium adsorption potentials (U^0, V_{NHE}) for the adsorption of hydrogen from a pH = 0 solution as a function of coverage (ML) onto Pt(111) (blue square), Pt(100) (black triangle), and Pt(110) (red diamond). Dotted lines are linear regressions of the plotted data. ..............................................124

Figure 4-2. Simulated cyclic voltammograms for hydrogen adsorption onto a bare surface from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110) electrode surfaces. Scan rate is 50 mVs. It is assumed 1 ML of hydrogen is the maximum coverage reached on each facet. ..............................................127
Figure 4-3. Favorable adsorption potential ranges ($V_{NHE}$) calculated for hydrogen and hydroxide adsorption from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110). Hydrogen adsorption potentials are calculated at 1/9 ML coverage. Hydroxide adsorption potentials shown in blue (bottom) are calculated at a coverage of 1/9 ML, those in green (middle) are 1/9 ML OH* and solvated by a single water molecule, and those in purple (top) are the minimum energy hydroxide and water co-adsorbed structures (MES). MES for Pt(111) and Pt(100) are 1/3 ML OH* and 1/3 ML H$_2$O* and for Pt(110) is 1/2 ML OH* and 1/2 ML H$_2$O*.

Figure 4-4. Simulated cyclic voltammograms for hydrogen and hydroxide adsorption from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110) electrode surfaces. Adsorption/desorption on Pt(100) and Pt(110) is taken to occur through a H/OH surface phase change process. Scan rate is 50 mV/s. 1 ML of hydrogen is the assumed maximum coverage reached on each facet. The hydroxide coverage is that of the minimum energy OH*+H$_2$O* structure, and is 1/3 ML OH* and 1/3 ML H$_2$O* on Pt(111) and Pt(100) and is 1/2 ML OH* and 1/2 ML H$_2$O* on Pt(110). The background data (faint lines) are experimentally measured cyclic voltammograms in 0.1 M HClO$_4$ at 50 mV/s on single crystal electrodes adapted from N. Garcia-Araez. The texture seen in the experimentally measured cyclic voltammograms would be better captured if the coverage dependence of hydrogen adsorption, hydroxide adsorption, and hydrogen and hydroxide co-adsorption were considered.

Figure 4-5. Equilibrium adsorption potential ($V_{NHE}$) calculated for K$^+$ adsorption from a 1M solution onto Pt(111) (blue diamonds), Pt(100) (green triangles), and Pt(110) (red squares) as a function of potassium coverage (ML). Equilibrium adsorption potentials neglect solvation stabilization of K$^+$ at the Pt surface, which would shift K$^+$ adsorption to more positive potentials.

Figure 4-6. Equilibrium adsorption potential ($V_{NHE}$) calculated for adsorption of 1 ML of hydrogen from a pH = 0 solution next to specifically adsorbed potassium (K$^+$) on Pt(111) (blue diamonds), Pt(100) (green triangles), and Pt(110) (red squares) as a function of adsorbed potassium coverage (ML).

Figure 4-7. Equilibrium adsorption potentials ($V_{NHE}$) calculated for hydrogen and hydroxide adsorption from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110). Hydrogen adsorption potentials are calculated at 1/9 ML coverage (left hand axis). Hydroxide adsorption potentials in purple (top bar) and green (3rd from top bar) are the same as in Figure 4-3. Hydroxide adsorption potentials in light purple (2nd bar from top) are calculated using the minimum energy hydroxide and water structures (MES) but with co-adsorbed potassium at 1/9 ML on Pt(111) and Pt(100) and at 1/4 ML on Pt(110). Hydroxide adsorption potentials given by the light green bar (bottom) are calculated with 1/9 ML OH*, 1/9 ML H$_2$O*, and 1/9 ML K*. The equilibrium adsorption potential is given by the right most edge of the bar (hydrogen adsorption, white bar, left hand axis) or by the left most edge (hydroxide adsorption).

Figure 4-8. Simulated cyclic voltammograms for hydrogen and hydroxide adsorption from a pH = 0 solution via a phase change reaction onto a) Pt(110) and b) Pt(100) electrode surfaces in the absence (dotted lines) and presence (solid lines) of
specifically adsorbed potassium. Scan rate is 50 mV/s. The hydroxide coverage is of the minimum energy OH*+H₂O* structure, and is 1/3 ML OH* and 1/3 ML H₂O* on Pt(100) and is 1/2 ML OH* and 1/2 ML H₂O* on Pt(110). Hydrogen coverage is 1ML on all three facets. K* coverage is 1/9 ML on Pt(100) and 1/4 ML on Pt(110). The absence of specifically adsorbed potassium represents the conditions expected in acid electrolytes and the presence of specifically adsorbed potassium represents the conditions expected in basic electrolytes, with the coverage of K* varying with pH.

Figure 4-9. Equilibrium formation potential for hydroxide in its minimum energy structure with co-adsorbed water from adsorbed water on Pt(110) for formation next to specifically adsorbed potassium as a function of potassium coverage (ML). The solid line is a linear regression, intended only as a guide to the general trend.

Figure 4-10. Pt-O bond length (Å) for adsorbed hydroxide and adsorbed water as a function of K* coverage (ML).

Figure 4-11. Hydrogen bond length (Å) between adsorbed hydroxide and adsorbed water with hydroxide as the hydrogen bond donor and as the hydrogen bond acceptor as a function of K* coverage (ML).

Figure 4-12. Charge on adsorbed hydroxide and adsorbed water molecules as a function of K* coverage on Pt(110).

Figure S4-1. Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamond) or by implicit solvation (red square) (VASSP), on the favorability to specifically adsorb potassium on Pt(111), as given by its equilibrium adsorption potential (V_{NHE}).

Figure S4-2. Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamond) or by implicit solvation (red square), on the favorability to specifically adsorb potassium on Pt(100), as given by its equilibrium adsorption potential (V_{NHE}).

Figure S4-3. Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamonds) or by implicit solvation (red square), on the favorability to specifically adsorb potassium on Pt(110), as given by its equilibrium adsorption potential (V_{NHE}).

Figure S4-4. Simulated cyclic voltammograms for hydrogen adsorption/desorption on (H*, black line), hydroxide adsorption/desorption (OH*, blue line), and their sum (H*+OH*, red line) for adsorption on Pt(100). The sum does not include competitive adsorption. The hydrogen adsorption/desorption cyclic voltammogram includes the coverage dependence calculated with DFT and configurational entropy, while hydroxide adsorption/desorption only includes the effect of the configurational entropy on the coverage dependence of hydroxide adsorption. Maximum hydrogen coverage is 1 ML while that of hydroxide is 1/3 ML in the minimum energy hydroxide+water structure (1/3 ML OH* 1/3 ML H₂O*). The scan rate is 50 mV/s, the temperature 300K, and adsorption occurs from a pH=0 electrolyte.
Figure S4-5. Simulated cyclic voltammogram for the sum of hydrogen adsorption/desorption and hydroxide adsorption/desorption (dark red line) for adsorption on Pt(100), from Figure S4-13. The background gives the experimentally measured cyclic voltammogram for hydrogen and hydroxide adsorption onto a Pt(100) single crystal electrode in a 0.1 M HClO4 electrolyte solution (faint red line) as adapted from N. Garcia-Araez. The simulated cyclic voltammogram shown here (and in Figure S4-4) do not include a phase change reaction or competitive adsorption of hydrogen and hydroxide.

Figure S4-6. Pt(111) Minimum energy water structure 6 H$_2$O* in 3x3 unit cell (6/9 ML H$_2$O).

Figure S4-7. Pt(111) Minimum energy water structure 6 H$_2$O* in 3x3 unit cell with 1/9 ML K*.

Figure S4-8. Pt(111) Minimum energy hydroxide+water structure 3OH*+ 3 H$_2$O* in 3x3 unit cell (3/9 ML OH, 3/9 ML H$_2$O).

Figure S4-9. Pt(111) Minimum energy hydroxide+water structure 3OH*+ 3 H$_2$O* in 3x3 unit cell with K* 1/9 ML (3/9 ML OH, 3/9 ML H$_2$O, 1/9 ML K*).

Figure S4-10. Pt(100) Minimum energy water structure 6 H$_2$O* in 3x3 unit cell (6/9 ML H$_2$O).

Figure S4-11. Pt(100) Minimum energy water structure 6 H$_2$O* in 3x3 unit cell with 1/9 ML K*.

Figure S4-12. Pt(100) Minimum energy hydroxide+water structure 3OH*+ 3 H$_2$O* in 3x3 unit cell (3/9 ML OH, 3/9 ML H$_2$O).

Figure S4-13. Pt(100) Minimum energy hydroxide+water structure 3OH*+ 3 H$_2$O* in 3x3 unit cell with K* 1/9 ML (3/9 ML OH, 3/9 ML H$_2$O, 1/9 ML K*).

Figure S4-14. Pt(100) Minimum energy water structure with 1 ML H* and 1/9 ML K* in 3x3 unit cell (6/9 ML H$_2$O, 1/9 ML K*, 1 ML H*).

Figure S4-15. Pt(110) Minimum energy water structure 4 H$_2$O* in 2x2 unit cell (1 ML H$_2$O).

Figure 5-1. The Pt(553) (a) and Pt(533) (b) surfaces with 1 ML (1 H per step Pt atom) of hydrogen adsorbed at the step.

Figure 5-2. a) Equilibrium adsorption potential of hydrogen onto the steps of Pt(553) (blue diamond) and Pt(533) (green triangle). Configurational entropy of the adsorbate is not included. Lines represent best linear fits to the data. b) Equilibrium adsorption potential for hydrogen adsorption as a function of coverage on Pt(111) (blue diamond), the terrace of Pt(533) (purple triangle), and the terrace of Pt(553) (red square). Adsorption on the terrace is modeled with the step occupied with 1 ML.
H*. The coverage dependence shown here does not include configurational entropy of the adsorbate on the surface. Lines represent best linear fits to the data. Figure 5-3. Stable surface adsorption potential ranges for H* (clear bar), OH* (blue bar) and solvated OH*+2H2O* (green bar) on the steps of Pt(533) and Pt(553).

Figure 5-4. Simulated and experimental cyclic voltammograms for a Pt(553) electrode. Simulated CVs are included in acid (free from co-adsorbed alkali, red dashed line) and base (with co-adsorbed alkali, blue solid line). Experimentally measured cyclic voltammograms measured in 0.1 M HClO₄ (dashed black line) and in 0.05 M NaOH (solid black line) are taken from van der Niet et al. Simulated and measured voltammograms both use a scan rate of 50 mV/s. Simulated CVs due not include hydroxide on terraces that would account for the experimental features at $V > 0.6 \text{ V}_\text{RHE}$.

Figure 5-5. Simulated and experimental cyclic voltammograms for a Pt(533) electrode. Simulated CVs are included in acid (free from co-adsorbed alkali, red dashed line) and base (with co-adsorbed alkali, blue solid line). Experimentally measured cyclic voltammograms measured in 0.1 M HClO₄ (dashed black line) and in 0.05 M NaOH (solid black line) are taken from van der Niet et al. Simulated and measured voltammograms both use a scan rate of 50 mV/s. Simulated CVs due not include hydroxide on terraces that would account for the experimental features at $V > 0.6 \text{ V}_\text{RHE}$.

Figure 5-6. The equilibrium phase change potential at the step of Pt(553) and Pt(533) for the desorption of 1ML of hydrogen (defined per number of step atoms) and adsorption of 1/3 ML OH* and 2/3 ML H₂O*, without (red bar) and with (blue bar) the co-adsorption of Na* (at 1/3 ML, next to the step).

Figure 5-7. 1 OH* + 2H₂O* (at 1/3 ML OH*) on the step of Pt(553) with co-adsorbed Na* near the step.

Figure S5-1. Equilibrium adsorption potentials for hydrogen adsorbed on Pt(111) (blue diamonds), the terrace of Pt(553) (green triangle), and the terrace of Pt(553) with the step occupied by a monolayer (ML) of adsorbed hydrogen (red square). Lines are intended as a guide to the eye.

Figure S5-2. Simulated cyclic voltammogram for competitive hydrogen and hydroxide adsorption on the step of Pt(553) in the presence (solid blue line) and absence of a co-adsorbed Na* (dashed red line). CV's simulated at 50 mV/s. Simulated CV's only include adsorption at the step. Simulated CV's correspond to a phase change reaction for 1ML H* at the step to desorb (adsorb) and 1/3 ML OH* to adsorb (desorb); coverage dependence of adsorption is ignored. This results in a much broader peak than what is measured experimentally. Experimental cyclic voltammogram is shown in the background measured in 0.1 M HClO₄ (grey dashed line) and 0.05 M NaOH (grey solid line) adapted from.She

Figure S5-3. Simulated cyclic voltammogram for competitive hydrogen and hydroxide adsorption on the step of Pt(553) in the presence (solid blue line) and absence of a
co-adsorbed Na* (dashed red line). CV’s simulated at 50 mV/s. Simulated CV’s only include adsorption at the step. Simulated CV’s correspond to a phase change reaction for 1ML H* at the step to desorb (adsorb) and 1/3 ML OH* to adsorb (desorb); coverage dependence of adsorption is ignored. This results in a much broader peak than what is measured experimentally. Experimental cyclic voltammogram is shown in the background measured in 0.1 M HClO₄ (grey dashed line) and 0.05 M NaOH (grey solid line) adapted from¹.  

Figure S5-4. Platinum-oxygen bond lengths for adsorbed hydroxide and adsorbed water on the step of Pt(553) in the absence and the presence of sodium adsorbed near the step as a function of sodium and hydroxide coverage.  

Figure S5-5. a) 1ML H* on the step of Pt(553). b) Pt(553) with 1ML H* on the step and 1ML H* on the step of Pt(553). c) 1/3 ML OH* at the step of Pt(553). d) 1/3 ML OH* + 2/3 ML H₂O* adsorbed on the step of Pt(553).  

Figure S5-6. a) 1/3 ML OH* + 4 H₂O* adsorbed on/near the step of Pt(553). b) 1/3 ML OH* + 2H₂O*+ 1/3 ML Na* adsorbed on/near the step of Pt(553). c) 1/3 ML OH* + 4H₂O*+Na* adsorbed on/near the step of Pt(553). d) 1 ML H* + 3H₂O on the step of Pt(553).  

Figure S5-7. 1 ML H* + 3H₂O + Na* adsorbed on/near the step of Pt(553).  

Figure S5-8. a) 1ML H* on the step of Pt(553). b) Pt(553) with 1ML H* on the step and 1ML H* on the step of Pt(553). c) 1/3 ML OH* at the step of Pt(553). d) 1/3 ML OH* + 2/3 ML H₂O* adsorbed on the step of Pt(553). 

Figure S5-9. a) 1/3 ML OH* + 4 H₂O* adsorbed on/near the step of Pt(553). b) 1/3 ML OH* + 2H₂O*+ 1/3 ML Na* adsorbed on/near the step of Pt(553). c) 1/3 ML OH* + 4H₂O*+Na* adsorbed on/near the step of Pt(553). d) 1 ML H* + 3H₂O on the step of Pt(553).  

Figure S5-10. 1 ML H* + 3H₂O + Na* adsorbed on/near the step of Pt(553).  

Figure 6-1. The background shows an experimentally measured cyclic voltammogram on a single crystal Pt(776) electrode in 0.1 M HClO₄ at 50 mV/s (black line) adapted from Farias et al.⁴⁷. The foreground (blue curve) shows the sum of the deconvolution functions fit to the experimental data at low potentials (below 0.5 V_RHE), assuming that adsorption on the step and on the terrace can be separated. Competitive adsorption of H* and OH* at the step is fit with a Gaussian function (equation 3) and adsorption of H* on the terrace is fit with an inverse hyperbolic cosine function (equation 1).  

Figure 6-2 a) Charge density on the step as given by the Gaussian functions fit to experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps³⁷, 42, 47, 50 versus the theoretical charge density assuming 1 electron is transferred per platinum step site. Data collected in acid electrolytes (orange squares) and basic electrolytes (blue diamonds). Linear regressions are given, assuming the data pass through the origin. b) Charge density on the step as given by
the Gaussian functions fit to experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps\textsuperscript{42, 48, 50-53} versus the theoretical charge density assuming 1 electron is transferred per platinum site. Data collected in acid electrolytes (orange squares) and basic electrolytes (blue diamonds). Linear regressions are given, assuming the data pass through the origin. c) Experimental charge density on the 111 terrace as given by the hyperbolic cosine fit (equation 1) to cyclic voltammograms on single crystal electrodes, plotted versus the theoretical charge density assuming 1 electron is transferred per platinum terrace site. The terrace charge density on single crystal surfaces with 110 steps\textsuperscript{37, 42, 47-50} (orange square), with 100 steps\textsuperscript{42, 48, 50-53} (blue diamond), and on the low index Pt(111) surface (green square) are shown. A linear regression is given, assuming the data pass through the origin. d) The experimentally measured potential of the sharp peak in current corresponding to hydrogen and hydroxide competitive adsorption at the step of single crystal surfaces with 110 steps\textsuperscript{37, 42, 47-50} (blue diamond and orange square) and with 100 steps\textsuperscript{42, 48, 50-53} (grey triangle, yellow circle) in both acidic and basic electrolytes.

Figure 6-3. Experimentally measured cyclic voltammogram with a stationary rotating disk Pt(pc) electrode (black line, background) and rotating electrode (400 rpm) (grey dotted line, background) in 0.1 M NaOH adapted from Rheinländer et al.\textsuperscript{45} and the sum of the deconvoluted cyclic voltammogram (red line, foreground).

Figure 6-4. Percent difference in calculated electrochemically active surface area (ECSA) between the traditional H-UPD method (solid orange) or the CO stripping method (dotted gray) and the deconvolution method. Negative difference indicates the compared method over-estimates surface area relative to the deconvolution method.

Figure 6-5. Fraction of 111-terrace and 100-step/terrace sites on shape controlled Pt-nanoparticles calculated using the deconvolution method and measured using the Bi, Ge adsorption methods (experimental data from Vidal-Iglesias et al.\textsuperscript{67}).

Figure S6-1. Experimentally measured cyclic voltammogram (black line, background) on Pt(pc) in 0.1 M HClO\textsubscript{4} adapted from Rheinländer et al.\textsuperscript{45} and the sum of the deconvoluted cyclic voltammogram (red line, foreground). The 110 step peak was fit with two Gaussian functions, as peak splitting is observed on stepped single crystal electrodes with narrow terraces (Pt(331) and Pt(110)) in perchloric acid solutions. This may explain the existence of the “middle” peak in the negative going scan near 0.2 V\textsubscript{RHE}.

Figure S6-2. Experimentally measured cyclic voltammogram with a stationary rotating disk Pt(pc) electrode (black line, background) and rotating electrode (400 rpm) (grey dotted line, background) in 0.1 M NaOH adapted from Rheinländer et al.\textsuperscript{45} and the sum of the deconvoluted cyclic voltammogram (red line, foreground).

Figure S6-3. Experimentally measured cyclic voltammogram (black line, background) on Pt(pc) in 0.1 M KOH adapted from Sheng et al.\textsuperscript{46} and the sum of the deconvoluted cyclic voltammogram (red line, foreground). Experimentally measured CV was shifted to more positive current density by ~ 6 µA/cm\textsuperscript{2} so that the double layer
charging current was centered about 0 μA/cm². Current density is per cm² of Pt area
calculated by Sheng et al.46  .............................................................................

Figure S6-4. Experimentally measured cyclic voltammogram (black line, background) on
Pt/C in 0.1 M KOH adapted from Sheng et al.46 and the sum of the deconvoluted
cyclic voltammogram (red line, foreground). Current density is per cm² of Pt area
calculated by Sheng et al.46  .............................................................................

Figure 7-1. Surface energy as a function of potential and hydrogen, hydroxide and water,
and oxygen coverage on Pt(111) (a), Pt(100) (b), and Pt(110) (c). Bold labels and
vertical lines define stability regions for the adsorbates. In the H* region, hydrogen
coverage increases as potential is decreased. In the OH*+H₂O* and O* region,
adsorbed oxygen species coverage increases as potential is increased. Due to the
strong adsorption of hydrogen and hydroxide (with co-adsorbed water) on Pt(100)
and Pt(110), there is no potential where the bare 100 or 110 surfaces are most stable....

Figure 7-2. Surface energy as a function of potential and coverage of adsorbed hydrogen,
hydroxide and water, and oxygen on Pt(111) (blue), Pt(100) (red), and Pt(110)
(black). The surface energy of the most stable coverage at any given potential is
plotted. ..................................................................................................................

Figure 7-3. a) Equilibrium nanoparticle shapes as given by Wulff constructions under the
following conditions (from left to right): UHV environment, 0 V RHE, 0.3 V RHE, and
0.7 V RHE. b) Fraction of total surface area of each facet (111, blue; 100, red; 110,
green) of a platinum surface as a function of potential given by Wulff construction.
For comparison, the UHV/bare surface energies give a Wulff construction that is
82.7% 111, 17.3 % 100, and 0% 110. ..................................................................

Figure 7-4. Cyclic voltammograms measured at 200 mV/s during conditioning of a
polycrystalline platinum electrode in argon saturated 0.1 M KOH. 100 cycles from -
0.9 to 0.3V vs Ag/AgCl are shown, with the first (black) and last (red) highlighted.
These cyclic voltammograms were measured after window opening cyclic
voltammograms (shown in Figure S7-7). ................................................................

Figure 7-5. Total site density (for 1 electron transferred per 111 site and 1.3 per 100 and
per 110 site, μC/cm²geo, or nanomole Pt/cm²geo) of 111 terrace (blue), 110
step/terrace (grey), and 100 (orange) step/terrace sites calculated by deconvoluting
the experimentally measured cyclic voltammograms shown in Figure S7-7. Also
shown is the total site density calculated from a CV measured after 200 cycles from
0.1 to 1.3 V RHE (after electrode conditioning) (AC – 1.05V) and that calculated after
an additional 50 cycles to 1.05 V RHE (50th). .....................................................

Figure S7-1. Pt(111) surface energy as a function of potential and coverage of adsorbed
hydrogen, hydroxide and water, and oxygen in an alkaline electrolyte (in the
presence of near-surface K*). Bold labels and vertical lines define regions of
stability for the different adsorbates. At low potentials, hydrogen coverage increases
with decreasing potential. At high potentials, adsorbed oxygen species coverage
increases with increasing potential.................................................................
Figure S7-2. Pt(100) surface energy as a function of potential and coverage of adsorbed hydrogen, hydroxide and water, and oxygen in an alkaline electrolyte (in the presence of near-surface K*). Bold labels and vertical lines define regions of stability for the different adsorbates. At low potentials, hydrogen coverage increases with decreasing potential. At high potentials, adsorbed oxygen species coverage increases with increasing potential.

Figure S7-3. Pt(110) surface energy as a function of potential and coverage of adsorbed hydrogen, hydroxide and water, and oxygen in an alkaline electrolyte (in the presence of near-surface K*). Bold labels and vertical lines define regions of stability for the different adsorbates. At low potentials, hydrogen coverage increases with decreasing potential. At high potentials, adsorbed oxygen species coverage increases with increasing potential.

Figure S7-4. Pt(111) surface energy as a function of potential and hydroxide and water, oxygen, and platinum surface oxide coverage (identical to Figure 7-1 in main paper but showing only the high potential region and including formation of a surface oxide).

Figure S7-5. Pt(100) surface energy as a function of potential and hydroxide and water, oxygen, and platinum surface oxide coverage (identical to Figure 7-2 in main paper but showing only the high potential region and including formation of a surface oxide).

Figure S7-6. Pt(110) surface energy as a function of potential and hydroxide and water, oxygen, and platinum surface oxide coverage (identical to Figure 7-3 in main paper but showing only the high potential region and including formation of a surface oxide).

Figure S7-7. Cyclic voltammograms measured at 100 mV/s on polycrystalline Pt in argon saturated 0.1 M KOH. 10 cycles to a positive potential limit of 0V, 10 cycles to 0.2V, and 10 cycles to 0.3V vs Ag/AgCl are shown.

Figure S7-8. Representative steady state cyclic voltammogram measured after electrode conditioning. The cyclic voltammogram was measured on a Pt(pc) electrode at 100 mV/s in 0.1 M KOH.

Figure S7-9. Fraction of 111 (blue), 100 (red), and 110 (green) surface sites calculated by Wulff construction from the potential dependent surface energies in an alkaline electrolyte (including the effect of an alkali cation, potassium, on hydroxide adsorption, shown in Figures S7-1, S7-2, and S7-3). The presence of a near surface cation weakens hydroxide adsorption, which yields a wider potential range over which bare Pt(111) is stable and increases the surface energy of Pt(100) and Pt(110) at high potentials. This results in a greater fraction of 111 sites at potentials equal to and greater than 0.4V_{RHE}, relative to those calculated in an acid electrolyte (Figure 7-3b).

Figure S7-10. Ratio of the surface site density (SA) after conditioning to that measured before conditioning plotted against the ratio of the bare surface energies (SE) to that...
of the surface energies calculated at 0.7 $V_{\text{RHE}}$ in the presence of a near-surface potassium cation. The x-axis represents a thermodynamic driving force for reconstruction calculated using DFT and the y-axis the experimentally measured extent of reconstruction.

Figure S7-11. Pt(111) 1/3 ML OH* + 1/3 ML H$_2$O* + 1/9 ML K* .................................................. 273

Figure S7-12. Pt(111) 1/3 ML O* + 1/9 ML K* .......................................................... 274

Figure S7-13. Pt(100) 1/3 ML OH* + 1/3 ML H$_2$O* + 1/9 ML K* .................................................. 274

Figure S7-14. Pt(110) 1/2 ML OH* + 1/2 ML H$_2$O* + 1/4 ML K* .................................................. 274

Figure S7-15. Pt(110) 1/2 ML O* + 1/4 ML K* .......................................................... 275

Figure S7-16. Pt(111) 1 ML PtO$_2$*, top view (left) and side view (right). ........................................ 275

Figure S7-17. Pt(100) 1 ML PtO*, top view (left) and side view (right). ........................................ 276

Figure S7-18. Pt(110) 1 ML PtO$_2$* (0.5 ML Pt$_2$O$_4$*), top view (left) and side view (right). .... 276

Figure 8-1. Equilibrium adsorption potentials of ammonium, tetramethyl-, tetraethyl-, tetrapropyl-, and benzyltrimethylammonium at 1/9 ML on Pt(111), Pt(100), and Pt(110). Potentials are calculated at a cation concentration of 1M and a temperature of 300K. van der Waals corrections are included. *The adsorption potential for benzyltrimethylammonium on Pt(110) is 1.75 $V_{\text{NHE}}$. .................................................. 286

Figure 8-2. Equilibrium adsorption potential of ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium at 1/9 ML on Pt(111) without and with six water molecules added near the surface adsorbate. van der Waals corrections are included. Adsorption of sodium is also shown for comparison, from Mills et al. (without vdW corrections)$^{39}$ .................................................. 288

Figure 8-3. Equilibrium adsorption potentials for ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium on Pt(111) as a function of cation coverage. van der Waal corrections are included. .................................................. 290

Figure 8-4. Equilibrium adsorption potentials for ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium on Pt(100) as a function of cation coverage. van der Waal corrections are included. .................................................. 291

Figure 8-5. Equilibrium adsorption potentials for ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium on Pt(110) as a function of cation coverage. van der Waal corrections are included. .................................................. 291

Figure 8-6. Cyclic voltammograms measured on Pt(pc) in 0.1 M KOH (red), 0.1 M tetramethylammonium hydroxide (TMAOH, blue), 0.1 M tetraethylammonium hydroxide (TEAOH, green), and 0.1 M benzyltrimethylammonium hydroxide (BTMAOH, teal) at 100 mV/s. .................................................. 293
Figure 8-7. Total electrochemically active surface area and relative site density of 111 (blue), 100 (red), and 110 (green) sites calculated by deconvoluting cyclic voltammograms measured on Pt(pc) in 0.1 M KOH, 0.1 M tetramethylammonium hydroxide (TMAOH), and 0.1 M tetraethylammonium hydroxide (TEAOH) (CVs shown in Figure 8-6). CVs measured in 0.1 M benzyltrimethylammonium hydroxide could not be deconvoluted, given the lack of discernable contributions from 111, 110, and 100 sites. Surface area is given in units of total charge per square centimeter of geometric electrode area, assuming one electron is transferred per 111 site and 1.33 electrons transferred per every 110 and 100 site.

Figure 8-8. Fraction of 111 (blue diamond), 100 (red square), and 110 (green triangle) sites blocked by tetramethylammonium or tetraethylammonium adsorption as a function of the number of surface sites blocked per adsorbate (calculated assuming 3 of the 4 alkyl chains adsorb and block 1 surface site for every CH₃ unit). The fraction of sites blocked are calculated from the changes in total surface area (relative to that measured in 0.1 M KOH) calculated by deconvoluting experimentally measured cyclic voltammograms (Figure 8-7). Linear regressions are shown with a slope of 0.12 for 111, 0.12 for 100, and 0.01 for 120.

Figure S8-1. Equilibrium adsorption potentials calculated for adsorption of ammonium, tetramethylammonium, tetraethylammonium, and tetrapropylammonium at 1/9 ML on Pt(111) calculated without (red) and with (blue) DFT+D2 van der Waals corrections.

Figure S8-2. Structure of adsorbed benzyltrimethylammonium at 1/9 ML on (from top to bottom) Pt(111), Pt(100), and Pt(110) (showing the top down view on the left and a view from the side on the right).

Figure S8-3. Equilibrium adsorption potential of ammonium, tetramethyl-, tetraethyl-, and tetrapropyl-ammonium at 1/9 ML as a function of the number of water molecules added near the surface adsorbate. van der Waals corrections are included. Adsorption of sodium is also shown for comparison, from Mills et al. (without vDW corrections) Equilibrium adsorption potentials calculated for adsorption of ammonium, tetramethylammonium, tetraethylammonium, and tetrapropylammonium at 1/9 ML on Pt(111) calculated without (red) and with (blue) DFT+D2 van der Waals corrections.

Figure 9-1. HOR/HER polarization curves measured on a polycrystalline platinum rotating disk electrode at 2500 rpm in H₂ saturated 0.1 M LiOH, 0.1 NaOH, 0.1 M KOH, and 0.1 M CsOH at 22°C.

Figure 9-2. Equilibrium adsorption potentials calculated for hydrogen adsorption at 1 ML on Pt(111) (a), Pt(100) (b), and Pt(110) (c) as a function of the coverage of co-adsorbed Li, Na, K, Cs.

Figure 9-3. Equilibrium adsorption potentials calculated for hydroxide (and water) adsorption at 1/3 ML (3OH*+3H₂O*) from an adsorbed water bilayer (6H₂O*) on Pt(100) (a) and Pt(110) (b) as a function of the coverage of alkali metal cation co-adsorbed on the surface.
Figure 9-4. Experimentally measured exchange current densities plotted against the DFT predicted hydroxide adsorption potential in the presence of 0.22 ML of co-adsorbed Li, Na, K, and Cs.

Figure 9-5. Volcano plot of the experimentally measured rate of the hydrogen oxidation reaction and the DFT calculated hydroxide adsorption potential on Ru(0001), Ir(111), Au(111), Pt(111), and Pt(100) in the presence of co-adsorbed potassium, as well as Pt(110) in the presence of co-adsorbed Li, Na, K, and Cs (with the experimentally measured rate on Pt(pc)). Hydroxide adsorption is considered with co-adsorbed water, at 1/3 ML OH*, 1/3 ML H2O*. Cation coverage is 1/9 ML on all surfaces except Pt(110), where the cation coverage is 2/9 ML. Red lines are drawn to highlight the volcano shape. Rate of the HOR/HER measured on Ru, Ir, Au, and Pt(111) single crystal electrodes are from Strmcnik et al. and on Pt(111), Pt(100), and Pt(110) single crystal electrodes from Markovic et al.

Figure 9-6. Schematic diagram for a proposed hydrogen (proton) desorption mechanism in acid and alkaline electrolytes which proceed through an intermediate state (TS) where a partially solvated water molecule (acid) or hydroxide anion (alkaline) interacts directly with the electrode surface. IS indicates the initial state, TS the transition state, and FS the final state.

Figure S9-1. Equilibrium adsorption potentials calculated for Li, Na, K, and Cs adsorption on to Pt(111) (a), Pt(100) (b), and Pt(110) (c) as a function of coverage from a solution cation concentration of 1 M at 300 K. Horizontal lines (black) indicate the equilibrium potential for the HOR/HER at pH = 14.

Figure S9-2. Equilibrium adsorption potentials calculated for adsorption of Li, Na, K, and Cs at 1/9 ML onto a bare (red) and solvated (blue) Pt(111) surface. The surface is solvated with a water bilayer (6 H2O*). The solid black line corresponds to the equilibrium potential for the HOR/HER in an acid electrolyte (pH = 0) and the dashed black line to the equilibrium potential for the HOR/HER in a basic electrolyte (pH = 14). The presence of solvent (water) near the electrode surface significantly promotes alkali metal cation adsorption (by 0.8 - 1 V).

Figure S9-3. Hydroxide adsorption potentials plotted against the hydrogen adsorption potential on Ru(0001), Ir(111), Au(111), Pt(111), Pt(100), and Pt(110). The hydroxide adsorption potential is calculated in the presence of adsorbed/near-surface potassium. The hydroxide adsorption potential on Pt(110) is calculated in the presence of Li, Na, K, and Cs.

Figure 10-1. Hypothetical dependence of the HOR/HER reaction rate in an alkaline electrolyte on the surface step density as expected for a single site or dual site HOR mechanism, for reaction rates measured on stepped single crystal Pt surfaces. The rates measured on Pt(110) and Pt(111) are known.

Figure 10-2. The experimentally measured rate of the hydrogen oxidation reaction as a function of the DFT calculated hydroxide adsorption potential (a more positive potential indicates weaker adsorption). Patterned blue circles correspond to rates measured in acid, solid red circles are measured in base (with the OH* adsorption
potential calculated in the presence of K*), and patterned red circles are the experimentally measured rates on Pt(pc) in the presence of various alkali metal cations, given in Chapter 9. The solid black lines are added as a guide to highlight the volcano trend.
LIST OF TABLES

Table 2-1. Conventional cubic cell dimension used for fcc metals

Table 2-2. Cation adsorption equilibrium potentials to fcc (111) electrode surfaces, $U_0 [V – NHE]$ calculated using DFT methods and equation 11

Table 2-3. Experimental cation solvation free energies, eV, at 300 K and 1M

Table 2-4. Values of $\Delta G_{ads}\Delta U$ for cation adsorption to fcc(111) metal surfaces. These values represent net electron transfer upon adsorption, calculated via equation 8

Table 2-5. Cation adsorption equilibrium potentials, $U^0$ (V-NHE), for a Pt(111) electrode calculated via the fully solvated double-reference method

Table S2-1. VASP energies (eV) for bare fcc(111) surfaces and single atoms adsorbed to fcc(111) surfaces

Table S2-2. VASP gas phase cation energies and energy corrections used to calculate solution phase cation free energies at 300 K and 1M using equations 5 and 6. All values are in eV

Table S2-3. Dipole moments (e Å) for bare fcc(111) surfaces ($\mu$) and surfaces with adsorbed atoms ($\mu_{C}$)

Table S2-4. Gas phase water properties at 300K (eV)

Table S3-1. Cu (111)-halide binding energy (1/2 $X_{2(g)}$ to $X^*$, 0K non-ZPVE corrected) for each possible adsorption site (Calculated using PW91 exchange-correlation functional). Energies in bold represent lowest energy site. Energy in eV

Table S3-2. Cu (100)-halide binding energy (1/2 $X_{2(g)}$ to $X^*$, 0K non-ZPVE corrected) for each possible adsorption site (Calculated using PW91 exchange-correlation functional). Energies in bold represent lowest energy site. Energy in eV


Table S3-4. Standard halogen reduction/dissolution potentials at 1 M halide concentration and 1 atm halogen gas partial pressure ($V_{NHE}$)

Table S3-5. Halide anion experimentally measured solvation energies at 1 M halide concentration
Table S3-6. Diatomic halogen energy and entropy contributions to total free energy at 300 K

Table S3-7. Halide anion energy and entropy contributions to total free energy at 300 K

Table S3-8. Cu (100)-I DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

Table S3-9. Cu (100)-F DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

Table S3-10. Cu (211)-F DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

Table S3-11. Cu (211)-I DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

Table S3-12. Cu (111)-F DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

Table S3-13. Cu (111)-I DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

Table S3-14. Cu (100)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1 ML halide coverage. Energy in eV.

Table S3-15. Cu (111)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1 ML halide coverage. Energy in eV.

Table S3-16. Cu (100)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage. Energy in eV.

Table S3-17. Cu (111)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage. Energy in eV.

Table S3-18. Cu (211)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage. Energy in eV.
Table S3-19. Equilibrium adsorption potentials ($V_{NHE}$) for adsorption on Cu(111) as a function of halide coverage calculated using diatomic gas phase energy method. ........ 107

Table S3-20. Equilibrium adsorption potentials ($V_{NHE}$) for adsorption on Cu(100) as a function of halide coverage calculated using diatomic gas phase energy method. ........ 107

Table S4-1. Adsorption site analysis for K* (a-c) and H* (d-f) at 1/9 ML on Pt(111), Pt(100), and Pt(110). ................................................................. 153

Table S4-2. Aqueous free energy of K$^+$ (aq) and H$^+$ (aq) calculated using the experimental solvation energy method and the computational hydrogen electrode method (with the equivalent method for potassium, using its standard dissolution potential). ........ 154

Table S4-3. Free energy H$_2$, H$_2$O(aq), and OH$^-$ (aq). ......................................................... 154

Table S4-4. Dipole moments for K* on Pt(111), Pt(100), and Pt(110) as a function of coverage. ................................................................................ 155

Table S4-5. Charge on K* as evaluated by a Bader charge analysis as a function of coverage on Pt(111), Pt(100), and Pt(110). ................................................................. 156

Table S4-6. Gibbs free energy of interaction between K* and H* as a function of coverage on Pt(111), Pt(100), and Pt(110). ......................................................... 158

Table S4-7. Charge on hydrogen when co-adsorbed at 1 ML with K* as a function of K* coverage on Pt(111), Pt(100), and Pt(110). ................................................................. 158

Table S4-8. Adsorption potential of 1/9 ML OH* on Pt(111), Pt(100), and Pt(110) in the absence and for OH* on Pt(110) in the presence of 1/9 ML K* ......................................................... 158

Table S4-9. Equilibrium adsorption potential of 1/9 ML K* into H$_2$O and OH+H$_2$O* structures on Pt(111) (100) and (110). Calculated using the potassium dissolution potential method. Includes dipole correction. ................................................................. 159

Table S5-1. Equilibrium adsorption potentials calculated for hydroxide and water adsorption on the step of Pt(553) at a 1/3 ML coverage of hydroxide with and without a hydrogen atom adsorbed at the step. ................................................................. 194

Table S5-2. Interaction parameters used in competitive adsorption model to simulate cyclic voltammograms. .................................................................................. 195

Table S5-3. Equilibrium adsorption potential of hydrogen adsorbed at 1 ML on the steps of Pt(553) and Pt(533) in the absence and the presence of 1/3 ML sodium adsorbed near the step. ................................................................. 197

Table S5-4. Hydrogen bond length between hydroxide and water (2 co-adsorbed water molecules per adsorbed hydroxide) adsorbed at the step of Pt(553) in the absence and presence of sodium co-adsorbed near the step as a function of the coverage of adsorbed hydroxide and adsorbed water. ................................................................. 197
Table S5-5. Calculated surface normal dipole moments for OH*, OH+2H₂O*, and OH*+4H₂O* adsorbed at the step of Pt(553) and Pt(533). Coverage is defined as number of adsorbed hydroxide molecules per surface step Pt atom (In cases where Na* is co-adsorbed, sodium coverage matches the hydroxide coverage). Unit cell has one step row which is 3 Pt atoms wide (1/3 ML coverages) or 4 Pt atoms wide (1/4 ML coverages) (with appropriate terrace width). A surface normal dipole moment change on adsorption of -0.4 eÅ and assuming a double layer thickness of 3 Å gives an electrosorption valency of 1.13 electrons for hydroxide. A smaller change in magnitude gives an electrosorption valency closer to the 1 electron transfer expected for hydroxide adsorption (which is the case with hydroxide adsorption in the absence of co-adsorbed water).

Table S6-1. References for all of the experimentally measured cyclic voltammograms used in this study and their respective miller index and microfacet notations.

Table S6-2. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms (CV's) on single crystal electrodes with 110 steps measured in an acid electrolyte. The Pt(776) experimentally measured CV and the sum of the deconvoluted CV are shown in Figure 6-1 in the main paper.

Table S6-3. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps measured in a basic electrolyte.

Table S6-4. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in an acid electrolyte.

Table S6-5. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in a basic electrolyte. *Pt(311) has a short 2 atom wide 100 terrace with a 111 step (2n-1, 1, 1; n(100)x(111), where n=2).

Table S6-6. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps measured in an acid electrolyte.

Table S6-7. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps measured in a basic electrolyte.

Table S6-8. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in an acid electrolyte.

Table S6-9. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in a basic electrolyte.
Table S6-10. Parameters used to deconvolute experimentally measured cyclic voltammograms on polycrystalline and nanoparticle platinum electrodes in both acidic and basic electrolytes. The cyclic voltammogram measured on Pt(pc) in perchloric acid was deconvoluted using two Gaussian peaks to represent adsorption on 110 sites.

Table S6-11. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on polycrystalline and nanoparticle Pt electrodes measured in acidic and basic electrolytes.

Table S6-12. Total site density (in units of µC/cm²geo, where the number of platinum sites can be calculated assuming 1 electron transferred per site, after accounting for the appropriate number of electrons transferred (assume 1 electron per site in H-upd method, assume 2 electrons per site in the CO stripping method, and calculated 1 electron per 111 site and 1.33 electrons per each 110 and 100 site (from DFT) in the deconvolution method)) calculated with the H-UPD method, CO stripping method, and our deconvolution method.

Table S6-13. Fraction of total sites which correspond to 111, 100 and 110 type sites, calculated from cyclic voltammograms measured on shape controlled platinum nanoparticles by Devivaraprasad et al. in NaOH. While the absolute values differ between the method used here and the methods used by Devivaraprasad et al., the trend in which nanoparticles show the highest relative proportion of 100 type sites matches.

Table S6-14. Fraction of total sites which correspond to 111, 100 and 110 type sites, calculated from cyclic voltammograms measured on shape controlled platinum nanoparticles by Vidal-Iglesias et al. While the absolute values differ between the method used here and the methods used by Vidal-Iglesias et al., the trend in which nanoparticles show the highest relative proportions of 111 and 100 types sites both match between the two methods.

Table S7-1. Fraction of 111, 100, and 110 surface sites calculated by Wulff construction as a function of potential in a non-adsorbing acid electrolyte and in an alkaline electrolyte containing potassium cations. The surface fractions calculated in an alkaline electrolyte only consider the effect of potassium on hydroxide adsorption (as the effect on hydrogen adsorption is small). Fraction of sites also shown for bare nanoparticle surfaces (in UHV).

Table S8-1. Difference in DFT energy for benzyltrimethylammonium adsorbed at 1/9 ML on Pt(111), Pt(100), and Pt(110) with the benzyl ring parallel or perpendicular to the electrode surface. A negative difference in energy means the parallel configuration (ring adsorbed) is more stable.

Table S8-2. Surface normal dipole moments for the quaternary ammonium organic cations adsorbed on Pt(111) at 1/9 ML without and with explicit water molecules.

Table 9-1. HOR/HER exchange current densities (i₀) measured on platinum in 0.1 M alkaline electrolytes.
Table S9-2. Surface normal dipole moment generated on adsorption of Li, Na, K, and Cs on Pt(111), Pt(100), Pt(110) at a coverage of 1/9 ML. .................................................................332

Table S9-3. Tafel slopes and transfer coefficients (α) calculated from the experimentally measured mass transport corrected (using the irreversible Koutecky-Levich equation\(^1\)) HOR/HER current densities near 0 V\(_{RHE}\) (-0.10 to 0.20 V\(_{RHE}\))......................333

Table S9-4. HOR/HER exchange current densities (i\(_0\)) measured on platinum in 0.1 M alkaline electrolytes, calculated from a linear fit to a plot of log(i\(_k\)) vs. overpotential for the HOR and for the HER (mass transport corrected using the irreversible Koutecky-Levich equation\(^1\)). ...............................................................334
ACKNOWLEDGEMENTS

I would first like to thank my dissertation advisors Michael Janik and Michael Hickner for their unending support, guidance, and of course for the many things I have learned from them during my time in graduate school. Within the first few minutes of meeting Mike Janik, I knew that he was passionate about research and that I could learn a lot working in the Janik lab; I am glad to say that the last few years have even surpassed my expectations.

I am also grateful for the support of my family; my mother for convincing me that I could achieve whatever I set my mind to, my father for encouraging me to work hard and indulging my desire to build things at a young age, and my grandparents for always being interested in my work and teaching me about math and science while I was growing up. I am thankful for the support from my aunts and uncles and cousins as well, who have, on more than one occasion, taken my word for it that I will finish my education soon.

Finally, I would like to thank all of my friends and colleagues at Penn State, as well as my friends outside of State College. Thanks to everyone in the Janik and Hickner labs for all of the help and for always answering even my stupider questions. Thanks to Praveen for teaching me how to run electrochemistry experiments, Tom for helping me to understand when DFT is useful, and equally importantly, when it is not, and Sneha for always listening to my complaints when research was difficult. Thanks to Gaurav, Joel, and Jonayat for helping me try to better understand quantum mechanics (which required significant patience), and to TJ and Raymond for their help in the lab. Good luck to those left in the Janik lab - Gaurav, Joel, Jonayat, Haoran, Shyam, Sharad, Bryan, Siqi, Prithvi, Bo, and Li – I wish you all the best. Last but certainly not least, thanks to Maggie, Tom, Sneha, Charles, Dan, Mike, Lily, and Julie for helping to keep me sane and making sure I spent my free time doing something fun.
Chapter 1

Introduction

1.1. Motivation

The structure and composition of the electrode-electrolyte interface (Figure 1-1) can affect the rate, mechanism, and selectivity of electrocatalytic reactions. The position of solvent molecules and the concentration of ions near the electrode surface are a function of the bulk electrolyte composition (including the solvent identity, ion identity, and ion concentration) and the applied electrochemical potential. This interface is a fundamental component of all electrochemical devices, including fuel cells, which provide an efficient means for the conversion of chemical energy into electrical energy, and electrolyzers, which convert electrical energy into chemical energy. Hydrogen fuel cells have been used to power commercially available electric vehicles\textsuperscript{1-2} and provide electrical power and water for manned space missions\textsuperscript{3}. Hydrogen fuel cells and electrolyzers have also been proposed as an integral component of grid scale energy storage\textsuperscript{4-5}, necessary for supporting clean but intermittent renewable energy sources (such as solar and wind)\textsuperscript{6}. The widespread use of hydrogen fuel cells and water electrolyzers however, requires further reductions in cost and increases in operating lifetime\textsuperscript{7,8}. Key to the development of lower cost and highly stable electrocatalysts is an understanding of how the structure and composition of the electrode-electrolyte interface effects both catalyst activity and stability.

Proton exchange membrane (PEM) hydrogen fuel cells have reached a high level of performance, giving high power densities and efficiencies\textsuperscript{7}, however their high cost limits their widespread use\textsuperscript{7}. A significant portion of this cost arises from the need for expensive noble metal (primarily platinum) catalysts\textsuperscript{8}, as most other metals are not stable in the acid environment.
created by the proton exchange membrane for long periods of time. While significant research has focused on the design of high surface area platinum nanoparticles or highly active platinum alloys (to maximize the activity per unit mass of platinum), the use of an alkaline electrolyte would allow non-noble metal catalysts to be used (as well as potentially lower cost membranes and ionomers), and could therefore represent a lower cost alternative to the well-developed PEM fuel cell. Recent evidence however, suggests that the rate of the hydrogen oxidation reaction (occurring on the anode of a hydrogen fuel cell) is significantly slower in alkaline electrolytes than in acid electrolytes, even on the most active catalysts for this reaction (Pt, Pd, Ir, Rh). This suggests that an alkaline hydrogen fuel cell would have significantly reduced performance compared to an acid fuel cell. Understanding the mechanism by which pH so significantly effects the rate of the hydrogen oxidation and evolution reactions (HOR/HER) is necessary for the development of high performance and low cost alkaline fuel cells and electrolyzers.
Figure 1-1. Schematic of the double layer structure near a negatively charged electrode surface in an aqueous electrolyte solution (with the bulk electrolyte above the surface; not shown). The inner Helmholtz plane is comprised of water molecules and ions adsorbed on the electrode surface, the outer Helmholtz plane a high concentration of charge to counter the charge on the electrode surface, and the diffuse layer, containing anions and cations which continue to screen the charge at the electrode surface until the disordered arrangement of anions and cations in the bulk electrolyte is reached. For a metal electrode, the negative charge is distributed across the surface.
1.2. Background

1.2.1. pH and Alkali Cation Effects on Electrocatalysis

In addition to the significant effects of pH on the rate of the hydrogen oxidation reaction, pH has also been shown to affect many other electrocatalytic reactions. For example, the rate of the oxygen reduction reaction (ORR) is faster at lower overpotentials in an alkaline electrolyte on Ag(111)\textsuperscript{15} and Ag(100) (by almost 4 orders of magnitude at 0.8 V\textsubscript{RHE})\textsuperscript{16} than in an acid electrolyte. Meng et al. also found the ORR to be slightly faster (7-10 times) in alkaline electrolytes on Fe/N/C based noble-metal free catalysts\textsuperscript{17}. In contrast, the ORR on Pt(111) in non-adsorbing perchloric acid or alkaline sodium hydroxide was found to be pH independent\textsuperscript{18}. CO oxidation and CO stripping (where carbon monoxide adsorbed on a surface is oxidatively removed in a CO free electrolyte) are faster in alkaline electrolytes on many electrocatalysts, including on Au(100)\textsuperscript{16}, polycrystalline Au and Pt (with Au becoming more active for CO oxidation in an alkaline electrolyte than Pt)\textsuperscript{19}, and on Pt/C, Ir/C, Rh/C, and Pd/C (as given by the onset potential for CO stripping)\textsuperscript{14}. The local pH near the electrode surface (which may change as a function of reaction rate) has also been argued to impact the selectivity of CO\textsubscript{2} electroreduction\textsuperscript{20-21}. These effects of pH on electrocatalytic reaction rates have been typically attributed to a change in the coverage of a site blocking spectator species, an effect on the adsorption strength of a reactive intermediate, or in driving changes in the relative rates of competing reactions, changing the product selectivity.

In an aqueous or hydrated polymer electrolyte, changing the pH not only effects the concentration of protons or hydroxide at the electrode-electrolyte interface, but also shifts the equilibrium potentials for any reaction consuming or producing protons (or hydroxide) including the hydrogen oxidation/evolution reactions (HOR/HER) and the oxygen reduction/evolution
reactions (ORR/OER). This shift follows the Nernst equation, moving to lower absolute potentials with increasing pH. The change in potential on an absolute or the normal/standard hydrogen electrode scale (NHE, where the equilibrium potential for HOR/HER at a pH of 0 is defined as 0 V_{NHE}) can change the magnitude of the electric field near the surface, driving solvent (water) molecules to re-orient relative to the electrode surface. These solvent molecules near the electrode surface may interact with adsorbates on the electrode surface, through hydrogen bonding or by screening charge on these adsorbed species, affecting the thermodynamics of adsorption and kinetics of reactions at this interface. Re-orientation of the solvent from changes in electric field near the surface may alter the magnitude of this interaction.

The change in absolute potential of the equilibrium potential for a given reaction on changing pH may also drive the adsorption of different spectator or reactive species (which do not depend on pH) to become favorable at potentials where the reaction of interest occurs. Adsorption of anions at high potentials to many surfaces is well known\textsuperscript{22}, including the adsorption of bi(sulfate)\textsuperscript{23-25} and the halide anions (chloride, bromide, and iodide; fluoride is typically considered non-adsorbing\textsuperscript{26-28}. The shift in reaction potential on an absolute scale with increasing pH to lower potentials may allow for the specific adsorption of cations, including the alkali metal cations present in aqueous alkaline electrolytes or the organic cations present in alkaline polymer electrolytes. Adsorbed or near-surface (within the double layer) anions and cations, even as spectators in an electrocatalytic reaction, can affect the rate and mechanism of these reactions.

The effect of spectator ions can be occur through three main mechanisms. First, if the spectator ion is specifically adsorbed, it may block active sites on the catalyst surface, reducing the overall reaction rate of a reaction which occurs at potentials where the ion is adsorbed. Second, adsorbed or near-surface ions may interact with adsorbed species which are intermediates in the reaction, altering how strongly they interact with the surface, which may then
effect the rate of the reaction. Lastly, adsorbed or near-surface ions may directly interact with reaction intermediates at a transition state, altering the energy of this state (the activation energy), thereby directly changing the rate of the reaction.

Many anions specifically adsorb to metal electrode surfaces and effect the rate of electrocatalytic reactions. For example, (bi)sulfate\textsuperscript{23, 29-31} and halide anions\textsuperscript{28, 32-33} adsorb to platinum electrode surfaces at high potentials and decrease the rate of the oxygen reduction reaction, via primarily a simple site blocking mechanism\textsuperscript{32-37}. This effect can be so significant, that even blocking a small number of sites with a small anion with repulsive interactions (cyanide) which blocks adsorption of larger anions (which would block more sites), leads to a higher oxygen reduction rate at high potentials\textsuperscript{38}.

The alkali metal cations present in alkaline electrolytes have been shown to also effect reaction rates, including that of oxygen reduction\textsuperscript{39}, methanol oxidation\textsuperscript{39}, and CO stripping\textsuperscript{40} on platinum electrodes, as well as the rate and selectivity of CO\textsubscript{2} electroreduction on copper\textsuperscript{41-42} and silver\textsuperscript{41, 43} electrodes, but the mechanism by which these effects occur is not entirely clear. In contrast to the case with anions, there is only limited, indirect experimental evidence which suggests that alkali metal cations may specifically adsorb to electrode surfaces, including radiotracer studies suggesting alkali and alkaline earth metal cation adsorption on platinum\textsuperscript{44-47} and quartz crystal microbalance measurements which suggest Cs\textsuperscript{+} adsorption to platinum electrodes\textsuperscript{48-49}. Direct electron transfer due to adsorption of an alkali metal cation onto a metal electrode in an aqueous electrolyte has not been observed. Strmcnik et al. suggested that alkali metal cations present near the electrode surface (though not necessarily adsorbed) may affect the binding of adsorbed hydroxide, an intermediate in oxygen reduction, methanol oxidation, and CO stripping\textsuperscript{39}, to platinum electrodes, explaining the effect of these cations on the rates of these reactions.
1.2.2. pH and Alkali Cation Effects on the Thermodynamics of Hydrogen/Hydroxide Adsorption

pH and the alkali metal cations present in alkaline electrolytes have been found to not only effect electrocatalytic reaction rates, but also perturb the binding strength or thermodynamics of adsorption of hydrogen and hydroxide, though the mechanism by which this occurs is unknown. These effects are most clearly seen on single crystal electrode surfaces, where only one particular facet or arrangement of atoms are exposed to the electrolyte environment; platinum single crystal electrodes in particular have seen significant study. On Pt(111), the electrolyte pH has little effect on the adsorption of hydrogen (on a relative hydrogen electrode scale, where the effect of the changing concentration of protons on the adsorption thermodynamics has already been accounted for assuming a Nernstian shift), but shifts the onset of hydroxide adsorption and increases the maximum hydroxide coverage, as given by cyclic voltammetry\textsuperscript{50-51}. Figure 1-2 shows a cyclic voltammogram measured (CV) on Pt(111) in an acid and an alkaline electrolyte, highlighting these effects\textsuperscript{51}. The broad low potential peak (0-0.4 \text{ V\,RHE}) corresponds to hydrogen adsorption; the broad shape indicating strong repulsive interactions between adsorbed hydrogen, which has been supported with density functional theory (DFT) calculations and cyclic voltammograms simulated from first principles, which match experiment\textsuperscript{52}. The high potential peak in current (0.5-0.9 \text{ V\,RHE}) corresponds to hydroxide adsorption (desorption) in the positive (negative) going scan. Not only does pH effect the shape of the high potential hydroxide adsorption peak, but the identity of the alkali metal cation present in an alkaline electrolyte also effects the location of this peak\textsuperscript{39-40}. 
Figure 1-2. Cyclic voltammograms measured on Pt(111) in an acidic (0.1 M HClO₄) and basic (0.1 M NaOH) electrolyte at a scan rate of 50 mV/s. Figure adapted from Garcia et al., Ref. 50, with permission from the PCCP Owner Societies.

On the other low index facets of platinum, Pt(110) and Pt(100), pH also effects the shape and location of peaks in current measured by cyclic voltammetry. On Pt(110) a relatively narrow peak at low potentials (0.1-0.35 V_RHE) shifts to more positive potentials with increasing pH\textsuperscript{40, 53}

The effect of pH on the cyclic voltammogram measured on Pt(100) is more subtle, with the broad mid-potential peak (0.2-0.5 V_RHE) shifting slightly and gaining additional features with increasing pH\textsuperscript{54}. CO displacement experiments, which measure the charge transferred to an electrode when an ionic adsorbate is displaced by strongly adsorbing carbon monoxide, and measurements of the potential of zero displaced (or total) charge, on both Pt(100)\textsuperscript{54-55} and Pt(110)\textsuperscript{53}, have shown that these CV features correspond to competitive hydrogen and hydroxide adsorption. Therefore, it is clear that pH effects the thermodynamics of adsorption of either hydrogen, hydroxide, or both species on Pt(100) and Pt(110), but additional study is needed to identify the mechanism by which these effects occur. Slight differences in the location of the narrow peak on Pt(110) in alkaline electrolytes with different alkali metal cations (Li\textsuperscript{+}, Na\textsuperscript{+}) (and significant differences with
Be$^{+2}$) have been observed as well$^{40}$.

Higher order stepped platinum facets comprised of 111-like terraces with either 110 or 100 type steps also show a strong effect of pH on the location of the sharp, low potential peaks measured by cyclic voltammetry$^{56}$. These sharp peaks (0.125 V$_{RHE}$ on 110-stepped surfaces, 0.27 V$_{RHE}$ on 100-stepped surfaces$^{56}$) shift to more positive potentials (on an RHE scale) with increasing pH; this is an anomalous sub-Nernstian shift$^{56}$. While these sharp peaks are known to correspond to adsorption on the step site (as it is in the same location (potential) on all surfaces showing the same type of step (110 vs 100), for terraces wider than ~ 3 atoms), it is not known what species adsorb to yield this sharp peak. While traditionally assumed to correspond to hydrogen adsorption along the step$^{57-58}$, it has been recently proposed that the sharp shape and anomalous pH dependence of the peak can only be explained if the peak corresponds to competitive hydrogen and water adsorption$^{59-60}$ or hydrogen and hydroxide or oxygen adsorption$^{51-56}$. Repulsive interactions between adsorbed hydrogen and water/hydroxide/oxygen$^{51, 61}$ or attractive interactions between water/hydroxide/oxygen adsorbed along the step would yield a sharper peak than what would be expected for hydrogen alone.

Similar CO-displacement experiments to those carried out on the low index Pt(110) and Pt(100) electrodes cannot uniquely determine the competitive adsorption of hydrogen with an anionic species along the step of a stepped surface, as the charge transferred along the step is convoluted with the charge transferred on the terrace (due to hydrogen adsorption on the terrace at potentials where the sharp peak corresponding to adsorption along the step occurs). Density functional theory has therefore been used to examine water, hydroxide, and oxygen adsorption on Pt(553) (with 110 type steps) and Pt(533) (with 100 type steps), finding that competitive adsorption of hydrogen and hydroxide may be possible only on the step of the Pt(533) surface, but the effect of near-surface solvation on the adsorption of these species was not considered$^{62}$. Recent DFT results using an implicit, continuum solvation model suggest hydrogen and water
competitive adsorption along 110 type steps, but this type of model may not accurately capture hydrogen bonding interactions between adsorbates (OH*, H2O*) and water near the electrode surface (near-surface solvation).

The lack of understanding of hydrogen and hydroxide adsorption as well as the effects of alkali metal cations and pH on hydrogen and hydroxide adsorption across the low index platinum surfaces, Pt(111), Pt(100), and Pt(110), as well as stepped platinum surfaces, motivates the use of ab initio computational modeling techniques, such as density functional theory (DFT), to probe the thermodynamics of adsorption. DFT allows for the adsorption of each species (alkali metal cations, hydrogen, hydroxide, oxygen, and water) to be considered in the absence of any competing adsorption or reactions, which complicate the interpretation of experimental results. Further, the interaction between these adsorbed species, in particular between adsorbed or near-surface alkali metal cations and hydrogen, hydroxide, oxygen, and water can be explicitly and independently evaluated, which cannot be done through experiment alone.

1.3. Hypothesis and Research Objectives

Previous experimental studies show that alkali metal cations, present in an alkaline electrolyte, effect the rate and mechanism of many electrochemical reactions and support the general hypothesis that they sit close to the electrode surface and either block surface reaction sites, affect the binding strength of reactive intermediates, and/or effect the energy of reaction transition states, directly altering activation energies and rates of electrocatalytic reactions.

Using a combined computational and experimental approach, the following research questions and specific hypotheses will be evaluated:

1) Under what conditions (ion concentration, pH, electrochemical potential) is the specific adsorption of alkali metal cations to metal electrodes favorable? Hypothesis: At low
potentials and high electrolyte pH, alkali metal cations will specifically adsorb to some transition metal electrodes (within the electrochemical window of water).

2) If specific adsorption of alkali metal cations is favorable, does the specifically adsorbed cation interact with common reaction intermediates, such as adsorbed hydrogen or adsorbed hydroxide? Does this explain the experimentally observed effects of pH on cyclic voltammograms measured on Pt(110) and Pt(100) electrodes? *Hypothesis: The specifically adsorbed cation either weakens hydroxide adsorption or strengthens hydrogen adsorption, which would explain the experimentally observed effects of pH on the cyclic voltammograms.*

3) Does hydroxide competitively adsorb with hydrogen on along the steps of stepped platinum surfaces, similar to that seen/suggested on Pt(100) and Pt(110)? *Hypothesis: The stronger binding of both hydrogen and hydroxide to Pt steps due to their lower coordination relative to surface atoms on Pt(111) drives adsorption of both species to be competitive and favorable at low potentials.*

4) How does adsorption of hydrogen, hydroxide, oxygen, and alkali cations on the low index platinum facets effect platinum electrode stability as a function of pH and electrochemical potential? *Hypothesis: The strong binding of hydrogen and hydroxide on to Pt(110) and Pt(100) surfaces drives these surfaces to be comparable in stability/surface energy to that of the Pt(111) surface (which has the lowest surface energy in the absence of adsorption).*

5) If the alkali metal cation mediates the effect of pH, is the rate of the hydrogen oxidation reaction dependent on the identity of the alkali metal cation present in an alkaline electrolyte? *Hypothesis: As the adsorption of H* and OH* appear to be both pH and alkali cation dependent, and may be reactive intermediates in the hydrogen oxidation
reaction, the rate of the hydrogen oxidation reaction will depend on the alkali metal cation present in an alkaline electrolyte.

To answer these research questions, density functional theory modeling will be used to examine alkali metal cation specific adsorption to metal surfaces, the adsorption of hydrogen and hydroxide to Pt surfaces, and the effect of alkali metal cations on hydrogen and hydroxide adsorption. Experiments will be performed the measure the effect of the identity of the alkali metal cation on the rate of the hydrogen oxidation reaction.

1.4. Computational Methods

Density functional theory (DFT) is a computational tool that can be used to calculate the ground state energy and electronic structure of a set of atoms, based on their nuclear coordinates. Forces between atoms can be calculated and these forces can be minimized to find the (local) minimum energy ground state structure (geometry optimization) or can be used to propagate the motion of these atoms through space and time at a finite, non-zero temperature (ab initio molecular dynamics). Further, various techniques have been developed to explore the DFT calculated potential energy surface near a particular state or structure (including the nudged elastic band and dimer methods). This allows for the identification of saddle points in the potential energy surface, corresponding to activation energy barriers between reactant and product states at local minima in energy. DFT is therefore a powerful tool useful for studying many phenomena branching many fields, including studying the thermodynamics, kinetics, and mechanisms of chemical and catalytic reactions.
1.4.1. Density Functional Theory

Calculating the ground state energy of a set of atoms involves understanding the interactions between the nuclei, between the electrons, and between the electrons and nuclei. Given that the electrons are significantly lighter (and respond to changes in their environment faster) than most nuclei, the problem can be simplified to finding the energy of the system at a fixed set of nuclei positions, called the Born-Oppenheimer approximation. To optimize the nuclear positions, forces between the atoms can be calculated, the nuclei positions moved to minimize the force, and the ground state energy re-calculated. This process can be repeated until some convergence criteria, for example, on the forces between the atoms, or on the total system energy, are met. For a system of electrons and nuclei, the energy of the system cannot be calculated using classical (Newtonian) mechanics, as the system exhibits quantum behavior. Calculating the ground state energy requires using quantum mechanics, through solving the Schrödinger wave equation.

The time-independent Schrödinger wave equation, shown in Equation 1, is an eigenvalue equation relating the Hamiltonian \((H)\), containing all of the interactions acting on the electrons, to the total ground state energy \((E)\) and the electron wave function \(\psi\), the eigenstates of the Hamiltonian.

\[
H \psi = E \psi \quad [1]
\]

The electron wave function defines all of the properties of the electrons in a given system; for a single electron wave function, the squared modulus of the wave function \((|\psi|^2)\) represents the probability density of finding the electron within a given physical space (volume). Equation 1 can be written more explicitly by defining the interactions in the Hamiltonian; shown in Equation 2 for a set of atoms with fixed nuclear coordinates:
\[
\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 + \sum_{r=1}^{N} \sum_{\alpha=1}^{M} \frac{Z_\alpha}{r_i} + \sum_{i=1}^{N} \sum_{j<i}^{N} \frac{1}{|r_j - r_i|} = E\psi,
\]

where the first term corresponds to the kinetic energy of each electron \(i\) (of \(N\) total electrons) with mass, \(m\) (with \(\hbar\) the Planck constant); the second term corresponds to the electrostatic interaction between nuclei \(\alpha\) (of \(M\) total nuclei) with charge \(Z_\alpha\) and each electron at position \(r_i\); and the last term in the Hamiltonian corresponds to the electrostatic interaction between each of the electrons. Solving the Schrödinger wave equation requires finding the wave function and corresponding ground state energy which satisfy Equation 2. The wave function \(\psi\) can be approximated as a product of individual, single electron wave functions, \(\psi = \psi_1(r)\psi_2(r) \ldots \psi_N(r)\), and is therefore a function of all of the electronic coordinates, \(r_i\). This means that even for a very small system, the complete wave function is multidimensional, with three 3 dimensions for each electron. For example, for a small molecule like water (H\(_2\)O) with 10 electrons, the wave function is a 30-dimensional function, and for a platinum cluster with 100 atoms, the wave function is a 23,400-dimensional function. Given the many-body nature of the problem, where the wave function of any individual electron depends on that of all the other electrons, finding an approximate solution to the Schrödinger wave equation, even for small systems, requires significant computational resources. An exact, analytical solution to the Schrödinger wave equation is known only for systems containing a single electron. The density functional theory method provides a means to approximate a solution to the ground state energy and wave function, with a significantly reduced computational intensity.

Only the central ideas outlining the density functional theory method are described here, for a more thorough and practical introduction, the reader is referred to the DFT textbook by D. Sholl and J. Steckel\(^{68}\).

The underlying principle behind the density functional theory method is that the Schrödinger wave equation can be restated, from depending on the position of every single
electron, to instead depending only on the total charge density of all of the electrons at a given position in space. This restatement can be made as a result of the Hohenberg-Kohn theorems\textsuperscript{69}, which state that the ground state energy is a unique functional of the charge density, and that the density which minimizes the total energy is the exact ground state charge density.

To apply the Hohenberg-Kohn theorems, the ground state density is obtained using the Kohn-Sham equations\textsuperscript{70}, which only explicitly involve a single electron:

$$\left[ -\frac{1}{2} \nabla^2 + V_{NE}(r) + V_H(r) + V_{XC}(r) \right] \phi_i(r) = \epsilon_i \phi_i(r) \text{ and } \rho(r) = \sum_{i=1}^{N} |\phi_i(r)|^2 . \quad [3]$$

The first term in the Hamiltonian on the left hand side corresponds to the kinetic energy, the second term to the potential which defines the electrostatic interaction between the nuclei and electrons, the third term to the Hartree potential, which defines the electrostatic interaction between a single electron ($i$) and the total electron density defined by all of the electrons ($\rho(r)$), and the last term to the electron exchange and correlation potential. $\rho(r)$ is the total charge density.

The electron exchange and correlation potential is defined as a functional derivative of the exchange and correlation energy. While Equation 3 gives an exact solution of the ground state energy, the functional form of the exchange and correlation (XC) functional is unknown. It contains contributions from electron exchange, which is a quantum property requiring the wave function to be anti-symmetric (commonly referred to as the Pauli exclusion principle), as well as electron correlation, which arises from electrons being able to correlate their motion, which was lost when the Schrodinger equation was reframed to depend only on the charge density and not the explicit all electron wave function. The exchange and correlation functional additionally contains a correction to a “self-interaction” error present in the Hartree potential; the $i^{th}$ electron is present in the total charge density, so the Hartree potential includes an interaction between the $i^{th}$ electron and itself. Approximate exchange and correlation functionals are typically defined as
functions of the known exchange and correlation potential of the uniform electron gas (where the
electron density is constant through all space); local density approximation (LDA) functionals use
only the local charge density to calculate the exchange and correlation potential, and gradient
density approximation functionals (GGA) additionally use the gradient of the density.

Even with the only approximate exchange and correlation functional, DFT has proven to
provide an effective combination of accuracy and computational efficiency⁷¹, significantly
reducing the computational intensity of finding an approximate solution of the Schrödinger wave
equation for multi-electron systems. DFT provides a means to calculate the energy of and
minimize the forces between a set of atoms, useful for studying the structural, chemical, and
electronic properties of diverse materials. It has seen widespread use in studying catalysis, where
reaction rates and mechanisms can be predicted and identified to better understand experimental
measurements, as well as in predicting the behavior of new catalyst materials, which have never
before been tested experimentally⁷¹.

1.4.2. *Ab Initio* Thermodynamics

To calculate thermodynamics for adsorption and reaction during heterogeneous
(electro)catalysis, the energy of gas phase molecules/atoms, solution phase molecules, atoms, and
ions, and the energy of these species adsorbed on various electrically conductive surfaces
(catalytic electrode) are needed. More specifically, the Gibbs free energies of these species are
typically most important, as changes in free energy indicate the spontaneity of a reaction (and
reaction equilibrium conditions) and these changes can be directly related to the electrochemical
potential which can be measured or controlled experimentally. To calculate a Gibbs free energy,
statistical mechanics is needed to extend the energies calculated with DFT in vacuum at 0K (from
The Gibbs free energy of any given state is defined as:

\[ G(T, P) = U + pV - TS, \]  

where \( T \) and \( P \) are the temperature and pressure, \( U \) is the internal energy, \( V \) the volume, and \( S \) the entropy. The internal energy can be further decomposed to yield Equation 5:

\[ G(T, P) = E^{DFT} + ZPVE + E^{int} + pV - TS, \]

where \( E^{DFT} \) is the DFT energy of the system (at 0K), \( ZPVE \) is the zero point vibrational energy, and \( E^{int} \) the translational, rotational, and vibrational energy at the temperature of interest. The entropy includes translational, rotational, and vibrational entropy. For a gas phase species, statistical mechanics relations can be used to directly calculate the zero-point energy and the translational, rotational, and vibrational energy and entropy contributions to the free energy. For a neutral liquid phase species, the free energy can be most easily be calculated by calculating the free energy of the species in the gas phase at a pressure equal to its vapor pressure at the temperature of interest. For an ionic solution phase species, its free energy can be most easily calculated by either, calculating the free energy of the ion in the gas phase, then adding on an experimentally measured solvation energy (or a solvation energy calculated with a continuum solvation model) or by calculating the free energy of a neutral species and using an experimentally measured electrochemical potential where the neutral species and ionic species are in equilibrium (such as in the computational hydrogen electrode method\textsuperscript{72}, where the potential in which aqueous phase protons and gas phase hydrogen at standard state are in equilibrium is defined to be exactly 0 V\textsubscript{NHE}). Finally, for an adsorption reaction (or reaction on the electrode surface), the free energy of the adsorbate is most conveniently calculated by assuming it only retains vibrational energy and entropy (with complete loss of translation and rotational degrees of freedom), and that the vibrational energy and entropy of the surface are un-perturbed by the
presence of the adsorbate, such that the free energy of the bare surface is simply the DFT 0K energy ($E^{DFT}$).

### 1.4.3. Solvation Near the Electrode Surface

Of particular importance in modeling electrocatalytic reactions is the inclusion of the effects of the presence of electrolyte (solvent+ions) near the electrode surface, which may affect the binding strength of spectator species and reactive intermediates as well as the activation energy of elementary steps for electrocatalytic reactions. In the case of aqueous or hydrated polymer electrolytes, this involves capturing the behavior of water and the distribution of ions near the electrode surface. The behavior of water, namely its ability to screen charge on or near the electrode surface and to hydrogen bond with species adsorbed on the surface, is dependent on both its local and long-range structure (governed by hydrogen bonding) as well as its dynamic motion. This long range structure and the dynamic motion of water as well as the long range structure of the distribution of ions near the electrode surface are difficult to capture with density functional theory, as the computational intensity limits the length and time scales over which simulations can be performed. This means the effects of electrolyte near the electrode surface must be approximated.

While solvation of a species (ion, atom, molecule) in the bulk solution is also certainly important, in many cases thermodynamic cycles can be used which obviate the need to explicitly calculate with DFT the energy of a solution phase species. For example, the free energy of an aqueous phase proton can be calculated using the computational hydrogen electrode method\textsuperscript{72}, and the free energy of a water molecule in liquid water can be calculated by finding the free energy of a water molecule in the gas phase at the partial pressure in which water in the gas phase is in equilibrium with that in solution, such that the difference in free energy between the two
There are many methods which can be used to approximate the effects of solvation, in bulk solution or near an electrode surface, but they can be grouped into two main categories, implicit solvation models and explicit solvation models. With an implicit solvation model, the effect of solvation is approximated by placing the species of interest (solution phase ion, atom, molecule, or electrode surface) in a continuum dielectric (with a dielectric constant equal to that of the bulk solvent), and evaluating the interaction of that dielectric with the electron density at/near the surface of the species of interest. For a more thorough discussion, see Cramer and Truhlar. An explicit solvation model involves placing explicit solvent molecules near the species of interest and modeling the energy and geometry of the solvent molecules with density functional theory.

Both implicit and explicit solvation models represent an approximation to the “real” solvation environment and both have advantages and disadvantages. Implicit solvation models, while relatively computationally inexpensive, typically require some parameter to be fit against experimentally measured solvation energies, as the variation in the dielectric constant of the solvent near a solution phase species or surface is typically not known a priori. Though many implicit solvent models can accurately capture bulk solution solvation energies, it is unclear whether these models alone will be able to, for example, capture the effects of hydrogen bonding to an adsorbate on an electrode surface. While explicit solvent methods do not require any fitting, the computational intensity of density functional theory puts strict limits on the length and time scales over which the behavior of the explicit solvent can be examined; a small number of explicit solvent molecules examined in a static structure or dynamically over only a short period of time may not accurately reproduce the behavior of the real solvent. Even with a static explicit solvent structure, density functional theory is only guaranteed to find a local minimum energy structure, not a global minimum. Further, to capture the free energy of the static explicit solvent, the
vibrational, translational, rotational, and configurational entropy must be accounted for, which is non-trivial to calculate for solvent near an electrode surface.

While this paints a bleak picture for accurately capturing the effects of solvation with density functional theory using an explicit solvation model, fortunately, only differences in free energy, and therefore differences in entropy (and enthalpy), are important. Capturing the effects of solvent near the electrode-electrolyte interface on adsorption or on activation energies using a static, explicit solvent, therefore only requires assuming the entropy of the solvent is relatively un-perturbed by the presence of the adsorbate or during transition state.

A variety of explicit solvation methods have been developed, typically using known minimum energy water structures. For example, a water bilayer (water molecules arranged in a continuous hydrogen bonded hexameric structure\textsuperscript{76}) has been used to solvate adsorbates as well as reaction transition states on a variety of 111 transition metal surfaces, including hydrogen adsorbed on Pt(111)\textsuperscript{77} and adsorbed oxygen species on Pt(111)\textsuperscript{78}. The double reference method uses a larger static solvent minimum energy structure, filling the vacuum region above the surface with a minimum energy structure mimicking the 3 dimensional structure of ice\textsuperscript{79} and has been used, for example, to examine methanol oxidation\textsuperscript{80} and the adsorption of hydrogen, hydroxide, and oxygen to Pt(111)\textsuperscript{81}. Individual or small clusters of solvent molecules have also been used\textsuperscript{82-84} to approximate the effects of solvation on adsorption and reaction on many transition metal surfaces.

1.4.4. Near Surface Electric Field

Related to the effects of solvent near the electrode surface are the effects of the near-surface electric field, which is partially screened by the electrolyte near the electrode surface (through the double layer). The thermodynamics of adsorption or reaction to or on the surface can
be corrected, to a first order approximation, for the energy of interaction of the near surface electric field with the dipole moment generated on adsorption or reaction (which can be calculated using density functional theory). The electric field near the surface can be calculated by dividing the potential drop across the double layer (typically taken as the electrode potential of interest) by the double layer thickness (typically approximated as 3 Å). A second order approximation amounts to calculating the polarizability of the surface-adsorbate bond, and can be calculated using DFT by applying an electric field normal to the electrode surface. For simple adsorbates, such as hydrogen, both the dipole moment and applied electric field have a negligible effect on the adsorption thermodynamics. This effect may be larger (non-negligible) with a more charged adsorbate (creating a larger surface normal dipole moment) or more polarizable surface-adsorbate bond. The structure of electrolyte near the electrode-electrolyte interface may also be affected by the near-surface electric field.

1.5 Experimental Methods

To better understand the effects of pH and alkali metal cations on the electrode-electrolyte interface, it is useful to compare density functional theory calculations with the experimentally measured effects. One of the more powerful types of electrochemistry techniques are voltammetric techniques, where the voltage of the working electrode, the electrode of interest, is controlled, and the response in current is measured. Controlling the potential sets one of the thermodynamic variables, the energy of the electron, which is as a reactant (product) in an electrochemical reduction (oxidation) reaction. The measured current indicates the rate of the reaction. For a thorough discussion of the behavior of the electrochemical environment and the many types of electrochemistry techniques, the reader is referred to Bard and Faulkner.

Linear sweep and cyclic voltammetry are two of the more common voltammetric
techniques used to study electrochemical reactions. In both linear sweep and cyclic voltammetry, the potential is varied linearly at some constant scan rate; in linear sweep voltammetry, this is carried out from low to high or high to low potential, in cyclic voltammetry, the potential is continuously cycled from low to high or high to low potential. Cyclic voltammetry is particularly useful for studying electrocatalysis, as both the adsorption of reactive species, as well as continuous catalytic reactions, can be examined. For an ion adsorption reaction, the location of a cyclic voltammetric peak in current indicates the potential where adsorption (or desorption in the backwards cycle) is favorable, and can be readily converted to a Gibbs free energy change for adsorption. For a fast adsorption reaction, the shape of a peak in a cyclic voltammogram is dictated by the interactions between adsorbates on the surface; a broad peak typically indicates repulsive interactions (as a greater change in potential is required to drive changes in coverage) and a narrow peak, attractive interactions. For a slow adsorption reaction, the shape of the peak, in particular, the asymmetry of the peak across the y-axis (zero current), is correlated with the rate of the adsorption reaction. A slower reaction drives a greater separation between the location of the adsorption peak and the desorption peak, as more time is required (which for a fixed scan rate means a greater change in potential) for the same coverage of species to adsorb/desorb.

For the study of a continuous electrocatalytic reaction (such as hydrogen oxidation), hydrogen gas can be dissolved in the electrolyte, and a linear sweep or cyclic voltammogram measured about the equilibrium potential for the reaction. The relationship between current and voltage near the equilibrium potential is dependent on the intrinsic catalytic activity, a more active catalyst will give a higher rate (current) for a small change in potential near the equilibrium potential (where the total rate is zero) and a less active catalyst will give only a small change in current. In the absence of mass transport limitations, the current-voltage response typically exhibits an exponential relationship, following the Butler-Volmer equation. Extrapolating the measured current to the equilibrium potential allows the exchange current density to be
calculated, representing the rate of the forward or backward reactions at this potential (which sum to zero); this can be used to represent the intrinsic catalytic activity of the electrode.

The exchange current density only represents the true intrinsic kinetics if mass transport does not limit the reaction rate near the equilibrium potential or if the effects of mass transport can be corrected. For reactants which have low solubility in the electrolyte solution (such as hydrogen gas), measuring the rate free from mass transport limitations on a stationary electrode can be difficult. In this case, a rotating disk electrode can be used in an electrolyte saturated with the reactant. This electrode exhibits well-defined mass transport, such that the effect of mass transport on the reaction rate can be calculated by varying the rotational speed (and therefore the rate of mass transfer), and used to correct the measured rate. Reactions which are very fast and have reactants with low solubility may require a higher rate of mass transport than that provided by the rotating disk electrode; for example, hydrogen oxidation in an acid electrolyte on Pt can only be measured on supported Pt nanoparticles at low loading or in an operating PEM fuel cell, where transport of hydrogen gas to well dispersed Pt nanoparticles has been optimized.

Performing these voltammetric measurements requires the use of a three electrode cell. A three electrode cell allows the potential of the working electrode, the electrode of interest, to be independently controlled. In a two electrode cell, the potential difference between the two electrodes is dependent on the current and the nature of the reactions occurring on both electrodes. By adding a reference electrode, which maintains a constant, preferably known potential, and through which no current flows (such that it maintains a constant potential), the potential of the working electrode can be measured and controlled relative to that of the reference electrode (and independently of the counter electrode). Reference electrodes are typically constructed such that a very fast or very stable reaction occurs at the electrode surface; so long as no current flows through the reference electrode, this reaction remains at equilibrium; its equilibrium potential determining the potential of the reference electrode.
1.6. Summary of Chapters

This dissertation investigates the mechanism by which pH and alkali cations effect the adsorption of hydrogen, hydroxide, and water; reactive intermediates in many electrocatalytic reactions, as well as the rate of the hydrogen oxidation reaction. Chapters 2 and 3 report the investigation of the thermodynamics of alkali metal cation specific adsorption to metal electrode surfaces and of halide specific adsorption onto copper electrode surfaces using density functional theory. Adsorption of the alkali metal cations is favorable and competitive with hydrogen adsorption under conditions of low potential and high electrolyte pH on Pt(111) and Pd(111). On adsorption, these alkali cations retain some of their charge (contributing to the difficulty in observing alkali cation specific adsorption experimentally with cyclic voltammetry) and interact strongly with water near the electrode surface; this could affect the adsorption of reaction intermediates or activation barriers for reactions which occur under these conditions (such as hydrogen oxidation/evolution and CO2 electroreduction). Chapter 3 illustrates that adsorption of Cl, Br, and I anions are favorable at relatively low potentials on copper electrodes (Cu(111), Cu(100), Cu(211), which could affect reactions at low potentials on these surfaces; recent experimental evidence has shown the rate and product selectivity of CO2 electroreduction is halide anion dependent.

Chapters 2 and 3 additionally examine various methods of referencing the free energy of an aqueous phase ion (using experimentally measured dissolution potentials or solvation energies) and of approximating the effect of near-surface solvation (presence of electrolyte near the electrode surface) on adsorption thermodynamics using explicit water molecules. The use of a local minimum energy water structure, with a small number of water molecules, is found to reproduce the effect of solvation given by an ice-like minimum energy water structure with significantly more water molecules, reducing the computational intensity required to examine
solvation effects. Near-surface water significantly promotes the adsorption of these cations to more positive potentials (by ~ 1 V), as they retain some of their positive charge. In contrast, the halide anions, in general, adsorb neutrally to copper electrode surfaces, and show only a minor interaction with near surface water. Understanding what dictates the effect of near surface solvation is important for determining when it can be safely neglected (to reduce computational expense) and when it cannot.

Chapter 4 explores the effects of pH and alkali metal cations on hydrogen, hydroxide, and water adsorption onto the low index facets of platinum, Pt(111), Pt(100), and Pt(110). Experimental measurements have shown previously that the sharp peak in current measured by cyclic voltammetry at low potentials on Pt(110)\textsuperscript{40, 53}, and the broad peak on Pt(100)\textsuperscript{54} shift to more positive potentials on a relative hydrogen electrode scale with increasing pH, but the cause for this was unknown. The results show that alkali metal cation adsorption is favorable on all three low index Pt facets, and once on the surface, the alkali cations exhibit a small interaction with co-adsorbed hydrogen and a significant weakening of hydroxide adsorption. The cations retain some of their charge on adsorption and disrupt the OH* - H\textsubscript{2}O* hydrogen bonding network. This effect increases with increasing cation coverage, which is expected on increasing the electrolyte pH (as the adsorption of H* and OH* are shifted to lower potentials, further into the region where alkali cation adsorption is favorable, with increasing pH). This low potential peak measured by cyclic voltammetry corresponds to the competitive adsorption of H* and OH* on Pt(100) and Pt(110), and shifts to more positive potentials with increasing pH due to the cation induced weakening of hydroxide adsorption. Understanding the shift in these peaks is important as their shift is correlated with the pH dependence of the hydrogen oxidation reaction\textsuperscript{13}.

Chapter 5 extends the work performed in Chapter 4 to stepped platinum surfaces, examining alkali metal cation, hydrogen, hydroxide, and water adsorption on the 110 type steps of Pt(553) and the 100 type steps of Pt(533) as well as hydrogen adsorption on the 111-like
terraces of Pt(553) and Pt(533). The strong binding of hydrogen and hydroxide along the step results in their competitive adsorption (on both types of steps), which has been proposed previously\textsuperscript{51, 56}. Alkali metal cation adsorption is very favorable along the step (such that cations may be adsorbed even in intermediate to low pH electrolytes), and similar to the low index facets, weakens hydroxide and water co-adsorbed along the step. Cyclic voltammograms were simulated using the density functional theory results and compared directly to experiment, showing agreement both in acid (in the absence of a co-adsorbed alkali metal cation) and base (in the presence of an alkali cation). The experimentally measured location of the sharp, step associated peaks, corresponding to competitive H*/OH* adsorption along the step, and the broad peak, corresponding to repulsive hydrogen adsorption along the terrace, in both acidic and basic electrolytes, are described well with density functional theory.

Chapter 6 uses the results of Chapter 4 and Chapter 5 to develop a method to deconvolute experimentally measured cyclic voltammograms on polycrystalline platinum electrodes. Hydrogen and hydroxide competitive adsorption along 110 and 100 steps of stepped, single crystal Pt surfaces are relatively independent of the width of the terrace and the locations of the sharp peaks measured by cyclic voltammetry on these single crystal surfaces match those measured on polycrystalline or nanoparticle platinum. Arbitrary functions (Gaussian) can be fit to these sharp, step associated peaks, and to the broad terrace associated peak (hyperbolic cosine) such that the contributions to the cyclic voltammogram in the low potential region (0-0.5 V\textsubscript{RHE}) can be deconvoluted. These functions can then be integrated and the total charge transferred in each peak calculated, to estimate the total number or total surface area of 110 and 100 step sites as well as 111 terrace sites. This is an improvement over the traditional “H-UPD” method used to calculate the electrochemically active surface area of an electrode (an accurate measure of which is necessary to properly compare intrinsic catalytic activity across catalysts), which may over-count step sites and include contributions from hydrogen evolution or oxidation at low potentials.
This method however has only been validated for surfaces comprised predominately of 111-like terraces. As hydrogen and hydroxide adsorption on other terraces and types of step sites may overlap with these features, it may not be possible to perform this deconvolution for all rough Pt electrodes.

Chapter 7 uses the energetics calculated with DFT for the adsorption of hydrogen, hydroxide and water, and alkali metal cations on the low index Pt facets in Chapter 4 and new calculations examining oxygen adsorption (in the absence and presence of an alkali cation) and surface oxide formation to calculate the surface energy of Pt(111), Pt(100), and Pt(110) in acid and alkaline electrolytes as a function of electrochemical potential, spanning the electrochemical window of water, from low potentials (near 0 V RHE) to high potentials (near 1-1.3 V RHE). These surface energies define the stability of platinum nanoparticles as well as platinum surface faceting/structure in an aqueous, electrochemical environment. While the Pt(111) surface is the most stable surface in vacuum (with no adsorbates), Pt(100) and Pt(110) become more stable in the electrochemical environment at low potentials where hydrogen adsorbs to high coverage, and high potentials where hydroxide and water or oxygen adsorb. The calculated surface energies are used to generate Wulff constructions, illustrating the lowest energy nanoparticle shapes and relative site fractions as a function of potential. The Wulff constructions and relative site fractions indicate how a Pt nanoparticle synthesized in an electrochemical environment may be faceted as a function of potential, or how a nanoparticle or polycrystalline Pt surface will restructure. These results are compared to the changes in surface site exposure seen on experimentally cycling a polycrystalline platinum electrode in an alkaline electrolyte to high potentials, where a surface oxide forms. A growth in 110 sites is seen, which is found to be the lowest energy surface at potentials where platinum surface oxide is reduced (0.7-0.9 V RHE). The calculated surface energies may also explain the growth of 100 sites seen on square wave cycling of spherical Pt nanoparticles to low potentials, as the 100 surface is lowest in energy at low potentials (near 0
In Chapter 8, both experiment and density functional theory are used to examine the specific adsorption of quaternary ammonium cations (tetramethylammonium, tetraethylammonium, tetrapropylammonium, and benzyltrimethylammonium) to platinum electrode surfaces. These cations are commonly used to impart ionic conductivity to polymers in hydroxide conducting membranes, for use in polymer alkaline fuel cells or electrolyzers. Experimentally measured cyclic voltammograms show that the presence of the quaternary ammonium cations significantly reduces the current measured in the low potential region (0-0.5 V_{\text{RHE}}) relative to voltammograms measured in 0.1 M KOH. This suggests the quaternary ammonium cations block surface sites at low potentials, with the fraction of surface sites blocked increasing with alkyl chain length (or presence of benzyl ring, with benzyltrimethylammonium blocking the most sites). The voltammogram deconvolution method outlined in Chapter 6 is used to identify that the quaternary ammonium cations block more 110 and 100 sites than 111 sites. Density functional theory results show that these quaternary ammonium cations specifically adsorb at low potentials in alkaline electrolytes, explaining how these cations block surface sites. van der Waals attraction between the cation and the surface contributes significantly to adsorption; while this drives cations with longer alkyl chains to adsorb more favorably, an opposite trend is seen in the effects of near surface solvation, where longer alkyl chains drive water further from the surface. This work suggests that shorter alkyl chain cations should be used (in polymer alkaline fuel cells) as they block fewer sites on the electrode surface, though additional study is needed to examine their effects on hydrogen oxidation or oxygen reduction (reactions important in hydrogen fuel cells). Experimental measurements additionally suggest these quaternary ammonium cations may oxidize on a Pt electrode at high potentials, which could limit their stability in an alkaline fuel cell.

In Chapter 9, a combined computational and experimental approach is used to examine
the effects of alkali metal cations on the rate of the hydrogen oxidation reaction in an alkaline electrolyte. In Chapters 4 and 5 the anomalous effects of pH on the thermodynamics of hydrogen and hydroxide adsorption, which are correlated with the pH dependence of the hydrogen oxidation reaction, are explained as a consequence of alkali metal cation specific adsorption and their subsequent weakening of hydroxide adsorption. In this chapter, the rate of the hydrogen oxidation reaction in an alkaline electrolyte is found (experimentally) to depend on the identity of the alkali cation that is present in the alkaline electrolyte, following the trend in activity Li > Na > K > Cs. Density functional theory is used to extend the work discussed in Chapter 4 to examine the specific adsorption of each of these cations on Pt(111), Pt(100), and Pt(110) and examine any differences between the cations in their effects on hydrogen adsorption and hydroxide adsorption. The adsorption strength of hydroxide, a proposed intermediate of the hydrogen oxidation reaction in alkaline electrolytes, on Pt(110), the most active low index Pt facet for hydrogen oxidation, is found to correlate with the experimentally measured rate, with Li showing the smallest weakening of hydroxide adsorption and the highest rate, and Cs showing the greatest weakening and the lowest rate. While the mechanism for the hydrogen oxidation reaction cannot be uniquely defined, this work highlights that the effect of the cations on the HOR rate cannot be captured by considering only the binding strength of hydrogen (which is relatively unaffected by the alkali cations).

Conclusions and recommendations for future work for further understanding the effects of pH, alkali metal cations, and organic cations on the rate and mechanism of the hydrogen oxidation reaction are given in Chapter 10.
1.7. References


33


Chapter 2

Alkali Cation Specific Adsorption onto fcc(111) Transition Metal Electrodes


*J.N.M. performed the DFT calculations without surface solvation, I.T.M. performed the DFT calculations with solvation, both contributed to writing the manuscript.

Abstract

The presence of alkali cations in electrolyte solutions is known to impact the rate of electrocatalytic reactions, though the mechanism of such impact is not conclusively determined. We use density functional theory (DFT) to examine the specific adsorption of alkali cations to fcc(111) electrode surfaces, as specific adsorption may block catalyst sites or otherwise impact surface catalytic chemistry. Solvation of the cation-metal surface structure was investigated using explicit water models. Computed equilibrium potentials for alkali cation adsorption suggest that alkali and alkaline earth cations will specifically adsorb onto Pt(111) and Pd(111) surfaces in the potential range of hydrogen oxidation and hydrogen evolution catalysis in alkaline solutions.

2.1. Introduction

The electrode/electrolyte interfacial structure affects electrocatalytic kinetics. The position of solvent molecules and the ion distribution near the electrode surface varies with electrode, solvent, ion identity and concentration, and electrode potential. At sufficiently polarized electrodes, ions may specifically adsorb, transferring charge and bonding directly with the electrode surface. Anion specific adsorption, particularly sulfate and sulfonate adsorption, has received much attention due to its relevance to proton exchange membrane fuel cells\textsuperscript{1-2}. Similarly,
organic cations used in anion exchange membrane fuel cells (AEMFC) could specifically adsorb
to electrode surfaces, blocking active sites and impacting catalytic activity. Cation specific
adsorption has seen limited investigation, but experimental evidence shows alkali and alkaline
earth metal cations in alkaline solutions effect the rates of oxygen reduction on Au and Pt\textsuperscript{3}, and
hydrogen and methanol oxidation on Pt\textsuperscript{4}, reactions important to fuel cell electrochemistry.
Hydrogen oxidation is proposed to be several orders of magnitude slower in an alkaline
environment than in an acidic environment\textsuperscript{5}. The mechanism of cation effects on kinetics may
vary between systems and reactions, and is generally not conclusively determined. The specific
adsorption of cations to the electrode surface may impact electrokinetic rates. Herein, we use
Density Functional Theory (DFT) to determine the favorability of alkali metal cation specific
adsorption onto close packed transition metal surfaces. This favorability is determined through a
DFT-calculated free energy of adsorption, and is compared to that of hydrogen adsorption on
each of the surfaces. Methods to approximate the effects of solvation on cation adsorption are
examined.

Alkali metal cations can specifically adsorb to metal electrode surfaces at low potentials,
and these specific interactions could impact the rates of electrochemical surface reactions.
Examining ion specific adsorption experimentally is difficult due to the complex nature of the
aqueous electrolyte-electrode interface; the adsorption of a species often occurs simultaneously
with the adsorption of protons or hydroxide or with a catalytic reaction. Continuum and atomistic
force-field modeling of the electrode-electrolyte interfacial structure has provided insight into
how ions are distributed at this interface\textsuperscript{6-9}. These models, however, cannot accurately describe
specific adsorption, where electron transfer between the ion and the electrode leads to direct
bonding. Quantum chemical methods, such as DFT, are necessary to examine the specific
bonding interactions between an ion and electrode surface. While anion adsorption has been well
studied, computationally\textsuperscript{2, 10-12}, spectroscopically\textsuperscript{13-16}, and microscopically\textsuperscript{17-18} cation specific
adsorption in electrochemical systems is not as extensively investigated.

If anion and cation adsorption can be separated from proton or hydroxide adsorption, a variety of experimental methods can be used to probe the adsorption. Vibrational spectroscopy has been used to examine sulfate\textsuperscript{13, 19}, acetate\textsuperscript{20-21}, and hydroxide\textsuperscript{15} adsorption and has, for example, helped elucidate the sulfate/bisulfate species and coverage adsorbed to a platinum electrode from an aqueous sulfuric acid solution\textsuperscript{19}. Scanning tunneling microscope (STM) imaging determined the structure of co-adsorbed anions and solvent water molecules on a Pt(111) surface in sulfuric acid solution\textsuperscript{17}. STM and surface X-ray scattering (SXS), along with traditional electrochemical techniques such as cyclic voltammetry, have elucidated the structure and favorability (F<Cl<Br<I) of halide adsorption on low index platinum surfaces\textsuperscript{18}. IR reflection-absorption spectroscopy and in-situ STM have been used to examine sulfate adsorption on a Au(111) electrode in aqueous perchloric-sulfuric acid electrolytes\textsuperscript{13}. While anion specific adsorption has received much attention, alkali metal cation adsorption has limited experimental evidence. Voltammetry and in-situ nano-gravimetry\textsuperscript{22} and electrochemical impedance spectroscopy\textsuperscript{23} show that Cs\textsuperscript{+} can specifically adsorb to polycrystalline platinum from dilute sulfuric acid-cesium sulfate solutions. Radiotracer studies support this result\textsuperscript{24}. Electrokinetic studies, with extensive contributions from Marković and co-workers, suggest that alkali metal cations, as well as anions, can have a strong effect on electrocatalytic reactions, whether the ion is near the electrode or adsorbed to its surface\textsuperscript{1, 3-4, 25}.

Halides\textsuperscript{26}, (bi)sulfate\textsuperscript{1}, and alkali metal cations\textsuperscript{3-4} in an electrolyte solution have been shown to affect the rate of electrocatalytic reactions. While the mechanistic cause for these effects, in many cases, is unknown, specific adsorption of these ionic species onto the electrode surface could play a role. Bisulfate/sulfate specific adsorption onto a platinum electrode exhibits a site blocking effect on the rate of oxygen reduction\textsuperscript{1}. Alkali metal cations can affect the rate of oxygen reduction, hydrogen oxidation, and methanol oxidation in alkaline electrolytes, and non-
specific interactions have been proposed to explain these effects. Lithium, potassium, and barium cations in an alkaline electrolyte affect the rate of oxygen reduction on platinum and gold (100) and (111) electrodes. Proposed mechanisms to explain the observed effect of alkali metal cation on HOR, ORR, and MeOR include the non-covalent interaction of solution phase, partially solvated cations with hydroxide adsorbed on the metal surface, but these cations, in a manner similar to the effect of anions on ORR, may also specifically adsorb to the electrode surface at low potentials. Specific adsorption could lead to site blocking effects or otherwise perturb the catalytic, electronic, or structural properties of the electrode.

DFT has been used to model anion adsorption onto various metal electrode surfaces, but, to our knowledge, no one has applied DFT methods to examine alkali cation specific adsorption in electrochemical systems. Our group as well as Jinnouchi and co-workers have used DFT to investigate bisulfate/sulfate adsorption onto platinum and create simulated linear sweep voltammograms of the adsorption process. The double reference method, a DFT approach developed in the Neurock group to approximate the effects of solvation and electrode potential within a DFT simulation, has been used to probe acetate and phosphate adsorption onto platinum electrodes. Many DFT methods have also been used to probe the adsorption of hydroxide onto a variety of metal surfaces.

Determining when cation adsorption is favorable gives insight into whether the specific adsorption of these cations could be responsible for, or contribute to, their effects on electrocatalytic kinetics. We use DFT to model the specific adsorption of H, Li, Na, K, Cs, and Ba cations onto fcc (111) transition metal surfaces. These cations are commonly used in alkaline electrolytes and represent a simpler model system, both computationally and experimentally, than an AEMFC’s organic cations. DFT calculations are used to estimate the equilibrium adsorption potentials of these ions. Capturing the ion-electrode adsorption properties is challenging due to the presence of both solvent and electric fields in the electrode-electrolyte interfacial region. We
use surface dipole/field interactions to approximate the electric field influence. The effects of solvation are approximated by including explicit, static water molecules near the electrode surface and adsorbates. The use of static water structures introduces an unknown error in representing solvation, and we examine a series of approaches to assess the variability introduced. A fully solvated and charged double-reference model is used for comparison. Our results suggest that alkali metal cations may specifically adsorb to Pt(111) and Pd(111) surfaces at low coverage near potentials where hydrogen oxidation occurs in high pH electrolytes.

2.2. Methods

Electronic structure calculations were performed using the Vienna ab initio Simulation Package, with a plane wave basis set and the Perdew-Wang (PW91) exchange-correction functional. The Projector Augmented Wave (PAW) approach was used to model core potentials. A 5x5x1 Monkhorst-Pack mesh was used to sample k-space. The cutoff energy for the plane-wave basis set was 450 eV and structural optimization was complete when forces on atoms were less than 0.02 eV Å⁻¹. Due to pseudo-slab interactions, dipole corrections were included in the surface normal direction (IDIPOL=3, LDIPOL=TRUE).

Experimental metal lattice constants were used, as given in Table 2-1. A 3x3 surface cell modeled the electrode surface, leading to a 1/9 monolayer adsorption of alkali metals. Surface slabs contained four layers of depth and the bottom two layers were frozen during optimization. Hollow sites were most favorable for adsorption for all cations on all of the surfaces considered, and the energy difference between hcp and fcc sites was negligible.
Table 2-1. Conventional cubic cell dimension used for fcc metals\textsuperscript{38}.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag(111)</td>
<td>4.09</td>
</tr>
<tr>
<td>Au(111)</td>
<td>4.08</td>
</tr>
<tr>
<td>Ni(111)</td>
<td>3.52</td>
</tr>
<tr>
<td>Pd(111)</td>
<td>3.89</td>
</tr>
<tr>
<td>Pt(111)</td>
<td>3.92</td>
</tr>
</tbody>
</table>

2.2.1. Calculating Cation Adsorption Equilibrium Potential

The specific adsorption process for a cation onto a metal surface can be written as a reaction:

\[
* + C^+_{aq} + e^- \rightarrow C^* \tag{1}
\]

where \( * \) represents the bare surface, \( C^+_{aq} \) the aqueous solvated cation, and \( C^* \) the adsorbed species. The Gibbs energy of adsorption as a function of electrode potential on an absolute potential scale, \( U_{abs} \), can be written as:

\[
\Delta G_{ads}(U_{abs}) = G_{C^*} - G_* - G_{C(aq)} + eU_{abs} \tag{2}
\]

where \( e \) represents the absolute value of the electron charge and \( G_x \) is the chemical potential of species \( x \). The free energy of the cation adsorbed to the surface \( G_{C^*} \) is calculated as:

\[
G_{C^*} = E_{C^*}^{DFT} + ZPVE - TS_{vib} \tag{3}
\]

where \( E_{C^*}^{DFT} \) is the DFT energy of the adsorbed cation system, \( ZPVE \) accounts for the zero point vibrational energy, and \( TS_{vib} \) is the vibrational entropy of the adsorbed species. The free energy of the bare surface \( G_* \) is approximated presuming adsorption does not alter the electrode entropy:

\[
G_* = E_{*}^{DFT} \tag{4}
\]
The cation free energy in aqueous alkaline solution is approximated by calculating the free energy of the cation in the gas phase and adding an experimentally measured solvation free energy for the cation in a 1 M solution ($\Delta G^0_{solvation}$):

$$G^*_{C_{aq}} = G^*_{C_{(g)}} + \Delta G^0_{solvation} \tag{5}.$$ 

The cation free energy in the gas phase, $G^*_{C_{(g)}}$, is calculated by adding a translational entropy correction ($-TS_{trans}$) at standard conditions to the DFT calculated energy:

$$G^*_{C_{(g)}} = E^*_{C_{(g)}} - TS_{trans} \tag{6}.$$ 

Solvation free energies are taken at standard conditions and, therefore, adsorption free energies are determined relative to 1 M concentrations of the cations in aqueous solutions. Adsorption free energies at other concentrations could be calculated provided activity corrections to the non-standard state are available.

Equations 1 and 2 express specific adsorption as occurring with a single electron transferred to form the adsorbed species. For most adsorption configurations considered, the cation retains a partial positive charge and a dipole moment is established in the surface normal direction. The free energy change of adsorption is corrected to include the interaction of this dipole moment with an interfacial electric field:

$$\Delta G_{ads}(U_{abs}) = G^*_C - G^*_0 - G^*_C + eU_{abs} + \frac{\mu_C - \mu_s}{d}(U_{abs} - U_{pzc}) \tag{7}$$

where $\mu_s$ is the dipole moment of the bare surface, $\mu_C$ is the dipole moment of the surface-cation system, $U_{pzc}$ is the electrode potential at zero charge, and $d$ is the distance between the electrode surface and the solution phase countercharge within an approximate, classical Helmholtz model. We use a $d$ value of 3 Å, consistent with that used by others within a concentrated electrolyte. This dipole correction effectively allows the adsorption to occur with
partial electron transfer. Equation 8, the derivative of $\Delta G_{ads}$ with respect to $U$, gives the net electron transfer upon adsorption:

$$\frac{d \Delta G_{ads}}{dU} = 1 + \frac{\mu_{C^*} - \mu_*}{d}$$

(8)

The equilibrium adsorption potential, $U^0_{abs}$, can be solved for by setting $\Delta G_{ads}$ to zero in equation 7:

$$U^0_{abs} = -G_{C^*} + G_* + G_{C^*} + U_{pzc} \left( \frac{\mu_{C^*} - \mu_*}{d} \right) + \frac{\mu_{C^*} - \mu_*}{d}$$

(9)

At potentials above $U^0_{abs}$, little cation specific adsorption would be expected. Potentials significantly below $U^0_{abs}$ would be expected to attain at least the $\frac{1}{9}$ ML coverage used in the DFT model.

The adsorption equilibrium potential can be shifted to the scale of a normal hydrogen electrode by using the conversion:

$$U^0_{NHE} = U^0_{abs} - 4.6 \text{ V}$$

(10)

The value of 4.6 V is consistent with that calculated by DFT methods and is in the experimental range of 4.4-4.8 V.

In this work, we take $U_{pzc}$ as zero on a NHE scale, consistent with the approach used by others when employing a similar model to examine surface adsorbate interactions. Equations 9 and 10 may be combined to give the cation equilibrium adsorption potential on a NHE scale as

$$U^0_{NHE} = \frac{-G_{C^*} + G_* + G_{C^*} + e + 4.6V}{e + \frac{\mu_{C^*} - \mu_*}{d}}$$

(11)

This method for calculation of $U^0_{NHE}$ neglects the additional stabilization of the adsorbed cation due to solvation, though cation solvation in the bulk electrolyte phase is included in the $\Delta G^0_{solvation}$ value. The non-solvated $U^0_{NHE}$ value is, therefore, expected to provide a minimum adsorption equilibrium potential, with solvation stabilization pushing adsorption to higher potentials.
2.2.2. Surface Solvation

To examine the potential impact of surface cation solvation, we evaluate the Gibbs free energy change of adsorption for H\(^+\), Na\(^+\), and Ba\(^{+2}\) cations onto a Pt(111) surface with solvation provided by a varying number of explicit water molecules. We chose the Pt(111) surface due to the relevance of Pt to fuel cell catalysis and because our non-solvated results suggest Pt will show the greatest competition between H\(^+\) and alkali cations for adsorption sites. To include solvation, equation 1 for the cation adsorption process can be rewritten as:

\[
(H_2O)_n^* + C_{aq}^+ + e^- \rightarrow C(H_2O)_n^*
\]  

where \((H_2O)_n^*\) represents the surface with \(n\) H\(_2\)O molecules adsorbed and \(C(H_2O)_n^*\) represents the cation adsorbed and solvated by \(n\) H\(_2\)O molecules. Were we able to represent both surface structures with a dynamic ensemble of H\(_2\)O structures that allowed explicit determination of the free energy change due to cation addition, an exact free energy change for equation 12 could be determined. We, however, resort to using a static H\(_2\)O structure due to computational requirements of DFT. This leaves open a question as to whether the static structure of \(n\) H\(_2\)O molecules, in their configuration either before or after C\(^*\) addition, is a true representation of the dynamic ensemble.

For all solvation calculations, the structure of \(C(H_2O)_n^*\) was generated by sequentially adding more water molecules to a structure optimized with \(n-1\) H\(_2\)O molecules. Multiple local minimum energy structures were calculated, with the lowest energy structure reported. Despite this approach, it is not possible to assure that a global minimum energy structure is reached once even a few water molecules are included. We attempted to perform a reasonable extent of local minima sampling and to assure consistency between cations. For \((H_2O)_n^*\), we evaluated three alternatives for determining their static energy as described below.

With solvation included, equation 7 may be rewritten as
\[
\Delta G_{ads}(U_{abs}) = G_{C(H_2O)_n^*} - G_{(H_2O)_n^*} - G_{C^+} + eU_{abs} + \frac{\mu_{C^*} - \mu_*}{d}(U_{abs} - U_{pzc})
\]  (13)

where \( G_{C(H_2O)_n^*} \) is the free energy of the cation adsorbed on the Pt(111) surface with \( n \) H\(_2\)O molecules and \( G_{(H_2O)_n^*} \) is the free energy of \( n \) H\(_2\)O molecules adsorbed on the Pt(111) surface prior to cation addition. Dipole moments now represent the values for the solvated cation system and the \((H_2O)_n^*\) systems. These two free energy values are calculated similarly to equation 3, but include the harmonic vibrational degrees of freedom of the adsorbed water molecules in the entropy and ZPVE corrections. Three methods were compared for referencing the initial energy of the explicit water molecules. The fixed water method kept the water molecules in the \((H_2O)_n^*\) structure fixed at their optimal positions in the \(C(H_2O)_n^*\) structure while removing the cation. This un-relaxed initial state is likely un-physically high in energy. A relaxed water approach used a relaxed initial water state, attempting to represent the minimum energy structure of \( n \) static H\(_2\)O molecules on the Pt(111) surface. The relaxed water method is identical to the fixed water method except the water molecules adsorbed near the platinum surface are relaxed after the cation has been removed, to yield the initial solvated surface energy.

A third method referenced the \((H_2O)_n^*\) Gibbs free energy as that of \( n \) water molecules in the gas phase at 300K at the vapor pressure above an aqueous solution together with a bare surface. The free energy of gas phase water was calculated by equation 14,

\[
G_{H_2O(g)} = E^{DFT}_{H_2O(g)} + ZPVE - TS_{tot}
\]  (14)

where \( E^{DFT}_{H_2O(g)} \) is the DFT calculated energy of a single water molecule in the gas phase and \( S_{tot} \) includes entropy corrections to account for the water molecule’s internal vibrational, rotational, and translational entropy. Using this reference, the adsorption free energy calculated via equation 13 also embeds the interaction energies of water with Pt(111) and each other, relative to the free energy of bulk phase water molecules.

To compare with these three methods, the surface-adsorbate bond was also modeled in a
fully solvated state using the double-reference method. 24 water molecules were placed between the periodic platinum slabs, completely filling the vacuum region between the slabs at a density of 0.86 g/cm$^3$ and optimized to form an ice-like structure. To investigate the adsorption of a cation, a water molecule was removed near the surface and replaced with a cation. The cell was then charged using a varying number of electrons to adjust the potential within the cell; the potential of an inserted vacuum region and that of the water region are used as the two references to determine the electrode potential as a function of the added charge. The equilibrium adsorption potential can be calculated similarly to equation 12, with 24 water molecules in the reactant state and a single bulk phase water free energy added to the final 23 water-cation state Gibbs free energy. With the double-reference method, the free energy of each state becomes potential dependent, and the interaction of the adsorbate with the interfacial field arises from electrode charging (and balancing homogeneous countercharge) rather than being added with the approximate dipole interaction. This allows for the effects of solvation and the effects of electrode potential to be accounted for in the cation adsorption process.

### 2.3. Results and Discussion

Table 2-2 reports the DFT calculated cation adsorption equilibrium potentials for the alkali and Ba$^{2+}$ cations to fcc(111) surfaces on the NHE scale. These values were calculated without including ion solvation at the electrode surface, and as such, should be considered minimum values with adsorption possibly occurring at potentials more positive to these values due to solvation stabilization. Tables S2-1 and S2-2 in supplementary information include the DFT energies for each structure as well as the corrections for ZPVE, entropy and aqueous cation solvation. Table 2-3 reports the experimental free energies of solvation for each cation at standard
state. These values range from -2.67 eV for Cs\(^+\) to -13.0 eV for Ba\(^{2+}\), clearly confirming that cation solvation must be considered. Table S2-2 lists the entropy corrections for gas phase ions which range from 0.197 to 0.529 eV.

Table 2-2. Cation adsorption equilibrium potentials to fcc (111) electrode surfaces, \(U^0[V - NHE]\) calculated using DFT methods and equation 11.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Pt</th>
<th>Pd</th>
<th>Ni</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>-0.07</td>
<td>-1.30</td>
<td>-0.90</td>
<td>-0.98</td>
<td>-0.80</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>0.09</td>
<td>-1.63</td>
<td>-1.19</td>
<td>-1.35</td>
<td>-1.09</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.05</td>
<td>-2.06</td>
<td>-1.61</td>
<td>-1.85</td>
<td>-1.68</td>
</tr>
<tr>
<td>K(^+)</td>
<td>-1.29</td>
<td>-2.76</td>
<td>-2.40</td>
<td>-2.74</td>
<td>-2.64</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>-0.65</td>
<td>-2.63</td>
<td>-2.11</td>
<td>-2.52</td>
<td>-2.44</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2-3. Experimental cation solvation free energies, eV, at 300 K and 1M.

<table>
<thead>
<tr>
<th>Cation</th>
<th>(\Delta G_{\text{SOLV}}^0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>-11.411</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>-4.985</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>-3.887</td>
</tr>
<tr>
<td>K(^+)</td>
<td>-3.151</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>-2.674</td>
</tr>
</tbody>
</table>

We analyse the impact of the dipole corrections before discussing the conclusions reached from the adsorption potentials. Figure 2-1 shows the change in adsorption free energy as a function of potential for three of the cations, \(H^+, K^+, \) and Ba\(^{2+}\) on the Pt(111) surface, both with (equation 7) and without (equation 2) the dipole correction. The adsorbed \(H^+\) retains no net charge, as evidenced by the lack of change in the surface dipole moment after adsorption, and therefore the adsorption free energies with and without dipole corrections are identical. Other cations retain a positive net charge, contributing to a slope of \(\Delta G_{\text{ads}}\) versus \(U\) which is less than 1. This slope is equal to the net electron transfer upon adsorption, and these values are given in Table 2-4. Net electron transfers around 1 for \(H^+\) indicate full electron transfer. As no positive charge remains, the solvation interaction with the \(H^+\) surface is not expected to differ significantly.
from that of the bare surface. The adsorption potential for $H^+$ on Pt of -0.07 V is within the experimentally measured hydrogen adsorption region on Pt(111). This value is slightly lower than that typically reported using the computational hydrogen electrode approach, suggesting some variability introduced by the use of the $H^+$ cation free energy and experimental solvation energy as compared to the use of a gas-phase $H_2$ free energy.

![Figure 2-1. Free energy of adsorption for $H^+$, $K^+$, and $Ba^{2+}$ onto a Pt(111) electrode as a function of electrode potential. Adsorption free energies are reported with (equation 7) and without (equation 2) dipole corrections. Without dipole correction: red - $K^+$, green - $Ba^{2+}$; with dipole correction: light blue - $K^+$, orange - $Ba^{2+}$; purple - $H^+$ with and without dipole correction.]

Table 2-4. Values of $\frac{\Delta G_{ads}}{\Delta U}$ for cation adsorption to fcc(111) metal surfaces. These values represent net electron transfer upon adsorption, calculated via equation 8.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$H^+$</th>
<th>$Li^+$</th>
<th>$Na^+$</th>
<th>$K^+$</th>
<th>$Cs^+$</th>
<th>$Ba^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>1.00</td>
<td>0.81</td>
<td>0.72</td>
<td>0.64</td>
<td>0.63</td>
<td>1.60</td>
</tr>
<tr>
<td>Pd</td>
<td>1.00</td>
<td>0.82</td>
<td>0.75</td>
<td>0.67</td>
<td>0.67</td>
<td>1.67</td>
</tr>
<tr>
<td>Ni</td>
<td>1.00</td>
<td>0.84</td>
<td>0.78</td>
<td>0.70</td>
<td>0.69</td>
<td>1.71</td>
</tr>
<tr>
<td>Au</td>
<td>1.00</td>
<td>0.81</td>
<td>0.74</td>
<td>0.65</td>
<td>0.61</td>
<td>1.60</td>
</tr>
<tr>
<td>Ag</td>
<td>1.01</td>
<td>0.84</td>
<td>0.78</td>
<td>0.69</td>
<td>0.66</td>
<td>1.68</td>
</tr>
</tbody>
</table>

For other ions, the surface dipole moment upon adsorption is significant, generally increasing with ion size. The dipole correction does not vary significantly across metals, though Pt and Au consistently show the largest dipole moments while Ni and Ag have the smallest.
Examining the $\frac{\Delta G_{ads}}{\Delta U}$ values, $Li^+$ generally transfers close to $0.8 \, e^{-}$ while $Cs^+$ transfers closer to $\frac{2}{3} \, e^{-}$. Partial electron transfer may be interpreted as signifying full electron transfer with adsorption, followed by a non-Faradic current required to maintain constant electrode potential arising from the need to counteract the established surface dipole. The established dipole moment is significant enough to suggest that the adsorbed alkali cations will be stabilized further by solvation.

The cation adsorption free energies provide indication as to whether cation specific adsorption will occur in potential ranges of interest for HOR/HER catalysis in alkali containing electrolytes. The $H^+$ adsorption potential is significantly more positive than all other cations on all metals, prior to any consideration of any adsorbed cation solvation. Provided both $H^+$ and alkali cations are present at concentrations of 1M, the $\Delta G_{ads}$ will be significantly more negative for $H^+$ at any potential and alkali cations are not likely to compete for adsorption sites. At a pH of 14, the $H^+$ adsorption potential would shift negatively by 0.826 V-NHE. At this low $H^+$ concentration, the free energies of adsorption of $Na^+$ and $Cs^+$ become more favourable than $H^+$ adsorption on Pt(111), with $K^+$ becoming close as well. The $Na^+$, $K^+$, and $Cs^+$ free energies on Pd (111) also near that of $H^+$ at pH 14. As solvation of $H^+$ is not likely to alter the adsorption free energies, these initial non-solvated values are a reasonable estimate for $H^*$ formation. Specifically adsorbed alkali cations are expected to be stabilized by solvation interactions, pushing their equilibrium adsorption potentials further positive and suggesting greater competition with hydrogen for adsorption sites during HOR/ORR in base.

### 2.3.1. Surface Solvation

The effects of surface solvation have been investigated by adding 1-10 explicit water molecules on a platinum surface during the adsorption of H, Na, and Ba. Equation 13 is used to calculate the adsorption equilibrium potentials with solvation included, using three reference
energies for surface water prior to cation adsorption. Values are compared with those calculated using the fully-solvated double-reference method. The values calculated with the double reference method are given in Table 2-5.

Table 2-5. Cation adsorption equilibrium potentials, \( U^0 \) (V-NHE), for a Pt(111) electrode calculated via the fully solvated double-reference method.

<table>
<thead>
<tr>
<th>Cation</th>
<th>( U^0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>-0.18</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.32</td>
</tr>
<tr>
<td>Ba(^{2+})</td>
<td>-0.13</td>
</tr>
</tbody>
</table>

Figure 2-2 illustrates the adsorption equilibrium potentials calculated for proton adsorption as a function of the number of water molecules solvating the surface adsorbate. Using the fixed water and relaxed water references, calculated equilibrium potentials yield similar potentials for hydrogen adsorption, suggesting the presence of hydrogen adsorbed on the surface does not strongly perturb the relaxed water structure. Solvation does not significantly alter the adsorption potential, as evidenced by flat adsorption potentials as a function of the number of water molecules included for the fixed and relaxed water references. These values also agree well with the double-reference method calculated adsorption equilibrium potential. The gas phase water reference leads to adsorption becoming progressively less favourable as more water molecules are added, as this approach penalizes the movement of water molecules from the bulk electrolyte to the surface region due to their lack of long range solvation interactions and liquid phase entropy. This third method of referencing solvation should be neglected.

For solvated sodium and barium specific adsorption (Figures 2-3 and 2-4) the fixed water method gives much more favourable adsorption potentials than the relaxed water method. Here the cations retain most of their positive charge and strongly influence the adjacent water structure. For the fixed water reference, the energy of the water structure prior to cation addition is unreasonably unstable due to requiring the water to take on the structure it would prefer in the
presence of the cation. Therefore, the fixed water reference method should be considered less reliable, and these adsorption potentials improperly too positive.

Figure 2-2. Equilibrium adsorption potential for H$^+$ adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using three references for the energy of the surface-water system before cation addition: gas phase reference (red square), fixed water reference (purple x), relaxed water reference (blue triangle). A flat line is included to show the value calculated with the fully solvated DR Method (green line).

Figure 2-3. Equilibrium adsorption potential for Na$^+$ adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using three references for the energy of the surface-water system before cation addition: gas phase reference (red square), fixed water reference (purple x), relaxed water reference (blue triangle). A flat line is included to show the value calculated with the fully solvated DR Method (green line).
Figure 2-4. Equilibrium adsorption potential for Ba\(^{2+}\) adsorption onto the Pt(111) surface calculated including the effects of explicit surface solvation (equation 13), given for a varying number of water molecules included in the solvation model. Data points are included using three references for the energy of the surface-water system before cation addition: gas phase reference (red square), fixed water reference (purple x), relaxed water reference (blue triangle). A flat line is included to show the value calculated with the fully solvated DR Method (green line).

Figure 2-5 illustrates the optimized solvated structures for an \(n\) of 6 (and all structures for all values of \(n\) are illustrated in supplementary information). Comparing Figures 2-5a and b suggests adsorbed H only slightly perturbs the water structure, and only 1 of the 6 water molecules appears to interact directly with the adsorbed H. From Figure 2-5c and d, Na and Ba have 4 H\(_2\)O molecules closest to them, with direct interactions forming a partial 1\(^{st}\) solvation shell at the electrode surface. Figure 2-5e gives the solvated structure for Na adsorbed on a Pt(111) surface with 23 H\(_2\)O molecules, used in the double reference method. Here again the sodium is surrounded closest by about 4 water molecules. Relative to the un-solvated surfaces, Na and Ba atoms move slightly further from the Pt(111) surface when solvated, though we did not observe any insertion of water molecules between the cations and the surface. Attempts to locate such non-specifically adsorbed states lead either to specific adsorption or a less stable structure.
Figure 2-5. Solvated surface structures on Pt(111) in 3x3 unit cell. a) Pt(111) with 6 H$_2$O molecules. b) Pt(111) + H with 6 H$_2$O molecules. c) Pt(111) + Na with 6 H$_2$O molecules. d) Pt(111) + Ba with 6 H$_2$O molecules. e) Pt(111) + Na with 23 H$_2$O molecules used in the double reference method.

The relaxed water reference gives the most physically reasonable reference initial states, with $n$ water molecules in a minimum energy structure on both the bare surface and about the cation following specific adsorption. With approximately 6 water molecules included, the calculated adsorption potentials for hydrogen, sodium, and barium approach the potentials calculated with the fully-solvated double reference method. This suggests that a smaller, more computationally tractable number of water molecules (with no density control due to a vacuum region) can reasonably model a density controlled static solvent. Further, the dipole correction approach provides a similar estimate of the impact of interface electrification on cation specific adsorption as the double-reference method.

We conclude that the relaxed water reference of double-reference method provide the most reasonable approach to providing a solvation approximation using static water. These
methods still neglect longer range solvation effects, though the convergence of the adsorption potential with respect to the number of water molecules suggests that these likely have little quantitative impact. A greater unknown contribution to the adsorption free energy is the entropy loss associated with the strong water-cation interactions. To fully capture the thermodynamics of the water adsorption process would require a molecular dynamics model, for example, to better estimate the entropy and enthalpy of the water molecules fully solvated in bulk solution. We take the non-solvated cation adsorption equilibrium potentials to estimate a minimum equilibrium adsorption potential. The relaxed water/double-reference method values provide a maximum estimate due to neglecting the entropy penalty of water solvating the surface cations. The values reported are for the single 1/9 ML coverage, and the significant retention of charge for the specifically adsorbed alkali cations suggests that adsorption will be strongly coverage dependent, becoming less favourable at higher coverages due to cation-cation repulsion.

The effects of solvation on the favourability of Na\(^+\) and Ba\(^{2+}\) cation adsorption are significant, greater than 1 eV for adsorption onto the Pt(111) surface. Solvation of the metal-cation bond screens and stabilizes the charge that remains on the cations when they adsorb to the surface, making the adsorption process more favourable. Solvation has a much smaller effect on the adsorption of a hydrogen cation, as shown in Figure 2-2, which is expected given its almost neutral charge on the surface and very small surface-hydrogen dipole moment. Given the large stabilizing effect of solvation on the cation adsorption process, it is likely that all cations considered could compete with hydrogen on Pt(111) for adsorption sites during HOR/HER in alkaline solutions. If the maximum range of solvation corrections on Pt(111) are presumed transferable to the other (111) surfaces, competitive cation adsorption could be relevant on all of these metals. These results suggest the possible presence of cations on electrode surfaces in the HOR/HER range in alkali hydroxide electrolytes, at least at 1/9 ML coverage and on Pt(111) and Pd(111) surfaces. The >1V range between the non-solvated and solvated values,
together with the inability to firmly quantify the solvation effect on specific adsorption, limit the conclusiveness of DFT calculations in determining the extent of specific adsorption as a function of electrode potential. More advanced approaches to estimating free energies of solvation that allow for consideration of extended electrode surfaces would help further clarify this phenomena, though these are complicated by difficulties in modelling the impact of the surface and electrification on solvation dynamics.

2.4. Summary and Conclusion

Density functional theory calculations were used to examine the specific adsorption of alkali cations to fcc(111) electrode surfaces. The adsorption equilibrium potential for cations, below which adsorption may occur to a significant degree, was estimated both with and without consideration of solvation of the adsorbed cations. Results suggest alkali and alkali-earth cations can specifically adsorb at low coverage in alkaline solutions around potentials where hydrogen oxidation or evolution catalysis may occur. Competitive cation adsorption is most favourable on Pt(111) but may occur to a lesser degree on other metals as well. Specific adsorption free energies are most favourable on electrode surfaces in the order of Pt(111) > Pd(111) > Ni(111) > Ag(111), Au(111). On all metals, alkali cations will transfer a partial electron upon adsorption, and the surface dipole moment thereby created will reduce the potential dependence of the adsorption free energy and motivate direct solvation by surface water molecules.

Surface solvation can be estimated by including approximately 6 static water molecules about the adsorbed cation. When the arrangement of these water molecules is relaxed both before and after cation adsorption, the adsorption free energy matches well with that calculated with the more computationally demanding double-reference method approach. The unknown error introduced by the use of a single structure of static water molecules and not considering the
impact of cation interactions on the solvation entropy limits the conclusiveness of calculated adsorption free energies. Solvation of cations is much more significant than that of adsorbed hydrogen, and the surface dipole moment provides a reasonable screening value for determining whether solvation will impact the stability of adsorbed single-atom species.

2.5. Acknowledgements

This work was supported by the National Science Foundation, Grant # CBET- 1264104.

2.6. References


2.7 Supplementary Information

Table S2-1. VASP energies (eV) for bare fcc(111) surfaces and single atoms adsorbed to fcc(111) surfaces.

<table>
<thead>
<tr>
<th>E_DFT</th>
<th>H⁺</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cs⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>-177.80</td>
<td>-181.64</td>
<td>-181.05</td>
<td>-180.60</td>
<td>-180.71</td>
<td>-181.94</td>
</tr>
<tr>
<td>Ni</td>
<td>-183.83</td>
<td>-185.04</td>
<td>-186.70</td>
<td>-186.29</td>
<td>-186.35</td>
<td>-186.54</td>
</tr>
<tr>
<td>Au</td>
<td>-110.01</td>
<td>-112.48</td>
<td>-112.37</td>
<td>-111.94</td>
<td>-112.06</td>
<td>-112.25</td>
</tr>
<tr>
<td>Ag</td>
<td>-91.86</td>
<td>-94.96</td>
<td>-94.24</td>
<td>-93.90</td>
<td>-93.94</td>
<td>-94.12</td>
</tr>
</tbody>
</table>

Table S2-2. VASP gas phase cation energies and energy corrections used to calculate solution phase cation free energies at 300 K and 1M using equations 5 and 6. All values are in eV.

<table>
<thead>
<tr>
<th>Cation</th>
<th>E_DFT</th>
<th>TS_TRANS</th>
<th>ΔG_SOLV</th>
<th>G_{C⁺,aq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>H⁺</td>
<td>12.527</td>
<td>0.197</td>
<td>-11.411</td>
<td>1.378</td>
</tr>
<tr>
<td>Li⁺</td>
<td>5.344</td>
<td>0.414</td>
<td>-4.985</td>
<td>0.950</td>
</tr>
<tr>
<td>Na⁺</td>
<td>5.183</td>
<td>0.460</td>
<td>-3.887</td>
<td>0.901</td>
</tr>
<tr>
<td>K⁺</td>
<td>4.347</td>
<td>0.481</td>
<td>-3.151</td>
<td>0.780</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>3.874</td>
<td>0.528</td>
<td>-2.674</td>
<td>0.737</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>15.388</td>
<td>0.529</td>
<td>-13.04</td>
<td>1.883</td>
</tr>
</tbody>
</table>

Table S2-3. Dipole moments (e Å) for bare fcc(111) surfaces (µₐ) and surfaces with adsorbed atoms (µ_C⁺).

<table>
<thead>
<tr>
<th>Metal alone</th>
<th>H⁺</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cs⁺</th>
<th>Ba²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>0.0166</td>
<td>0.000832</td>
<td>-0.567</td>
<td>-0.813</td>
<td>-1.06</td>
<td>-1.11</td>
</tr>
<tr>
<td>Pd</td>
<td>0.00834</td>
<td>0.0172</td>
<td>-0.520</td>
<td>-0.733</td>
<td>-0.971</td>
<td>-0.997</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.0131</td>
<td>-0.0211</td>
<td>-0.506</td>
<td>-0.689</td>
<td>-0.906</td>
<td>-0.941</td>
</tr>
<tr>
<td>Au</td>
<td>0.0279</td>
<td>0.0205</td>
<td>-0.549</td>
<td>-0.764</td>
<td>-1.03</td>
<td>-1.13</td>
</tr>
<tr>
<td>Ag</td>
<td>0.0124</td>
<td>0.0295</td>
<td>-0.471</td>
<td>-0.635</td>
<td>-0.913</td>
<td>-1.02</td>
</tr>
</tbody>
</table>

Table S2-4. Gas phase water properties at 300K (eV).

<table>
<thead>
<tr>
<th>E_DFT</th>
<th>ZPVE</th>
<th>TS_VIB+ROT+TRANS</th>
<th>U+PV</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>-14.272</td>
<td>0.5645</td>
<td>0.6733</td>
<td>0.1035</td>
<td>-14.278</td>
</tr>
</tbody>
</table>
Figure S2-1. Relaxed solvated Pt(111) surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O
Figure S2-2. Relaxed solvated Pt(111)+H surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O
Figure S2-3. Relaxed solvated Pt(111)+Na surface. a) 1 H₂O b) 2 H₂O c) 3 H₂O d) 4 H₂O e) 5 H₂O f) 6 H₂O g) 7 H₂O h) 8 H₂O i) 9 H₂O j) 10 H₂O
Figure S2-4. Relaxed solvated Pt(111)+Ba surface. a) 1 H$_2$O b) 2 H$_2$O c) 3 H$_2$O d) 4 H$_2$O e) 5 H$_2$O f) 6 H$_2$O g) 7 H$_2$O h) 8 H$_2$O i) 9 H$_2$O j) 10 H$_2$O
Chapter 3

Electrochemical Specific Adsorption of Halides on Cu 111, 100, and 211: A Density Functional Theory Study


**Abstract**

The specific adsorption of ions onto electrode surfaces can affect electrocatalytic reactions. Density functional theory is used to investigate the specific adsorption of aqueous F\(^-\), Cl\(^-\), Br\(^-\), and I\(^-\) onto Cu (111), (100), and (211) surfaces. The adsorption is increasingly favorable in the order of F\(^-\) < Cl\(^-\) < Br\(^-\) < I\(^-\). The adsorption has a weak dependence on the surface facet, with adsorption most favorable on Cu (100) and least favorable on Cu (111). Potential ranges where specific adsorption would be expected on each facet are reported. The thermodynamics of bulk copper halide formation are also investigated as a function of potential. CuX formation occurs at potentials slightly more positive of halide specific adsorption and of copper oxidation in aqueous electrolytes. Specifically adsorbed halides and bulk CuX may be present during a variety of electrochemical reactions carried out over a Cu electrode in halide containing electrolyte solutions.
3.1. Introduction

Copper is an important transition metal used in a diverse range of applications, including catalysis for both gas phase\(^1\) and electro-chemical reactions\(^2\)-\(^3\), wiring interconnects in semiconductor circuit manufacturing\(^4\), and ship building where its resistance to corrosion is important in a salt-water environment\(^5\). The electrochemical properties of Cu determine the rate of corrosion or electrodeposition of Cu in an electrolytic environment, as well as the extent of its catalytic activity in electrochemical reactions. Ions in an electrolyte solution can affect these surface electrochemical processes, but due to the complexity of the electrochemical interface, it is difficult to determine the mechanism by which ions produce these effects. At the interface, the position of solvent molecules and distribution of ions strongly depend on the applied potential, the structure and composition of the electrode, identity and concentration of the ions, and solvent. Halide ions in an aqueous electrolyte solution can affect the rate of copper corrosion\(^6\), planarization\(^7\)-\(^8\), and catalytic reactions occurring on a copper electrocatalyst surface\(^9\)-\(^12\).

During specific adsorption, an ion or adsorbate forms a direct bond to the surface, as opposed to an electrostatic interaction at a longer distance, as illustrated in Figure 3-1. The specific adsorption of ions onto metal electrodes has been widely studied previously with notable contributions from Frumkin\(^13\), Stern\(^14\), Grahame\(^15\), and Parsons\(^16\). These contributions led to the development of a mathematical framework to describe the location of ions distributed by an electric field in an electrolyte solution and demonstrated that ions can specifically adsorb to the electrode surface. This phenomenon will affect both the electronic and structural properties of the electrode surface, altering its catalytic and electrochemical properties as well as blocking surface sites.
Figure 3-1. The specific adsorption reaction equation, in which an aqueous phase halide anion directly binds to the electrode surface, releasing an electron into the electrode/external circuit.

The specific adsorption of halides onto the copper surface has been proposed to explain the impact of halides on various processes\textsuperscript{7-8, 10, 12, 17}. Anions, such as Cl\textsuperscript{-}, Br\textsuperscript{-}, and I\textsuperscript{-}, in particular, strongly adsorb to many metal electrodes, due in part to their relatively small solvation energies\textsuperscript{18}. Magnussen presents a thorough review of halide specific adsorption onto a variety of transition metal surfaces\textsuperscript{19}. A series of electrochemical experiments suggest that halides specifically adsorb to copper and can affect its electrochemical deposition, passivation, and corrosion\textsuperscript{6, 8, 17, 19-21}. Specific adsorption or co-adsorption of halides enhances the adsorption of organic compounds including a polyether\textsuperscript{7} and benzotriazole\textsuperscript{8}, used to passivate copper surfaces in a process important to chemical-mechanical planarization used in semiconductor device manufacturing. Iodide adsorbed onto a copper surface enhances the inhibitory effect of 2-mercapto benzimidazole in the corrosion of copper\textsuperscript{6}. Specifically adsorbing halide ions also effect the roughness of electrodeposited polycrystalline copper\textsuperscript{17}. Electrochemical and X-ray experimental studies report anion adsorption onto copper adatoms deposited onto Pt(111)\textsuperscript{22-23} and Pt(100)\textsuperscript{24}.

Anions can affect the rate and mechanism of catalytic electrochemical processes. The specific adsorption of chloride\textsuperscript{25}, bisulfate, sulfate, and organic sulfonate ions\textsuperscript{26} to platinum electrodes affect the rate of the oxygen reduction reaction\textsuperscript{25, 27}. Halide anions can affect the rate and selectivity of carbon dioxide electroreduction over copper electrodes\textsuperscript{9-12}. The identity of the
halide strongly influences the selectivity and the kinetics of hydrocarbon formation\textsuperscript{12}. While the exact mechanism by which a halide impacts electrocatalysis is not fully understood, the variations in rate and selectivity may be attributed to the specific adsorption of halide anions onto the copper electrode. Ogura et al. suggest that specifically adsorbed halide anions increase the attraction between carbon dioxide and the copper electrode surface\textsuperscript{10, 12} and decrease the amount of hydrogen adsorbed on the copper surface\textsuperscript{12}. Determining the electrochemical conditions at which the specific adsorption of halides occurs onto copper surfaces is necessary prior to examining how these anions affect surface electrochemical processes.

While experimental electrochemistry can be used to examine surface and surface mediated processes, the presence of simultaneous electrochemical reactions such as dissolution, deposition, oxidation or other catalytic reactions impose a high degree of complexity towards studying ion specific adsorption. \textit{Ab initio} modeling techniques offer a convenient platform to examine the specific adsorption of ions exclusively, in the absence of other competing processes.

We employ Density Functional Theory (DFT), an \textit{ab initio} quantum mechanical technique, to probe the copper-halide interaction at an electronic structure level.

Other groups have applied DFT to examine halide specific adsorption, though the favorability of halide adsorption across Cu facets has not been previously examined. Roman et al. used DFT to examine the effect of halide specific adsorption on the work function of a variety of transition and alkaline earth metal surfaces\textsuperscript{28}. Ignaczak and Gomes\textsuperscript{29} used DFT to model halide adsorption onto Cu, Ag, and Au (100) metal clusters, showing adsorption is strongest with fluoride and weakest with iodide. This study, however, did not consider the solvation of the ions in solution and of the metal cluster surface. Similarly, Pašti and Mentus consider the adsorption of Cl, Br, and I onto Pt, Pd, Cu, and Au slabs using DFT, but their adsorption energetics referenced a gas phase halogen atom, as opposed to a solution phase halide anion\textsuperscript{30}. Gossenberger et al. use DFT to predict the trends in the adsorption of F, Cl, Br, and I as a function of coverage.
on Cu(111) and Pt(111)\textsuperscript{31}. The co-adsorption of sodium and chloride layers onto the Cu (100) and Cu (311) surfaces has also been investigated with DFT\textsuperscript{32}. These DFT studies neglected to consider solvation of ions prior to adsorption or when adsorbed on the electrode surface.

While DFT can reliably determine the electronic structure of specifically adsorbed halide-electrode systems, incorporating solvation effects is non-trivial due to restricted time and length scales of the simulation. One approach is to employ force-fields in classical molecular dynamics to increase the simulation scale, although this method is then limited by the accuracy of the trained potentials. In particular, the force-field representation of the specific, halide-metal bond is challenging. Jeon et al. used this approach to study the corrosion of a solvated copper surface in the presence of chloride in solution\textsuperscript{33}, with a simplified halide-electrode interaction model.

In this study, we use DFT to examine the electrochemical adsorption of F, Cl, Br, and I anions from an aqueous solution to Cu (111), Cu (100), and Cu (211) surfaces. The free energies of specific adsorption are determined as a function of electrode potential. Explicit water molecules are added to each copper surface to incorporate the effect of solvation on the thermodynamic favorability of adsorption of F\textsuperscript{−} and I\textsuperscript{−}. Our results suggest that the halide anions (from a 1M halide solution) favorably adsorb from aqueous solution on to the three copper surfaces at potentials generally above -1 V\textsubscript{NHE}.

Shao et al.\textsuperscript{21} and Soares et al.\textsuperscript{20} both suggest that a solid CuCl phase can form during copper electrodeposition from a chloride containing electrolyte, influencing the mechanism of formation and properties of the electrodeposit relative to deposition carried out in a halide free electrolyte. We also evaluate the thermodynamic favorability of bulk copper halide (CuX or CuX\textsubscript{2}) formation as a function of electrode potential.
3.2. Methods

3.2.1 Computational Methods

All DFT calculations were performed with the Vienna Ab initio Simulations Package (VASP 5.2.12)\textsuperscript{34-36}, using the projected augmented wave (PAW)\textsuperscript{37,38} method. The calculations used the Perdew-Burke-Ernzerhof (PBE)\textsuperscript{39-40} exchange and correlation functional described within the generalized gradient approximation (GGA)\textsuperscript{39}. The plane wave basis set cut-off energy was 450 eV. Optimization was conducted until the electronic energies were converged to within $10^{-5}$ eV with an ionic convergence limit of 0.02 eV Å\textsuperscript{-1}. For the surface calculations, a 5×5×1 Monkhorst Pack\textsuperscript{41} mesh k-point sampling was used for the 3×3 unit cell, 7×7×1 for the 2×2 unit cell, and 9×9×1 for the 1×1 unit cell, while for the bulk structures a 7×7×7 mesh was used. All calculations were spin restricted. Vibrational modes were calculated by Cartesian displacements of each adsorbate by 0.01 Å in each direction to create a Hessian matrix. Dipole corrections (LDIPOLE=TRUE) were applied in the surface normal direction (IDIPOLE=3) to prevent interaction between periodic surface slabs.

The copper surfaces were constructed using a periodic supercell with a thickness of 4 layers, with the bottom two layers constrained to the bulk configuration with an experimental lattice constant of 3.61 Å\textsuperscript{42}. Three different unit cells were used to examine the effect of halide surface coverage ($\theta$). A 3×3 unit cell was used to represent $\theta = 1/9$ ML halide adsorbed on Cu (100) and $\theta = 1/9$ ML, 2/9 ML, and 3/9 ML on Cu (111). A 2×2 unit cell was used to examine $\theta = 1/4$ ML and $\theta = 1/2$ ML on Cu(100) and $\theta = 1/2$ ML on Cu (111). A 1×1 unit cell represented $\theta = 1$ ML adsorption. The FCC site was found to be the most favorable adsorption site for all halides on the (111) surface facet, as found by others\textsuperscript{28}. The three fold site was found to be most favorable for Cl, Br, and I, and the bridge site for F on the (100) surface facet. The edge-bridge site was
most favorable for Cl on the (211) surface facet; it was assumed all other halides also preferred the edge-bridge site for the (211) facet. Site adsorption energies are given in the Supplementary Information. Bulk CuX and CuX\textsubscript{2} were modeled using structures reported in\textsuperscript{43} for X = Cl, Br, and I. No structure was given for CuI\textsubscript{2} and therefore it was not considered.

The free energies of the solution phase halides were computed using two alternative methods; a more detailed description follows in section 2.2. The first, the diatomic gas phase method, involves calculating the Gibbs free energy of the diatomic halide molecule (\(G_{X_2(g)}\)) in the gas phase (assuming ideal gas behavior), then using the experimentally measured standard reduction potential (\(U_{X_2}\)) to determine the free energy of the halide in aqueous solution (\(G_{X_2(aq)}\)). This is similar to the computational hydrogen electrode method\textsuperscript{44}. The second method, the solvation energy method, computes the Gibbs free energy of a gas phase halide ion (\(G_{X(g)}\)) then adds an experimentally measured solvation free energy change (\(\Delta G_{solv}^{exp}\)) to determine the free energy of the ion in aqueous solution (\(G_{X(aq)}\)).

3.2.2. Specific Adsorption Equilibrium Potentials

The specific adsorption process is described by Equation 1.

\[
Cu^* + X^-_{aq} \leftrightarrow Cu - X + e^-
\]  

[1]

\(Cu^*\) represents an empty copper surface site and \(Cu - X\) represents a halide adsorbed onto a surface site. Equations 2 and 3 show how the free energy of the aqueous anion can be replaced with that of the gas phase diatomic halogen, where Equation 3 is valid when the free energy change of halide dissolution is zero, at the equilibrium dissolution potential \(U_{X_2}(\Delta G_{X_2}^{Diss} = 0 @ U = U_{X_2})\).

\[
X_2 + 2e^- \leftrightarrow 2X^-_{aq}
\]  

[2]
\[ G_{X_{ads}} = \frac{1}{2} G_{X_{2}} - eU_{X_{2}} \]  

The Gibbs free energy change of adsorption (\( \Delta G_{X}^{ads} \)) (Equation 4) as a function of electrode potential on an NHE scale (\( U_{NHE} \)) is calculated using this diatomic gas phase method

\[ \Delta G_{X}^{ads}(U_{NHE}) = G_{Cu-X} - G_{Cu} - \frac{1}{2} G_{X_{2}} + eU_{X_{2}} - eU_{NHE} + \frac{\mu_{Cu-X} - \mu_{Cu}}{d}(U_{NHE} - U_{PZC}) \]  

where \( G_{Cu} \) represents the energy of the bare copper surface, \( G_{Cu-X} \) is the energy of a halide adsorbed on the copper surface, \( G_{X_{2}} \) is the gas phase free energy of diatomic halogen, and \( U_{X_{2}} \) is the standard dissolution potential, measured experimentally\(^{45-46}\). The standard dissolution potentials used for each halide are tabulated in the Supplementary Information. The final term in Equation 4, \( \frac{\mu_{Cu-X} - \mu_{Cu}}{d}(U_{NHE} - U_{PZC}) \) represents the change in free energy on interaction between the surface dipole moment \( \mu_{Cu-X} - \mu_{Cu} \) and the electrode-electrolyte interfacial electric field, \( (U_{NHE} - U_{PZC})/d \) in a Helmholtz approximation\(^{44}\). \( U_{PZC} \), the potential of zero charge, is approximated as 0 on an NHE scale. The equilibrium adsorption potential, \( U_{0}^{NHE} \), is found by setting \( \Delta G_{X}^{ads} \) to zero and solving for the potential:

\[ U_{0}^{NHE} = \frac{G_{Cu-X} - G_{Cu} - \frac{1}{2} G_{X_{2}} + U_{X_{2}}}{e^{-} - \frac{\mu_{Cu-X} - \mu_{Cu}}{d}} \]  

The free energy of the bare surface (\( G_{Cu} \)) is equal to the DFT optimized energy (\( E_{Cu}^{DFT} \)), neglecting any change in surface phonons due to adsorption. The free energy of the surface with the adsorbed halide (\( G_{Cu-X} \)) includes an entropy correction (\( TS_{Cu-X}^{vib} \)) to account for the added vibrational modes of the surface-halide bond and a zero point vibrational energy (ZPVE), as shown in Equation 6. The gas phase free energy of the diatomic halogen molecule includes a correction for vibrational energy (ZPVE) and entropy as well as translational and rotational entropy (\( TS_{X_{2}}^{gas} \)), as given in Equation 7.

\[ G_{Cu-X} = E_{Cu-X}^{DFT} + ZPVE - TS_{Cu-X}^{vib} \]
\[ G_{X_2} = E_{X_2}^{DFT} + ZPVE - TS_{X_2}^{gas} \]  

[7]

All vibrational and entropic contributions are calculated at 300K. Calculated energies, entropy corrections, and Gibbs free energies are tabulated in the Supplementary Information.

For the solvation energy method, the free energy of the solvated anion \( G_{X^{-}(aq)} \) is estimated as shown in Equation 8.

\[ G_{X^{-}(aq)} = E_{X^{-}}^{DFT} - TS_{X^{-}}^{gas} + \Delta G_{solv}^{exp} \]  

[8]

The free energy of specific adsorption and the equilibrium adsorption potential are then calculated as:

\[ \Delta G_{ads}^{ads}(U_{NHE}) = G_{Cu-X} - G_{Cu} - G_{X^{-}(aq)} + e(U_{NHE} + 4.6) + \frac{\mu_{Cu-X} - \mu_{Cu}}{d}(U_{NHE} - U_{PZC}) \]  

[9]

\[ U_{NHE}^0 = \frac{G_{Cu-X} - G_{Cu} - G_{X^{-}} - 4.6 e^{-}}{e^{-} - \frac{\mu_{Cu-X} - \mu_{Cu}}{d}} \]  

[10]

The free energy of the solution phase halide \( G_{X^{-}(aq)} \) is calculated by adding entropy corrections for gas phase translational entropy \( TS_{X^{-}}^{gas} \) and an experimentally measured free energy change of solvation \( \Delta G_{solv}^{exp} \). The experimental solvation energies of the halides are tabulated in the Supplementary Information. To shift the calculated equilibrium adsorption potentials \( U^0 \) from an absolute potential scale \( U_{abs} \) to the normal hydrogen electrode scale \( (U_{NHE}) \), the potential of an electron in vacuum on an NHE scale \( (U_{e^-} = -4.6 \text{ V}_{\text{NHE}}) \) is used. As both the standard dissolution potentials and the solvation free energies are given for a 1M halide solution, the reported adsorption free energies and equilibrium adsorption potentials are at these conditions.

To compare the free energy of adsorption at different coverages, the free energy was normalized by the surface area of the unit cell.
3.2.3. Surface Solvation

The presence of bulk electrolyte near the electrode surface can strongly influence surface reactions. For example, water molecules can solvate the partial charge of a molecule adsorbed on a surface, making its adsorption more favorable. Approximations to account for the effects of solvation include continuum based methods, where the quantum environment is surrounded by a dielectric medium with a dielectric constant equal to that of the electrolyte of interest, and force field based methods\textsuperscript{14, 33, 51-53}. Alternatively, explicit water molecules can be treated with DFT near the surface-adsorbate bond\textsuperscript{54}. These can be arranged as water bi-layers\textsuperscript{55,56} or individual molecules with a number density selected to allow convergence of pertinent properties\textsuperscript{57}. In this study, we incorporate surface solvation by including explicit water molecules. For cases of strong ion adsorption, where only small surface dipole moments occur in the adsorbed state, the effect of electrode surface solvation is minor. The use of a small number of explicit water molecules allows for the estimation of this effect without significantly increasing the computational intensity.

To estimate the effects of surface solvation, individual water molecules were added near the adsorbate on the surface. The structure was relaxed, yielding the energy of the solvated, adsorbed state. The adsorbate was then removed, and the remaining water structure re-optimized to yield the energy of the solvated copper surface. This method was shown to give reasonable results for hydrogen and alkali metal cations on the Pt(111) surface, and should converge with a small (<6) number of water molecules\textsuperscript{57}. The free energy for solvated adsorption was calculated with Equation 11, using the solvation energy method where the bare reactant copper surface was replaced with the relaxed solvated surface and the product Cu-X surface was replaced with the solvated Cu-X surface.

\[
\Delta G^{ads-solv}_{X} (U_{NHE}) = G_{Cu-X(H_2O)_n} - G_{Cu(H_2O)_n} - G_{X^{-}} + e(U_{NHE} + 4.6) + \frac{\mu_{Cu-X} - \mu_{Cu}}{d}(U_{NHE} - U_{PZC}) \tag{11}
\]
The number of explicit water molecules, $n$, was varied. Equilibrium adsorption potentials were calculated by setting $\Delta G_X^{ads-solv} = 0$ and solving for $U_{NHE}^0$. While the vibrational entropy of the water molecules is included, additional contributions to the entropy of these water molecules near the electrode surface are neglected. Using the method outlined here, the water molecules in the initial and final state are near the electrode surface, and while they would have a presumably substantial difference in entropy relative to bulk, solution phase water, the only change in entropy not accounted for here is the change in entropy of the water layer due to its interaction with an adsorbed halide. The effect of surface solvation was investigated for fluoride and iodide adsorption on the Cu (111), (100), and (211) surfaces. The behavior of the adsorption of the other halides investigated here, Cl$^-$ and Br$^-$, on the solvated surface are expected to fall between those of fluoride and iodide, due to their solvation energies and surface dipole moments falling intermediate to those of fluoride and iodide$^{47,58}$.

### 3.2.4. Bulk CuX & CuX$_2$ Formation

The Gibbs free energy of CuX ($\Delta G_{CuX}^{bulk}$) and CuX$_2$ ($\Delta G_{CuX_2}^{bulk}$) formation were determined as a function of electrode potential using Equations 12 and 13:

$$\Delta G_{CuX}^{bulk}(U_{NHE}) = G_{CuX} - G_{Cu} - \frac{1}{2} G_{X_2} + eU_{X_2} - eU_{NHE} \quad \text{[12]}$$

$$\Delta G_{CuX_2}^{bulk}(U_{NHE}) = G_{CuX_2} - G_{Cu} - G_{X_2} + 2eU_{X_2} - 2eU_{NHE} \quad \text{[13]}$$

The gas phase diatomic method was used to represent the free energy of the aqueous halide ion. Bulk phase thermodynamics neglect phonon contributions to the free energy, using only the 0K energy values. The calculated formation free energies are therefore only an estimate and the expected increase in entropy due to phonon contributions in the halides make our estimated values an overestimate of the formation free energy.
3.3. Results and Discussion

3.3.1. Non-solvated Specific Adsorption Potential

We first evaluate the internal consistency between the two reference approaches for the solvated halide ion free energy. Figure 3-2 is a parity plot between halide molecular dissolution potentials calculated as $U_{X_2}^{DFT} = \frac{1}{2}(\epsilon_{X_2} - \epsilon_{X_{aq}})$ and the experimentally measured dissolution potentials. This plot captures the variance between the solvation energy method and diatomic gas phase energy method based on experimentally measured potentials. Differences in calculated potentials between the two methods are relatively small, all less than 0.35 V, with the largest deviation observed for chloride. The small magnitude of these deviations shows internal consistency between the two methods, but illustrates that the calculated equilibrium adsorption potentials cannot be reliably more precise than this difference (~0.35 V).

Figure 3-2. Parity plot between DFT calculated diatomic halogen dissolution potentials and experimental dissolution potentials. (Solid red line gives y=x.)

Figure 3-3 shows the calculated adsorption potentials, $U_{NHE}^{0}$, for $F^-$, $Cl^-$, $Br^-$, and $I^-$ adsorption onto Cu (111), (211), and (100) at $\theta = 1/9$th monolayer coverage using the experimental solvation energy method. Equilibrium adsorption potentials calculated using the
diatomic gas phase energy method are given in the Supplementary Information. Specific adsorption of the halides is favorable at any potential more positive of those indicated in Figure 3-3; the Gibbs free energy change upon adsorption is zero at the indicated potential and becomes more negative as the potential is made more positive of the equilibrium adsorption potential. The adsorption potentials follow a periodic trend across all of the surfaces, with fluoride adsorption least favorable and iodide adsorption most favorable. This is opposite to the binding energy trend found by Ignaczak and Gomes and Pašti and Mentus, due to our referencing of the aqueous anion including its solvation energy, with fluoride having the largest solvation energy and iodide the smallest. The calculated equilibrium adsorption potentials for Cl$^-$ and I$^-$ are similar to those calculated by Gossenberger et al. for adsorption onto Cu (111). Halide adsorption is most favorable on the Cu (211) and Cu (100) surfaces, followed by the Cu (111) surface.

![Figure 3-3](image)

**Figure 3-3.** Equilibrium adsorption potentials for F$^-$, Cl$^-$, Br$^-$, and I$^-$ adsorption at $\theta = 1/9$ ML onto Cu (111) (green), Cu (211) (beige), and Cu (100) (blue) calculated using the experimental anion solvation energy method. The surface adsorbed state was not solvated.

Intermediate coverages of adsorbed F, Cl, Br, and I were investigated on Cu (111) and Cu (100). Both the qualitative trend in adsorption favorability between the halides and their quantitative adsorption potentials on Cu (111) are similar to those calculated by Gossenberger et
Plots of the calculated adsorption potentials versus the halide coverage can be found in Supplementary Information. In general, on Cu (111), at low coverages, the favorability of adsorption decreases slightly with increasing coverage, until some critical coverage is reached where adsorption becomes significantly unfavorable. This significant decrease in adsorption favorability, between 1/3 ML and 1/2 ML, could be due to steric hindrance between neighboring adsorbates as the coverage increases. Generally, the adsorption of halides up to 1/3 to 1/2 ML is favorable on Cu(111) at similar potential to 1/9 ML and at potentials lower than bulk copper halide formation. The adsorption of halides up to a higher coverage of 1 ML on Cu(111) requires significantly positive potentials (U>0.75 V NHE) and is always thermodynamically less favorable than bulk copper chloride formation, as discussed in section 3.3. This is due to the large electrostatic repulsion and steric hindrance of the adsorbed halide on the surface at such a high coverage (1 ML). On the more open Cu (100) surface, adsorption of 1ML of Cl* or Br* occurs at potentials only slightly more positive than lower coverages, and is more favorable than formation of bulk copper halide.

The adsorbate-surface interaction on adsorption at θ = 1/9 ML was further investigated by determination of the charge of the adsorbed anion and the dipole moment along the surface normal. The dipole moments along the surface normal following specific adsorption are shown in Figure 3-4. Dipole moments are largest with fluoride and smallest with iodide, reflecting a greater retention of negative charge on the fluoride when adsorbed and least charge retention on the iodide. The Cu (211) surface gives the largest dipole moment for each of the halides, possibly due to the corrugated structure of the surface. The magnitude of the dipole moments for the examined halides and Cu surface facets are relatively small compared to those reported for ions that bond more ionically to the surface. For example, the calculated dipole moments of alkali metals adsorbed on the Pt (111) surface range from -0.58 > μ > -1.1 eÅ\(^57\). The variation in halide charges, determined with Bader charge analysis\(^59\,61\), are in agreement with the surface dipole
trends. The calculated Bader charges of the halides are presented in the Supplementary Information. The trend in halide Bader surface charge is also periodic, with fluoride retaining the most charge and iodine the least, with little sensitivity to the surface facet. Both the greater charge transfer upon adsorption and the equilibrium adsorption potentials suggest I\(^-\) binds most strongly to the Cu surfaces. The small adsorbed halide-surface dipole moments suggest relatively strong non-ionic adsorption, suggesting that the effect of water/electrolyte on the adsorption process should be relatively small. Water typically acts to stabilize charge separation, making adsorption more favorable; this solvation effect is minimized when the charges/dipole moments are small. Interestingly, we find that iodine generates a small but negative surface normal dipole moment on adsorption to Cu (111) and Cu (100) (Figure 3-4), opposite in sign to the other halides, even though it retains negative charge (Supplementary Information). This effect has been investigated by Roman et al. who suggest this trend is due to the strong polarizability of iodine relative to the other halides \(^6\).

Figure 3-4. Surface-halide dipole moment (along surface normal direction) on F\(^-\), Cl\(^-\), Br\(^-\), and I\(^-\) adsorption at θ = 1/9 ML onto Cu (111) (green), Cu (211) (beige), and Cu (100) (blue).
3.3.2. Surface Solvation

The effect of 1-6 explicit water molecules on the adsorption of 1/9th monolayer of fluoride and iodide onto Cu (111), Cu (100), and Cu (211) was investigated. Figure 3-5 shows the final converged solvated structure for fluoride adsorbed on Cu (211), Cu (111), and Cu (100). Explicit water molecules were added until the change in adsorption potential on the addition of another water molecule was less than 0.06 V, except in the case of F\(^{-}\) on Cu (111), which is converged to within 0.01 V of the average of the adsorption potentials for each solvated structure. The change in adsorption potential as a function of the number of explicit H\(_2\)O molecules for both fluoride and iodide on the three copper facets are given in the Supplementary Information. Figure 3-6 shows the equilibrium adsorption potential (\(U^0_{\text{NHE}}\)) for the adsorption of fluoride and iodide species on the three surfaces with and without solvating water molecules.

![Solvated structures of F adsorbed to the three Cu surface facets: a) F + 4 H\(_2\)O on Cu (211) b) F + 6 H\(_2\)O on Cu (111) c) F + 5 H\(_2\)O on Cu (100). Cu (orange, large species) and F (blue) are shown in space filling representation with water (O-red, H-white) shown in ball and stick representation. Dashedlines represent hydrogen bonds.](image-url)
As shown in Figure 3-6, explicit water molecules have a negligible effect on iodide adsorption on the copper surface. This is expected due to the small dipole moment between the adsorbed iodide and the copper surface. The effect of explicit water molecules on the fluoride adsorption is more pronounced as expected from the larger dipole moment between the surface and the fluoride ion. While the effect of solvation on the iodide adsorption by explicit water method is independent of the copper facet, the effect on the fluoride adsorption favorability is significant on all three surfaces. The solvation effect is greater on the Cu (100) > Cu (111) > Cu (211) surface, with solvation making fluoride adsorption more favorable on the Cu (100) surface by about 0.6 V. Though surface solvation brings the F\(^-\) adsorption equilibrium potentials towards that of I\(^-\), the solvation effect is considerably less than the difference in adsorption potentials between the two ions.

Figure 3-6. Equilibrium adsorption potentials for fluoride (blue) and iodide (red) calculated using the solvation energy method for adsorption to bare and solvated copper surfaces. Cross hatched bars are the potentials calculated without surface solvation, solid bars include converged surface solvation.
The effects of F* solvation are sensitive to the surface facet and do not exactly track the dipole moments. For example, as given in Figure 3-4, the dipole moment is greatest on the Cu (211) surface with both iodide and fluoride adsorption, but the effect of solvation is negligible to low on Cu (211) with iodide and fluoride adsorption. The solvation effect on fluoride adsorption is less on Cu (211) than Cu (100), which could be due to the stepped nature of the Cu (211) surface, interrupting the organized water structure which would form on the other surface facets.

We expect that for Cl− and Br−, with adsorbed charges and dipole moments between those of F− and I−, the effects of solvation will also lie between those of fluoride and iodide, with the magnitude of the effect being less than 0.6 V. Thus in neglecting the effect of surface solvation, the computed adsorption potentials are offset by less than 0.6 V, with the solvation effect being the greatest for fluoride and least for iodide adsorption on the copper surfaces under consideration.

3.3.3. Bulk Cu-Halide Formation

Figure 3-7 compares the potential dependent free energies of Cu (111) specific chloride adsorption with the formation of bulk CuCl and CuCl2. Additional potential dependent free energy phase diagrams for the other halides are presented in the Supplementary Information.

In comparing the potential-dependent free energies, the equilibrium formation potential of CuCl is only slightly more positive than that of low coverage halide adsorption, suggesting bulk CuCl may be present during a variety of electrochemical reactions. At potentials below -0.36 V_NHE, both specific adsorption and bulk chloride formation are not stable (ΔG > 0). At potentials above -0.36 V_NHE, 1/9 ML of specifically adsorbed chloride on Cu (111) is stable (above -0.68 V_NHE on (211) and above -0.52 eV on (100)). As specific adsorption can occur rapidly, surfaces above these potentials in 1M Cl− solution would have adsorbed Cl. Above -0.17 V_NHE, CuCl bulk
formation becomes stable ($\Delta G < 0$), and transformation from bulk Cu to bulk CuCl can initiate. The formation of bulk CuCl occurs at potentials more positive than that of Cu$_2$O formation, suggesting in 1M Cl$^-$ solution, copper oxidation and copper chloride formation may compete or formation of oxychlorides may occur. Adsorption of Cl onto Cu (211) and Cu (100) surface facets is more favorable than on to the Cu(111) facet, therefore, the window between adsorption and bulk CuCl formation is slightly larger for these facets. At significantly positive potentials, above 1.2 V$_{NHE}$, a phase transition occurs to form bulk CuCl$_2$. Both this transition and formation of a full monolayer coverage ($\theta = 1$ML) of specifically adsorbed chloride require highly positive potentials past which Cu metal would be present in an aqueous electrolyte. Potentials above 1.23V$_{NHE}$ may either break down the electrolyte or trigger side reactions involving other species, and are well into the Cu$_x$O formation potential region. Similar trends are seen with the bulk copper bromides and copper iodide, with low coverage halide adsorption occurring at potentials slightly (generally 0.5-1 V) more negative than bulk CuX formation, and high coverage of adsorbed halide and CuX$_2$ formation requiring significantly more positive potentials.
Figure 3-7. Favorability of bulk CuCl formation, bulk CuCl$_2$ formation, and chloride adsorption onto Cu(111) as a function of potential. Dotted lines represent chloride specific adsorption (light yellow 1/9 ML, dark red 1ML) and solid lines represent bulk copper chloride formation (purple CuCl, blue CuCl$_2$). The vertical dashed lines separate regions of the most favorable surface or bulk state as a function of potential, as indicated by the labels within the four regions below the $\Delta G=0$ line.

3.3.4. Effect on electrochemical reactions

Given the low potential at which halide specific adsorption occurs, adsorbed halides may affect a variety of electrochemical processes. Copper deposition and dissolution (+0.34 $V_{\text{NHE}}$ to Cu$^{2+}$ and +0.52 $V_{\text{NHE}}$ to Cu$^{1+}$) occurs at potentials more positive of the calculated equilibrium adsorption potentials at 1/9 ML coverage. This suggests at least a low coverage of specifically
adsorbed halide, or possibly bulk CuX if kinetically accessible, are present during copper plating or dissolution in a 1M halide solution. Specifically adsorbed halides and CuX may also be present during copper oxidation to cuprous oxide (-0.360 V_{NHE} @ pH=14). Another important electro-catalytic reaction frequently studied on copper electrodes, CO$_2$ electroreduction, occurs at negative potentials (-1.5 < U < -0.5 V_{RHE}). We would expect a low coverage of specifically adsorbed Cl, Br, and I over portions of this range, with differences between facet and solvation considerations impacting the exact potential at which halide specific adsorption occurs. If specific adsorption, even with solvation considered, is not favorable on any facet throughout this range. A low coverage of specifically adsorbed halide could impact CO$_2$ electroreduction carried out in Cl$^-$, Br$^-$, and I$^-$ containing electrolytes. Our analysis neglects the effects of the co-adsorption of other species on halide adsorption. The co-adsorption of hydrogen, cations, or other anionic species could impact the favorability of halide specific adsorption depending on the co-adsorbed species.

The conversion of copper to bulk CuX occurs well within the range of many electrochemical reactions as well, becoming favorable thermodynamically at potentials 0.2-1 V more positive than the equilibrium potential for halide adsorption at 1/9 ML. Not considered here are the kinetic limitations of converting bulk Cu metal to bulk CuX, or the competing conversion to Cu$_2$O in aqueous electrolytes. Our DFT calculations suggest bulk CuX and CuX$_2$ formation occurs at potentials positive of Cu oxidation and CuX$_2$ at potentials positive of bromine and iodine evolution.

Further atomistic scale research is necessary to precisely determine the effects of the specifically adsorbed halide on specific reaction mechanisms and kinetics. The effect on electrochemical and electrocatalytic reactions by the specifically adsorbed halides could occur by a simple site blocking effect, or through a more complicated interaction where the binding
strength or coverage of reactive intermediates are affected by the presence of specifically adsorbed halide.

3.4. Conclusion

We used DFT to examine the energetics of halide specific adsorption (F\textsuperscript{−}, Cl\textsuperscript{−}, Br\textsuperscript{−}, I\textsuperscript{−}) on three Cu facets (111, 100, 211) using a computational free energy approach. The surface-halide interaction is probed using the surface normal dipole moment, the charge of the adsorbed halide, and the effect of surface solvation by explicit water molecules. The results suggest that Cl, Br, and I begin to favorably adsorb to low index copper facets to a low coverage (θ = 1/9 ML) at low potentials (-1.0 V\text{NHE} < U < -0.36 V\text{NHE}, using non-solvated values), putting their adsorption well within the range of many electrochemical and electrocatalytic reactions on copper. Adsorption to higher coverages (θ ≥ 1/2 ML) may occur on Cu (100). Adsorption follows a periodic trend and is most favorable with iodide and least favorable with fluoride. Between the Cu facets investigated, halide adsorption is most favorable on Cu (100) and least favorable on Cu (111). The effect of surface solvation is minimal and is largest with F\textsuperscript{−} adsorption, making adsorption more favorable by up to 0.6 eV. Formation of bulk CuX can also occur at low potentials, typically only 0.2-1 V more positive than that of low coverage halide specific adsorption, depending on halide species and surface facet considered. Specific adsorption of halides from electrolyte solutions and the formation of bulk CuX may affect the rate and mechanism of copper dissolution, deposition, and oxidation. Specific adsorption of Cl\textsuperscript{−}, Br\textsuperscript{−}, and I\textsuperscript{−} may also affect CO\textsubscript{2} electroreduction over copper.
3.5. Acknowledgements

This work was supported by the National Science Foundation, Grant # CBET – 1264104 and The Pennsylvania State University Diefenderfer Graduate Fellowship.

3.6. References


### 3.7 Supplementary Information

Table S3-1. Cu (111)-halide binding energy (1/2 X$_{2\text{g(0)}}$ to X$^*$, 0K non-ZPVE corrected) for each possible adsorption site (Calculated using PW91 exchange-correlation functional). Energies in bold represent lowest energy site. Energy in eV.

<table>
<thead>
<tr>
<th></th>
<th>Atop</th>
<th>Bridge</th>
<th>FCC</th>
<th>HCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-2.21</td>
<td>-2.57</td>
<td>-2.67</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>-1.25</td>
<td>-1.57</td>
<td>-1.65</td>
<td>-1.65</td>
</tr>
<tr>
<td>Br</td>
<td>-1.14</td>
<td>-1.43</td>
<td>-1.50</td>
<td>-1.50</td>
</tr>
<tr>
<td>I</td>
<td>-1.01</td>
<td>-1.29</td>
<td>-1.35</td>
<td></td>
</tr>
</tbody>
</table>

Table S3-2. Cu (100)-halide binding energy (1/2 X$_{2\text{g(0)}}$ to X$^*$, 0K non-ZPVE corrected) for each possible adsorption site (Calculated using PW91 exchange-correlation functional). Energies in bold represent lowest energy site. Energy in eV.

<table>
<thead>
<tr>
<th></th>
<th>Atop</th>
<th>Bridge</th>
<th>3-fold</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-2.98</td>
<td>-3.42</td>
<td>-3.40</td>
</tr>
<tr>
<td>Cl</td>
<td>-2.00</td>
<td>-2.35</td>
<td>-2.43</td>
</tr>
<tr>
<td>Br</td>
<td>-1.86</td>
<td>-2.17</td>
<td>-2.31</td>
</tr>
<tr>
<td>I</td>
<td>-1.68</td>
<td>-1.97</td>
<td>-2.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Starting Site</th>
<th>Converged Site</th>
<th>Energy (3x2 4 Layer Cu(211)+Cl) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>T</td>
<td>-2.19</td>
</tr>
<tr>
<td>Atop-3</td>
<td>SB</td>
<td>-2.21</td>
</tr>
<tr>
<td>EB</td>
<td>EB</td>
<td>-2.66</td>
</tr>
<tr>
<td>F1</td>
<td>F1</td>
<td>-2.35</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>-2.17</td>
</tr>
<tr>
<td>F2</td>
<td>EB</td>
<td>-2.66</td>
</tr>
</tbody>
</table>

Table S3-4. Standard halogen reduction/dissolution potentials at 1 M halide concentration and 1 atm halogen gas partial pressure (V$_\text{NHE}$)$^{45,56}$.

<table>
<thead>
<tr>
<th>Standard Dissolution Potential (V$_\text{NHE}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
</tr>
<tr>
<td>Cl</td>
</tr>
<tr>
<td>Br</td>
</tr>
<tr>
<td>I</td>
</tr>
</tbody>
</table>

Table S3-5. Halide anion experimentally measured solvation energies at 1 M halide concentration$^{47}$.

<table>
<thead>
<tr>
<th>Solvation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$^-$</td>
</tr>
<tr>
<td>Cl$^-$</td>
</tr>
<tr>
<td>Br$^-$</td>
</tr>
<tr>
<td>I$^-$</td>
</tr>
</tbody>
</table>

Table S3-6. Diatomic halogen energy and entropy contributions to total free energy at 300 K.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{DFT}}$ (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>PV (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_2$</td>
<td>-4.09</td>
<td>-0.07</td>
<td>0.85</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>-5.35</td>
<td>-0.02</td>
<td>1.18</td>
<td>0.03</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>-3.66</td>
<td>-0.02</td>
<td>1.04</td>
<td>0.03</td>
</tr>
<tr>
<td>I$_2$</td>
<td>-3.34</td>
<td>-0.02</td>
<td>1.10</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Table S3-7. Halide anion energy and entropy contributions to total free energy at 300 K.

<table>
<thead>
<tr>
<th></th>
<th>DFT (eV)</th>
<th>TS (eV)</th>
<th>PV (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F^-</td>
<td>-4.40</td>
<td>0.45</td>
<td>0.03</td>
</tr>
<tr>
<td>Cl^-</td>
<td>-3.90</td>
<td>0.48</td>
<td>0.03</td>
</tr>
<tr>
<td>Br^-</td>
<td>-3.62</td>
<td>0.51</td>
<td>0.03</td>
</tr>
<tr>
<td>I^-</td>
<td>-3.34</td>
<td>0.53</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Figure S3-1. Equilibrium adsorption potential for F^-, Cl^-, Br^-, and I^- onto Cu (111) (green), Cu (211) (beige), and Cu (100) (blue) calculated using the diatomic gas-phase energy method.

Figure S3-2. Calculated Bader charge of specifically adsorbed F^-, Cl^-, Br^-, and I^- on Cu (111) (green), Cu (211) (beige), and Cu (100) (blue).
Figure S3-3. Equilibrium adsorption potential for fluoride adsorption (blue diamond) and iodide adsorption (red square) on to Cu (211) as a function of the number of explicit water molecules solvating the surface-adsorbate bond.

Figure S3-4. Equilibrium adsorption potential for fluoride adsorption (blue diamond) and iodide adsorption (red square) on to Cu (111) as a function of the number of explicit water molecules solvating the surface-adsorbate bond.
Figure S3-5. Equilibrium adsorption potential for fluoride adsorption (blue diamond) and iodide adsorption (red square) on to Cu (100) as a function of the number of explicit water molecules solvating the surface-adsorbate bond.

Figure S3-6. Bulk formation and surface adsorption free energy vs. potential diagram for Br\textsuperscript{−} adsorption at 1/9 ML (yellow circle), 2/9 ML (yellow square), 1/3 ML (orange triangle), 1/2 ML (yellow diamond), and 1 ML (orange circle) onto Cu (111) and bulk CuBr (purple line) and CuBr\textsubscript{2} (blue line) formation. Vertical line (black, dashed) indicates potential where CuBr\textsubscript{2} becomes more favorable than CuBr (potential dependence of bulk formation not shown).
Figure S3-7. Bulk formation and surface adsorption free energy vs. potential diagram for I\(^-\) adsorption at 1/9 ML (yellow circle), 2/9 ML (yellow square), 1/3 ML (orange triangle), and 1/2 ML (orange circle) onto Cu (111) and bulk CuI formation (purple square).

Figure S3-8. Bulk formation and surface adsorption free energy vs. potential diagram for Cl\(^-\) adsorption at 1/9 ML (yellow circle), 1/4 ML (yellow square), 1/2 ML (orange triangle), and 1 ML (orange circle) onto Cu (100) and bulk CuCl (purple line) and CuCl\(_2\) (blue line) formation. Vertical line (black, dashed) indicates potential where CuCl\(_2\) formation becomes more favorable than CuCl (potential dependence of bulk formation not shown).
Figure S3-9. Bulk formation and surface adsorption free energy vs. potential diagram for Br⁻ adsorption at 1/9 ML (yellow circle), 1/4 ML (yellow square), 1/2 ML (orange triangle), and 1 ML (orange circle) onto Cu (100) and bulk CuBr (purple line) and CuBr₂ (blue line) formation. Vertical line indicates potential where bulk formation of CuBr₂ becomes more favorable than CuBr (potential dependence of bulk formation not shown).

Figure S3-10. Bulk formation and surface adsorption free energy vs. potential diagram for I⁻ adsorption at 1/9 ML (yellow circle), 1/4 ML (yellow square), 1/2 ML (orange triangle), and 1 ML (orange circle) onto Cu (100) and bulk CuI (purple line) formation.
Table S3-8. Cu (100)-I DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

<table>
<thead>
<tr>
<th></th>
<th>E_{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(100) – I</td>
<td>-124.99</td>
<td>0.01</td>
<td>0.17</td>
<td>-125.08</td>
</tr>
<tr>
<td>Cu(100) – 1 H2O</td>
<td>-136.16</td>
<td>0.59</td>
<td>0.12</td>
<td>-135.63</td>
</tr>
<tr>
<td>Cu(100) – 2 H2O</td>
<td>-150.95</td>
<td>1.30</td>
<td>0.33</td>
<td>-149.82</td>
</tr>
<tr>
<td>Cu(100) – 3 H2O</td>
<td>-165.56</td>
<td>1.96</td>
<td>0.41</td>
<td>-163.81</td>
</tr>
<tr>
<td>Cu(100) – 4 H2O</td>
<td>-180.14</td>
<td>2.62</td>
<td>0.62</td>
<td>-177.85</td>
</tr>
<tr>
<td>Cu(100) – I – 1 H2O</td>
<td>-139.17</td>
<td>0.60</td>
<td>0.28</td>
<td>-138.73</td>
</tr>
<tr>
<td>Cu(100) – I – 2 H2O</td>
<td>-154.00</td>
<td>1.31</td>
<td>0.42</td>
<td>-152.90</td>
</tr>
<tr>
<td>Cu(100) – I – 3 H2O</td>
<td>-168.56</td>
<td>1.98</td>
<td>0.56</td>
<td>-166.88</td>
</tr>
<tr>
<td>Cu(100) – I – 4 H2O</td>
<td>-183.15</td>
<td>2.63</td>
<td>0.71</td>
<td>-180.90</td>
</tr>
</tbody>
</table>

Table S3-9. Cu (100)-F DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

<table>
<thead>
<tr>
<th></th>
<th>E_{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(100) – F</td>
<td>-126.71</td>
<td>0.02</td>
<td>0.11</td>
<td>-126.76</td>
</tr>
<tr>
<td>Cu(100) – 1 H2O</td>
<td>-136.17</td>
<td>0.59</td>
<td>0.25</td>
<td>-135.72</td>
</tr>
<tr>
<td>Cu(100) – 2 H2O</td>
<td>-150.96</td>
<td>1.30</td>
<td>0.33</td>
<td>-149.83</td>
</tr>
<tr>
<td>Cu(100) – 3 H2O</td>
<td>-165.49</td>
<td>1.94</td>
<td>0.38</td>
<td>-163.74</td>
</tr>
<tr>
<td>Cu(100) – 4 H2O</td>
<td>-180.00</td>
<td>2.59</td>
<td>0.59</td>
<td>-177.71</td>
</tr>
<tr>
<td>Cu(100) – 5 H2O</td>
<td>-194.68</td>
<td>3.28</td>
<td>0.74</td>
<td>-191.78</td>
</tr>
<tr>
<td>Cu(100) – F – 1 H2O</td>
<td>-141.06</td>
<td>0.66</td>
<td>0.23</td>
<td>-140.53</td>
</tr>
<tr>
<td>Cu(100) – F – 2 H2O</td>
<td>-156.20</td>
<td>1.35</td>
<td>0.35</td>
<td>-155.02</td>
</tr>
<tr>
<td>Cu(100) – F – 3 H2O</td>
<td>-170.94</td>
<td>2.05</td>
<td>0.47</td>
<td>-169.14</td>
</tr>
<tr>
<td>Cu(100) – F – 4 H2O</td>
<td>-185.50</td>
<td>2.71</td>
<td>0.64</td>
<td>-183.13</td>
</tr>
<tr>
<td>Cu(100) – F – 5 H2O</td>
<td>-200.23</td>
<td>3.40</td>
<td>0.68</td>
<td>-197.17</td>
</tr>
</tbody>
</table>
Table S3-10. Cu (211)-F DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

<table>
<thead>
<tr>
<th></th>
<th>E\text{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(211) – F</td>
<td>-128.51</td>
<td>0.04</td>
<td>0.04</td>
<td>-128.49</td>
</tr>
<tr>
<td>Cu(211) – 1 H2O</td>
<td>-137.72</td>
<td>0.60</td>
<td>0.17</td>
<td>-137.22</td>
</tr>
<tr>
<td>Cu(211) – 2 H2O</td>
<td>-152.10</td>
<td>1.27</td>
<td>0.17</td>
<td>-150.91</td>
</tr>
<tr>
<td>Cu(211) – 3 H2O</td>
<td>-166.96</td>
<td>1.96</td>
<td>0.38</td>
<td>-165.20</td>
</tr>
<tr>
<td>Cu(211) – 4 H2O</td>
<td>-181.61</td>
<td>2.66</td>
<td>0.51</td>
<td>-179.22</td>
</tr>
<tr>
<td>Cu(211) – F – 1 H2O</td>
<td>-142.80</td>
<td>0.66</td>
<td>0.24</td>
<td>-142.28</td>
</tr>
<tr>
<td>Cu(211) – F – 2 H2O</td>
<td>-157.30</td>
<td>1.32</td>
<td>0.36</td>
<td>-156.18</td>
</tr>
<tr>
<td>Cu(211) – F – 3 H2O</td>
<td>-172.01</td>
<td>2.01</td>
<td>0.52</td>
<td>-170.28</td>
</tr>
<tr>
<td>Cu(211) – F – 4 H2O</td>
<td>-186.70</td>
<td>2.71</td>
<td>0.59</td>
<td>-184.29</td>
</tr>
</tbody>
</table>

Table S3-11. Cu (211)-I DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

<table>
<thead>
<tr>
<th></th>
<th>E\text{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(211) – I</td>
<td>-126.53</td>
<td>0.01</td>
<td>0.17</td>
<td>-126.62</td>
</tr>
<tr>
<td>Cu(211) – 1 H2O</td>
<td>-137.73</td>
<td>0.60</td>
<td>0.24</td>
<td>-137.27</td>
</tr>
<tr>
<td>Cu(211) – 2 H2O</td>
<td>-152.27</td>
<td>1.26</td>
<td>0.28</td>
<td>-151.16</td>
</tr>
<tr>
<td>Cu(211) – 3 H2O</td>
<td>-167.03</td>
<td>1.98</td>
<td>0.39</td>
<td>-165.26</td>
</tr>
<tr>
<td>Cu(211) – 4 H2O</td>
<td>-181.63</td>
<td>2.63</td>
<td>0.54</td>
<td>-179.29</td>
</tr>
<tr>
<td>Cu(211) – I – 1 H2O</td>
<td>-140.70</td>
<td>0.62</td>
<td>0.31</td>
<td>-140.26</td>
</tr>
<tr>
<td>Cu(211) – I – 2 H2O</td>
<td>-155.18</td>
<td>1.28</td>
<td>0.33</td>
<td>-154.07</td>
</tr>
<tr>
<td>Cu(211) – I – 3 H2O</td>
<td>-170.00</td>
<td>1.98</td>
<td>0.50</td>
<td>-168.29</td>
</tr>
<tr>
<td>Cu(211) – I – 4 H2O</td>
<td>-184.63</td>
<td>2.64</td>
<td>0.63</td>
<td>-182.33</td>
</tr>
</tbody>
</table>
Table S3-12. Cu \((111)\)-F DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(111) – F</th>
<th>Edft (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111) – F</td>
<td>-128.91</td>
<td>0.03</td>
<td>0.11</td>
<td>-128.94</td>
</tr>
<tr>
<td>Cu(111) – 1 H2O</td>
<td>-138.59</td>
<td>0.63</td>
<td>0.21</td>
<td>-138.08</td>
</tr>
<tr>
<td>Cu(111) – 2 H2O</td>
<td>-153.21</td>
<td>1.30</td>
<td>0.26</td>
<td>-152.04</td>
</tr>
<tr>
<td>Cu(111) – 3 H2O</td>
<td>-167.81</td>
<td>1.95</td>
<td>0.42</td>
<td>-166.07</td>
</tr>
<tr>
<td>Cu(111) – 4 H2O</td>
<td>-182.53</td>
<td>2.65</td>
<td>0.50</td>
<td>-180.12</td>
</tr>
<tr>
<td>Cu(111) – 5 H2O</td>
<td>-197.01</td>
<td>3.33</td>
<td>0.67</td>
<td>-194.02</td>
</tr>
<tr>
<td>Cu(111) – 6 H2O</td>
<td>-211.60</td>
<td>4.00</td>
<td>0.74</td>
<td>-207.98</td>
</tr>
<tr>
<td>Cu(111) – F – 1 H2O</td>
<td>-143.51</td>
<td>0.69</td>
<td>0.20</td>
<td>-142.92</td>
</tr>
<tr>
<td>Cu(111) – F – 2 H2O</td>
<td>-158.30</td>
<td>1.37</td>
<td>0.30</td>
<td>-157.03</td>
</tr>
<tr>
<td>Cu(111) – F – 3 H2O</td>
<td>-172.99</td>
<td>2.03</td>
<td>0.37</td>
<td>-171.13</td>
</tr>
<tr>
<td>Cu(111) – F – 4 H2O</td>
<td>-187.45</td>
<td>2.72</td>
<td>0.53</td>
<td>-184.98</td>
</tr>
<tr>
<td>Cu(111) – F – 5 H2O</td>
<td>-201.86</td>
<td>3.37</td>
<td>0.65</td>
<td>-198.82</td>
</tr>
<tr>
<td>Cu(111) – F – 6 H2O</td>
<td>-216.54</td>
<td>4.04</td>
<td>0.82</td>
<td>-212.90</td>
</tr>
</tbody>
</table>

Table S3-13. Cu \((111)\)-I DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage with and without surface solvation. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(111) – I</th>
<th>Edft (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111) – I</td>
<td>-127.10</td>
<td>0.01</td>
<td>0.16</td>
<td>-127.18</td>
</tr>
<tr>
<td>Cu(111) – 1 H2O</td>
<td>-138.43</td>
<td>0.60</td>
<td>0.23</td>
<td>-137.96</td>
</tr>
<tr>
<td>Cu(111) – 2 H2O</td>
<td>-152.75</td>
<td>1.24</td>
<td>0.37</td>
<td>-151.70</td>
</tr>
<tr>
<td>Cu(111) – 3 H2O</td>
<td>-167.68</td>
<td>1.95</td>
<td>0.45</td>
<td>-165.97</td>
</tr>
<tr>
<td>Cu(111) – 4 H2O</td>
<td>-182.40</td>
<td>2.66</td>
<td>0.50</td>
<td>-179.99</td>
</tr>
<tr>
<td>Cu(111) – I – 1 H2O</td>
<td>-141.27</td>
<td>0.62</td>
<td>0.40</td>
<td>-140.89</td>
</tr>
<tr>
<td>Cu(111) – I – 2 H2O</td>
<td>-155.59</td>
<td>1.25</td>
<td>0.56</td>
<td>-154.66</td>
</tr>
<tr>
<td>Cu(111) – I – 3 H2O</td>
<td>-170.52</td>
<td>1.97</td>
<td>0.60</td>
<td>-168.88</td>
</tr>
<tr>
<td>Cu(111) – I – 4 H2O</td>
<td>-185.23</td>
<td>2.67</td>
<td>0.69</td>
<td>-182.92</td>
</tr>
</tbody>
</table>

Table S3-14. Cu \((100)\)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1 ML halide coverage. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(100) – X 1ML</th>
<th>Edft (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-15.01</td>
<td>0.03</td>
<td>0.11</td>
<td>-15.03</td>
</tr>
<tr>
<td>Br</td>
<td>-14.43</td>
<td>0.01</td>
<td>0.13</td>
<td>-14.47</td>
</tr>
<tr>
<td>I</td>
<td>-11.81</td>
<td>0.00</td>
<td>0.14</td>
<td>-11.87</td>
</tr>
</tbody>
</table>
Table S3-15. Cu \((111)\)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1 ML halide coverage. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(111) –X 1ML</th>
<th>E_{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-14.73</td>
<td>0.02</td>
<td>0.08</td>
<td>-14.76</td>
</tr>
<tr>
<td>Br</td>
<td>-13.95</td>
<td>0.01</td>
<td>0.00</td>
<td>-13.87</td>
</tr>
<tr>
<td>I</td>
<td>-10.59</td>
<td>0.00</td>
<td>0.14</td>
<td>-10.66</td>
</tr>
</tbody>
</table>

Table S3-16. Cu \((100)\)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(100) –X 1/9 ML</th>
<th>E_{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-126.71</td>
<td>0.02</td>
<td>0.11</td>
<td>-126.76</td>
</tr>
<tr>
<td>Cl</td>
<td>-125.69</td>
<td>0.02</td>
<td>0.13</td>
<td>-125.73</td>
</tr>
<tr>
<td>Br</td>
<td>-125.31</td>
<td>0.01</td>
<td>0.18</td>
<td>-125.41</td>
</tr>
<tr>
<td>I</td>
<td>-124.99</td>
<td>0.01</td>
<td>0.17</td>
<td>-125.08</td>
</tr>
</tbody>
</table>

Table S3-17. Cu \((111)\)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(111) –X 1/9 ML</th>
<th>E_{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-128.91</td>
<td>0.03</td>
<td>0.11</td>
<td>-128.94</td>
</tr>
<tr>
<td>Cl</td>
<td>-127.84</td>
<td>0.03</td>
<td>0.11</td>
<td>-127.87</td>
</tr>
<tr>
<td>Br</td>
<td>-127.44</td>
<td>0.01</td>
<td>0.20</td>
<td>-127.56</td>
</tr>
<tr>
<td>I</td>
<td>-127.10</td>
<td>0.01</td>
<td>0.16</td>
<td>-127.18</td>
</tr>
</tbody>
</table>

Table S3-18. Cu \((211)\)-halide DFT energy, zero point vibrational energy, vibrational entropy and Gibbs free energy calculated at 300K and 1/9 ML halide coverage. Energy in eV.

<table>
<thead>
<tr>
<th>Cu(211) –X 1/9 ML</th>
<th>E_{DFT} (eV)</th>
<th>ZPVE (eV)</th>
<th>TS (eV)</th>
<th>G (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>-128.51</td>
<td>0.04</td>
<td>0.04</td>
<td>-128.49</td>
</tr>
<tr>
<td>Cl</td>
<td>-127.408</td>
<td>0.03</td>
<td>0.13</td>
<td>-127.45</td>
</tr>
<tr>
<td>Br</td>
<td>-126.95</td>
<td>0.02</td>
<td>0.08</td>
<td>-126.97</td>
</tr>
<tr>
<td>I</td>
<td>-126.53</td>
<td>0.01</td>
<td>0.17</td>
<td>-126.62</td>
</tr>
</tbody>
</table>
Figure S3-11. Cu (100)-F (a) and solvated structures for Cu (100)-F 1 H$_2$O (b), Cu (100)-F 2 H$_2$O (c), Cu (100)-F 3 H$_2$O (d), Cu (100)-F 4 H$_2$O (e), and Cu (100)-F 5 H$_2$O (f).

Figure S3-12. Cu (100)-I (a) and solvated structures for Cu (100)-I 1 H$_2$O (b), Cu (100)-I 2 H$_2$O (c), Cu (100)-I 3 H$_2$O (d), and Cu (100)-I 4 H$_2$O (e).
Figure S3-13. Cu (100)-I (a) and solvated structures for Cu (100)-I 1 H₂O (b), Cu (100)-I 2 H₂O (c), Cu (100)-I 3 H₂O (d), and Cu (100)-I 4 H₂O (e).

Figure S3-14. Cu (111)-F (a) and solvated structures for Cu (111)-F 1 H₂O (b), Cu (111)-F 2 H₂O (c), Cu (111)-F 3 H₂O (d), Cu (111)-F 4 H₂O (e), Cu (111)-F 5 H₂O (f), and Cu (111)-F 6 H₂O (g).
Figure S3-15. Cu (111)-I (a) and solvated structures for Cu (111)-I 1 H₂O (b), Cu (111)-I 2 H₂O (c), Cu (111)-I 3 H₂O (d), and Cu (111)-I 4 H₂O (e).
Figure S3-16. Cu (211)-F (a) and solvated structures for Cu (211)-F 1 H₂O (b), Cu (211)-F 2 H₂O (c), Cu (211)-F 3 H₂O (d), and Cu (211)-F 4 H₂O (e).
Figure S3-17. Cu (211)-I (a) and solvated structures for Cu (211)-I 1 H₂O (b), Cu (211)-I 2 H₂O (c), Cu (211)-I 3 H₂O (d), and Cu (211)-I 4 H₂O (e).
Figure S3-18. Cu (211) solvated bare surfaces for Cu (211) 1 H$_2$O (a), Cu (211) 2 H$_2$O (b), Cu (211) 3 H$_2$O (c), and Cu (211) 4 H$_2$O (d).
Figure S3-19. Cu (111) solvated bare surfaces for Cu (111) 1 H_{2}O (a), Cu (111) 2 H_{2}O (b), Cu (111) 3 H_{2}O (c), Cu (111) 4 H_{2}O (d), Cu (111) 5 H_{2}O (e), and Cu (111) 6 H_{2}O (f).
Figure S3-20. Cu (100) solvated bare surfaces for Cu (100) 1 H₂O (a), Cu (100) 2 H₂O (b), Cu (100) 3 H₂O (c), Cu (100) 4 H₂O (d), and Cu (100) 5 H₂O (e).

Figure S3-21. Equilibrium adsorption potential (V_{NHE}) vs. halide coverage on Cu(111) calculated using diatomic gas phase energy method (coverage of 1 ML given in Table S3-19).
Figure S3-22. Equilibrium adsorption potential ($V_{\text{NHE}}$) vs. halide coverage on Cu(100) calculated using diatomic gas phase energy method (coverage of 1 ML for F* and I* given in Table S3-20).

Table S3-19. Equilibrium adsorption potentials ($V_{\text{NHE}}$) for adsorption on Cu(111) as a function of halide coverage calculated using diatomic gas phase energy method.

<table>
<thead>
<tr>
<th>Cu(111) $U^0$ ($V_{\text{NHE}}$)</th>
<th>0.11 ML</th>
<th>0.22 ML</th>
<th>0.33 ML</th>
<th>0.5 ML</th>
<th>1 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>F*</td>
<td>0.26</td>
<td>0.30</td>
<td>0.38</td>
<td>0.83</td>
<td>18.8</td>
</tr>
<tr>
<td>Cl*</td>
<td>-0.14</td>
<td>-0.10</td>
<td>-0.06</td>
<td>0.71</td>
<td>2.28</td>
</tr>
<tr>
<td>Br*</td>
<td>-0.39</td>
<td>-0.33</td>
<td>-0.29</td>
<td>0.72</td>
<td>2.69</td>
</tr>
<tr>
<td>I*</td>
<td>-0.69</td>
<td>-0.63</td>
<td>-0.58</td>
<td>0.96</td>
<td>5.20</td>
</tr>
</tbody>
</table>

Table S3-20. Equilibrium adsorption potentials ($V_{\text{NHE}}$) for adsorption on Cu(100) as a function of halide coverage calculated using diatomic gas phase energy method.

<table>
<thead>
<tr>
<th>Cu(100) $U^0$ ($V_{\text{NHE}}$)</th>
<th>0.11 ML</th>
<th>0.25 ML</th>
<th>0.5 ML</th>
<th>1 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>F*</td>
<td>0.14</td>
<td>0.33</td>
<td>0.32</td>
<td>17.0</td>
</tr>
<tr>
<td>Cl*</td>
<td>-0.31</td>
<td>-0.25</td>
<td>-0.14</td>
<td>-0.01</td>
</tr>
<tr>
<td>Br*</td>
<td>-0.54</td>
<td>-0.50</td>
<td>-0.27</td>
<td>-0.15</td>
</tr>
<tr>
<td>I*</td>
<td>-0.89</td>
<td>-0.87</td>
<td>-0.27</td>
<td>2.09</td>
</tr>
</tbody>
</table>
Chapter 4

pH and Alkali Cation Effects on the Pt Cyclic Voltammogram Explained Using Density Functional Theory


Abstract

Platinum electrode cyclic voltammograms show features at low potentials which correspond to adsorption/desorption processes on Pt(111), Pt(100), and Pt(110) facets that have traditionally been ascribed to hydrogen adsorption. The 100 and 110 associated features exhibit a dependence on pH beyond the expected Nernstian shift. Herein we use density functional theory (DFT) to explain these shifts. We examine the specific adsorption of hydrogen, hydroxide, water, and potassium onto the low index facets of platinum, Pt(111), Pt(100), and Pt(110). In support of a growing body of evidence, we show that the low potential features which correspond to adsorption/desorption on Pt(100) and Pt(110) contain contributions from the competitive or co-adsorption of hydroxide. This allows us to simulate cyclic voltammograms for Pt(100) and Pt(110), as well as Pt(111), which match experimentally measured cyclic voltammograms in a pH = 0 electrolyte. Furthermore, we find that potassium cations can specifically adsorb to all three low index facets of platinum, weakening the binding of hydroxide. As potassium specific adsorption becomes more favorable with increasing pH, this allows us to explain the measured pH dependence of these features and to simulate cyclic voltammograms for the three low index facets of platinum which match experiment in a pH = 14 electrolyte. This has significant
implications in catalysis for hydrogen oxidation/evolution, as well as for any electrocatalytic reaction which involves adsorbed hydroxide.

4.1. Introduction

Adsorption of hydrogen (H⁺) and hydroxide (OH⁻) onto platinum electrodes forms reactive surface intermediates involved in many electrocatalytic reactions, including hydrogen oxidation and evolution,¹⁴ oxygen reduction and evolution,⁵⁻⁷ CO oxidation and stripping,⁸⁻¹¹ and methanol oxidation.⁸, ¹² However, the thermodynamics of hydrogen and hydroxide adsorption onto platinum in an electrochemical environment, as examined by cyclic voltammetry, are still debated. Changes in pH give an un-explained shift in the thermodynamics of hydrogen and hydroxide adsorption, beyond the Nernstian shift expected due to the change in concentration/activity of hydrogen and hydroxide. In this work we examine the effects of pH and the presence of a specifically adsorbed alkali metal cation, potassium, on the adsorption of protons, hydroxide, and water onto platinum electrode surfaces.

Polycrystalline platinum electrodes show three pronounced features in cyclic voltammograms within the 0-0.5 V_RHE (Reversible Hydrogen Electrode) range.⁴, ¹³ A series of single crystal electrode cyclic voltammetry studies, including the three low index platinum facets, have facilitated assigning these peaks to the 111, 100, and 110 facets, and they are typically referred to as hydrogen adsorption/desorption features.⁴, ¹⁴⁻¹⁶ Higher order facets can readily be de-convoluted to contributions from flat 111 terraces and contributions from 100 and 110 steps.¹⁶⁻¹⁷ The width of the terrace in the higher order facets has only a minor effect on adsorption, though there are subtle differences in the shape of low potential features between 110 steps on high order facets with wide terraces,¹⁷ those with short terraces (Pt(211))¹⁸, and the low index Pt(110) facet.¹⁴⁻¹⁵ Ultra-high vacuum studies support this de-convolution to contributions from steps and
terraces on higher order platinum facets, at least for hydrogen and oxygen adsorption. While these low potential features in cyclic voltammograms on platinum have traditionally been thought to be due to hydrogen adsorption/desorption, a growing body of evidence strongly suggests that hydroxide adsorption also contributes to these features on all platinum surfaces except for Pt(111) (and 111 terraces). This competitive or co-adsorption of hydrogen and hydroxide on Pt(100), Pt(110), and Pt steps seems intuitive given the expected stronger binding of hydrogen and hydroxide to these lower coordinated surfaces. The Feliu group has previously used the co-adsorption of H and OH on platinum steps to explain the magnitude and shape of these low potential features measured in acid. CO displacement experiments, which give a significantly lower potential of zero charge for stepped platinum surfaces than for Pt(111), further corroborate this competitive adsorption, suggesting hydroxide adsorption can occur at lower potentials on steps than on Pt(111). Rigorous thermodynamic analyses performed by Garcia-Araez et al. and Gómez et al. show that these features can be de-convoluted into contributions from hydrogen adsorption and contributions from hydroxide adsorption on Pt(100) and Pt(110) electrodes.

Recent density functional theory (DFT) calculations have shown that the free energy to dissociate adsorbed water to co-adsorbed hydrogen and hydroxide is positive on Pt(111) but negative on Pt(100), Pt(110), and Pt steps, showing it is thermodynamically favorable to co-adsorb hydrogen and hydroxide on these surfaces. Kolb et al. showed stronger binding for H, OH, and water on the Pt(100) step edge and stronger binding for OH on the Pt(110) step edge relative to Pt(111), though they neglect the effect of co-adsorbed water, which would act to stabilize adsorbed OH and further promote water dissociation. In contrast to these findings, Karlberg et al. use DFT to model cyclic voltammograms for hydrogen adsorption on Pt(111) and Pt(100) electrode surfaces that match experiment well, even though hydroxide competitive adsorption on Pt(100) is neglected. The involvement of hydroxyl adsorption in these low potential features,
therefore, remains unclear.

The low potential features measured by cyclic voltammetry on Pt(100), Pt(110) and Pt steps, show a dependence on pH beyond the expected Nernstian shift,\textsuperscript{4, 17} which has yet to be explained. The broad peak associated with hydrogen adsorption on Pt(111) is relatively pH independent, experiencing only the Nernstian shift corresponding to the change in concentration of protons, leaving the peak unaltered on a RHE scale.\textsuperscript{17} van der Niet et al. showed that, on well-defined single crystal electrodes, the low potential feature on stepped platinum electrodes is at a lower potential in acid than in base on a RHE scale (where the Nernstian shift is already accounted for).\textsuperscript{17} The low potential feature for facets which contain (110) or (100) steps both shift by \textasciitilde10 mV\textsubscript{RHE}/pH unit.\textsuperscript{17} The broad low potential peak on Pt(111) remains unchanged by pH, though the high potential (111) associated hydroxide adsorption peak changes shape between an acid electrolyte and a basic electrolyte.\textsuperscript{17} A similar trend was seen previously in phosphate containing electrolytes with polycrystalline platinum.\textsuperscript{13} Sheng et al. find identical results with polycrystalline platinum, showing two sharp low potential peaks, presumed to correspond to adsorption on Pt(110) and Pt(100), which shift almost linearly with pH.\textsuperscript{4} This non-Nernstian shift is important to catalysis, as the location of these peaks on the relative hydrogen electrode scale correlates with the rate of the hydrogen oxidation reaction. A CV peak shift to more positive potentials by \textasciitilde0.15 V on increasing the pH from 0 to 13 correlates with a roughly two order of magnitude decrease in the hydrogen oxidation/evolution reaction rate, when compared to the rate measured in acid in an operating PEM fuel cell under conditions free from mass transfer limitations.\textsuperscript{4, 35-36}

This sub-Nernstian shift has so far gone unexplained. van der Niet et al. proposed that, in alkaline media, relatively more hydroxide may be adsorbed than in acidic media, that the electrosorption valency of hydroxide may not be unity, or that a low coverage of oxygen may be co-adsorbed with hydroxide, giving this peak its experimentally measured pH dependence on an
RHE scale.\textsuperscript{17} It is unclear, however, why the electrosorption valency or ratio of adsorbed hydroxide to adsorbed oxygen would be pH dependent. Sheng et al. suggest that the shift of these low potential peaks with pH could be due to co-adsorbed or competitively adsorbed hydroxide, but provide no insight into why this competition should be pH dependent on a RHE scale.\textsuperscript{4} Sheng et al. assumed this shift was a direct measure of hydrogen binding energy, but provide no explanation as to why the binding strength of hydrogen on Pt(100) or (110) would depend on pH.\textsuperscript{4} One possible explanation for this shift with pH, not considered previously, is the presence of specifically adsorbed alkali metal cations on the electrode surface as the pH is increased, as alkali cation specific adsorption becomes more favorable relative to proton adsorption with increasing pH.

Alkali metal cation specific adsorption onto platinum electrodes has only limited direct experimental evidence, though recent density functional theory efforts show their adsorption is favorable at high pH and low potential onto Pt(111),\textsuperscript{37-38} Pt(100), and Pt(110).\textsuperscript{38} Indirect experimental evidence includes radiotracer studies showing sodium and cesium adsorption from alkaline solutions onto platinum electrodes\textsuperscript{39} as well as studies showing their co-adsorption with various anions, including (bi)sulfate\textsuperscript{40-43} and cyanide,\textsuperscript{44-45} supported by direct STM imaging and DFT calculations.\textsuperscript{44-48} Nanogravimetric electrochemical experiments show the specific adsorption of cesium at low potentials in a sulfuric acid electrolyte as well as its co-adsorption with (bi)sulfate.\textsuperscript{49-50} A building body of evidence suggests the presence of alkali metal cations effects a variety of electrochemical reactions, including hydrogen oxidation and evolution,\textsuperscript{51-52} methanol oxidation,\textsuperscript{51, 53} formate oxidation,\textsuperscript{54} ethylene glycol oxidation,\textsuperscript{55-57} CO oxidation and stripping,\textsuperscript{58-59} oxygen reduction\textsuperscript{51} and evolution,\textsuperscript{60-61} and CO\textsubscript{2} electroreduction.\textsuperscript{62} It has been unclear, however, whether these effects occur due to specific cation adsorption or influence from non-specific adsorption of cations in the electrochemical double layer.

Herein, we use density functional theory to examine the specific adsorption of hydrogen,
hydroxide, water, and potassium onto Pt(111), Pt(100), and Pt(110) electrode surfaces. We find that hydrogen binds more strongly to Pt(100) and Pt(110) electrodes than to Pt(111), in contrast to experimentally measured cyclic voltammograms which show desorption from Pt(110) at potentials lower than the corresponding peak on Pt(100) and intermediate to the broad peak seen with Pt(111). We then show that adsorption of hydroxide is also much more favorable on Pt(100) and Pt(110) than on Pt(111) and would occur within the traditional “hydrogen adsorption region” on stepped platinum surfaces. This lends concrete thermodynamic evidence to support that these low potential peaks measured on stepped platinum surfaces in cyclic voltammetry correspond to the competitive adsorption of hydrogen and hydroxide. While we only investigate the low index facets of platinum, a significant body of electrochemical results suggest that the behavior of higher order platinum facets and polycrystalline platinum electrodes can be at least roughly de-convoluted into contributions from the low index facets.\textsuperscript{4, 16-17}

Furthermore, we find that potassium cations can favorably adsorb to low coverages on Pt(111), Pt(100), and Pt(110) and could compete with hydrogen adsorption in high pH electrolytes. We find specifically adsorbed potassium has no effect on the adsorption energetics of hydrogen, but a significant effect on the adsorption of hydroxide. The effect matches the pH dependence of these low potential peaks measured on stepped or polycrystalline platinum electrodes. As the pH is increased, not only is a counter-cation such as potassium added to the electrolyte, but the absolute potential of the electrode is lowered, thereby making the reductive potassium specific adsorption more favorable, increasing its coverage on the surface. Co-adsorbed potassium disrupts the solvation of adsorbed hydroxide, destabilizing the surface hydroxide, and driving the adsorption peak measured in cyclic voltammetry to higher potentials at higher pH. We compare our results with a significant body of both computational and experimental work, including prior DFT simulations and both electrochemical and UHV surface science studies.
4.2. Methods

4.2.1. Computational Details

Density functional theory (DFT) was used to probe the specific adsorption thermodynamics of hydrogen, hydroxide, potassium, and water onto Pt(111), Pt(100), and Pt(110) electrode surfaces. Electronic structure calculations were performed using the Vienna ab initio Simulations Package (VASP),\textsuperscript{63-65} using a plane wave basis set and the Perdew-Wang (PW91) exchange-correlation functional.\textsuperscript{66} The Projector Augmented Wave (PAW) approach was used to describe the ion-core interactions.\textsuperscript{67-68} A 5x5x1 Monkhorst-Pack mesh\textsuperscript{69} was used to sample k-space for the 3x3 and 4x4 unit cells, and 7x7x1 mesh was used for the 2x2 unit cells. The cutoff energy for the plane-wave basis set was 450 eV and the structural optimization was complete when the magnitude of the forces on the atoms were less than 0.02 eV Å\textsuperscript{-1}. The DFT energies are converged to within 0.03 eV with respect to the k-space sampling mesh and the plane-wave cutoff energy. Dipole corrections were included in all surface calculations in the surface normal direction (LDIPOL = TRUE, IDIPOL = 3). The experimentally measured Pt lattice constant of 3.92 Å was used.\textsuperscript{70} All surface calculations used a 4 layer slab, with the bottom two layers frozen during optimization. An adsorption site preference analysis was performed for each adsorbate alone on each surface at 1/9 ML (in the 3x3 unit cell). Results are given in Table S4-1 of the supplementary information. K* preferred the 3-fold hollow site on all three facets. H* preferred the FCC site on Pt(111) and bridge site on Pt(100) and Pt(110). OH* preferred atop sites on Pt(111) and Pt(110) and bridge sites on Pt(100). OH* was also modeled with co-adsorbed water, with results given in the section “Surface solvation and adsorbed water”. Bader charge analysis was performed using the implementation developed by the Henkelman group.\textsuperscript{71-73}
4.2.2. Calculating Equilibrium Adsorption Potentials

The procedure for calculating the equilibrium adsorption potentials for alkali metal cations, hydrogen, and anion adsorption has been described previously\textsuperscript{37, 74-75} and is reviewed here.

The adsorption reaction for an aqueous cation, including a proton and potassium ion, can be written as a reduction reaction:

\[ * + C_{aq}^+ + e^- \rightarrow C^* \]  
\[ \text{(1)} \]

where * represents a bare surface site, \( C_{aq}^+ \) and \( C^* \) the solution phase and surface adsorbed cation, respectively, and \( e^- \) an electron from the electrode. Similarly, the adsorption of an anion such as hydroxide can be written as an oxidation reaction:

\[ * + OH_{aq}^- \rightarrow OH^* + e^- \]  
\[ \text{(2)} \]

where \( OH_{aq}^- \) and \( OH^* \) represent solution phase and adsorbed hydroxide, respectively. The Gibbs free energy change for each adsorption reaction as a function of electrode potential on an absolute scale are

\[ \Delta G_{ads}^{C^+}(U_{abs}) = G_{c^*} - G_c - G_{C_{aq}^+} + |e|U_{abs} \]  
\[ \text{(3)} \]

\[ \Delta G_{ads}^{OH^-}(U_{abs}) = G_{OH^*} - G_c - G_{OH_{aq}^-} - |e|U_{abs} \]  
\[ \text{(4)} \]

for reactions 1 and 2, respectively. \( \Delta G_{ads}^{C^+}(U_{abs}) \) and \( \Delta G_{ads}^{OH^-}(U_{abs}) \) are the free energy changes for each respective adsorption reaction, \( G_{c^*} \) and \( G_{OH^*} \) the free energy of adsorbed cation and adsorbed hydroxide, \( G_{C_{aq}^+} \) and \( G_{OH_{aq}^-} \) the free energy of solution phase cation and hydroxide, respectively, \( G_c \) the free energy of a bare surface site, and \( |e|U_{abs} \) the free energy of an electron on an absolute potential scale.

The free energy of the adsorbed species \( X^* \), \( G_{X^*} \) is calculated as

\[ G_{X^*} = E_X^{DFT} + ZPVE - TS_{vib} \]  
\[ \text{(5)} \]
where $E^{DFT}_X$ is the DFT energy of the adsorbed species-surface state, ZPVE the zero-point vibrational energy, and $T_S_{vib}$ the vibrational entropy of the surface-adsorbate bond (and of the bonds in the adsorbate, in the case of adsorbed hydroxide). It is assumed the phonon modes of the metal electrode surface are not perturbed by the adsorbate. The free energy of the surface is therefore calculated as

$$G_s = E^{DFT}_s \quad [6]$$

To calculate the free energy of the solution phase cations $G_{Caq}^+$ and $G_{Haq}^+$, two different methods are used. The aqueous potassium cation free energy, $G_{Kaq}^+$, is calculated by finding the free energy of the cation in the gas phase, accounting for translational entropy, then adding on an experimentally measured solvation energy for the cation in a 1M solution ($\Delta G_{solv}^0$):

$$G_{Kaq}^+ = E^{DFT}_{K^g} - T_S_{trans} + \Delta G_{solv}^0 \quad [7]$$

The free energy of the aqueous phase proton, $G_{Haq}^+$, is calculated using the computational hydrogen electrode $^{76}$, as given by reaction 8 and equation 9:

$$H_2(g) \rightarrow 2H^+_aq + 2e^- \quad [8]$$

$$G_{Haq}^+ = \frac{2eU_0 + G_{H_2}}{2} \quad U_0 = 0.00 \text{ V}_{NHE} @ pH = 0 \quad [9]$$

We find the solvation energy method described above for finding the free energy of $G_{Kaq}^+$ and previously for finding the free energy of an aqueous phase halide$^{75}$ matches the approach of using an experimental dissolution potential to within 0.3 eV. A comparison for the aqueous free energy of K$^+$ and H$^+$ calculated using the two methods are given in Table S4-2 in the supplementary information.

The free energy of the solution phase hydroxide, $G_{OHaq}$, is calculated using an approach
similar to the computational hydrogen electrode method, using the hydrogen oxidation reaction and its known potential in a pH = 14 solution (-0.826 V$_{NHE}$). The overall reaction is:

$$H_2(g) + 2OH^- \rightarrow 2H_2O_{aq} + 2e^-$$  \[10\]

Since the overall free energy change for this reaction is known, from its equilibrium potential, and the free energies of $H_2(g)$ and $H_2O_{aq}$ can easily be calculated, the free energy of the solution phase hydroxide anion can be found, as given by equation 11:

$$G_{OH_{aq}} = \frac{2G_{H_2O} - 2eU_0 - G_{H_2}}{2} \quad U_0 = -0.826 \text{ V}_{NHE} \ @ \ pH = 14$$  \[11\]

where $G_{H_2O}$ and $G_{H_2}$ are the free energies of solution phase water and gas phase hydrogen molecules, respectively. $G_{H_2O}$ and $G_{H_2}$ are calculated by:

$$G_{H_2O_{aq}} = E_{H_2O_{g}}^{DFT} - TS_{gas} + ZPVE + U_{int} + PV$$  \[12\]

$$G_{H_2(g)} = E_{H_2(g)}^{DFT} - TS_{gas} + ZPVE + U_{int} + PV$$  \[13\]

where $TS_{gas}$ is the translational, rotational, and vibrational entropy of the molecule, ZPVE is the zero point vibrational energy, $U_{int}$ is the internal energy of the molecule, and PV is the pressure-volume contribution to the gas phase free energy. $G_{H_2O_{aq}}$ is calculated as the free energy of gas phase water at a partial pressure equal to the vapor pressure of a 300K aqueous solution (0.035 bar), where $G_{H_2O_{aq}} = G_{H_2O_{g}}$. Calculated free energies can be found in the supplementary information.

Finally, equations 3 and 4 can be expanded to include corrections to the free energy due to the interaction of the surface normal dipole moment with the interfacial electric field, yielding equations 14 and 15:

$$\Delta G^+_{ads}(U_{NHE}) = G_C^- - |e|(U_{NHE} + 4.6) + |e|(U_{NHE} - U_{pzc}) \frac{\mu_C^+ - \mu_s}{d} - G_s - G_{C_{aq}}^+$$  \[14\]

$$\Delta G^-_{ads}(U_{NHE}) = G_{(OH)^+} - |e|U_{NHE} - |e|(U_{NHE} - U_{pzc}) \frac{\mu_{(OH)}^- - \mu_s}{d} - G_s - G_{OH_{aq}}^-$$  \[15\]
with $\frac{\mu_{C^+} - \mu_\ast}{d}$ the change in surface normal dipole moment on adsorption divided by $d$, the Helmholtz thickness, taken to be $3\text{Å}^{76}$. The adsorption free energy of the cation, $\Delta G_{ads}^{\pm\text{aq}}(U_{\text{NHE}})$, is shifted from an absolute to the normal hydrogen electrode scale (NHE) using the 4.6V difference between scales observed experimentally$^{77-79}$ and replicated computationally.$^{80}$ This correction is not needed for hydrogen adsorption when using the computational hydrogen electrode as it references the NHE scale.

In all cases the temperature is taken as 300K and the concentration of each species 1M unless otherwise noted. All entropic contributions to free energy are calculated using traditional statistical mechanics relationships. Vibrational energy and entropy are calculated using vibrational frequencies calculated by VASP, by computing the Hessian matrix from atomic displacements of 0.01Å in each Cartesian direction.

To calculate equilibrium adsorption potentials, equations 14 and 15 are solved for the potential, $U_{\text{NHE}}$, where $\Delta G_{ads} = 0$.

### 4.2.3. Surface Solvation and Adsorbed Water

Aqueous electrolyte near the electrode surface has little effect on the adsorption of hydrogen,$^{34, 37}$ but can have a significant effect on the adsorption of alkali cations$^{37}$ and hydroxide.$^{18, 81}$

To model the effect of surface solvation on potassium adsorption, we evaluate the Gibbs free energy change for adsorption of potassium at 1/9 ML on Pt(111), Pt(100), and Pt(110) with 1, 3, or 6 explicit water molecules placed near the surface adsorbate bond. The method used here has been described previously.$^{37, 75}$ 1, 3, or 6 water molecules are placed near potassium on the electrode surface, the structure is relaxed and the free energy calculated; the potassium atom is
then removed, the structure relaxed again, and the free energy of the solvated clean surface calculated. While it is not guaranteed that the global minimum energy water structure is found, this method does not require knowledge of the near-surface water structure, which is long range and metal surface dependent. Using a small number of explicit water molecules allows for solvation effects on adsorption free energy to be approximated without greatly increasing computational effort. Furthermore, while the free energy calculated here only includes the vibrational energy and entropy of the water structure, thereby neglecting configurational entropy of the dynamic water, we assume the difference in these properties between the initial and final states here to be small. The Gibbs free energy change for potassium cation adsorption onto the solvated electrode surface is calculated in a manner similar to equation 14, shown in equation 16:

\[
\Delta G_{ads}^{C_{aq}}(U_{NHE}) = G_{(H_2O)_nC^+} - |e|(U_{NHE} + 4.6) + |e|(U_{NHE} - U_{pzc}) \frac{\mu_{C^+} - \mu_*}{d} - G_{(H_2O)_n}^{C^+} \tag{16}
\]

where \(G_{(H_2O)_nC^+}\) is the adsorbed surface state containing 1/9 ML potassium and 1, 3, or 6 water molecules, and \(G_{(H_2O)_n}^{C^+}\) is the solvated bare surface state.

We also model the effect of implicit solvation on the adsorption of potassium at 1/9 ML onto Pt(111), Pt(100), and Pt(110), using the implicit solvation model implemented in VASP by the Hennig and Arias groups.\(^8\) We use the default solvent parameters defined for water\(^8\) with an ENCUT=800.

To model the effect of adsorbed water on the adsorption of hydroxide on Pt(111) and Pt(100), the minimum energy hydroxide-water co-adsorbed structure was found in the prior literature and replicated on a 3x3 surface. For Pt(111), the minimum energy structure is a hexagonal arrangement of 1/3 ML OH\(^*\) and 1/3 ML H\(_2\)O\(^*\) as determined from DFT\(^8,8^3-8^6\) and UHV STM imaging, low energy electron diffraction (LEED), and spectroscopic techniques.\(^8^7-8^9\) The minimum energy water structure on Pt(111) was the 2/3 ML ice like bi-layer.\(^8^6\) For Pt(100), the
minimum energy hydroxide and water structure is a square-like alternating arrangement of OH* and H₂O* at 1/3 ML H₂O* and 1/3 ML OH*, and the minimum energy water structure was 2/3 ML H₂O* as determined by DFT.⁹⁰ This coverage of OH* on Pt(100) compares well with that found by Gómez et al.¹⁴ and Garcia-Araez et al.⁹¹ in electrochemical cyclic voltammetry in perchloric acid.

For hydroxide and water adsorption on Pt(110), no known minimum energy structure could be found. As it is well known that the minimum energy structure of adsorbed hydroxide and water on platinum maximizes the number of hydrogen bonds between OH* and H₂O* ⁸³, two structures were considered; an alternating square arrangement of 1/3 ML H₂O* and 1/3 ML OH* in a 3x3 unit cell, and an alternating square arrangement of 1/2 ML H₂O* and 1/2 ML OH* in a 2x2 unit cell. 1/2 ML H₂O* and 1/2 ML OH* in a 2x2 unit cell was found to be lower in energy (per OH*).

The free energy to adsorb or form hydroxide in these minimum energy structures (MES) of co-adsorbed hydroxide and water is calculated by removing half of the hydrogen atoms, as protons, from an adsorbed water layer to form the co-adsorbed hydroxide and water layer. This hydroxide formation free energy is given in equation 17.

\[
\Delta G_{\text{ads,MES}}^{\text{OH}}(U_{\text{NHE}}) = G_{(H_2O)_{n-x}OH_x^*} + xeU_{\text{NHE}} + xeU_{\text{NHE}} \frac{\mu_{(OH)}^* - \mu^*}{d} - G_{(H_2O)_n^*} + xG_{H_{aq}^+} \tag{17}
\]

\(G_{(H_2O)_{n-x}OH_x^*}\) is the free energy of the co-adsorbed hydroxide and water structure, \(G_{(H_2O)_n^*}\) the free energy of the adsorbed water reactant structure, and \(x\) the number of protons/electrons removed.

To further investigate the effect of co-adsorbed water on hydroxide adsorption, the adsorption of hydroxide on each of the three facets was also investigated at low coverage (1/9 ML) with 1 co-adsorbed water molecule. The free energy of adsorption is then calculated as given by equation 18, equivalent to equation 16:
\[ \Delta G_{\text{ads}}^{OH^-}(U_{\text{NHE}}) = G_{(H_2O)_nOH} + eU_{\text{NHE}} + eU_{\text{NHE}} \frac{\mu_{(OH)^*} - \mu_*}{d} - G_{(H_2O)_n^*} - G_{OH_{\text{aq}}} \] [18]

Equation 17 differs from Equation 18 in that protons are desorbed from the water structure instead of hydroxide adsorbed into the water structure. Both methods are equivalent, assuming the pH used is the same in each case, and only differ in the stoichiometry used in the explicit solvation shell.

While the absolute energy and free energy change of adsorption will certainly depend on the particular water structure evaluated, both for water adsorbed onto and near the electrode surface, we find that the trend in adsorption across facets or with co-adsorbed alkali cation are independent of water structure, and hold even when only one water molecule solvates the electrode surface.

Images of all water and co-adsorbed hydroxide and water structures on each of the three facets are given in the supplementary information. A comparison of the different approaches for calculating the hydroxide adsorption free energy is given in the supplementary information.

4.2.4. Quantifying Adsorbate-Adsorbate Interactions

To quantify the interaction between one adsorbate and another on the same surface, the free energy of “interaction” is calculated using the following reaction:

\[ X_1^* + X_2^* = (X_1X_2)^* + * \] [19]

where \( X_1^* \) and \( X_2^* \) are independent adsorbates, and \( (X_1X_2)^* \) represents the two species adsorbed in the same surface unit cell. The free energy change for this reaction is simply:

\[ \Delta G_{X_1-X_2} = G_{(X_1X_2)^*} + G_* - G_{X_1^*} - G_{X_2^*} \] [20]

where a positive \( \Delta G_{X_1-X_2} \) describes a repulsive \( X_1-X_2 \) adsorbate interaction.
4.2.5. Computational Cyclic Voltammograms

Cyclic voltammograms for adsorption of ionic species were modeled by solving for the rate of adsorption with electron transfer as a function of potential, scan rate, and species coverage under the assumption that adsorption is equilibrated at all potentials. This approach has been previously described for modeling the CV features associated with (bi)sulfate adsorption.\textsuperscript{74} The equilibrium constant for adsorption of an ionic species, $X$, can be written as:

$$K_{X^*}(U, \theta_{X^*}) = \exp \left( \frac{-\Delta G_{X^*}(U, \theta_{X^*})}{RT} \right) = \frac{\theta_{X^*}}{\theta^*_a a_X(aq)}$$  \hspace{1cm} [21]

where $\theta_{X^*}$ is the coverage of adsorbed species $X$, $\theta^*_a$ is the coverage of bare or unoccupied surface sites, $a_X(aq)$ is the activity of ionic species $X$ in solution, $R$ is the gas constant, $T$ the temperature, and $\Delta G_{X^*}(U, \theta)$ the Gibbs free energy of adsorption of species $X$ to the electrode surface as a function of its coverage and the electrode potential $U$. The potential ($U$) is defined as a function of time, $t$, and scan rate, $\nu$ from an initial starting potential $U_0$:

$$U = U_0 + \nu t$$  \hspace{1cm} [22]

Finally the voltammetric current density due to adsorption of species $X$ can be written as:

$$j_{X^*} = \left( \frac{m \times e}{A} \right) \frac{d\theta_{X^*}}{dt}$$  \hspace{1cm} [23]

where $m$ is the maximum coverage and $A$ is the area of the unit cell. The cyclic voltammograms are each simulated at a scan rate of 50 mV/s and a surface atom density, considering transfer of one electron per surface atom, of 241 $\mu$C/cm$^2$ for Pt(111),\textsuperscript{34} 209 $\mu$C/cm$^2$ for Pt(100),\textsuperscript{34} and 147 $\mu$C/cm$^2$ for Pt(110).\textsuperscript{92} The reverse scan in the cyclic voltammogram is given by $-j_{X^*}$.

The Gibbs free energy of adsorption, $\Delta G_{X^*}$, is calculated as described in equation 14. For the adsorption reactions which are explicitly coverage dependent, an approximation to the configurational entropy\textsuperscript{34} is added to the Gibbs free energies of adsorption calculated by equation 14. The configurational entropy is defined as:
\[
S = k_B \ln \left( \frac{1 - \theta}{\theta} \right). \tag{24}
\]

A linear function is fit to a plot of \( \Delta G_{X^*} \) vs. \( \theta_{X^*} \), plugged into the adsorption equilibrium constant expression, equation 21, which is then solved with equations 22 and 23 to simulate the cyclic voltammogram, in terms of \( f_{X^*} \) vs \( U \).

Cyclic voltammograms are simulated for both coverage dependent adsorption and electrochemical “phase-change” reactions, which have been simplified here to be coverage independent. While the free energy change for the phase change reaction does depend on the coverage of each species before and after the phase change, only one coverage of each species is examined. In the electrochemical phase change, hydrogen is desorbed (adsorbed) and hydroxide adsorbed (desorbed). Phase change reactions are simulated for competitive hydrogen and hydroxide adsorption on Pt(100) and Pt(110). For both facets, the starting hydrogen coverage is 1 ML and the final hydroxide coverage is given by the respective minimum energy co-adsorbed hydroxide and water structure (1/3 ML OH* on Pt(100) and 1/2 ML OH* on Pt(110)). This phase change reaction is given in reaction 25.

\[
(H_2O)_n xH^* \rightarrow yOH^* (n - y)H_2O^* + (x + y)e^- + (x + y)H_{aq}^+ \tag{25}
\]

\[
\Delta G_{H^* \rightarrow OH^*H_2O^*}(U_{NHE}) = G_{yOH^* (n-y)H_2O^*} + (x+y)eU_{NHE} - G_{(H_2O)_n xH^*} - (x+y)G_{H_{aq}^+} \tag{26}
\]

The same procedure is used to calculate the Gibbs free energy change for the reaction as is used in equations 14 and 15, yielding equation 26. The effect of co-adsorbed potassium on the phase change reaction is also considered, using equation 26, where now the free energy of the adsorbed hydrogen and adsorbed hydroxide states also contain co-adsorbed potassium (at the
same coverage in both states). Dipole moment changes were neglected here, as they were small in both cases, giving a change in reaction free energy of less than 0.005 eV when included.

4.3. Results

4.3.1. Hydrogen Adsorption

The adsorption of hydrogen onto Pt(111), Pt(100), and Pt(110) as a function of coverage was modeled using DFT. Adsorption favorability is given by the calculated equilibrium adsorption potential in Figure 4-1. Since hydrogen adsorption is a reduction process, adsorption is favorable (the ΔG becomes negative) at any potential more negative of the equilibrium adsorption potential.

![Figure 4-1](image)

Figure 4-1. Equilibrium adsorption potentials (U°, V_NHE) for the adsorption of hydrogen from a pH = 0 solution as a function of coverage (ML) onto Pt(111) (blue square), Pt(100) (black triangle), and Pt(110) (red diamond). Dotted lines are linear regressions of the plotted data.

The adsorption of hydrogen on Pt(111) is significantly dependent on coverage, relative to the other low index facets, with adsorption becoming less favorable as the coverage is increased. This is a well-known phenomenon that has been observed both experimentally by cyclic
voltammetry\textsuperscript{14, 29, 92} and temperature programmed desorption (TPD) in ultra-high vacuum (UHV) experiments,\textsuperscript{93-95} as well as computationally.\textsuperscript{34, 95-96} This strong coverage dependence has been ascribed to significant repulsion between the hydrogen adsorbates.\textsuperscript{14, 92-94} The calculated slope of adsorption potential vs. coverage compares well with the slope of the adsorption energy vs. coverage calculated by Karlberg et al. with DFT (0.15 \textsuperscript{34} vs. 0.128 eV/ML).\textsuperscript{34} The slope calculated here also compares well to that derived from cyclic voltammetric experiments in HClO\textsubscript{4} via rigorous thermodynamic analysis by Garcia-Araez et al. and Gómez et al. (0.303 \textsuperscript{29}, 0.295 \textsuperscript{15}, 0.285 \textsuperscript{14} vs. 0.267 eV/ML (our slope with configurational entropy included)). The negative of the intercept, which gives the $\Delta G$ of adsorption when $\theta_{H^*} = 0$, matches experiment as well (-0.285 to -0.291 eV\textsuperscript{14-15, 29} vs. -0.256 eV).

The adsorption of hydrogen onto Pt(100) and Pt(110) is significantly more favorable than on Pt(111), which is to be expected given their lower surface atom coordination. On Pt(100), the intercept at zero coverage compares well to that found by Garcia-Araez et al. (-0.386 eV \textsuperscript{29} vs. -0.404 eV), with our DFT results suggesting slightly stronger binding than found experimentally. The calculated slope of adsorption potential vs coverage also differs slightly (0.073 eV/ML \textsuperscript{29} vs. 0.021, or 0.160 eV/ML, with configurational entropy), with our DFT calculations suggesting a slightly stronger repulsion when configurational entropy is included than what is measured experimentally in an electrochemical environment. Our DFT results for H adsorption on Pt(100) matches prior DFT work well; our slope is similar to that found by Karlberg et al. (0.034 eV/ML \textsuperscript{34} vs. 0.021 eV/ML). The small dependence on coverage suggests only weak repulsion between adsorbed hydrogen atoms on Pt(100). The trend in hydrogen adsorption favorability between Pt(111) and Pt(100) calculated here matches TPD data from UHV experiments, with hydrogen desorbing at a higher temperature, indicating stronger binding, and with a narrower desorption peak, indicating less repulsion between adsorbates on Pt(100) and 100 steps than on Pt(111) and 111 terraces.\textsuperscript{19-21, 97} The deviation in the electrochemical environment may be due to the
competitive or co-adsorption of hydroxide onto the Pt(100) surface, as suggested previously,\textsuperscript{14, 17, 91} but this has not been previously evaluated using DFT techniques. We examine this in the following sections.

The favorability of hydrogen adsorption on Pt(111) deviates significantly from that measured in electrochemical experiments, where hydrogen adsorption appears to be less favorable and occurs at lower potentials on Pt(111) and 110 steps than on the other low index facets.\textsuperscript{14-17, 22, 29, 59, 92} TPD and DFT data suggest hydrogen adsorption favorability on Pt(110) (1x2) bridge sites and 110 steps on Pt(553) fall intermediate to that of hydrogen adsorption on 100 steps and 111 terraces on higher order Pt(533) and Pt(211),\textsuperscript{19-21, 98} roughly matching what our DFT results suggest, but conflicting with electrochemical experimental results.

To more easily visualize the discrepancy between DFT/UHV and electrochemical experiments, cyclic voltammograms are simulated for hydrogen adsorption and are given in Figure 4-2. Configurational entropy contributions have been added to the data shown in Figure 4-1 to produce the cyclic voltammograms. They are each simulated at a scan rate of 50 mV/s, a surface site atom density of 241 μC/cm\textsuperscript{2} for Pt(111), 209 μC/cm\textsuperscript{2} for Pt(100), and 147 μC/cm\textsuperscript{2} for Pt(110) and under the assumption that hydrogen adsorption reaches a maximum coverage of 1 monolayer (ML) on each of the three facets.

Following the discussion from Figure 4-1, the simulated cyclic voltammogram for hydrogen adsorption on Pt(111) matches experiment well, in terms of both the absolute location of the peak and its broad shape, indicating significant repulsion between adsorbed hydrogen on this surface.\textsuperscript{14, 17} The shape and location of the hydrogen adsorption peak on Pt(100) is close to what is measured experimentally,\textsuperscript{14, 17} but the simulated voltammogram peak for hydrogen adsorption on Pt(110) occurs at potentials significantly more positive of those measured experimentally,\textsuperscript{14, 17} by about 0.2 V. Both the minor deviation from experiment for the hydrogen adsorption on Pt(100) and the significant deviation for hydrogen adsorption on Pt(110) seen in
Figure 4-2 may be due to a variety of effects, but it has been suggested previously\textsuperscript{14, 17, 91, 99} that hydroxide adsorption may occur near potentials where hydrogen adsorption occurs on Pt(100) and Pt(110) resulting in a co-adsorption or competitive adsorption of hydrogen and hydroxide at low potentials. The effect of this competitive or co-adsorption on cyclic voltammetry has not been examined previously using \textit{ab initio} methods such as DFT, and is considered in the next section.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4-2.png}
\caption{Simulated cyclic voltammograms for hydrogen adsorption onto a bare surface from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110) electrode surfaces. Scan rate is 50 mV/s. It is assumed 1 ML of hydrogen is the maximum coverage reached on each facet.}
\end{figure}

\subsection*{4.3.2. Hydroxide and Solvated Hydroxide Adsorption}

In an effort to identify the discrepancy between the simulated CV in Figure 4-2 and experiment for Pt(100) and Pt(110) electrode surfaces, the adsorption of hydroxide and its co-adsorption with water onto Pt(111), Pt(100), and Pt(110) are considered. As has been found previously,\textsuperscript{18, 81} the presence of co-adsorbed water has a significant effect on the adsorption
favorability of hydroxide onto platinum. Therefore, we simulate hydroxide alone at low coverage, hydroxide with one co-adsorbed water molecule at low coverage, and hydroxide with a co-adsorbed water bi-layer at varying coverages.

Figure 4-3 gives the favorable adsorption potential ranges for hydroxide adsorption, both at low coverage (1/9 ML) and in the optimal OH/H₂O co-adsorbed minimum energy structures (MES). Images of these adsorbed structures are given in the supplementary information. Co-adsorbed water reduces the equilibrium adsorption potential for hydroxide on all of the low index platinum facets, as hydrogen bonds with neighboring water stabilizes surface OH*. For comparison, the adsorption potential range of 1/9 ML hydrogen is shown. The well-known “double layer” region can be seen on Pt(111) with a roughly 0.4 V window separating hydrogen adsorption from hydroxide adsorption. Experimentally, hydroxide adsorption on Pt(111) is known to begin around 0.55 V_NHE with a sharp peak just below 0.8 V_NHE in perchloric acid,¹⁴ which compares well to the potential shown in Figure 4-3 when co-adsorbed water is included. Fully describing hydroxide adsorption as a function of coverage requires modeling the adsorbed hydroxide-water bilayer structure, which is not explicitly known for Pt(110) and has only been recently evaluated for Pt(100). We find our results with the adsorbed water/bi-layer structure are comparable to those with just one water molecule adsorbed, and therefore leave a more detailed analysis of particular water structures for future work.
Figure 4-3. Favorable adsorption potentials ranges ($V_{\text{NHE}}$) calculated for hydrogen and hydroxide adsorption from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110). Hydrogen adsorption potentials are calculated at 1/9 ML coverage. Hydroxide adsorption potentials shown in blue (bottom) are calculated at a coverage of 1/9 ML, those in green (middle) are 1/9 ML OH* and solvated by a single water molecule, and those in purple (top) are the minimum energy hydroxide and water co-adsorbed structures (MES). MES for Pt(111) and Pt(100) are 1/3 ML OH* and 1/3 ML H$_2$O* and for Pt(110) is 1/2 ML OH* and 1/2 ML H$_2$O*.

Hydroxide adsorption can occur at low potentials on Pt(100) and Pt(110) within the traditional “hydrogen adsorption region”, as shown by the overlapping H* and OH* potential ranges in Figure 4-3. Supporting assertions by Clavilier et al.,$^{23}$ van der Niet et al.,$^{17}$ Gómez et al.,$^{28}$ and García-Araez et al.,$^{15, 22, 29, 91}$ hydroxide could co-adsorb or compete with hydrogen adsorption on Pt(100) and Pt(110), driving hydrogen desorption to lower potentials on these facets than what is predicted by DFT for isolated hydrogen adsorption. Relative to Pt(111), not only do Pt(100) and Pt(110) bind hydrogen more strongly, but also bind hydroxide (and co-adsorbed water) more strongly, matching both intuition and experiment, where there is no clear hydroxide adsorption feature at high potentials in cyclic voltammograms on Pt(100) and Pt(110).

The DFT trend in hydroxide adsorption favorability with co-adsorbed water across the low index platinum facets matches well with results from thermally programmed desorption
(TPD) in UHV experiments. The adsorption of water on a platinum surface that has been pre-covered with adsorbed oxygen has been shown to produce mixed OH+H₂O layers on platinum surfaces. The formation of these mixed, hydrogen bonded adlayers drives the desorption of water to higher temperatures, indicating stronger binding relative to water adsorption on a bare surface. The temperature of the water desorption peak from TPD from an oxygen pre-covered surface then indicates the relative stability of the adsorbed hydroxide and water layer. The hydroxide and water adlayer is least stable on Pt(111) (200K) and most stable on facets containing 100 and 110 steps, including Pt(533) (270K) and Pt(553) (235K), respectively. While we match the trend between Pt(111) and stepped surfaces, we predict the opposite stability trend between 100 steps and 110 steps; this could be due to an interaction between step and terrace sites on the higher order facets which is not captured by our single facet DFT slab models.

The overlap of the hydrogen adsorption and hydroxide adsorption regions on Pt(100) and Pt(110) are further supported by prior DFT studies which evaluated the dissociation of water on platinum steps and terraces. Fajín et al. predicted the co-adsorption energy of H and OH on Pt(111), Pt(100), and Pt(110) and show that the energy to co-adsorb both species from water molecule dissociation, which should be proportional to the width of the “double layer” region separating the adsorption of both species in a CV, is positive on Pt(111) but negative on Pt(100) and Pt(110). This suggests that the hydrogen adsorption region and hydroxide adsorption region do not overlap on Pt(111) but do overlap on Pt(100) and Pt(110). A similar conclusion is reached examining the results of Peköz et al. While Fajín et al. show the same trend in stability between hydroxide adsorbed on Pt(100) and Pt(110) as we do here (Figure 4-3), they do not consider the effects of co-adsorbed water on the binding strength of hydroxide.

Cyclic voltammograms were again simulated, but now including the possibility of competitive adsorption of hydrogen and solvated hydroxide on Pt(100) and Pt(110) (Figure 4-4).
Figure 4-4. Simulated cyclic voltammograms for hydrogen and hydroxide adsorption from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110) electrode surfaces. Adsorption/desorption on Pt(100) and Pt(110) is taken to occur through a H/OH surface phase change process. Scan rate is 50 mV/s. 1 ML of hydrogen is the assumed maximum coverage reached on each facet. The hydroxide coverage is that of the minimum energy OH*+H₂O* structure, and is 1/3 ML OH* and 1/3 ML H₂O* on Pt(111) and Pt(100) and is 1/2 ML OH* and 1/2 ML H₂O* on Pt(110). The background data (faint lines) are experimentally measured cyclic voltammograms in 0.1 M HClO₄ at 50 mV/s on single crystal electrodes adapted from N. Garcia-Araez. The texture seen in the experimentally measured cyclic voltammograms would be better captured if the coverage dependence of hydrogen adsorption, hydroxide adsorption, and hydrogen and hydroxide co-adsorption were considered.

To model competitive adsorption of hydrogen and hydroxide, we considered the possibility of a phase change, that is, that the surface went from being predominately covered by hydrogen to predominately covered by hydroxide and water (and the reverse for the backwards scan in the cyclic voltammogram). Our DFT results suggest hydrogen and hydroxide adsorption would be less competitive on Pt(100), which is supported by cyclic voltammograms on Pt(100) single crystals, where the low potential peak can be fairly well de-convoluted to show co-adsorption when the hydrogen coverage is low. However, the H/OH phase change reaction represents a computationally more tractable modeling choice. It allows for consistent treatment of near surface
water between the Pt(100) and Pt(110) facets, especially in the presence of co-adsorbed potassium, which has a strong interaction with water, as considered in a later section. Cyclic voltammograms for the co-adsorption of hydrogen and hydroxide on Pt(100), assuming no interaction between adsorbed hydrogen and hydroxide, are provided in the supplementary information for comparison.

Figure 4-4 illustrates the cyclic voltammograms for the phase change reaction for hydrogen desorption and hydroxide+water adsorption on Pt(100) and Pt(110) (and the reverse reaction for the backward scan in the cyclic voltammogram). The competitive adsorption of hydroxide shifts the low potential peak on Pt(110) to lower potentials, by ~0.12 V, and the peak on Pt(100) by ~0.01 V, relative to isolated hydrogen adsorption/desorption (relative to Figure 4-2). The order of the low potential peaks for adsorption on Pt(100) and Pt(110) now matches that given by experimentally measured CV’s in 0.1 M perchloric acid. The peak corresponding to adsorption on Pt(110) is ~0.13 V below the Pt(100) peak (~0.15 V \textsuperscript{4}, 0.13 V \textsuperscript{17}). Furthermore, we also capture the absolute location of the peaks very well compared to experimental CV’s in perchloric acid. We predict the peak on Pt(110) to be ~0.07 V more positive than what is measured experimentally on (110) steps\textsuperscript{4,17} and within the center of the broader peak measured on low index Pt(110)\textsuperscript{14,29} We predict the peak on Pt(100) to be ~0.05 V more positive than what is measured experimentally on (100) steps\textsuperscript{4,17} and ~0.05 V more negative than on low index Pt(100)\textsuperscript{14,29} The magnitude and narrow width of these competitive adsorption peaks also match experiment much better than for isolated hydrogen adsorption\textsuperscript{14,17} The competitive adsorption exchange yields 1.5 electrons per surface atom for Pt(110) and 1.33 electrons per surface atom for Pt(100). The background of Figure 4-4 shows experimentally measured CV’s on single crystal Pt(111), Pt(110), and Pt(100) electrodes measured in 0.1 M perchloric acid, adapted from N. Garcia-Araez.\textsuperscript{29} This lends great support to the conclusion that the low potential peaks measured in cyclic voltammetry on Pt(100), Pt(110), and higher order facets which contain 100 and 110
steps represent the desorption (adsorption) of hydrogen and the adsorption (desorption) of hydroxide, as proposed previously by others.\textsuperscript{14, 23, 28, 99} The texture seen in the experimentally measured CV’s may be due to the coverage dependence of hydrogen adsorption, hydroxide adsorption, and their competitive adsorption (which is neglected in the simulated CV’s shown in Figure 4-4) on extended Pt(100) and Pt(110) surfaces\textsuperscript{29}, as these features are absent in higher order single crystal CV’s which contain 100 and 110 steps.\textsuperscript{17} For comparison, Figure 4-4 also contains the simulated hydrogen adsorption CV for adsorption onto Pt(111) as given in Figure 4-2 as well as the simulated CV for hydroxide adsorption onto Pt(111), which has been presented previously by Rossmeisl et al. and whose methods we use here to describe hydroxide adsorption on Pt(111)\textsuperscript{104}. The Pt(111) CV is reasonably captured without considering H/OH exchange due to the $\sim$0.4 V separation between these processes.

With it established that the low potential peaks measured in cyclic voltammetry on Pt(100), Pt(110), stepped, and polycrystalline platinum are due to the co- or competitive adsorption of hydrogen and hydroxide, we can investigate the mechanism of how pH effects the location of these peaks. As the pH is increased, the electrochemical window in an aqueous solution is driven to more negative potentials on an absolute scale, making the specific adsorption of a cation in the $\text{H}^*$ potential range more favorable. We next consider the specific adsorption of a potassium cation and its effects, once specifically adsorbed, on hydrogen adsorption and hydroxide adsorption.

4.3.3. Potassium Cation Adsorption

Variations in pH could affect the specific adsorption of hydrogen and hydroxide/water via a few different, but related, mechanisms. Increasing pH causes a negative shift in the absolute potential at which hydrogen and hydroxide adsorb, since their concentrations, and therefore their
activity, change with pH. This change will not alter the H/OH adsorption potentials on a relative hydrogen electrode scale. The change in absolute potential could alter the interfacial water structure at the electrode surface, change the electric field or ion distribution near the electrode surface, and increase the favorability to adsorb cations other than protons that are present in the electrolyte solution.

The absolute potential affects the structure and dynamics of water near the electrode surface, however, the presence of water near the electrode surface has a negligible effect on hydrogen adsorption. The change in electric field near the surface, beyond changing the water structure, would affect the binding of adsorbates which generate a strong surface normal dipole moment. The changes in dipole moment on the adsorption of hydrogen and hydroxide, however, are small. This leaves the interaction with cations other than protons as an important part of the mechanism for how increasing pH can shift the adsorption favorability of hydrogen and hydroxide. The favorability to specifically adsorb $K^+$ was investigated, as well as the effects of $K^*$ on the binding of hydrogen and hydroxide.

Figure 4-5 gives the equilibrium adsorption potentials calculated for adsorption of $K^+$ from a 1 M electrolyte solution to Pt(111), Pt(100), and Pt(110) as a function of $K^*$ coverage. The adsorption potentials shown in Figure 4-5 do not include the effects of electrolyte near the electrode surface, which would act to stabilize the partially charged $K^*$ state, which generates a relatively significant surface normal dipole moment upon adsorption. The charge on potassium, calculated by a Bader charge analysis, and the surface normal dipole moments are tabulated as a function of $K^*$ coverage for adsorption onto each of the three facets in Table S4-4 and S4-5 in the supplementary information. Effects of surface solvation are discussed shortly.
Figure 4-5. Equilibrium adsorption potential ($V_{\text{NHE}}$) calculated for $K^+$ adsorption from a 1M solution onto Pt(111) (blue diamonds), Pt(100) (green triangles), and Pt(110) (red squares) as a function of potassium coverage (ML). Equilibrium adsorption potentials neglect solvation stabilization of $K^*$ at the Pt surface, which would shift $K^*$ adsorption to more positive potentials.

Adsorption of $K^*$ is favorable within the electrochemical window of water in an alkaline electrolyte (lower limit -0.826 $V_{\text{NHE}}$ for HER/HOR at pH=14) up to a coverage of 1/4 ML on all three of the low index facets of platinum. Therefore we expect low coverage $K^*$ specific adsorption to be competitive with hydrogen adsorption at low potentials on Pt(111), Pt(100), and Pt(110) in an alkaline electrolyte. Solvation by water near the electrode surface would drive adsorption to higher coverages within this window. This would also make $K^*$ specific adsorption competitive with hydrogen adsorption in lower pH electrolytes. Figure 4-5 also shows that the adsorption of $K^+$ onto all three low index Pt facets is strongly coverage dependent, and, as such, we would not expect the coverage of $K^*$ to exceed 1/3 ML on Pt(111) or 1/2 ML on Pt(100) and Pt(110). Given the size of the potassium cation and the small positive charge it retains on adsorption (Table S4-5), this strong dependence on coverage is primarily due to electrostatic repulsion at low coverages and a combination of electrostatic repulsion and steric hindrance at high coverages.
To examine the effects of electrolyte near the electrode surface on the adsorption of K\(^+\), the favorability of K\(^+\) adsorption at 1/9 ML on Pt(111), Pt(100), and Pt(110) was examined in the presence of 1, 3, and 6 explicit water molecules placed near the surface adsorbate and with an implicit solvation model implemented in VASP\(^8\). Our group previously concluded, for the Pt(111) surface, that the adsorption favorability of alkali cations is roughly converged with 6 explicit water molecules.\(^3\) These adsorption potentials are plotted in Figures S6, S7, and S8 in the supplementary information. The effect of including explicit water molecules on all of the three facets is to make adsorption more favorable by \(\sim 0.6-0.8\) eV. Implicit solvation shows a similar effect. Water near the electrode surface can stabilize the charge retained on potassium after its specific adsorption, making adsorption more favorable.

Potassium cations can specifically adsorb to Pt(111), Pt(100), and Pt(110) in the H\(^*\) potential region in alkaline electrolytes and could affect the adsorption of hydrogen or hydroxide. With the effects of surface solvation approximated, they may specifically adsorb at low coverage in lower pH electrolytes as well, even including in a pH = 0 electrolyte. We next examine if alkali cation specific adsorption can cause the experimentally observed shifts in the H/OH exchange potentials with pH on Pt(110) and Pt(100) by examining K/H and K/OH co-adsorption.

### 4.3.4. Hydrogen and Potassium Co-adsorption

Figure 4-6 shows the calculated hydrogen adsorption potential at 1 ML coverage on Pt(111), Pt(100), and Pt(110) as a function of co-adsorbed potassium coverage, from \(\theta_{K^*} = 0\) to 0.25ML. The interaction between K\(^*\) and H\(^*\) is slightly repulsive at all coverages investigated on each of the three facets. This makes hydrogen adsorption less favorable, driving its equilibrium adsorption potential lower. This repulsive interaction is strongest on Pt(111) and Pt(100), but the overall magnitude of the interaction is weak, never exceeding 0.15 eV. The effect is almost
negligible on Pt(110). Further examination of this interaction, including the free energy of interaction between adsorbed hydrogen and adsorbed potassium (Table S4-6) and the change in the charge of adsorbed hydrogen in the presence of specifically adsorbed potassium (Table S4-7) is given in the supplementary information.

Figure 4-6. Equilibrium adsorption potential ($V_{\text{NHE}}$) calculated for adsorption of 1 ML of hydrogen from a pH = 0 solution next to specifically adsorbed potassium ($K^*$) on Pt(111) (blue diamonds), Pt(100) (green triangles), and Pt(110) (red squares) as a function of adsorbed potassium coverage (ML).

Given that the interaction between adsorbed hydrogen and adsorbed potassium is almost negligible on Pt(110) and that the interaction is repulsive on Pt(100), this interaction cannot explain the experimentally measured shift of the Pt(100) and Pt(110) low potential CV peaks to higher potential with increasing pH. The presence of co-adsorbed potassium, favored by higher pH, weakens hydrogen binding, whereas experimentally, the adsorption peak shifts to higher potentials, suggesting stronger hydrogen binding as pH is increased.\textsuperscript{4,17}

This leads us to consider the effect of specifically adsorbed potassium on hydroxide adsorption to explain these experimentally measured effects, as we showed that these low
potential peaks on Pt(110) and Pt(100) are actually due to the competitive adsorption of hydrogen and hydroxide (Figure 4-4).

4.3.5. Hydroxide-Water-Potassium Co-adsorption

We established in the section entitled “Hydroxide and solvated hydroxide adsorption” that the low potential adsorption peaks measured in cyclic voltammetry on Pt(100) and Pt(110)\(^4\) are the competitive or co-adsorption of hydrogen and hydroxide (Figure 4-4). Experimentally, these peaks shift to higher potentials with increasing pH.\(^4\)\(^,\)\(^,\)\(^,\)\(^1\)\(^7\) The previous section showed that this shift cannot be explained by the interaction of specifically adsorbed potassium and specifically adsorbed hydrogen (Figure 4-6). We therefore consider that specifically adsorbed potassium may affect the adsorption of hydroxide and water. Given that potassium tends to retain some of its charge on adsorption (Tables S4-4 and S4-5), it seems logical that the interaction between K* and OH*+H\(_2\)O* could be significant, at least more so than the interaction with non-polar H*.

To examine the interaction between K* and OH*+H\(_2\)O*, the hydroxide adsorption potential was calculated for K* and OH* co-adsorption in three structures: 1) OH* at 1/9 ML next to 1/9 ML K* on Pt(111), Pt(100), and Pt(110), 2) the adsorption of OH* at 1/9 ML next to 1/9 ML K* and 1/9 ML H\(_2\)O* on Pt(111), Pt(100), and Pt(110), and 3) the adsorption of OH* in the minimum energy OH+H\(_2\)O structure next to K* [at 1/9 ML K*, 1/3 ML OH* and 1/3 ML H\(_2\)O* on Pt(111) and Pt(100), and K* at 1/4 ML, OH 1/2 ML, and H\(_2\)O 1/2 ML on Pt(110)]. The adsorption potentials calculated with water included are given in Figure 4-7. Without water included (K* 1/9 ML, OH* 1/9 ML), the interaction was found to be significantly attractive, counter to what was found for all of the structures that include co-adsorbed water; these results are given separately in supplementary information (Table S4-8).
Figure 4-7. Equilibrium adsorption potentials ($V_{NHE}$) calculated for hydrogen and hydroxide adsorption from a pH = 0 solution onto Pt(111), Pt(100), and Pt(110). Hydrogen adsorption potentials are calculated at 1/9 ML coverage (left hand axis). Hydroxide adsorption potentials in purple (top bar) and green (3rd from top bar) are the same as in Figure 4-3. Hydroxide adsorption potentials in light purple (2nd bar from top) are calculated using the minimum energy hydroxide and water structures (MES) but with co-adsorbed potassium at 1/9 ML on Pt(111) and Pt(100) and at 1/4 ML on Pt(110). Hydroxide adsorption potentials given by the light green bar (bottom) are calculated with 1/9 ML OH*, 1/9 ML H$_2$O*, and 1/9 ML K*. The equilibrium adsorption potential is given by the right most edge of the bar (hydrogen adsorption, white bar, left hand axis) or by the left most edge (hydroxide adsorption).

Specifically adsorbed K* drives the adsorption of OH* with co-adsorbed H$_2$O* to more positive potentials, making surface hydroxide formation less stable. This effect matches the experimentally measured trend in cyclic voltammetry; as the pH is increased and potassium adsorption made more favorable, the low potential peaks on Pt(100) and Pt(110) shift to more positive potentials. There is no effect on the broad Pt(111) low potential peak because OH* adsorption occurs at potentials significantly more positive of this H* adsorption/desorption peak.

To better compare with experiment, cyclic voltammograms are again simulated for the phase change reaction, but now with and without the presence of specifically adsorbed potassium.

Figure 4-8 plots the cyclic voltammogram simulated at 50 mV/s and 300K for the phase
change reactions on Pt(100) and Pt(110) in the presence of specifically adsorbed potassium. As potassium specific adsorption becomes more favorable as pH is increased, the simulated voltammograms with co-adsorbed K* represent the expected CVs in an alkaline electrolyte. These CVs compare very well with those experimentally measured in 0.1 M KOH. While we predict the competitive adsorption of hydrogen and hydroxide in an alkaline solution on Pt(110) at a slightly higher potential, 0.35 \( V_{\text{RHE}} \), than what is measured experimentally, 0.28 \( V_{\text{RHE}} \), we predict the location of the competitive adsorption peak on Pt(100) very well, 0.41 vs \(-0.4 \ V_{\text{RHE}}\) measured experimentally. More importantly, we capture the shift with pH very well between CV’s measured in 0.1 M HClO₄ and 0.1 M KOH; for Pt(110) we calculate a shift of 0.155 \( V_{\text{RHE}} \) compared to \(-0.15 \ V_{\text{RHE}}\). For Pt(100) our calculated shift of 0.09 is a little less than what is measured experimentally, \(-0.13 \ V_{\text{RHE}}\). The presence of specifically adsorbed K* at high pH weakens the binding of solvated hydroxide, and therefore shifts the H*/OH* replacement/phase change potential to more positive values.
Figure 4-8. Simulated cyclic voltammograms for hydrogen and hydroxide adsorption from a pH = 0 solution via a phase change reaction onto a) Pt(110) and b) Pt(100) electrode surfaces in the absence (dotted lines) and presence (solid lines) of specifically adsorbed potassium. Scan rate is 50 mV/s. The hydroxide coverage is of the minimum energy OH*+H2O* structure, and is 1/3 ML OH* and 1/3 ML H2O* on Pt(100) and is 1/2 ML OH* and 1/2 ML H2O* on Pt(110). Hydrogen coverage is 1ML on all three facets. K* coverage is 1/9 ML on Pt(100) and 1/4 ML on Pt(110). The absence of specifically adsorbed potassium represents the conditions expected in acid electrolytes and the presence of specifically adsorbed potassium represents the conditions expected in basic electrolytes, with the coverage of K* varying with pH.

Figure 4-9 plots the formation potential for surface hydroxide as a function of potassium coverage, illustrating that as the K* coverage is increased, the favorability to adsorb hydroxide progressively decreases. This results in the hydroxide equilibrium adsorption potential rising to more positive potentials at higher K* coverages. This trend matches very well with the results by Sheng et al.\textsuperscript{4} and van der Niet et al.,\textsuperscript{17} which show that as the pH increases, the “hydrogen binding energy”, which we have now concluded is actually a H*/OH* replacement reaction energy, increases as well, with a slope of about $-10 \text{ mV}_{\text{RHE}}/\text{pH}$ unit. As the pH of the electrolyte is increased, the favorability to adsorb potassium increases, increasing the potassium coverage on the surface, making hydroxide adsorption less favorable, causing the 110 and 100 CV peaks measured at low potentials to shift to more positive potentials. It is difficult to compare our slope
of hydroxide adsorption potential versus K* coverage directly to experiment, as that requires a precise evaluation of K* adsorption energy vs. coverage which is too dependent on the imprecision of using static H₂O molecules to solvate K* in DFT calculations.

Figure 4-9. Equilibrium formation potential for hydroxide in its minimum energy structure with co-adsorbed water from adsorbed water on Pt(110) for formation next to specifically adsorbed potassium as a function of potassium coverage (ML). The solid line is a linear regression, intended only as a guide to the general trend.

The conclusion that K* co-adsorption weakens hydroxide adsorption in the solvated environment is counterintuitive, given the expected attraction between K* and OH*. To better understand why K* reduces the favorability to form OH*H₂O*, the surface Pt-O bond lengths, the OH*H₂O* hydrogen bond lengths, and the charge on molecular OH* and H₂O* are evaluated as a function of potassium coverage for adsorption onto the Pt(110) surface. As the potassium coverage is increased, the Pt-O bond length in the 1/2 ML OH* 1/2 ML H₂O* structure increases significantly, as given in Figure 4-10. This is consistent with the weakening of the Pt-O bond, for oxygen in both adsorbed hydroxide and adsorbed water, as the potassium coverage is increased. This weakening contributes to the decrease in favorability to adsorb hydroxide as the potassium coverage is increased.
Figure 4-10. Pt-O bond length (Å) for adsorbed hydroxide and adsorbed water as a function of K* coverage (ML).

A more complex interaction is seen in Figure 4-11, which plots the OH*-H₂O* (with hydroxide as the hydrogen bond donor) hydrogen bond length and the H₂O*-OH* (with hydroxide as the hydrogen bond acceptor) hydrogen bond length as a function of potassium coverage. The “hydroxide as donor” hydrogen bond length between adsorbed hydroxide and adsorbed water decreases with increasing potassium coverage, while the hydrogen bond length with hydroxide as the acceptor increases with increasing potassium coverage. The magnitude of the change with potassium coverage is larger for hydroxide as the donor, given by the larger slope in Figure 4-11. As the potassium coverage is increased, bonding to the surface through oxygen seems to weaken, while hydrogen bonding between adsorbed hydroxide and adsorbed water strengthens, with the net effect of the structure becoming less stable, as indicated by the more positive hydroxide adsorption potentials with increasing potassium coverage.
Figure 4-11. Hydrogen bond length (Å) between adsorbed hydroxide and adsorbed water with hydroxide as the hydrogen bond donor and as the hydrogen bond acceptor as a function of K* coverage (ML).

Finally, the charge on the adsorbed OH* and H₂O* molecules can be evaluated as a function of K* coverage on Pt(110). Figure 4-12 shows the charge on adsorbed OH* and the charge on H₂O*, calculated via a Bader charge analysis, vs K* coverage. As the coverage of K* is increased, both OH* and H₂O* take on more negative charge. This is expected as K* retains some positive charge on adsorption, allowing for a stabilization of more negative charge above the surface as the coverage of K* is increased.

Figure 4-12. Charge on adsorbed hydroxide and adsorbed water molecules as a function of K* coverage on Pt(110).
Though the bond lengths and change in charges show a complex set of interactions, the presence of increasing amounts of K* on the Pt(110) surface drives solvated $\text{OH}_{\text{aq}}^-$ adsorption to be less favorable. Increasing coverage of K* produces a greater negative charge, primarily on the oxygen of OH*, lengthens the Pt-O bond to both OH* and H$_2$O*, and causes a restructuring of the OH* H$_2$O* hydrogen bonding network.

While the absolute potentials calculated here do depend on the particular co-adsorbed hydroxide and water structures that we have used, the qualitative results are consistent across the multiple structures and the Pt(110) and (100) surfaces considered. Hydroxide adsorption occurs well into the hydrogen adsorption region on Pt(100) and Pt(110) and the presence of specifically adsorbed potassium weakens hydroxide binding, as supported by the calculations with one co-adsorbed water molecule at a low hydroxide coverage (Figure 4-7). Non-specifically adsorbed K$^+$ ions in the surface region may cause similar effects, though we have not examined this with DFT as our calculations indicate specific adsorption of potassium will occur.

### 4.4. Conclusions

The presence of reactant and spectator ions, atoms, and molecules near or adsorbed onto the electrode surface can have a complex effect on the rates and mechanisms of electrocatalytic reactions. Density functional theory was used to show that the sharp, low potential peaks in current measured experimentally by cyclic voltammetry on Pt(100), Pt(110), and higher order stepped and polycrystalline platinum are the co-adsorption or competitive adsorption of hydrogen and hydroxide. The experimentally measured variation of these peak positions with pH is due to specifically adsorbed alkali metal cations. The presence of specifically adsorbed potassium does not significantly impact H* adsorption, but weakens the binding of hydroxide on the electrode
surface. Less stable OH* drives the Pt(110) and (100) peaks to higher potentials on a relative hydrogen electrode scale as the pH is increased, as observed experimentally. These conclusions could have a significant impact on the electrocatalytic properties of platinum electrodes, especially for reactions which involve specifically adsorbed hydroxide. This DFT work lends significant support to the idea that hydroxide can be present on 100, 110, and stepped platinum surfaces at much lower potentials than on Pt(111). This work also illustrates the importance of alkali cation specific adsorption in effecting the adsorption of hydroxide. The shift in favorability of hydroxide adsorption with pH, which we show is due to the presence of specifically adsorbed potassium, correlates with a two order of magnitude change in the rate of hydrogen oxidation/evolution from acid to basic electrolytes. Understanding alkali cation effects on adsorbed reaction intermediates is therefore technologically significant.

4.5. Acknowledgements

The authors gratefully acknowledge support from the National Science Foundation DMREF Grant #1436206. I.T. McCrum acknowledges support from The Pennsylvania State University Diefenderfer Graduate Fellowship and NSF NRT #1449785.

4.6. References


### 4.7 Supplementary Information

Table S4-1. Adsorption site analysis for K* (a-c) and H* (d-f) at 1/9 ML on Pt(111), Pt(100), and Pt(110).

#### a) Pt(111) K* Adsorption Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>-210.230</td>
</tr>
<tr>
<td>Bridge</td>
<td>-210.306</td>
</tr>
<tr>
<td>HCP</td>
<td><strong>-210.317</strong></td>
</tr>
<tr>
<td>FCC</td>
<td>-210.312</td>
</tr>
</tbody>
</table>

#### b) Pt(100) K* Adsorption Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>-205.243</td>
</tr>
<tr>
<td>Bridge</td>
<td>-205.331</td>
</tr>
<tr>
<td>3-fold</td>
<td><strong>-205.432</strong></td>
</tr>
</tbody>
</table>

#### c) Pt(110) K* Adsorption Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>-197.676</td>
</tr>
<tr>
<td>Short bridge</td>
<td>-197.765</td>
</tr>
<tr>
<td>FCC</td>
<td><strong>-198.084</strong></td>
</tr>
<tr>
<td>Long bridge</td>
<td>-198.018</td>
</tr>
</tbody>
</table>

#### d) Pt(111) H* Adsorption Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>-211.021</td>
</tr>
<tr>
<td>Bridge</td>
<td>-211.019</td>
</tr>
<tr>
<td>HCP</td>
<td>-211.007</td>
</tr>
<tr>
<td>FCC</td>
<td><strong>-211.057</strong></td>
</tr>
</tbody>
</table>

#### e) Pt(100) H* Adsorption Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>-206.080</td>
</tr>
<tr>
<td>Bridge</td>
<td><strong>-206.259</strong></td>
</tr>
<tr>
<td>3-fold</td>
<td>-205.897</td>
</tr>
</tbody>
</table>

#### f) Pt(110) H* Adsorption Site

<table>
<thead>
<tr>
<th>Site</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atop</td>
<td>-198.769</td>
</tr>
<tr>
<td>Short bridge</td>
<td><strong>-198.852</strong></td>
</tr>
<tr>
<td>FCC</td>
<td>-198.280</td>
</tr>
</tbody>
</table>
Table S4-2. Aqueous free energy of $K^+(aq)$ and $H^+(aq)$ calculated using the experimental solvation energy method and the computational hydrogen electrode method (with the equivalent method for potassium, using its standard dissolution potential).

<table>
<thead>
<tr>
<th>Exp Solvation Energy (eV)</th>
<th>Comp. Hydrogen Electrode (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_{C_+(gas)} + \Delta G_{solv}^{exp}$</td>
<td>$\frac{1}{2} G_{H_2(g)} + 4.6$</td>
</tr>
<tr>
<td>$G_{K(s)} + E_{diss}^{exp} + 4.6$</td>
<td></td>
</tr>
<tr>
<td>$H^+(aq)$</td>
<td>0.842</td>
</tr>
<tr>
<td>$K^+(aq)$</td>
<td>0.780</td>
</tr>
</tbody>
</table>

Table S4-3. Free energy $H_2$, $H_2O(aq)$, and $OH^-(aq)$.

<table>
<thead>
<tr>
<th>Free Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2(g)$ 1 atm</td>
</tr>
<tr>
<td>$H_2O (aq)$</td>
</tr>
<tr>
<td>$OH^-(aq)$ 1 M</td>
</tr>
</tbody>
</table>
Table S4-4. Dipole moments for K* on Pt(111), Pt(100), and Pt(110) as a function of coverage.

<table>
<thead>
<tr>
<th>Pt(111) K* Coverage</th>
<th>Dipole moment (eÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare 3x3</td>
<td>0.012</td>
</tr>
<tr>
<td>Bare 2x2</td>
<td>0.005</td>
</tr>
<tr>
<td>1/9 ML</td>
<td>-1.060</td>
</tr>
<tr>
<td>1/4 ML</td>
<td>-0.650</td>
</tr>
<tr>
<td>1/3 ML</td>
<td>-1.274</td>
</tr>
<tr>
<td>1/2 ML</td>
<td>-0.481</td>
</tr>
<tr>
<td>3/4 ML</td>
<td>-0.496</td>
</tr>
<tr>
<td>1 ML</td>
<td>-0.793</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pt(100) K* Coverage</th>
<th>Dipole moment (eÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare 3x3</td>
<td>0.003</td>
</tr>
<tr>
<td>Bare 2x2</td>
<td>0.001</td>
</tr>
<tr>
<td>1/9 ML</td>
<td>-1.027</td>
</tr>
<tr>
<td>1/4 ML</td>
<td>-0.737</td>
</tr>
<tr>
<td>1/2 ML</td>
<td>-0.614</td>
</tr>
<tr>
<td>3/4 ML</td>
<td>-0.496</td>
</tr>
<tr>
<td>1 ML</td>
<td>-0.440</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pt(110) K* Coverage</th>
<th>Dipole moment (eÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare 3x3</td>
<td>-0.033</td>
</tr>
<tr>
<td>Bare 2x2</td>
<td>-0.014</td>
</tr>
<tr>
<td>1/9 ML</td>
<td>-0.926</td>
</tr>
<tr>
<td>1/4 ML</td>
<td>-0.743</td>
</tr>
<tr>
<td>1/2 ML</td>
<td>-0.979</td>
</tr>
<tr>
<td>3/4 ML</td>
<td>-0.873</td>
</tr>
<tr>
<td>1 ML</td>
<td>-0.784</td>
</tr>
</tbody>
</table>
Table S4-5. Charge on K* as evaluated by a Bader charge analysis as a function of coverage on Pt(111), Pt(100), and Pt(110).

<table>
<thead>
<tr>
<th>Pt(111) K* Coverage</th>
<th>Average Bader Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/9 ML</td>
<td>+ 0.834</td>
</tr>
<tr>
<td>1/4 ML</td>
<td>+ 0.723</td>
</tr>
<tr>
<td>1/3 ML</td>
<td>+ 0.621</td>
</tr>
<tr>
<td>1/2 ML</td>
<td>+ 0.550</td>
</tr>
<tr>
<td>3/4 ML</td>
<td>+ 0.335</td>
</tr>
<tr>
<td>1 ML</td>
<td>+ 0.252</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pt(100) K* Coverage</th>
<th>Average Bader Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/9 ML</td>
<td>+ 0.832</td>
</tr>
<tr>
<td>1/4 ML</td>
<td>+ 0.751</td>
</tr>
<tr>
<td>1/2 ML</td>
<td>+ 0.560</td>
</tr>
<tr>
<td>3/4 ML</td>
<td>+ 0.472</td>
</tr>
<tr>
<td>1 ML</td>
<td>+ 0.435</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pt(110) K* Coverage</th>
<th>Average Bader Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/9 ML</td>
<td>+ 0.835</td>
</tr>
<tr>
<td>1/4 ML</td>
<td>+ 0.792</td>
</tr>
<tr>
<td>1/2 ML</td>
<td>+ 0.708</td>
</tr>
<tr>
<td>3/4 ML</td>
<td>+ 0.604</td>
</tr>
<tr>
<td>1 ML</td>
<td>+ 0.563</td>
</tr>
</tbody>
</table>

Figure S4-1. Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamond) or by implicit solvation (red square) (VASPsol), on the favorability to specifically adsorb potassium on Pt(111), as given by its equilibrium adsorption potential ($V_{\text{NHE}}$).
Figure S4-2. Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamond) or by implicit solvation (red square), on the favorability to specifically adsorb potassium on Pt(100), as given by its equilibrium adsorption potential ($V_{\text{NHE}}$).

Figure S4-3. Effect of surface solvation, approximated by adding 1, 3, or 6 explicit water molecules near the electrode (blue diamonds) or by implicit solvation (red square), on the favorability to specifically adsorb potassium on Pt(110), as given by its equilibrium adsorption potential ($V_{\text{NHE}}$).
Table S4-6. Gibbs free energy of interaction between K* and H* as a function of coverage on Pt(111), Pt(100), and Pt(110).

<table>
<thead>
<tr>
<th>Surface</th>
<th>( \Delta G_{K-H} ) interaction (eV) (per H*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td></td>
</tr>
<tr>
<td>K* 1/9 ML H* 1 ML</td>
<td>0.094</td>
</tr>
<tr>
<td>K* 1/4 ML H* 1 ML</td>
<td>0.197</td>
</tr>
<tr>
<td>Pt(100)</td>
<td></td>
</tr>
<tr>
<td>K* 1/9 ML H* 1 ML</td>
<td>0.044</td>
</tr>
<tr>
<td>K* 1/4 ML H* 1 ML</td>
<td>-0.094</td>
</tr>
<tr>
<td>Pt(110)</td>
<td></td>
</tr>
<tr>
<td>K* 1/9 ML H* 1 ML</td>
<td>-0.005</td>
</tr>
<tr>
<td>K* 1/4 ML H* 1 ML</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table S4-7. Charge on hydrogen when co-adsorbed at 1 ML with K* as a function of K* coverage on Pt(111), Pt(100), and Pt(110).

<table>
<thead>
<tr>
<th>Surface</th>
<th>Average H* Bader charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td></td>
</tr>
<tr>
<td>H* 1ML</td>
<td>0.045</td>
</tr>
<tr>
<td>K* 1/9 ML H* 1 ML</td>
<td>0.079</td>
</tr>
<tr>
<td>K* 1/4 ML H* 1 ML</td>
<td>0.105</td>
</tr>
<tr>
<td>Pt(100)</td>
<td></td>
</tr>
<tr>
<td>H* 1ML</td>
<td>0.091</td>
</tr>
<tr>
<td>K* 1/9 ML H* 1 ML</td>
<td>0.122</td>
</tr>
<tr>
<td>K* 1/4 ML H* 1 ML</td>
<td>0.179</td>
</tr>
<tr>
<td>Pt(110)</td>
<td></td>
</tr>
<tr>
<td>H* 1ML</td>
<td>0.065</td>
</tr>
<tr>
<td>K* 1/9 ML H* 1 ML</td>
<td>0.124</td>
</tr>
<tr>
<td>K* 1/4 ML H* 1 ML</td>
<td>0.173</td>
</tr>
</tbody>
</table>

Table S4-8. Adsorption potential of 1/9 ML OH* on Pt(111), Pt(100), and Pt(110) in the absence and for OH* on Pt(110) in the presence of 1/9 ML K*.

<table>
<thead>
<tr>
<th>OH (aq) adsorption potential (V_NHE)</th>
<th>OH* (1/9 ML)</th>
<th>K* + OH* (1/9 ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111)</td>
<td>1.209</td>
<td>-</td>
</tr>
<tr>
<td>Pt(100)</td>
<td>0.548</td>
<td>-</td>
</tr>
<tr>
<td>Pt(110)</td>
<td>0.780</td>
<td>0.331</td>
</tr>
</tbody>
</table>
Table S4-9. Equilibrium adsorption potential of 1/9 ML K* into H₂O and OH+H₂O* structures on Pt(111) (100) and (110). Calculated using the potassium dissolution potential method. Includes dipole correction.

<table>
<thead>
<tr>
<th></th>
<th>K⁺(aq) Adsorption potential (V NHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(111) 1/9 ML K* 1/3 ML OH* 1/3 ML H₂O*</td>
<td>-0.491</td>
</tr>
<tr>
<td>Pt(100) 1/9 ML K* 1/3 ML OH* 1/3 ML H₂O*</td>
<td>-0.834</td>
</tr>
<tr>
<td>Pt(110) 1/4 ML K* 1/2 ML OH* 1/2 ML H₂O*</td>
<td>-1.017</td>
</tr>
</tbody>
</table>

4.7.1. Simulating Cyclic Voltammograms

As can be seen in Figure 4-4, the simulated cyclic voltammograms for the H/OH phase change reaction on Pt(100) and Pt(110) match experiment well, in terms of the general location (potential) and the size of the adsorption/desorption peak (in both acid and base (Figure 4-8)). The simulated cyclic voltammograms do not capture the finer details in the shape of both the adsorption peaks on Pt(100) and on Pt(110). This is due our neglecting three important points in the phase change model, as a computational simplification, which, if they were to be captured accurately with DFT, may reproduce all of the details of the experimentally measured cyclic voltammograms. Namely, in the phase change reaction simulated voltammograms, we have neglected the explicit coverage dependence of hydrogen, the coverage dependence of hydroxide, and the fact that they could compete for the same sites on each surface and could co-adsorb (though the interaction between adsorbed hydrogen and hydroxide should be small). As a simple example, consider Figures S4-4 and S4-5, where we have modeled the adsorption of H* and OH* on Pt(100) separately (not as a phase change reaction). While we still neglect competitive adsorption in this case, Figure S4-4 shows that this yields a much broader peak, removing some of the disagreement with experiment.
Figure S4-4. Simulated cyclic voltammograms for hydrogen adsorption/desorption on (H*, black line), hydroxide adsorption/desorption (OH*, blue line), and their sum (H*+OH*, red line) for adsorption on Pt(100). The sum does not include competitive adsorption. The hydrogen adsorption/desorption cyclic voltammogram includes the coverage dependence calculated with DFT and configurational entropy, while hydroxide adsorption/desorption only includes the effect of the configurational entropy on the coverage dependence of hydroxide adsorption. Maximum hydrogen coverage is 1 ML while that of hydroxide is 1/3 ML in the minimum energy hydroxide+water structure (1/3 ML OH* 1/3 ML H2O*). The scan rate is 50 mV/s, the temperature 300K, and adsorption occurs from a pH=0 electrolyte.

Figure S4-5. Simulated cyclic voltammogram for the sum of hydrogen adsorption/desorption and hydroxide adsorption/desorption (dark red line) for adsorption on Pt(100), from Figure S4-13. The background gives the experimentally measured cyclic voltammogram for hydrogen and hydroxide adsorption onto a Pt(100) single crystal electrode in a 0.1 M HClO4 electrolyte solution (faint red line) as adapted from N. Garcia-Araez. The simulated cyclic voltammogram shown here (and in Figure S4-4) do not include a phase change reaction or competitive adsorption of hydrogen and hydroxide.
Figure S4-6. Pt(111) Minimum energy water structure 6 H$_2$O* in 3x3 unit cell (6/9 ML H$_2$O).

Figure S4-7. Pt(111) Minimum energy water structure 6 H$_2$O* in 3x3 unit cell with 1/9 ML K*.

Figure S4-8. Pt(111) Minimum energy hydroxide+water structure 3OH*+ 3 H$_2$O* in 3x3 unit cell (3/9 ML OH, 3/9 ML H$_2$O).
Figure S4-9. Pt(111) Minimum energy hydroxide-water structure 3OH* + 3 H₂O* in 3x3 unit cell with K* 1/9 ML (3/9 ML OH, 3/9 ML H₂O, 1/9 ML K*).

Figure S4-10. Pt(100) Minimum energy water structure 6 H₂O* in 3x3 unit cell (6/9 ML H₂O).

Figure S4-11. Pt(100) Minimum energy water structure 6 H₂O* in 3x3 unit cell with 1/9 ML K*.
Figure S4-12. Pt(100) Minimum energy hydroxide+water structure 3OH*+ 3 H₂O* in 3x3 unit cell (3/9 ML OH, 3/9 ML H₂O).

Figure S4-13. Pt(100) Minimum energy hydroxide+water structure 3OH*+ 3 H₂O* in 3x3 unit cell with K* 1/9 ML (3/9 ML OH, 3/9 ML H₂O, 1/9 ML K*).

Figure S4-14. Pt(100) Minimum energy water structure with 1 ML H* and 1/9 ML K* in 3x3 unit cell (6/9 ML H₂O, 1/9 ML K*, 1 ML H*).
Figure S4-15. Pt(110) Minimum energy water structure 4 H₂O* in 2x2 unit cell (1 ML H₂O).

Figure S4-16. Pt(110) Minimum energy water structure 4 H₂O* in 2x2 unit cell with 1/4 ML K*.

Figure S4-17. Pt(110) Minimum energy hydroxide+water structure 2OH*+ 2 H₂O* in 2x2 unit cell (1/2 ML OH, 1/2 ML H₂O).
Figure S4-18. Pt(110) Minimum energy hydroxide+water structure 2OH*+ 2 H2O* in 2x2 unit cell with 1/4 ML K* (1/2 ML OH, 1/2 ML H2O, 1/4 ML K*).

Figure S4-19. Pt(110) Minimum energy water structure with 1 ML H* and 1/4 ML K* in 2x2 unit cell (1 ML H2O, 1/4 ML K*, 1 ML H*).
Chapter 5

First Principles Simulations of Cyclic Voltammograms on Stepped Pt(553) and Pt(533) Electrode Surfaces

This chapter is published as: McCrum, I.T.; Janik, M.J.; First Principles Simulations of Cyclic Voltammograms on Stepped Pt(553) and Pt(533) Electrode Surfaces. ChemElectroChem 2016, 3, 1609-1617.

Abstract

Density functional theory (DFT) calculations are used to examine hydrogen and hydroxide adsorption on stepped Pt(553) and Pt(533) surfaces and to simulate the associated cyclic voltammograms in both basic and acidic electrolytes. Hydrogen and hydroxide surface species are active intermediates or spectator species in many important electrocatalytic reactions, such as hydrogen oxidation, oxygen reduction, and methanol oxidation. We examine the adsorption of hydrogen, hydroxide, water, and a sodium cation onto the stepped platinum surfaces, Pt(553) and Pt(533). Due to the strong adsorption of both hydrogen and hydroxide (with co-adsorbed water) at the steps of Pt(553) and Pt(533), they will competitively adsorb on the step at low potentials. The presence of co-adsorbed sodium near the step weakens the adsorption of solvated hydroxide, which we identify as a possible cause of the non-Nernstian shift of the sharp step-associated peaks in changing from acidic to basic electrolytes. We also examine hydrogen adsorption at the terrace of Pt(553) and Pt(533), and simulate a low potential cyclic voltammogram on Pt(553) and Pt(533). The experimental CV is well-represented as a sum of step and terrace features, and the (553) and (533) CV features closely resemble those from the low index (111), (100), and (110) surface facets that match the local atom arrangements.
5.1. Introduction

Adsorbed hydrogen and hydroxide species are important intermediates or spectator species in many electrocatalytic reactions. These reactions include hydrogen oxidation and evolution, oxygen reduction, and methanol oxidation. While experimental techniques such as cyclic voltammetry (CV) can be used to elucidate adsorption thermodynamics, deconvoluting the involvement of multiple species that co-adsorb or competitively adsorb in the same potential range is challenging. Hydrogen and hydroxide have been shown to adsorb within the same low potential range (0-0.5 V versus a relative hydrogen electrode, RHE) to Pt(100) and Pt(110). Disordered or stepped single crystal, polycrystalline, or nanoparticle electrode surfaces expose multiple local surface environments, and deconvolution of the adsorption behavior among sites is also challenging. Attributing adsorption behavior to specific local sites is particularly important to the study of electrocatalysis. The sharp current peaks at low potentials, as measured by cyclic voltammetry on stepped platinum and polycrystalline platinum, exhibit anomalous non-Nernstian shifts with pH. This anomalous shift is correlated with a decrease in the rate of the hydrogen oxidation reaction by two orders of magnitude as the pH is increased.

The low potential (below 0.5 V_{RHE}) CV features on stepped or polycrystalline Pt electrodes are typically assumed to correspond to hydrogen adsorption/desorption; and this potential range is often termed the “H-upd” region. In our previous work, we used density functional theory (DFT) to show that the low potential peaks measured by cyclic voltammetry on Pt(100) and Pt(110) low index single crystal electrodes can be attributed to collective H* desorption (adsorption) and OH* adsorption (desorption) as the potential is scanned positively (negatively). This H*/OH* competitive adsorption drives the Pt(110) and Pt(100) associated adsorption peaks measured by cyclic voltammetry to lower potentials than what is predicted by DFT for H* desorption/adsorption alone. These low potential peaks shift by less than the
Nernstian shift with pH, which has been attributed to the specific adsorption of alkali metal cations.\textsuperscript{12-13} Alkali cation co-adsorption weakens the adsorption of hydroxide and co-adsorbed water on the electrode surface.\textsuperscript{5} Though this previous work explains the H*/OH* adsorption behavior of the low index platinum facets, the transferability of these findings to more complex stepped or polycrystalline surfaces has not been demonstrated.

Experimental studies have suggested that both H* and OH* may adsorb on stepped Pt facets at low potentials, though complexities of deconvoluting step and terrace features have complicated analysis. CO displacement studies support the conclusion that hydrogen and hydroxide competitively adsorb at low potentials on Pt(100) and Pt(110) single crystal electrode surfaces.\textsuperscript{7, 14} Similar experiments with stepped platinum electrodes, however, have not been able to conclusively identify hydroxide adsorption at low potentials, as adsorption on the step is convoluted with adsorption on the terrace.\textsuperscript{15-16} Chen et al. measured a total displaced charge using CO displacement which changes sign (from negative to positive with increasing potential) within the “H-upd region”, suggesting hydroxide adsorption at low potentials competitive with hydrogen desorption on polycrystalline platinum electrodes.\textsuperscript{17} Pohl et al. use potentiodynamic electrochemical impedance spectroscopy in both the absence and presence of dissolved oxygen to support that hydroxide can adsorb at low potentials on the steps of a Pt(331) surface.\textsuperscript{18} Schouten et al. suggested hydrogen and hydroxide or oxygen competitive adsorption on Pt steps to explain the narrow width of the sharp peaks measured by cyclic voltammetry, which could not be explained by hydrogen adsorption alone.\textsuperscript{19}

Density functional theory (DFT) can be used to examine specific adsorption in the absence of competing adsorption or surface reactions. The presence of an electric field and of solvent and ions near the electrode surface can affect the thermodynamics of adsorption, and including them rigorously in a DFT simulation is not trivial. A growing body of evidence suggests that the effect of near surface solvation and electric field on the adsorption of hydrogen
to platinum surfaces is small\textsuperscript{12, 20-21}, though a rigorous investigation on stepped surfaces is lacking. In contrast to this, the effect of solvation near the electrode surface has a significant effect on the adsorption of hydroxide\textsuperscript{5, 22-25}, where co-adsorbed water forms strong hydrogen bonds with adsorbed hydroxide. This effect may not be captured by implicit solvation (using a dielectric medium to solvate the surface), and as water is always present near the surface in an aqueous electrochemical environment, the effect of co-adsorbed water cannot be neglected.

Previous DFT studies have investigated hydrogen and hydroxide adsorption at stepped Pt surfaces. Kolb et al. used DFT to calculate the adsorption energy of hydrogen, hydroxide, and water at the steps and terraces of Pt(553) and Pt(533).\textsuperscript{26} They predicted hydrogen adsorption at the steps at higher potentials than what is seen in experimental cyclic voltammograms. They also observed strong hydroxide binding on the step of Pt(533), suggesting that H*/OH* competitive adsorption may occur. They neglected, however, to include explicit water interaction that could stabilize adsorbed hydroxide on both steps. Donadio et al.\textsuperscript{22} and Peköz et al.\textsuperscript{27} showed that the dissociation of water at the step of Pt(221) to form adsorbed hydroxide becomes more favorable as an increasing number of hydrogen bonded water molecules are co-adsorbed at the step, and that competitive adsorption of hydrogen and hydroxide becomes favorable with 2 co-adsorbed water molecules.\textsuperscript{27} Jinnouchi et al. recently examined the impact of implicit water solvation on the thermodynamics of hydroxide adsorption at a stepped surface.\textsuperscript{28} Co-adsorption of explicit water molecules with hydroxide at the step was found to significantly promote adsorption, though no significant promotion was seen if only an implicit water solvation model was used.

The complications in assigning the CV features to H*/OH* processes on stepped electrodes has led to significant discrepancies in explaining the non-Nerstian shifts of the sharp CV features. van der Niet et al. suggested that H*/OH* competitive or co-adsorption may explain these experimentally measured shifts on stepped platinum surfaces with pH.\textsuperscript{8} Although they discuss DFT and ultra-high vacuum (UHV) measurements of hydrogen and hydroxide adsorption,
they don’t provide a mechanistic explanation for why the adsorption of either species would be pH dependent on a reversible hydrogen electrode (RHE) scale.\(^8\) Recent work from Gómez-Marín et al. suggested that near surface water may have a significant effect on the adsorption of hydrogen at platinum steps and that the changing electric field near the surface with pH may alter the structure and interaction of near surface water with adsorbed hydrogen.\(^{29}\) Schwarz et al. used DFT to suggest that water binds very strongly to platinum step sites, such that competitive adsorption of hydrogen and water occurs at low potentials.\(^{30}\) They further show that a significant amount of charge can transfer to water adsorbed at step sites, which would give a non-unity electrosorption valency and explain a non-Nernstian shift with pH.\(^{30}\) While Schwarz et al. find that hydroxide adsorption occurs only at high potentials on platinum steps, they did not consider the effect of explicit co-adsorbed water molecules.

Herein, we use DFT to explicitly examine the thermodynamics of hydrogen and hydroxide adsorption on the steps and terraces of the Pt(553) and Pt(533) surfaces. We consider explicit solvation by co-adsorbed water molecules, and consider the impact of sodium co-adsorption. We support previous conclusions\(^{5,8,19}\) that the sharp low potential peaks measured in cyclic voltammograms on Pt(553) and Pt(533) (and any platinum stepped surface) correspond to the competitive adsorption of hydrogen and hydroxide. We calculate the relative coverage of adsorbed hydrogen and hydroxide as a function of electrode potential, simulating the low potential cyclic voltammograms of the (553) and (533) surfaces. We show that the step-associated peaks shift to higher potentials on a reversible hydrogen electrode (RHE) scale due to the effect of specifically adsorbed alkali metal cations.
5.2. Results and Discussion

The Pt(553) and Pt(533) surfaces are shown in Figure 5-1a and 5-1b, respectively, with hydrogen adsorbed at the step. We first consider the adsorption of hydrogen at the steps and terraces of Pt(553) and Pt(533). Next, we examine the adsorption of hydroxide and hydroxide with co-adsorbed water at the steps of Pt(553) and Pt(533). To compare with experiment, we simulate cyclic voltammograms for hydrogen adsorption at the terrace and hydrogen and hydroxide competitive adsorption at the steps of Pt(553) and Pt(533). Finally we examine the effect of a co-adsorbed alkali metal cation on the adsorption of hydrogen and hydroxide at the steps of Pt(553) and Pt(533).

Figure 5-1. The Pt(553) (a) and Pt(533) (b) surfaces with 1 ML (1 H per step Pt atom) of hydrogen adsorbed at the step.

5.2.1. H* Adsorption on Steps and Terraces of Pt(553) and Pt(533)

Figure 5-2a gives the equilibrium adsorption potential as a function of coverage for H* adsorption on the steps of Pt(553) and Pt(533). Hydrogen adsorption on these steps exhibits only a weak coverage dependence, which is slightly attractive on the Pt(553) step. Adsorption is stronger on the Pt(533) step (indicated by the more positive adsorption potential for hydrogen adsorption/desorption) than on the Pt(553) step. This trend in adsorption strength on the step...
between the two facets as well as the free energy of the adsorption at 0 V_{NHE} matches well with DFT results from Kolb et al. who calculate a ΔG of -0.41 eV on the same site of Pt(533) and -0.26 eV on Pt(553).26

Figure 5-2b gives the equilibrium adsorption potential as a function of coverage for H* adsorption on the terraces of Pt(553) and Pt(533) as well as on the low index Pt(111) facet (Pt(111) from5). These adsorption potentials are calculated with the step occupied by a full monolayer of adsorbed hydrogen. On both Pt(553) and Pt(533), terrace adsorbed hydrogen at low coverage is bound weaker (given by the less positive adsorption potential) than on the low index Pt(111) surface. Low coverage adsorption is more favorable when the step is vacant, but is still weaker than Pt(111) (see Figure S5-1 in supplementary information). On the Pt(533) surface, this repulsive effect from the occupied step is most apparent at low coverages; at high coverages of hydrogen on the terrace, the adsorption strength is similar to that on Pt(111).

Figure 5-2. a) Equilibrium adsorption potential of hydrogen onto the steps of Pt(553) (blue diamond) and Pt(533) (green triangle). Configurational entropy of the adsorbate is not included. Lines represent best linear fits to the data. b) Equilibrium adsorption potential for hydrogen adsorption as a function of coverage on Pt(111) (blue diamond), the terrace of Pt(533) (purple triangle), and the terrace of Pt(553) (red square). Adsorption on the terrace is modeled with the step occupied with 1 ML H*. The coverage dependence shown here does not include configurational entropy of the adsorbate on the surface. Lines represent best linear fits to the data.
Hydrogen adsorption is weaker on the terraces than on the steps of Pt(553) and Pt(533), which matches the trend in adsorption strength calculated by Kolb et al. at low hydrogen coverages.\textsuperscript{26} Hydrogen adsorption on the terraces is also more strongly dependent on coverage, showing significant repulsion as the coverage is increased, as is seen for hydrogen adsorption on Pt(111). These results match well with what is seen in TPD spectra for hydrogen adsorption on Pt(553) and Pt(533),\textsuperscript{31} where sharp desorption peaks are seen at higher temperatures (corresponding to stronger hydrogen adsorption on the steps with weak coverage dependence) and broad desorption peaks at lower temperatures (corresponding to weaker hydrogen adsorption on the terraces with strong, repulsive dependence on coverage).\textsuperscript{31-32}

The strong binding and weak coverage dependence of hydrogen to the steps of Pt(553) and Pt(533) surfaces suggests that peaks sharper than the broad peak corresponding to hydrogen adsorption on the terrace would be observed in cyclic voltammetry measurements, near 0.3 $V_{NHE}$ on Pt(553) and 0.45 $V_{NHE}$ on Pt(533). The experimentally measured peaks lie more negative of these potentials in both acidic and basic electrolytes (on a RHE scale), and are much sharper than the weak coverage dependence calculated here would suggest.\textsuperscript{5} These sharp experimentally measured peaks suggest strong attractive interactions\textsuperscript{33} and/or competitive adsorption\textsuperscript{34}. Furthermore, the location of these peaks shifts with pH on a RHE scale.\textsuperscript{8-10} We have previously considered this effect on the low index surfaces of platinum, and show that hydrogen adsorption/desorption on Pt(100) and Pt(110) is driven to lower potentials by concurrent hydroxide desorption/adsorption.\textsuperscript{5} We also concluded that the shift with pH could be explained by a weakening of hydroxide adsorption in the presence of specifically adsorbed alkali metal cations as pH is increased.\textsuperscript{5} Others have proposed that these low potential peaks on 100/110 surfaces or steps shift with pH due to a change in the interaction of near-surface water with adsorbed hydrogen\textsuperscript{29-30} or a non-unity electrosorption valency of adsorbed hydrogen or hydroxide.\textsuperscript{8}
next section, we consider the equilibrium adsorption potentials of OH* formation at the step to examine whether H* desorption from the step will be accompanied by OH* adsorption.

5.2.2. OH* Adsorption and OH*-H₂O* Co-adsorption on Steps of Pt(553) and Pt(533)

Figure 5-3 gives the potential ranges where hydroxide adsorption, hydroxide and water co-adsorption, and hydrogen adsorption are favorable on the steps of Pt(553) and Pt(533). Images of the co-adsorbed structures are given in the supplementary information, Figures S5-10, S5-11 and S5-13, S5-14. The end of each bar gives the equilibrium adsorption potential at low coverage (1/3 ML for H* and OH*); hydrogen (hydroxide) adsorption is more favorable at any potential more negative (positive) of the end of the bar. In the absence of co-adsorbed water, the calculated adsorption potentials for hydroxide match well with the adsorption free energies calculated by Kolb et al. at 0 V_RHE (0.27 eV on Pt(533) and 0.66 eV on Pt(553)).\textsuperscript{26} In the presence of explicit water molecules, hydroxide adsorption becomes more favorable on the step of Pt(533) and significantly more favorable on the step of Pt(553). This stabilization is due to the attractive hydrogen bonding interactions between adsorbed hydroxide and adsorbed water. Similar effects have been seen with hydroxide adsorption on Pt(111),\textsuperscript{24-25, 35-36} Pt(100),\textsuperscript{5, 23} and Pt(110),\textsuperscript{5} where solvation by explicit water molecules has been shown to be necessary to match experimentally observed adsorption thermodynamics.

When co-adsorbed water is neglected, it appears that competitive adsorption between hydrogen and hydroxide, as given by the overlap of their adsorption potential windows (Figure 5-3), would only occur on the Pt(533) step, a conclusion which Gomez-Marin and Feliu support\textsuperscript{29} from prior DFT results\textsuperscript{26} for adsorption in an alkaline electrolyte (though they note that solvation near the electrode surface may have a significant effect). It is clear from our DFT results that when co-adsorbed water is included, hydrogen and hydroxide competitively adsorb at low
potentials on the steps of both Pt(553) and Pt(533) at any pH (on a relative hydrogen electrode scale). This behavior is similar to that seen on the Pt(110) and Pt(100) low index surfaces, including the trend in adsorption favorability, where the 110 steps and Pt(110) low index surface bind hydroxide and water more strongly and hydrogen more weakly than the 100 steps and the Pt(100) surface.\textsuperscript{5,26,31}

Figure 5-3. Stable surface adsorption potential ranges for H\(^*\) (clear bar), OH\(^*\) (blue bar) and solvated OH\(^*\)+2H\(_2\)O\(^*\) (green bar) on the steps of Pt(533) and Pt(553).

To compare calculated adsorption free energies more directly to electrochemical experiments, cyclic voltammograms are simulated which include the competitive adsorption of hydrogen and hydroxide (with co-adsorbed water) on the steps of Pt(553) and Pt(533) and the adsorption of hydrogen on the terraces of Pt(553) and Pt(533).

5.2.3. Simulated Cyclic Voltammograms for Pt(553) and Pt(533)

The free energy of adsorption of hydrogen and hydroxide (with water) as a function of potential and coverage can be used to simulate cyclic voltammograms representing their adsorption/desorption. Although it is easy to capture the coverage dependence of the adsorption
energy of hydrogen, it is difficult to capture the coverage dependence of the adsorption energy of hydroxide and co-adsorbed water on the steps of Pt(553) and Pt(533) using DFT. The low coverage adsorption of hydroxide and water is particularly difficult to investigate on these surfaces as it requires a large unit cell along the direction of the step. Given the width of the terrace, the number of atoms that must be modeled to simulate a longer step, and therefore the computational time, grows significantly with step length. This also makes it difficult to investigate the interaction between adsorbed hydrogen and co-adsorbed hydroxide and water. Therefore, the DFT results are used to determinate the nature of the interactions, attractive or repulsive, between adsorbates but are limited in calculating the exact magnitude of the interaction. We compare the results of DFT calculations and experimental fits to the coverage dependent interactions before simulating CVs.

With DFT simulations we calculate a slope for hydroxide adsorption potential as a function of coverage as $-0.251 \text{ eV/ML (553)}$ and $-0.154 \text{ eV/ML (533)}$ (for $1 \text{OH}^* + 2 \text{H}_2\text{O}^*$; $-0.423 \text{ eV/ML (553)}$ and $-0.105 \text{ eV/ML (533)}$ were calculated for $1 \text{OH}^* + 4 \text{H}_2\text{O}^*$). These DFT results indicate an attractive interaction between OH* species on both surfaces. This compares well with the values fit to experiment of $-0.084 \text{ eV/ML}$ and $-0.425 \text{ eV/ML}$ on Pt(553) and Pt(533) respectively. Both DFT and experimental fits indicate attractive interactions (and/or repulsive interactions between the competing adsorbates, which would contribute to sharpening the experimentally measured peak\textsuperscript{34}), though experimental fits show a weaker attraction on the Pt(553) step and a stronger attraction on the Pt(533) step than what is calculated using DFT. We also find that the interaction between adsorbed hydrogen and adsorbed hydroxide and water is repulsive (see Table S5-1 in the Supplementary Information). This would further contribute to sharpening the cyclic voltammetric peak\textsuperscript{34}, as measured by experiment. While DFT results support an attractive interaction between adsorbed hydroxides and a repulsive interaction between co-adsorbed hydrogen and adsorbed hydroxide, we use the experimental fits for hydroxide
coverage dependence when simulating CVs due to the limited range of coverage evaluated with DFT. The difficulty in representing these interactions along the step with sufficient unit cells leaves the exact molecular structures responsible for the sharpness of these CV peaks undetermined. A table of the parameters used in the H*/OH* adsorption model can be found in the supplementary information.

Figures 5-4 and 5-5 show both experimental and simulated cyclic voltammograms for Pt(553) and Pt(533) (respectively) in an acidic electrolyte and in basic electrolytes at 300 K and a scan rate of 50 mV/s. We first discuss the acidic conditions, which are taken both experimentally and in simulation to not include adsorption of electrolyte ions other than protons and hydroxide. Basic conditions are discussed in the next section. The simulated CVs sum the features of the step and terraces. For the terraces, the adsorption energy and coverage dependence calculated with DFT yield a broad CV peak due to the repulsive interactions between adsorbed hydrogen. They also include sharp peaks corresponding to the competitive adsorption of hydrogen and hydroxide on the steps of Pt(553) and Pt(533). The simulated step contribution is generated using the adsorption energy and coverage dependence of hydrogen calculated using DFT, the adsorption energy of hydroxide with co-adsorbed water from DFT, and the coverage dependence of hydroxide and water derived from the experimental cyclic voltammograms. Experimental cyclic voltammograms in Figures 5-4 and 5-5 were measured in 0.1 M HClO4 and 0.05 M NaOH at 50 mV/s as adapted from van der Niet et al.8

We can see from Figures 5-4 and 5-5 that the simulated cyclic voltammograms capture very well both the location and the breadth of the wide peak corresponding to hydrogen adsorption on the terraces of Pt(553) and Pt(533) as well as the location of the sharp peak corresponding to the competitive adsorption of hydrogen and hydroxide on the steps of Pt(553) and Pt(533). Of course, in fitting the coverage dependence of hydroxide to experiment, we would expect the width of the sharp step peak to match experiment. However, a key insight provided by
DFT is that the step-associated peak positions are only matched when H* adsorption/desorption is taken to occur with concurrent OH* desorption/adsorption. Considering concurrent processes places the step-associated peak at 0.165 $\text{V}_{\text{RHE}}$ (553, expt. 0.125 $\text{V}_{\text{RHE}}$) and 0.263 $\text{V}_{\text{RHE}}$ (533, expt. 0.27 $\text{V}_{\text{RHE}}$). Treating these peaks as solely associated with H* adsorption/desorption would, inaccurately, place them at 0.29 $\text{V}_{\text{RHE}}$ (553) and 0.45 $\text{V}_{\text{RHE}}$ (533). The sharp peaks measured by cyclic voltammetry cannot correspond solely to hydrogen adsorption/desorption. We would not expect the interaction of the step with only adsorbed water to play a significant role in dictating the location of this peak, because we find it favorable for water to dissociate to form adsorbed hydroxide at the potential range of the peaks.

To illustrate the importance of considering hydroxide coverage dependence in the model, simulated cyclic voltammograms assuming no interaction between adsorbed hydrogen and adsorbed hydroxide are given as Figures S5-4 and S5-5 in the Supplementary Information.
Figure 5-4. Simulated and experimental cyclic voltammograms for a Pt(553) electrode. Simulated CVs are included in acid (free from co-adsorbed alkali, red dashed line) and base (with co-adsorbed alkali, blue solid line). Experimentally measured cyclic voltammograms measured in 0.1 M HClO$_4$ (dashed black line) and in 0.05 M NaOH (solid black line) are taken from van der Niet et al.$^8$. Simulated and measured voltammograms both use a scan rate of 50 mV/s. Simulated CVs due not include hydroxide on terraces that would account for the experimental features at $V > 0.6 \text{ V}_{\text{RHE}}$.

Figure 5-5. Simulated and experimental cyclic voltammograms for a Pt(533) electrode. Simulated CVs are included in acid (free from co-adsorbed alkali, red dashed line) and base (with co-adsorbed alkali, blue solid line). Experimentally measured cyclic voltammograms measured in 0.1 M HClO$_4$ (dashed black line) and in 0.05 M NaOH (solid black line) are taken from van der Niet et al.$^8$. Simulated and measured voltammograms both use a scan rate of 50 mV/s. Simulated CVs due not include hydroxide on terraces that would account for the experimental features at $V > 0.6 \text{ V}_{\text{RHE}}$. 
5.2.4. Effect of Specifically Adsorbed Cation on Hydroxide and Water Adsorption

We next examine the non-Nernstian shift of the sharp 533 and 553 low potential peaks with pH. We consider the effect of a specifically adsorbed alkali metal cation, in this case, sodium, on the adsorption of hydrogen at the step and on the adsorption of hydroxide and water at the step. We first calculated the equilibrium adsorption potential of the Na cation at the steps, and found values of \(-0.488 \, \text{V}_{\text{NHE}}\) (553) and \(-0.311 \, \text{V}_{\text{NHE}}\) (533). These values were calculated without micro-solvating the surface, which would further stabilize Na adsorption\(^{12}\). We conclude that Na cations will be adsorbed at the step within the H*/OH* range at high pH.

We next considered the impact of co-adsorbed Na* on H* adsorption. We find that the presence of specifically adsorbed sodium near the step of Pt(553) and Pt(533) has only a minor effect on the adsorption of hydrogen on the step, results are given in Table S5-3 of the Supplementary Information.

Figure 5-6 illustrates the effect of specifically adsorbed sodium on the adsorption of hydroxide and water at the step of Pt(553) and Pt(533). The phase change potential, defined as the potential where the free energy to convert a 1 ML coverage of hydrogen to 0.33 ML hydroxide (and 0.66 ML H\(_2\)O) is zero, is shown in Figure 5-6, both in the absence and in the presence of specifically adsorbed sodium. This phase change reaction is driven to more positive potentials by the presence of specifically adsorbed sodium. As Na* had only a minor effect on the adsorption of hydrogen, this suggests that the adsorption of hydroxide and water is weakened (made less favorable), in the presence of Na*. This matches what we have found previously for the low index facets of platinum.\(^{5}\) This is due to the distortion of the attractive hydrogen bonding network that forms between adsorbed hydroxide and adsorbed water due to the presence of Na*. Na* retains some of its positive charge on adsorption, and therefore interacts strongly with near surface and adsorbed water. In the presence of Na*, the hydrogen bonds between OH* and H\(_2\)O*
at the step are shortened and the bonds between OH* and H₂O* and the platinum surface atoms are lengthened (Figure S5-4 and Table S5-4 in Supplementary information). The surface normal dipole moments generated on sodium adsorption, which are related to the amount of charge retained by sodium are given in Table S5-5 in the supplementary information. The structure of 1OH*+2H₂O* adsorbed on the step with co-adsorbed Na* on Pt(553) is shown in Figure 5-7. Structures of all adsorbed/co-adsorbed species are given in the Supplementary Information.

![Graph showing phase change potential at 553 step and 533 step](image)

**Figure 5-6.** The equilibrium phase change potential at the step of Pt(553) and Pt(533) for the desorption of 1ML of hydrogen (defined per number of step atoms) and adsorption of 1/3 ML OH* and 2/3 ML H₂O*, without (red bar) and with (blue bar) the co-adsorption of Na* (at 1/3 ML, next to the step).

![Molecular structure](image)

**Figure 5-7.** 1 OH* + 2H₂O* (at 1/3 ML OH*) on the step of Pt(553) with co-adsorbed Na* near the step.
The calculated effect of specifically adsorbed sodium on the adsorption of hydroxide and water on the step can be used to simulate cyclic voltammograms in an alkaline environment, as shown in Figures 5-4 and 5-5. The presence of Na* near the step shifts the sharp, step-associated peak to more positive potentials due to the weakening of hydroxide and water adsorption. This provides an explanation for the non-Nernstian shift of these peaks with pH. On a RHE scale, the adsorption of Na* becomes more favorable with increasing pH, giving higher Na* coverages for the same $V_{\text{RHE}}$ as the pH increases. This increase in coverage can cause a shift of the low potentials peaks to more positive potentials as pH increases. The high Na* coverage we examine here (1 Na* per 3 step Pt atoms) is what we might expect at high pH (13-14), based on the potential at which sodium adsorption would be competitive with hydrogen and hydroxide adsorption at this coverage.

We note that the change of the surface normal dipole moment on adsorption of hydroxide and water at the step, in the absence and in the presence of a specifically adsorbed sodium cation, is significant (see Table S5-5 in supplementary information). This suggests an electrosorption valency which deviates from unity (1 electron per adsorbed hydroxide) for hydroxide adsorption with co-adsorbed water. This also contributes to the shift in the sharp low potential peaks in current measured by cyclic voltammetry with pH, as the expected Nernstian shift depends on the number of electrons transferred. While this could explain the experimentally measured shift in the sharp low potential peaks with pH in the absence of a specifically adsorbed alkali metal cation, experimental evidence suggests the identity of this cation also effects the location of these sharp peaks. Additional experimental work is necessary to examine the magnitude of each of these effects and to discern between the effects of adsorbed water and co-adsorbed water and hydroxide (on the cyclic voltammetric response). This could include in-situ spectroscopic measurements of adsorbed hydroxide and water and the effect of alkali cations on their spectroscopic response.
5.3. Conclusions

The co-adsorption of water significantly promotes the adsorption of hydroxide onto the steps of Pt(533) and Pt(553) surfaces, especially the 110-like steps, in an electrochemical environment. Due to the similarly strong adsorption of hydrogen on the steps, both H* and OH* formation are favorable in an overlapping electrode potential range. This leads to sharp peaks associated with the step features in cyclic voltammetry at low potentials, as high coverage H* is exchanged for co-adsorbed OH* and H₂O in the step region. DFT results also show a weakening of hydrogen adsorption on the terraces of platinum stepped surfaces relative to hydrogen adsorption on the low index Pt(111) facet. We have simulated cyclic voltammograms using our DFT results that match experimental CVs, demonstrating that a sum of terrace and step associated processes closely resembles the experimental broad and sharp features, respectively. We find that attractive interactions between adsorbed hydroxide and water lead to further sharpening of the step-associated peaks. Non-Nerstian shifts of the step-associated CV peaks are attributed to alkali cation induced destabilization of step-adsorbed OH* species.

Interpreting H* and OH* adsorption behavior on well-defined Pt electrodes could have significant implications in understanding electrocatalysis on platinum. Both H* and OH* have been proposed as intermediates in the hydrogen oxidation reaction, and OH* plays an important role in the rate of the oxygen reduction reaction. The low-potential CV features are also frequently used to determine electrochemically active surface area of Pt electrocatalysts. The low potential region of cyclic voltammograms measured on polycrystalline or nanoparticle platinum electrode surfaces cannot be considered to correspond to solely hydrogen adsorption, and should be considered as a convolution of H* adsorption/desorption on Pt(111)-like terraces and collective H*/OH* exchange on (100)-like and (110)-like steps and facets.
5.4. Computational Details

5.4.1. Computational Methods

Density functional theory (DFT) methods were used to examine the adsorption of hydrogen, hydroxide, water, and sodium to Pt(553) and Pt(533) stepped surfaces. The Vienna ab initio Simulation Package was used to perform electronic structure calculations.\textsuperscript{38-40} A plane wave basis set and the Perdew Wang (PW91) exchange-correlation functional was used.\textsuperscript{41} The projector augmented wave (PAW) approach was used to model core potentials.\textsuperscript{42-43} A 5\texttimes{}5\texttimes{}1 Monkhorst-Pack\textsuperscript{44} mesh was used to sample k-space for the 3\texttimes{}1 and 4\texttimes{}1 unit cells and a 7\texttimes{}7\texttimes{}1 mesh was used for the 2\texttimes{}1 unit cells. The basis set cutoff energy was 450 eV. Structural optimizations were performed until the forces on the atoms were less than 0.02 eV/Å. Dipole corrections in the surface normal direction were included in all surface calculations (LIDPOL = TRUE, IDIPOL = 3). The experimentally measured Pt lattice constant of 3.92 Å was used.\textsuperscript{45} A convergence test with respect to the number of metal layers in the surface slab was performed; the adsorption energy of hydrogen was converged to within 0.02 eV with a 4 layer slab. All surface calculations used at least a 4 layer slab, with the bottom half of the slab frozen during the optimization to mimic the behavior of the bulk metal. The preferred adsorption site was determined for each adsorbate at low coverage on the terrace and on the step of both the Pt(553) and the Pt(533) surfaces. Coverage is defined here as per step atom or per terrace atom, so 1 monolayer (ML) of hydrogen adsorbed at the step corresponds to 1 H\textsuperscript{*} per 1 Pt step atom, unless otherwise noted. Hydrogen preferred the bridge site on the step and the atop site of the terrace of both Pt(553) and Pt(533). Hydroxide preferred the bridge site of the steps of both Pt(553) and Pt(533); hydroxide adsorption on the terrace was not examined. When co-adsorbed with water adsorbed on a
neighboring atop site, hydroxide preferred the atop site on the steps of Pt(553) and Pt(533). The alkali cation preferred the HCP site just below the step on both Pt(553) and Pt(533).

5.4.2. Calculating Equilibrium Adsorption Potentials

The method for calculating the equilibrium adsorption potential for alkali metal cations, hydrogen, and hydroxide (anion) adsorption has been described previously. Described here is the approach for calculating the equilibrium adsorption potential for hydroxide, as an example, including surface solvation by explicit water molecules, and sodium co-adsorption.

The hydroxide adsorption reaction is shown in equation 1.

\[ H_2O_{(aq)} + \ast \rightarrow OH^\ast + H_{(aq)}^+ + e^- \]  

This reaction is thermodynamically equivalent to the adsorption of a hydroxide ion from solution, but is written to reference H\(^+\) and H\(_2\)O aqueous energies rather than the aqueous OH\(^-\) ion they are equilibrated with in solution.

The change in free energy for the hydroxide adsorption reaction can be written as:

\[ \Delta G_{ads}^{OH} = G_{OH^\ast} + G_{H_{(aq)}^+} - |e|U - G_{H_2O_{(aq)}} - G_* \]  

where \( G_{OH^\ast} \) is the free energy of the adsorbed hydroxide, \( G_{H_{(aq)}^+} \) is the free energy of the solution phase proton, \( |e|U \) is the free energy of the electron (given as the absolute value of the electron charge times the electrode potential on an absolute/vacuum scale), \( G_{H_2O_{(aq)}} \) the free energy of solution phase water, and \( G_* \) the free energy of the bare surface site where hydroxide will adsorb.

For the adsorbed species free energy, it is assumed that the major contribution to the entropy is the vibrational entropy of the adsorbed species, and that the vibrational entropy associated with the surface metal atoms is unperturbed by adsorption:

\[ G_* = E_{EDEM}^{DFT} \]
In equation 3, $E_{OH}^{DFT}$ is the DFT calculated energy of the bare surface. In equation 4, $E_{OH}^{DFT}$ is the DFT calculated energy of the surface with the adsorbate, $ZPVE$ is the zero-point vibrational energy, and $TS_{OH}^{vib}$ is the temperature times the vibrational entropy of the adsorbate adsorbed on the surface. The free energy of the solution phase water is:

$$G_{OH} = E_{OH}^{DFT} + ZPVE - TS_{OH}^{vib}$$  \[4\]

where $E_{H_2O}^{DFT}$ is the DFT calculated energy of water in the gas phase, $S_{H_2O}^{gas}$ is the vibrational, rotational, and translational entropy of gaseous water at the vapor pressure of interest, $U_{int}$ the internal energy of the molecule, and $pV$ is the pressure-volume contribution to the Gibbs free energy. Unless otherwise noted, all free energies are calculated at 300 K (giving a water vapor pressure of 0.035 bar, such that the free energy of gas phase water at this temperature and pressure is equal to the free energy of solution phase water at this temperature).

To calculate the free energy of the aqueous phase proton and place the electron potential on a hydrogen scale, the computational hydrogen electrode (CHE) model is used, giving

$$G_{H_2O(aq)} = E_{H_2O}^{DFT} + ZPVE - TS_{H_2O}^{gas} + pV + U_{int}$$  \[5\]

The free energy of the gas phase hydrogen molecule is calculated in a manner similar to that of the gas phase water molecule, but at a pressure of 1.01325 bar.

To calculate the equilibrium adsorption potential, equation 6 is inserted into equation 2, which is then solved for the potential that gives a zero free energy change of adsorption. This yields equation 7, which further includes a correction to the free energy for the interaction of the change in surface normal dipole moment on adsorption with the electric field.

$$U_{NHE}^{OH} = \frac{G_{OH^*} + \frac{1}{2}G_{H_2(g)} - G_{H_2O(aq)} - G_\ast}{|e| + |e| \frac{\mu_{OH^*} - \mu_\ast}{d}}$$  \[7\]
In equation 7, $\mu_{OH^*}$ is the surface normal dipole moment with the adsorbate adsorbed on the surface, $\mu_*$ is the surface normal dipole moment of the bare surface, and $d$ is the thickness of the double layer, which we assume to be 3 Å in the Helmholtz approximation. This dipole correction term also assumes the potential of zero charge (PZC) is zero.

5.4.3. Surface Solvation

To consider the effect of surface solvation on adsorption, the bare surface and adsorbate covered surface are solvated with a small number of explicit water molecules. A growing body of work suggests that near surface solvation has only a small effect on hydrogen adsorption. However, it can have a significant effect on the adsorption of hydroxide, to which the water molecules can hydrogen bond (promoting their co-adsorption on the surface). Explicit solvation also has a significant effect on the adsorption of the alkali metal cations, where we have previously shown that the cations retain some of their positive charge on adsorption and water molecules can stabilize and screen this charge, promoting the adsorption of the cation. We include the effects of near surface water on the adsorption of hydroxide and a sodium cation on Pt(553) and Pt(533).

In the case of adsorbed hydroxide, explicit water molecules are co-adsorbed next to the hydroxide, forming a hydrogen bond, as well as a bond to the surface. We examine the effect of a small number, 1-4 co-adsorbed water molecules, on hydroxide adsorption. The overall reaction is shown in equation 8.

$$xH_2O_{(aq)} + * \rightarrow OH^*(x - 1)H_2O^* + H^+_{(aq)} + e^-$$

[8]

The equilibrium adsorption potential is then calculated in the same manner as for hydroxide adsorption, as described previously. We have considered a limited number of hydrogen bonding configurations of the co-adsorbed water molecules. As the number of water molecules grows, it
becomes more likely that a local minimum energy structure is found. We therefore can only approximate the effect of solvation on hydroxide adsorption to the steps of Pt(553) and Pt(533), though this is a significant improvement over neglecting explicit water solvation entirely as strong hydrogen bonds are formed between H₂O* and OH* on the stepped surface. The equilibrium adsorption potential calculated here represents an “upper-limit” on the adsorption potential; a lower energy minima for the co-adsorbed state would yield a more negative adsorption potential for hydroxide.

As a useful estimate of the potential where hydrogen and hydroxide may competitively adsorb on the steps of Pt(553) and Pt(533), we calculate the “phase-change” potential, which represents the potential at which adsorbed hydrogen is replaced by hydroxide. The overall reaction is shown in equation 9.

\[ xH^*yH_2O^* \rightarrow OH^*(y-1)H_2O^* + (x+1)(H^*_aq + e^-) \]  

[9]

Calculating an equilibrium adsorption potential for this reaction follows the same methodology as described for hydroxide, and has been discussed previously.²

We consider the effect of an adsorbed cation, sodium, on the adsorption of hydrogen and hydroxide (and co-adsorbed water) on the steps of Pt(553) and Pt(533). The sodium is adsorbed near the step, and the equilibrium adsorption potential (or the free energy of adsorption) to adsorb hydrogen or hydroxide next to the cation is calculated. These results again rely on finding a reasonable minimum energy structure for H/OH, Na and solvating H₂O molecules at the step. We consider a number of minimum energy structures and report the most stable.
### 5.4.4. Simulating Cyclic Voltammograms

In order to more readily compare our results to experiment, we also simulate cyclic voltammograms using our DFT calculated equilibrium adsorption potentials on the Pt(553) and Pt(533) surfaces. The procedure follows what we have described previously\(^5\), but has been extended to include the explicit coverage dependence of the competitive adsorption of hydrogen and hydroxide (with co-adsorbed water) on the steps of Pt(553) and Pt(533). The cyclic voltammograms are simulated under the assumption that adsorption is equilibrated with solution at all potentials. For comparing to experimental cyclic voltammograms, the double layer charging current is taken from experiment at 0.5 V\(_{\text{RHE}}\) and added to the simulated voltammograms. We simulate the CV as a sum of the behavior of the step and terrace facets.

To simulate the Pt(553) and Pt(533) terrace contributions, we assume 1 electron transferred per surface site to give a surface site density 216.74 µC/cm\(^2\) (553) and 190.41 µC/cm\(^2\) (533). The free energy and the coverage dependence of hydrogen adsorption are calculated with DFT and the configurational entropy contribution to the coverage dependence is approximated by using the analytical configurational entropy of non-interacting adsorbates on a 2D surface.\(^5, 20, 48-49\) While this is an approximation given that the interaction between adsorbed hydrogen on the terraces is repulsive, it allows for simulated CV’s that compare well with experiment for hydrogen adsorption on Pt(111).\(^5, 20, 48-49\)

To simulate the cyclic voltammograms corresponding to hydrogen and hydroxide competitive adsorption at the steps of Pt(553) and Pt(533), we need to consider the coverage dependence of hydrogen adsorption and hydroxide adsorption at the step. This is straightforward using DFT for hydrogen adsorption, but difficult for hydroxide adsorption, given that we find the co-adsorption of water significantly promotes hydroxide adsorption. Since the step atoms represent only a small portion of the total atoms in the Pt(553) or Pt(533) unit cell, examining the
co-adsorption of hydroxide and water over a significant range of coverage would require a much larger unit cell than the 3-4 step-atom wide model used here. Therefore, to simulate the cyclic voltammograms which involve hydroxide adsorption, we estimate the coverage dependence of hydroxide such that the height and width of the simulated cyclic voltammograms match experimentally measured cyclic voltammograms for Pt(553) and Pt(533). We approximate that hydroxide adsorption blocks 3 step sites in the competitive adsorption site balance (which gives a maximum coverage of 1/3 ML OH* and 2/3 ML H2O* on the steps) due to the strong co-adsorption of 2 water molecules on the step. We compare and discuss our DFT simulated hydroxide coverage dependence with that estimated from experiment. Implicit in our consideration of coverage dependence is the interaction of co-adsorbed hydrogen and hydroxide (and water), which again we estimate with DFT over a limited range of coverage. The coverage dependence of hydrogen adsorption on the step is explicitly calculated with DFT and the configurational entropy contribution to the coverage dependence of hydrogen adsorption at the step is explicitly calculated using an analytical description for interacting adsorbates on a 1D step.19, 29, 50

5.5. Acknowledgements

I.T. McCrum acknowledges support from The Pennsylvania State University Diefenderfer Graduate Fellowship and NSF NRT #1449785. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1053575.
5.6. References


6. García-Araez, N.; Climent, V.; Feliu, J. M. Analysis of Temperature Effects on Hydrogen and OH Adsorption on Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) by Means of Gibbs Thermodynamics. *J. Electroanal. Chem.* 2010, 649, 69-82.


Figure S5-1. Equilibrium adsorption potentials for hydrogen adsorbed on Pt(111) (blue diamonds), the terrace of Pt(553) (green triangle), and the terrace of Pt(553) with the step occupied by a monolayer (ML) of adsorbed hydrogen (red square). Lines are intended as a guide to the eye.

Table S5-1. Equilibrium adsorption potentials calculated for hydroxide and water adsorption on the step of Pt(553) at a 1/3 ML coverage of hydroxide with and without a hydrogen atom adsorbed at the step.

<table>
<thead>
<tr>
<th>Pt(553)</th>
<th>1 OH*+2H* U° (V_RHE)</th>
<th>1 OH*+2H<em>O</em> near 1H* U° (V_RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.084</td>
<td>0.296</td>
</tr>
</tbody>
</table>
Table S5-2. Interaction parameters used in competitive adsorption model to simulate cyclic voltammograms.

The adsorption potential shown for hydrogen adsorption represents the y-axis intercept of the linear fit to the DFT calculated adsorption potentials; for adsorbed hydroxide, the coverage at which this potential was calculated is given below. All parameters were calculated using DFT, except for those shown in bold which were estimated from experimentally measured cyclic voltammograms. The interaction of adsorbed hydroxide and water as a function of coverage was calculated with DFT and is presented in the text of the paper in the section “Simulated cyclic voltammograms for Pt(553) and Pt(533)”. Interaction parameters are given in units of $V_{\text{RHE}}$/ML, where negative parameters correspond to a repulsive interaction and positive parameters correspond to attractive interactions. These can be converted to eV/ML by multiplying by negative one. The adsorption potentials calculated for hydroxide adsorption used in the interaction model were simulated as follows:

**Pt(553) OH* step**: 1OH*+4H2O* at ¼ ML  
**with Na*: 1OH*+2H2O* with Na* at 1/3 ML  
**Pt(533) OH* step**: 1OH*+4H2O* at ¼ ML  
**with Na*: 1OH*+2H2O* with Na* at ¼ ML

where coverage is defined as the number of adsorbed hydroxide molecules per surface Pt step atom. Coverage of adsorbed Na* is equal to that of adsorbed hydroxide here.

<table>
<thead>
<tr>
<th>Pt(553)</th>
<th>H* step</th>
<th>H* terrace</th>
<th>OH* step</th>
<th>OH* step with Na*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption potential ($V_{\text{RHE}}$ ($\theta_H \to 0$))</td>
<td>0.276</td>
<td>0.177</td>
<td>0.054</td>
<td>0.240</td>
</tr>
<tr>
<td>Interaction ($V_{\text{RHE}}$/ML)</td>
<td>0.063</td>
<td>-1.137</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Interaction with config. entropy ($V_{\text{RHE}}$/ML)</td>
<td>0.020</td>
<td>-0.214</td>
<td><strong>0.084</strong></td>
<td><strong>0.106</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pt(533)</th>
<th>H* step</th>
<th>H* terrace</th>
<th>OH* step</th>
<th>OH* step with Na*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorption potential ($V_{\text{RHE}}$ ($\theta_H \to 0$))</td>
<td>0.449</td>
<td>0.162</td>
<td>0.180</td>
<td>0.348</td>
</tr>
<tr>
<td>Interaction ($V_{\text{RHE}}$/ML)</td>
<td>-0.008</td>
<td>-0.067</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Interaction with config. entropy ($V_{\text{RHE}}$/ML)</td>
<td>-0.128</td>
<td>-0.144</td>
<td><strong>0.425</strong></td>
<td><strong>0.30</strong></td>
</tr>
</tbody>
</table>
Figure S5-2. Simulated cyclic voltammogram for competitive hydrogen and hydroxide adsorption on the step of Pt(553) in the presence (solid blue line) and absence of a co-adsorbed Na* (dashed red line). CV’s simulated at 50 mV/s. Simulated CV’s only include adsorption at the step. Simulated CV’s correspond to a phase change reaction for 1ML H* at the step to desorb (adsorb) and 1/3 ML OH* to adsorb (desorb); coverage dependence of adsorption is ignored. This results in a much broader peak than what is measured experimentally. Experimental cyclic voltammogram is shown in the background measured in 0.1 M HClO$_4$ (grey dashed line) and 0.05 M NaOH (grey solid line) adapted from$^8$.

Figure S5-3. Simulated cyclic voltammogram for competitive hydrogen and hydroxide adsorption on the step of Pt(533) in the presence (solid blue line) and absence of a co-adsorbed Na* (dashed red line). CV’s simulated at 50 mV/s. Simulated CV’s only include adsorption at the step. Simulated CV’s correspond to a phase change reaction for 1ML H* at the step to desorb (adsorb) and 1/3 ML OH* to adsorb (desorb); coverage dependence of adsorption is ignored. This results in a much broader peak than what is measured experimentally. Experimental cyclic voltammogram is shown in the background measured in 0.1 M HClO$_4$ (grey dashed line) and 0.05 M NaOH (grey solid line) adapted from$^8$. 
Table S5-3. Equilibrium adsorption potential of hydrogen adsorbed at 1 ML on the steps of Pt(553) and Pt(533) in the absence and the presence of 1/3 ML sodium adsorbed near the step.

<table>
<thead>
<tr>
<th></th>
<th>1 ML H* on step U° (V_{RHE})</th>
<th>1 ML H* on step with Na* U° (V_{RHE})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(553)</td>
<td>0.340</td>
<td>0.312</td>
</tr>
<tr>
<td>Pt(533)</td>
<td>0.458</td>
<td>0.425</td>
</tr>
</tbody>
</table>

Figure S5-4. Platinum-oxygen bond lengths for adsorbed hydroxide and adsorbed water on the step of Pt(553) in the absence and the presence of sodium adsorbed near the step as a function of sodium and hydroxide coverage.

Table S5-4. Hydrogen bond length between hydroxide and water (2 co-adsorbed water molecules per adsorbed hydroxide) adsorbed at the step of Pt(553) in the absence and presence of sodium co-adsorbed near the step as a function of the coverage of adsorbed hydroxide and adsorbed water.

<table>
<thead>
<tr>
<th>Pt(553) step</th>
<th>OH*-H_2O* bond length (Å)</th>
<th>OH*-H_2O* + Na* bond length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4 ML</td>
<td>1.572</td>
<td>1.533</td>
</tr>
<tr>
<td>1/3 ML</td>
<td>1.587</td>
<td>1.514</td>
</tr>
</tbody>
</table>
Table S5-5. Calculated surface normal dipole moments for OH*, OH+2H₂O*, and OH*+4H₂O* adsorbed at the step of Pt(553) and Pt(533). Coverage is defined as number of adsorbed hydroxide molecules per surface step Pt atom (In cases where Na* is co-adsorbed, sodium coverage matches the hydroxide coverage). Unit cell has one step row which is 3 Pt atoms wide (1/3 ML coverages) or 4 Pt atoms wide (1/4 ML coverages) (with appropriate terrace width). A surface normal dipole moment change on adsorption of -0.4 eÅ and assuming a double layer thickness of 3 Å gives an electrosorption valency of 1.13 electrons for hydroxide. A smaller change in magnitude gives an electrosorption valency closer to the 1 electron transfer expected for hydroxide adsorption (which is the case with hydroxide adsorption in the absence of co-adsorbed water).

<table>
<thead>
<tr>
<th>Pt(553) step</th>
<th>Bare (eÅ)</th>
<th>Na* (eÅ)</th>
<th>OH* (eÅ)</th>
<th>OH* + 2 H₂O* (eÅ)</th>
<th>OH* + 2 H₂O* + Na* (eÅ)</th>
<th>OH* + 4H₂O* (eÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4 ML</td>
<td>0.005</td>
<td>-0.508</td>
<td>-</td>
<td>-0.445</td>
<td>-0.764</td>
<td>-0.449</td>
</tr>
<tr>
<td>1/3 ML</td>
<td>0.005</td>
<td>-0.499</td>
<td>0.032</td>
<td>-0.421</td>
<td>-0.793</td>
<td>-0.097</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Pt(533) step</th>
<th>Bare (eÅ)</th>
<th>Na* (eÅ)</th>
<th>OH* (eÅ)</th>
<th>OH* + 2 H₂O* (eÅ)</th>
<th>OH* + 2 H₂O* + Na* (eÅ)</th>
<th>OH* + 4H₂O* (eÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/4 ML</td>
<td>0.033</td>
<td>-0.508</td>
<td>-</td>
<td>-0.559</td>
<td>-0.584</td>
<td>-0.697</td>
</tr>
<tr>
<td>1/3 ML</td>
<td>0.026</td>
<td>-0.503</td>
<td>-0.034</td>
<td>-0.502</td>
<td>-1.005</td>
<td>-0.165</td>
</tr>
</tbody>
</table>
Figure S5-5. a) 1ML H* on the step of Pt(553). b) Pt(553) with 1ML H* on the step and 1ML H* on the step of Pt(553). c) 1/3 ML OH* at the step of Pt(553). d) 1/3 ML OH* + 2/3 ML H₂O* adsorbed on the step of Pt(553).
Figure S5-6. a) 1/3 ML OH\(^*\) + 4 H\(_2\)O\(^*\) adsorbed on/near the step of Pt(553). b) 1/3 ML OH\(^*\) + 2H\(_2\)O\(^*\)+ 1/3 ML Na\(^*\) adsorbed on/near the step of Pt(553). c) 1/3 ML OH\(^*\) + 4H\(_2\)O\(^*\)+Na\(^*\) adsorbed on/near the step of Pt(553). d) 1 ML H\(^*\) + 3H\(_2\)O on the step of Pt(553).
Figure S5-7. 1 ML H* + 3H₂O + Na* adsorbed on/near the step of Pt(553).
Figure S5-8. a) 1ML H* on the step of Pt(533). b) Pt(533) with 1ML H* on the step and 1ML H* on the step of Pt(533). c) 1/3 ML OH* at the step of Pt(533). d) 1/3 ML OH* + 2/3 ML H₂O* adsorbed on the step of Pt(533).
Figure S5-9. a) 1/3 ML OH* + 4 H₂O* adsorbed on/near the step of Pt(533). b) 1/3 ML OH* + 2H₂O*+ 1/3 ML Na* adsorbed on/near the step of Pt(533). c) 1/3 ML OH* + 4H₂O*+Na* adsorbed on/near the step of Pt(533). d) 1 ML H* + 3H₂O on the step of Pt(533).
Figure S5-10. 1 ML H* + 3H_2O + Na* adsorbed on/near the step of Pt(533).
Chapter 6

Deconvoluting Cyclic Voltammograms To Accurately Calculate Pt Electrochemically Active Surface Area

This chapter is published as: McCrum, I.T.; Janik, M.J.; Deconvoluting Cyclic Voltammograms to Accurately Calculate Pt Electrochemically Active Surface Area. *JPCC*, 2017, 121, 6237-6245.

6.1. Abstract

An accurate measure of the electrochemically active surface area (ECSA) of an electrode is necessary to quantify electrocatalytic activity. Herein, we develop a method to de-convolute experimental cyclic voltammograms measured on platinum electrodes which predominately contain 111 terraces with 110 and 100 steps. We define simple functions which can be fit to experimental data to represent various contributions to the total voltammogram, including hydrogen adsorption on 111 terraces and competitive hydrogen and hydroxide adsorption on 110 and on 100 steps. We use our prior density functional theory (DFT) insight to accurately calculate the ECSA and the proportion of 111, 100, and 110 sites. We validate this method for experimental cyclic voltammograms measured on single crystal stepped platinum surfaces (with 111-terraces), where the surface area is known, then extend to polycrystalline and nanoparticle platinum electrodes.
6.2. Introduction

The electrochemically active surface area of an electrode is an important property, particularly for catalysis where the rate of an electrocatalytic reaction is directly proportional to the active surface area. Platinum is a highly active catalyst for many electrochemical reactions, including hydrogen oxidation and evolution\(^1\), oxygen reduction\(^2\), and methanol oxidation\(^3-4\). The high activity and cost of Pt has motivated significant work on the synthesis and study of high surface area platinum nanoparticles\(^1, 5-7\), nano-structures\(^8-12\), and platinum alloy electrodes\(^13-17\), where the surface activity of the platinum structure is maximized relative to its mass. Accurately measuring the platinum electrode surface area is of high importance in identifying structures and alloys which exhibit high catalytic activity. Furthermore, many electrocatalytic reactions show significant structure dependence, such as oxygen reduction\(^18-20\) and ammonia oxidation\(^21-24\), where designing a nano-structure or surface which preferentially exposes a particular facet is desired. Accurate quantification of both the total electrochemically active surface area and the relative proportions of given facets/step sites is necessary to properly attribute catalytic performance on an active site basis.

Many of the electrochemical techniques developed for estimating the electrochemically active surface area (ECSA) involve the adsorption or stripping (oxidative removal) of an adsorbate to or from the electrode surface. The most commonly used method for a platinum electrode is measuring the H-UPD (hydrogen under-potential deposition) area\(^25-28\), where the total integrated area of the low potential (\(\sim 0-0.4\) V on a reversible hydrogen electrode (RHE) scale) region of a cyclic voltammogram (CV) is used to give the total charge due to hydrogen adsorption. CO stripping\(^29-30\) and Cu stripping\(^30-31\) are also commonly used. For platinum, these methods have been compared with other, non-electrochemical methods for estimating surface area, such as BET measurements\(^32\) or TEM analysis\(^33-34\). All of these methods require knowledge
of the adsorbate coverage prior to desorption or stripping. If the desorption/stripping features on
different surface sites overlap, as is often the case\textsuperscript{35-37}, then an approximation to the total coverage
and total site density must be made. For H-UPD, it is typically assumed that 210 µC cm\textsuperscript{-2} of
hydrogen adsorbs on a polycrystalline Pt electrode surface. This value should be equal to the
product of the fractional coverage of H (before oxidative desorption), the density of H adsorption
sites per area, and the number of electrons transferred per H desorption event. However, as each
of these values varies with Pt facet, this charge density is somewhat arbitrary\textsuperscript{38}. Recent evidence
has also shown that the “H-UPD” region contains contributions from competitive hydroxide
adsorption on some Pt sites\textsuperscript{39-42}. The H-UPD method may also improperly count some current that
is due to catalytic hydrogen evolution and oxidation, depending on the choice of the lower
potential limit of the cyclic voltammogram. Polycrystalline and nanoparticle platinum electrode
surfaces are comprised of a mixture of facets and types of surface sites, which change as a
function of electrode history (restructuring or dissolution) and among synthesis techniques. The
use of a single charge density to define surface area limits the ability to properly compare
platinum electrodes.

In our previous work, we have used DFT to corroborate that the low potential peaks
measured by cyclic voltammetry (CV) on platinum electrodes include the co-adsorption or
competitive adsorption of hydrogen and hydroxide onto 110 and 100 facets\textsuperscript{39}. This competitive
adsorption drives the Pt(110) and Pt(100) associated CV peaks to lower potentials than what is
predicted by DFT for hydrogen adsorption alone. These low potential peaks shift by less than the
Nernstian shift with pH due to the specific adsorption of alkali metal cations\textsuperscript{43-44}. Alkali cation co-
adsorption weakens the adsorption of hydroxide on the electrode surface\textsuperscript{39}. We recently extended
this DFT analysis to the steps and terraces of Pt(553) and Pt(533) and concluded that competitive
adsorption of hydrogen and hydroxide occurs on their (110) and (100) steps\textsuperscript{40}, in agreement with
previous conclusions from Schouten et al.\textsuperscript{41} and van der Niet et al.\textsuperscript{42}. We find a similar effect of
the cation, and match the experimentally measured shifts in the location of the sharp CV peaks with pH\textsuperscript{40, 42}. Experimentally measured CVs on Pt(553) and Pt(533) were well represented by a linear combination of DFT simulated voltammograms for hydrogen adsorption on the terrace, hydrogen and hydroxide competitive adsorption on the steps, and a constant double layer charging current\textsuperscript{40}.

Using the calculated coverages of adsorbed hydrogen and hydroxide on the terraces and steps of Pt(553) and Pt(533) from DFT, herein we describe a method to accurately estimate electrode surface area for any platinum electrode surface that is comprised of primarily 111 terraces, with 110 and 100 steps. The low potential features (0.0-0.4 \text{V}_{\text{RHE}}) of aqueous phase CVs are deconvoluted to give the relative contributions of 111, 100, and 110 features. We first validate this approach by calculating the surface area and relative site density of single crystal higher order platinum electrodes, where the surface area and relative site densities of these three features are known. Following this validation, we apply this analysis to polycrystalline platinum and platinum nanoparticle electrodes, using CVs measured in both acidic and basic electrolytes\textsuperscript{45-46}. In examining experimentally measured cyclic voltammograms\textsuperscript{37, 42, 47-53}, we confirm that the location of the sharp adsorption peaks measured at low potentials on Pt 110 and 100 steps are relatively independent of terrace width for the single crystal higher order facets, for terrace widths above 2-3 atoms. We then compare the surface areas calculated with our approach to those measured using the standard H-UPD and CO stripping analysis as well as the relative site fractions to those estimated using Bi and Ge adsorption.
6.3. Methods

6.3.1. Deconvoluting Experimental Cyclic Voltammograms and Calculating Relative Surface Area

Significant experimental evidence\(^{42, 47, 50}\) suggests that stepped platinum surfaces comprised of 111 terraces with a terrace width greater than ~3 Pt atoms exhibit similar low potential features in cyclic voltammograms, suggesting that the terrace width has little effect on the adsorption strength of hydrogen on the terrace or on the competitive hydrogen and hydroxide adsorption at the step. Our previously published DFT results demonstrate that 553 (111 terrace and 110-like step) and 533 (111 terrace and 100-like step) low potential CV’s can be modeled as the sum of separate terrace and step features (as shown previously by Koper et al.\(^{54}\)). In a non-adsorbing electrolyte, we can deconvolute low potential CV’s into 111, 100, and 110 contributions. We describe a method to perform this deconvolution from experimental data, evaluate its efficacy with stepped single crystal platinum electrode data (Pt[n(111)x(110) and Pt[n(111)x(100)], where n indicates the terrace width), where the surface area is known, and extend it to polycrystalline platinum and Pt/C electrode cyclic voltammograms.

The low potential region (below ~ 0.5 \(V_{RHE}\)) of the CV measured on stepped Pt surfaces comprised of 111 terraces (with 110 and 100 steps) consists of 4 contributions: the double layer charging current, a broad feature, and two sharp features. The sharp peaks in current correspond to the competitive adsorption of hydrogen and hydroxide on Pt 100 and 110 steps. We fit these sharp peaks using two Gaussian functions, a lower potential 110 peak and a second 100 peak at higher potentials. The broad peak corresponding to hydrogen adsorption on 111-like terraces is fit with a hyperbolic cosine function, which has a more accurate fit than a broad Gaussian.

Step 1 in deconvoluting the low potential region of an experimentally measured cyclic voltammogram is to subtract the double layer charging current from the CV, which is assumed to
be constant over the entire low potential region. The double layer charging current is taken from the experimentally measured cyclic voltammogram at a potential where there are minimal faradaic reactions (between 0.45 \( V_{\text{RHE}} \) and 0.55 \( V_{\text{RHE}} \)).

Step 2 is to fit a broad inverse hyperbolic cosine function to the low potential region of the CV, to represent hydrogen desorption/adsorption on 111-like terraces. Two different inverse hyperbolic cosine functions were examined to represent hydrogen adsorption on the terraces, as shown in equations 1 and 2. Equation 1 is fit with two variable parameters and two arbitrary constants, to match the shape of the broad low potential hydrogen adsorption peak in the DFT simulated cyclic voltammogram on single crystal Pt(111). Equation 2 is fit with three parameters.

\[
j(U) = \frac{ad}{\cosh(Ub + c) + d} \tag{1}
\]
\[
j(U) = \frac{a}{\cosh\left(\frac{(U - b)^2}{c^2}\right)} \tag{2}
\]

In equations 1 and 2, \( j \) is the current density and \( U \) is the electrode potential. The \( a \) parameter is fit to the experimental data to set the magnitude of the peak, and the \( c \) parameter is fit to set the location (potential). \( b \) and \( d \) are constants, 28.959 \( V_{\text{RHE}}^{-1} \) and 112.61 \( \mu A \ cm^{-2} \), respectively, derived from a fit to the broad low potential CV peak simulated by DFT on single crystal Pt(111). In equation 2, \( a \) is fit to experimental data to set the magnitude, \( b \) the location (potential), and \( c \) the width and shape of the peak. Equation 1 was used in all analysis herein, as it fit the experimentally measured and DFT simulated voltammogram on Pt(111) better than equation 2. Equation 2 is provided as it fits the data nearly as well as equation 1 and has a more obvious correlation between the fit constants and the cyclic voltammetry features. The location of the peak is most easily determined by matching the experimentally measured onset of hydrogen adsorption (on the reverse or decreasing potential scan) on the 111-like terraces with the onset of
the broad hyperbolic cosine peak (typically near 0.2-0.4 V$_{\text{RHE}}$). Following Step 2, both the double layer charging current and the broad 111 fit are subtracted from the experimental data to leave the two sharp peaks.

Step 3 is to fit a Gaussian function to each of the sharp peaks measured at low potentials, corresponding to hydrogen and hydroxide competitive adsorption at 110 and 100 steps. Each Gaussian function, given by equation 3, is fit to the experimental data with three variable parameters.

$$j(U) = ae^{-(U-b)^2/2c^2} \quad [3]$$

The $a$ parameter is set to match the height of the sharp peak. The $b$ parameter sets the position of the center of the peak and is fit to the potential of the maximum current density measured, and $c$ is fit using the full width at tenth of maximum (FWTM) of the sharp peak ($FWTM = 2\sqrt{2\ln(10)}c$).

The sum of the four fit functions (the charging current, broad hyperbolic cosine function, and two sharp Gaussian functions) reproduce the measured cyclic voltammogram, except for any current due to hydrogen evolution or oxidation at low potentials (which is a catalytic reaction and therefore transfers multiple electrons per surface site). In some cases it may be difficult to determine the onset of hydrogen adsorption on the 111-like terraces, particularly when the onset of this peak overlaps with the competitive adsorption of hydrogen and hydroxide on 100 step sites, or when the double layer charging current is significant compared to the magnitude of the hydrogen and hydroxide adsorption peaks. In these cases, the fitting/deconvolution procedure will yield a better fit if performed iteratively. Further, adsorption on 111-like terraces and adsorption on 110 sites in acid may be convoluted with hydrogen gas evolution and oxidation; rotating the electrode has been shown to reduce this contribution$^{45}$.

With the fit functions determined and the scan rate known, the $j(U)$ functions are
analytically or numerically integrated to give the total charge associated with each CV feature. This total charge is used to calculate the surface area or site density of the 111 like terraces and 110 and 100 features. Our DFT results indicate that roughly 1 ML of H* will adsorb to the 111-like terraces over the complete broad feature, which extends to potentials where hydrogen evolution occurs, such that 1 electron is transferred per Pt atom of a 111 feature\(^\text{40}\). For the 110 and 100 features, our DFT results conclude that 1 ML of H* and 1/3 ML OH* specifically adsorb within the sharp low potential peaks, such that 1.33 electrons are transferred per Pt atom on these features\(^\text{40}\). Dividing the calculated total charge per unit of geometric area for each feature by the number of electrons transferred per site for each feature yields the total number of each type of site per unit geometric electrode area.

Implicit in this method are the assumptions that 1) all processes in the analyzed potential region are reversible, 2) the contributions from different sites are separable and, 3) these particular functions (given in equations 1, 2, and 3) accurately describe the shape of the various experimentally measured features. Experimentally measured cyclic voltammograms and impedance spectroscopy measurements suggest these low potential features are reversible given their symmetry in positive and negative scans and small charge transfer resistances, though less so in alkaline than in acid media\(^\text{41-42}\). While the choice of fitting function is somewhat arbitrary, we find these functions match our DFT simulated cyclic voltammograms\(^\text{39-40}\), where adsorption on a given site can be examined independently of any other type of site.

Polycrystalline or nanoparticle platinum surfaces may contain other types of sites beyond the 111 terraces and the 110 and 100 steps considered here, including 100 terraces, 110 terraces, and 111 steps. These surface sites are represented in many families of single crystal stepped surfaces, including Pt\([n(100)x(111)]\) and Pt\([n(100)x(110)]\) containing 100 terraces with 111 or 110 steps, and Pt\([n(110)x(100)]\) and Pt\([n(110x(111)]\) containing 110 terraces with 100 or 111 steps. Polycrystalline or nanoparticle platinum surfaces may also contain defect sites, many of
which can be represented by a combination of steps and short terrace sites. If the contributions to a cyclic voltammogram from each of these sites did not completely overlap and if the adsorption thermodynamics (of hydrogen and hydroxide onto these sites) were known, then a measured cyclic voltammogram on any Pt surface could be readily deconvoluted. However, contributions from these stepped surfaces do significantly overlap\textsuperscript{55-59}, the thermodynamics of hydrogen and hydroxide adsorption onto all of these sites are not well understood, and it is not known whether contributions from step sites and from terrace sites on these other stepped surfaces are separable (linearly additive). This may make it impossible to fully deconvolute all contributions from all types of sites on any polycrystalline or nanoparticle platinum surface, using hydrogen/hydroxide adsorption (in the low potential region of the CV) alone. We therefore limit the validation of this method to CV’s measured on Pt surfaces comprised of primarily 111 terraces (where adsorption on 111 terraces and 110 or 100 steps is well understood). Future work to understand adsorption on all stepped Pt surfaces may allow this method to be expanded and improved. For polycrystalline or nanoparticle platinum surfaces, when it is not known if the surface is comprised primarily of 111 terraces, this method may provide estimates of the exposure of various facets to be used in conjunction with surface site imaging (TEM) or counting (Bi, Ge adsorption) techniques.
6.4. Results and Discussion

6.4.1. Single Crystal Electrodes

We first deconvolute experimentally measured\textsuperscript{37, 42, 47-53} cyclic voltammograms on single crystal stepped platinum electrodes, where the surface area and relative site density (of step sites versus terrace sites) are known. Figure 6-1 illustrates an example cyclic voltammogram for a Pt(776) electrode measured in 0.1 M HClO\textsubscript{4} at 50 mV/s\textsuperscript{47}. The deconvoluted CV in Figure 6-1 represents the sum of 3 functions. The first is the constant double layer charging current, taken as the experimentally measured current at 0.5 V\textsubscript{RHE} (2.5 μA cm\textsuperscript{-2}). The second contribution is the broad hyperbolic cosine function fit to the onset of hydrogen adsorption on the terrace of Pt(776), near 0.35 V\textsubscript{RHE} (a=31.5 μA cm\textsuperscript{-2}, c=-3.2, see equation 1). Finally, a Gaussian function is fit to the sharp peak near 0.13 V\textsubscript{RHE} corresponding to hydrogen and hydroxide competitive adsorption at the 110 step sites on Pt(776) (a=75 μA cm\textsuperscript{-2}, b=0.13 V\textsubscript{RHE}, c=0.0055 V\textsubscript{RHE}, see equation 3). The assumption that the CV can be readily de-convoluted to contributions from the step and from the terrace holds true (as found previously by others\textsuperscript{54}). The deconvolution advantageously removes the low potential portion of the peak below 0.1 V\textsubscript{RHE}, due to the hydrogen evolution (oxidation) reaction on the negative (positive) scan.
Figure 6-1. The background shows an experimentally measured cyclic voltammogram on a single crystal Pt(776) electrode in 0.1 M HClO$_4$ at 50 mV/s (black line) adapted from Farias et al.\textsuperscript{47}. The foreground (blue curve) shows the sum of the deconvolution functions fit to the experimental data at low potentials (below 0.5 V$_{\text{RHE}}$), assuming that adsorption on the step and on the terrace can be separated. Competitive adsorption of H* and OH* at the step is fit with a Gaussian function (equation 3) and adsorption of H* on the terrace is fit with an inverse hyperbolic cosine function (equation 1).

We have applied this method to deconvolute experimental CV data\textsuperscript{37, 42, 47-53} measured on many single crystal stepped electrode surfaces, in both acid and alkaline electrolytes. Integrating the area under each fit function allows for the total charge transferred in the competitive adsorption of H* and OH* on the 110 and 100 steps and in the adsorption of hydrogen on the 111 terrace to be calculated. Figure 6-2a gives the total charge at the step plotted versus the theoretical charge density, assuming one electron is transferred per step site, for surfaces with 110 steps in both acidic (HClO$_4$) and basic electrolytes. Figure 6-2b shows the same for stepped surfaces with 100 steps. Figure 6-2c shows the total charge at the terrace of stepped surfaces with 110 steps or 100 steps plotted versus the theoretical charge density, assuming one electron is transferred per terrace site. The parameters used to fit these data, the total charges calculated, and a table of the literature from which each of the experimentally measured cyclic voltammograms were taken (along with the Miller index and microfacet notation for each stepped surface) are
given in the supplementary information. Figure 6-2d gives the location of the sharp step associated peak as a function of the terrace width (ratio of terrace sites to step sites).

Figure 6-2 a) Charge density on the step as given by the Gaussian functions fit to experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps\textsuperscript{37, 42, 47-50} versus the theoretical charge density assuming 1 electron is transferred per platinum step site. Data collected in acid electrolytes (orange squares) and basic electrolytes (blue diamonds). Linear regressions are given, assuming the data pass through the origin. b) Charge density on the step as given by the Gaussian functions fit to experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps\textsuperscript{42, 48, 50-53} versus the theoretical charge density assuming 1 electron is transferred per platinum site. Data collected in acid electrolytes (orange squares) and basic electrolytes (blue diamonds). Linear regressions are given, assuming the data pass through the origin. c) Experimental charge density on the 111 terrace as given by the hyperbolic cosine fit (equation 1) to cyclic voltammograms on single crystal electrodes, plotted versus the theoretical charge density assuming 1 electron is transferred per platinum terrace site. The terrace charge density on single crystal surfaces with 110 steps\textsuperscript{37, 42, 47-50} (orange square), with 100 steps\textsuperscript{42, 48, 50-53} (blue diamond), and on the low index Pt(111) surface (green square) are shown. A linear regression is given, assuming the data pass through the origin. d) The experimentally measured potential of the sharp peak in current corresponding to hydrogen and hydroxide competitive adsorption at the step of single crystal surfaces with 110 steps\textsuperscript{37, 42, 47-50} (blue diamond and orange square) and with 100 steps\textsuperscript{42, 48, 50-53} (grey triangle, yellow circle) in both acidic and basic electrolytes.
In Figures 6-2a and b, the total charge transferred at the 110 step and 100 step is greater than that given by assuming 1 electron transferred per Pt step atom. The slope of the linear regression shown in these figures is proportional to the electrosorption valency of the adsorbed species times the coverage of the adsorbed species. If we assume an electrosorption valency of 1 for both H* and OH*, then the total coverage of H* and OH* adsorbed at the step can be estimated from the slopes of the linear regressions shown in Figures 6-2a and b. In alkaline electrolytes, this gives a total coverage of ~ 1.3 ML for 110 steps and ~1.2 ML for 100 steps, with slightly lower coverage estimated for both step sites in acid. This matches well with what we would conclude from DFT with 1 ML of H* and 1/3 ML OH* competitively adsorbing at both 110 and 100 steps.\(^4\) In fitting the CVs to describe adsorption at the steps, there is a hysteresis (the adsorption/desorption process is less reversible) in these sharp peaks when the CV is measured in an alkaline electrolyte (apparent in Figure 6-3 for a polycrystalline Pt electrode); the deconvolution functions were fit to the positive going portion of the CV scan. As suggested by others, the hysteresis could be due to the slower rate of adsorption of H*, OH*, or both species in an alkaline electrolyte.\(^4\)\(^1\)\(^6\) The de-convoluted data further show that the location of the sharp 110 and 100 step-site peaks are independent of terrace width (above a ~3 atom wide terrace) and shift to more positive potentials with increasing pH (noted previously by others), as given by Figure 6-2d.

A similar analysis for the total charge transferred on the 111-like terrace sites in acid for surfaces with 110 and 100 steps is given in Figure 6-2c. While there is good agreement with DFT, where we expect ~ 1 ML of hydrogen to adsorb at the terrace, it is much more difficult to accurately fit a function to this broad low potential peak. A small change in the magnitude of the peak corresponds to a large change in the total charge (area under the peak), due to its breadth. It is also difficult to determine the onset potential of this peak when its high potential region
overlaps with adsorption at the step. This is particularly difficult with surfaces containing 100 steps, unless the sharp 100 adsorption peak is well defined.

Collectively, the reliable correlations between the deconvoluted experimental features (y-axes) and theoretical site densities (x-axes) in Figures 6-2a, 6-2b, and 6-2c validates our approach to attributing the individual CV features of complex multi-faceted surfaces. As this approach can determine the density of 111, 110, and 100 Pt atoms on well-defined step surfaces, we next apply the method to determine the density of each of these surface facets on polycrystalline and nanoparticle Pt electrodes.

6.4.2. Polycrystalline and Nanoparticle Platinum Electrodes

For polycrystalline and nanoparticle platinum surfaces, the surface area and relative proportion of 111, 100, and 110 sites is unknown. Many cyclic voltammograms measured on polycrystalline or nanoparticle Pt show the same features at low potentials seen on the stepped surfaces investigated in the previous section, namely a broad peak and two sharp peaks (plus the double layer charging contribution). A representative deconvolution is shown in Figure 6-3 for a cyclic voltammogram measured on polycrystalline Pt in 0.1 M NaOH\textsuperscript{45}. The sum of the deconvoluted functions match the experimental CV, especially when the electrode is rotated at 400 rpm, which reduces the contribution from hydrogen oxidation at low potentials in the positive going scan (as rotation reduces the near surface concentration of hydrogen generated by hydrogen evolution during the negative going scan). A polycrystalline surface may expose additional types of sites not considered here, such as 110-terraces, 100-terraces, and 111 steps, which give cyclic voltammetry features that overlap with those of surfaces containing 111-terraces, 110-steps, and 100-steps\textsuperscript{55-59}. The method should yield an accurate estimate of the total ECSA and relative site density if the polycrystalline surface is comprised primarily of 111-terraces.
Figure 6-3. Experimentally measured cyclic voltammogram with a stationary rotating disk Pt(pc) electrode (black line, background) and rotating electrode (400 rpm) (grey dotted line, background) in 0.1 M NaOH adapted from Rheinländer et al.\textsuperscript{45} and the sum of the deconvoluted cyclic voltammogram (red line, foreground).

Figure 6-4 gives the difference in total ECSA between our deconvoluted fit and the traditional H-UPD method for a polycrystalline Pt electrode in HClO\textsubscript{4} and NaOH\textsuperscript{45} as well as on polycrystalline Pt and Pt/C in KOH\textsuperscript{46}. Also shown in Figure 6-4 is the calculated surface area using the CO stripping method\textsuperscript{45}. These data are also given in Table S6-12 in the supplementary information, with additional fit data and discussion. From Figure 6-4, it is apparent that the traditional H-UPD method over-counts surface area by anywhere from 10-30%. This deviation results primarily from two contributions. The first is the traditional methods counting of charge due to hydrogen evolution or oxidation, which is a catalytic process (resulting in multiple turnovers/electron transfers per site). The second is the over-counting of step sites, where our DFT results show competitive hydrogen/hydroxide adsorption results in the transfer of greater than 1 electron per step site (1.33 electrons for 1 ML H\textsuperscript{*} and 1/3 ML OH\textsuperscript{*})\textsuperscript{40}. This suggests that the error in estimating surface area with the traditional H-UPD method for highly stepped or roughened surfaces may be even larger. The CO stripping method yields surface areas much
closer to those calculated by our deconvolution method, as the stripping occurs at high potentials (free from hydrogen oxidation and hydrogen evolution) and is less sensitive to the surface structure (step sites and terrace sites transfer a similar number of electrons).

Figure 6-4. Percent difference in calculated electrochemically active surface area (ECSA) between the traditional H-UPD method (solid orange) or the CO stripping method (dotted gray) and the deconvolution method. Negative difference indicates the compared method overestimates surface area relative to the deconvolution method.

Our method of deconvoluting the low potential region of cyclic voltammograms measured on Pt not only yields an estimate of the electrode surface area, but also allows for an estimation of the relative proportion of 110 step, 100 step, and 111 terrace-like features, without the need to run additional experiments (such as using Bi or Ge adsorption). As an example, we deconvolute the CV’s measured in an alkaline electrolyte on a variety of shape controlled Pt nanoparticles investigated by Devivaraprasad et al. and Vidal-Iglesias et al. They use bismuth adsorption, germanium adsorption, and TEM images to count the relative fraction of 111 and 100 terraces and characterize the nanoparticles. Devivaraprasad et al. find that Pt nanoparticles that expose more 100 sites (and fewer 111 sites) are less active for the oxygen
reduction reaction\textsuperscript{66}. While we differ in the fraction of 111 sites calculated using our deconvolution method, we agree with their trend of which Pt nanoparticles expose a higher proportion of 100 sites (results are given in Table S6-13 in the supplementary information). Though the deconvolution method counts 100 step sites (not 100 terrace sites, as counted by Ge adsorption), there is a sharp component of the cyclic voltammograms measured on stepped surfaces with 100 terraces which overlaps with that of the 100 step contribution\textsuperscript{56-57}. This may support why the trend in 100 terrace sites is captured with the deconvolution method, even though the total fraction of 100 terrace sites is under-counted at high 100 terrace fractions. We also match the trend in both the fraction of 100 sites and 111 sites measured by Vidal-Iglesias et al.\textsuperscript{67}, shown in Figure 6-5 (and Table S6-14), though we calculate the absolute fraction of 111 sites to be much greater than that measured by Bi adsorption\textsuperscript{67}.

![Figure 6-5](image-url)

**Figure 6-5.** Fraction of 111-terrace and 100-step/terrace sites on shape controlled Pt-nanoparticles calculated using the deconvolution method and measured using the Bi, Ge adsorption methods (experimental data from Vidal-Iglesias et al.\textsuperscript{67}).
The significant deviation between the surface site fractions calculated by the Bi and Ge adsorption methods and those calculated by the deconvolution method highlight the difficulties in extending this method to deconvolute a cyclic voltammogram measured on a polycrystalline or nanoparticle platinum surface. In cases where the surface is not comprised primarily of 111 terraces, this method may count other sites that have not been included in defining the method (primarily 100 terraces, 110 terraces, and 111 steps) as 111 terraces and, to a smaller extent 110 or 100 steps. This may not have a significant effect on counting the total electrochemically active surface area, as this method compares well with that calculated by CO stripping, at least for the cyclic voltammograms examined (Figure 6-4). However, this deviation in the calculated relative surface site fractions does suggest that the relative site fractions (111 terrace, 100 step, 110 step) calculated by the deconvolution method may only be accurate in cases where it is known that the surface is comprised primarily of 111-terraces (as seen with the single crystal electrodes in the previous section). Therefore, this method should not be blindly applied to any/all polycrystalline or nanoparticle platinum electrodes. It can be used in conjunction with other surface imaging (TEM, HRTEM) or site counting (Bi, Ge adsorption) techniques.

Comparing the rate of an electrocatalytic reaction across various electrocatalysts not only requires an accurate measure of the electrode surface area, but the rate may also depend on the surface structure. In estimating the relative proportions (or total number) of 111 terrace, 110 step, and 100 step, this deconvolution method may yield insight into why the reaction rate of a structure sensitive reaction may vary across platinum electrodes synthesized with different techniques and with varying degrees of atomic scale roughness.
6.5. Conclusions

We have defined a method for estimating platinum electrochemically active surface area. This method involves fitting Gaussian functions to the sharp low potential peaks in current measured by cyclic voltammetry at low potentials, corresponding to hydrogen and hydroxide competitive adsorption on 110 and 100 steps, and a broad inverse hyperbolic cosine function to hydrogen adsorption on the 111 terrace. We find this method fits cyclic voltammograms measured on higher order stepped platinum surfaces well, where we show that the total charge transferred in the sharp low potential peaks corresponds well with our DFT simulations.

In extending this method to examine polycrystalline platinum and platinum nanoparticle electrodes, we find that the traditional “H-UPD” method for estimating electrochemically active surface area may overestimate the total area or total number of platinum sites by up to 30% (relative to the deconvolution method and CO stripping). The method we have defined not only counts electrochemically active area, but de-convolutes the CV so that the total number of 111 terrace, 110 step, and 100 step sites can be explicitly determined. This method can be reliably applied to cyclic voltammograms measured in a non-adsorbing electrolyte on any platinum electrode comprised predominately of 111 terraces.

When applied to cyclic voltammograms measured on polycrystalline or nanoparticle platinum electrodes, significant deviations are seen in the fraction of 111-terrace sites counted by the deconvolution method and measured by Bi adsorption. The overestimation of 111-terrace sites suggests contributions from hydrogen or hydroxide adsorption on other types of surface sites may be inappropriately attributed to 111-terrace sites. Further study with both single crystal experiments and computational techniques is needed to fully understand the thermodynamics of hydrogen and hydroxide adsorption on these other sites (100-terraces, 110-terraces, and 111 steps; particularly for short terraces where adsorption on the step vs. terrace may not be
This method is of importance for electrocatalytic measurements on platinum, where an accurate determination of active surface area/sites is necessary for accurately measuring turnover frequencies of active sites.

### 6.6. Acknowledgement

We acknowledge support from The Pennsylvania State University Diefenderfer Graduate Fellowship and the National Science Foundation NRT #1449785. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number ACI-1053575.

### 6.7. References


35. García-Araez, N.; Climent, V.; Feliu, J. M. Analysis of Temperature Effects on Hydrogen and OH Adsorption on Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) by Means of Gibbs Thermodynamics. *J. Electroanal. Chem.* **2010**, *649*, 69-82.


6.8. Supplementary Information

Table S6-1. References for all of the experimentally measured cyclic voltammograms used in this study and their respective miller index and microfacet notations.

<table>
<thead>
<tr>
<th>Acids</th>
<th>Base</th>
<th>Miller Index</th>
<th>Microfacet</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(311)</td>
<td>52</td>
<td>50</td>
<td>(2n-1,1,1)</td>
<td>n(100)x(111)</td>
</tr>
<tr>
<td>Pt(553)</td>
<td>42</td>
<td>42</td>
<td>(n+1,n+1,n-1)</td>
<td>n(111)x(110)</td>
</tr>
<tr>
<td>Pt(533)</td>
<td>42</td>
<td>42</td>
<td>(n+1,n-1,n-1)</td>
<td>n(111)x(100)</td>
</tr>
<tr>
<td>Pt(554)</td>
<td>47</td>
<td>48</td>
<td>(n-1)(111)x(110)</td>
<td>10</td>
</tr>
<tr>
<td>Pt(544)</td>
<td>51</td>
<td>48</td>
<td>n(111)x(100)</td>
<td>9</td>
</tr>
<tr>
<td>Pt(755)</td>
<td>53</td>
<td>50</td>
<td>(n+1,n-1,n-1)</td>
<td>n(111)x(100)</td>
</tr>
<tr>
<td>Pt(775)</td>
<td>49</td>
<td>50</td>
<td>(n+1,n-1,n-1)</td>
<td>n(111)x(110)</td>
</tr>
<tr>
<td>Pt(776)</td>
<td>47</td>
<td>-</td>
<td>n(111)x(110)</td>
<td>13</td>
</tr>
<tr>
<td>Pt(13,13,12)</td>
<td>47</td>
<td>-</td>
<td>n(111)x(110)</td>
<td>25</td>
</tr>
<tr>
<td>Pt(pc)</td>
<td>45</td>
<td>45, 46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/C</td>
<td>-</td>
<td>46</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table S6-2. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms (CV’s) on single crystal electrodes with 110 steps measured in an acid electrolyte. The Pt(776) experimentally measured CV and the sum of the deconvoluted CV are shown in Figure 6-1 in the main paper.

<table>
<thead>
<tr>
<th>110 Steps Acid</th>
<th>DL charging current (µA/cm²)</th>
<th>111 cosine a (µA/cm²)</th>
<th>111 cosine c (unit-less)</th>
<th>110 a (µA/cm²)</th>
<th>110 b (V_RHE)</th>
<th>110 c (V_RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(776)</td>
<td>2.5</td>
<td>31.5</td>
<td>-3.2</td>
<td>75</td>
<td>0.13</td>
<td>0.0055</td>
</tr>
<tr>
<td>Pt(553)</td>
<td>2</td>
<td>29</td>
<td>-1.75</td>
<td>145</td>
<td>0.1275</td>
<td>0.009</td>
</tr>
<tr>
<td>Pt(554)</td>
<td>3</td>
<td>31</td>
<td>-2.5</td>
<td>95</td>
<td>0.125</td>
<td>0.0075</td>
</tr>
<tr>
<td>Pt(775)</td>
<td>4</td>
<td>30</td>
<td>-2</td>
<td>133</td>
<td>0.13</td>
<td>0.0065</td>
</tr>
<tr>
<td>Pt(13,13,12)</td>
<td>2.5</td>
<td>30.5</td>
<td>-3.75</td>
<td>25</td>
<td>0.1275</td>
<td>0.0055</td>
</tr>
</tbody>
</table>
Table S6-3. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps measured in a basic electrolyte.

<table>
<thead>
<tr>
<th>110 Steps</th>
<th>DL charging current (µA/cm²)</th>
<th>111 cosine a (µA/cm²)</th>
<th>111 cosine c (unit-less)</th>
<th>110 a (µA/cm²)</th>
<th>110 b (V RHE)</th>
<th>110 c (V RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(553)</td>
<td>5</td>
<td>22</td>
<td>-3.217</td>
<td>125</td>
<td>0.265</td>
<td>0.012</td>
</tr>
<tr>
<td>Pt(554)</td>
<td>4</td>
<td>26</td>
<td>-2.25</td>
<td>90</td>
<td>0.26</td>
<td>0.008</td>
</tr>
<tr>
<td>Pt(775)</td>
<td>4</td>
<td>26</td>
<td>-2</td>
<td>133</td>
<td>0.26</td>
<td>0.008</td>
</tr>
<tr>
<td>Pt(15,15,14)</td>
<td>1</td>
<td>10.5</td>
<td>-2.8</td>
<td>11</td>
<td>0.25</td>
<td>0.007</td>
</tr>
</tbody>
</table>

Table S6-4. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in an acid electrolyte.

\* V SCE

\*Two Gaussian functions were fit to the sharp double-peak experimentally measured on Pt(311). Pt(311) has a short 2 atom wide 100 terrace with a 111 step (2n-1, 1, 1; n(100)x(111), where n=2).

<table>
<thead>
<tr>
<th>100 Steps</th>
<th>DL charging current (µA/cm²)</th>
<th>111 cosine a (µA/cm²)</th>
<th>111 cosine c (unit-less)</th>
<th>100 a (µA/cm²)</th>
<th>100 b (V RHE)</th>
<th>100 c (V RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(533)</td>
<td>5</td>
<td>26</td>
<td>-2</td>
<td>90</td>
<td>0.27</td>
<td>0.017</td>
</tr>
<tr>
<td>Pt(544)</td>
<td>4</td>
<td>30</td>
<td>-2.75</td>
<td>82</td>
<td>0.285</td>
<td>0.01</td>
</tr>
<tr>
<td>Pt(755)</td>
<td>5</td>
<td>31</td>
<td>7.5</td>
<td>60</td>
<td>-0.045*</td>
<td>0.017</td>
</tr>
<tr>
<td>Pt(311)*</td>
<td>3</td>
<td>31</td>
<td>2</td>
<td>55</td>
<td>0.235</td>
<td>0.0225</td>
</tr>
<tr>
<td>Pt(311)*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>65</td>
<td>0.305</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table S6-5. Fitting parameters for deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in a basic electrolyte.

\*Pt(311) has a short 2 atom wide 100 terrace with a 111 step (2n-1, 1, 1; n(100)x(111), where n=2).

<table>
<thead>
<tr>
<th>100 Steps</th>
<th>DL charging current (µA/cm²)</th>
<th>111 cosine a (µA/cm²)</th>
<th>111 cosine c (unit-less)</th>
<th>100 a (µA/cm²)</th>
<th>100 b (V RHE)</th>
<th>100 c (V RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(533)</td>
<td>5</td>
<td>24</td>
<td>-3.217</td>
<td>85</td>
<td>0.415</td>
<td>0.017</td>
</tr>
<tr>
<td>Pt(544)</td>
<td>4</td>
<td>30</td>
<td>-2.5</td>
<td>58</td>
<td>0.415</td>
<td>0.015</td>
</tr>
<tr>
<td>Pt(755)</td>
<td>5</td>
<td>31</td>
<td>-3</td>
<td>75</td>
<td>0.418</td>
<td>0.016</td>
</tr>
<tr>
<td>Pt(311)*</td>
<td>5</td>
<td>31</td>
<td>1</td>
<td>120</td>
<td>0.416</td>
<td>0.025</td>
</tr>
</tbody>
</table>
Table S6-6. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps measured in an acid electrolyte.

<table>
<thead>
<tr>
<th>110 Steps Acid</th>
<th>111 total charge (μC/cm²)</th>
<th>110 total charge (1e⁻ per site) (μC/cm²)</th>
<th>110 total charge (1.33e⁻ per site) (μC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(776)</td>
<td>235.7</td>
<td>20.68</td>
<td>15.55</td>
</tr>
<tr>
<td>Pt(553)</td>
<td>217.0</td>
<td>65.42</td>
<td>49.19</td>
</tr>
<tr>
<td>Pt(554)</td>
<td>232.0</td>
<td>35.72</td>
<td>26.79</td>
</tr>
<tr>
<td>Pt(775)</td>
<td>224.5</td>
<td>43.34</td>
<td>32.51</td>
</tr>
<tr>
<td>Pt(13,13,12)</td>
<td>228.2</td>
<td>6.89</td>
<td>5.17</td>
</tr>
</tbody>
</table>

Table S6-7. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 110 steps measured in a basic electrolyte.

<table>
<thead>
<tr>
<th>110 Steps Base</th>
<th>111 total charge (μC/cm²)</th>
<th>110 total charge (1e⁻ per site) (μC/cm²)</th>
<th>110 total charge (1.33e⁻ per site) (μC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(553)</td>
<td>164.6</td>
<td>75.20</td>
<td>56.40</td>
</tr>
<tr>
<td>Pt(554)</td>
<td>194.6</td>
<td>36.10</td>
<td>27.07</td>
</tr>
<tr>
<td>Pt(775)</td>
<td>194.6</td>
<td>53.34</td>
<td>40.01</td>
</tr>
<tr>
<td>Pt(15,15,14)</td>
<td>196.4</td>
<td>9.65</td>
<td>7.24</td>
</tr>
</tbody>
</table>

Table S6-8. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in an acid electrolyte.

*Two Gaussian functions were fit to the sharp double-peak experimentally measured on Pt(311). Pt(311) has a short 2 atom wide 100 terrace with a 111 step (2n-1, 1, 1; n(100)x(111), where n=2).

<table>
<thead>
<tr>
<th>100 Steps Acid</th>
<th>111 total charge (μC/cm²)</th>
<th>100 total charge (1e⁻ per site) (μC/cm²)</th>
<th>100 total charge (1.33e⁻ per site) (μC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(533)</td>
<td>194.5</td>
<td>76.70</td>
<td>57.55</td>
</tr>
<tr>
<td>Pt(544)</td>
<td>224.5</td>
<td>41.11</td>
<td>30.83</td>
</tr>
<tr>
<td>Pt(755)</td>
<td>232.0</td>
<td>51.14</td>
<td>38.35</td>
</tr>
<tr>
<td>Pt(311)*</td>
<td>232.0</td>
<td>62.04</td>
<td>46.53</td>
</tr>
<tr>
<td>Pt(311)*</td>
<td>-</td>
<td>65.17</td>
<td>48.88</td>
</tr>
</tbody>
</table>
Table S6-9. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on single crystal electrodes with 100 steps measured in a basic electrolyte.

*Pt(311) has a short 2 atom wide 100 terrace with a 111 step (2n-1, 1, 1; n(100)x(111), where n=2).

<table>
<thead>
<tr>
<th>100 Steps Base</th>
<th>111 total charge (μC/cm²)</th>
<th>100 total charge (1e⁻ per site) (μC/cm²)</th>
<th>100 total charge (1.33e⁻ per site) (μC/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(533)</td>
<td>179.6</td>
<td>72.44</td>
<td>54.33</td>
</tr>
<tr>
<td>Pt(544)</td>
<td>194.6</td>
<td>36.10</td>
<td>27.07</td>
</tr>
<tr>
<td>Pt(755)</td>
<td>232.0</td>
<td>60.16</td>
<td>45.12</td>
</tr>
<tr>
<td>Pt(311)*</td>
<td>232.0</td>
<td>150.4</td>
<td>112.8</td>
</tr>
</tbody>
</table>

Figure S6-1. Experimentally measured cyclic voltammogram (black line, background) on Pt(pc) in 0.1 M HClO₄ adapted from Rheinländer et al.⁴⁵ and the sum of the deconvoluted cyclic voltammogram (red line, foreground). The 110 step peak was fit with two Gaussian functions, as peak splitting is observed on stepped single crystal electrodes with narrow terraces (Pt(331) and Pt(110)) in perchloric acid solutions. This may explain the existence of the “middle” peak in the negative going scan near 0.2 V_{RHE}. 
Figure S6-2. Experimentally measured cyclic voltammogram with a stationary rotating disk Pt(pc) electrode (black line, background) and rotating electrode (400 rpm) (grey dotted line, background) in 0.1 M NaOH adapted from Rheinländer et al.\textsuperscript{45} and the sum of the deconvoluted cyclic voltammogram (red line, foreground).

Figure S6-3. Experimentally measured cyclic voltammogram (black line, background) on Pt(pc) in 0.1 M KOH adapted from Sheng et al.\textsuperscript{46} and the sum of the deconvoluted cyclic voltammogram (red line, foreground). Experimentally measured CV was shifted to more positive current density by ~ 6 µA/cm\textsuperscript{2} so that the double layer charging current was centered about 0 µA/cm\textsuperscript{2}. Current density is per cm\textsuperscript{2} of Pt area calculated by Sheng et al.\textsuperscript{46}. 
Figure S6-4. Experimentally measured cyclic voltammogram (black line, background) on Pt/C in 0.1 M KOH adapted from Sheng et al.\textsuperscript{46} and the sum of the deconvoluted cyclic voltammogram (red line, foreground). Current density is per cm\textsuperscript{2} of Pt area calculated by Sheng et al.\textsuperscript{46}.

Table S6-10. Parameters used to deconvolute experimentally measured cyclic voltammograms on polycrystalline and nanoparticle platinum electrodes in both acidic and basic electrolytes. The cyclic voltammogram measured on Pt(pc) in perchloric acid was deconvoluted using two Gaussian peaks to represent adsorption on 110 sites.

*Total current in experimental CV was normalized to the total platinum area, not the geometric electrode area as calculated by Sheng et al.\textsuperscript{46}.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|c|c|c|c|c|c|c|}
\hline
& DL current & 111 a & 111 c & 110 a & 110 b & 110 c & 100 a & 100 b & 100 c \\
& (\mu A/cm\textsuperscript{2}) & (\mu A/cm\textsuperscript{2}) & (V\textsubscript{RHE}) & (\mu A/cm\textsuperscript{2}) & (V\textsubscript{RHE}) & (V\textsubscript{RHE}) & (\mu A/cm\textsuperscript{2}) & (V\textsubscript{RHE}) & (V\textsubscript{RHE}) \\
\hline
Pt(pc) 0.1 M HClO\textsubscript{4} & 4 & 30.0 & -4.00 & 54.0 & 0.123 & 0.026 & 32.0 & 0.330 & 0.035 \\
Pt(pc) 0.1 M NaOH & 10 & 24.0 & -5.00 & 75.0 & 0.300 & 0.026 & 48.0 & 0.415 & 0.023 \\
Pt(pc) 0.1 M KOH* & 8 & 16.3 & -6.25 & 44.0 & 0.275 & 0.028 & 32.5 & 0.395 & 0.017 \\
Pt/C 0.1 M KOH* & 14 & 20.0 & -6.50 & 55.0 & 0.285 & 0.024 & 10.0 & 0.395 & 0.025 \\
\hline
\end{tabular}
\end{table}
Table S6-11. Total charge calculated for each type of site after deconvoluting experimentally measured cyclic voltammograms on polycrystalline and nanoparticle Pt electrodes measured in acidic and basic electrolytes.

*Total current in experimental CV was normalized to the total platinum area not the geometric electrode area as calculated by Sheng et al. \(^{46}\).

<table>
<thead>
<tr>
<th></th>
<th>111 total charge ((\mu C/cm^2))</th>
<th>110 total charge (1e(^-) per site) ((\mu C/cm^2))</th>
<th>110 total charge (1.33e(^-) per site) ((\mu C/cm^2))</th>
<th>100 total charge (1e(^-) per site) ((\mu C/cm^2))</th>
<th>100 total charge (1.33e(^-) per site) ((\mu C/cm^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(pc) 0.1 M HClO(_4)</td>
<td>224.5</td>
<td>70.4</td>
<td>52.8</td>
<td>56.1</td>
<td>42.1</td>
</tr>
<tr>
<td>Pt(pc) 0.1 M NaOH</td>
<td>179.6</td>
<td>97.8</td>
<td>73.3</td>
<td>55.3</td>
<td>41.5</td>
</tr>
<tr>
<td>Pt(pc) 0.1 M KOH(^*)</td>
<td>121.6</td>
<td>61.8</td>
<td>46.3</td>
<td>27.7</td>
<td>20.8</td>
</tr>
<tr>
<td>Pt/C 0.1 M KOH(^*)</td>
<td>149.7</td>
<td>66.2</td>
<td>49.6</td>
<td>12.5</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table S6-12. Total site density (in units of \(\mu C/cm^2_{geo}\), where the number of platinum sites can be calculated assuming 1 electron transferred per site, after accounting for the appropriate number of electrons transferred (assume 1 electron per site in H-upd method, assume 2 electrons per site in the CO stripping method, and calculated 1 electron per 111 site and 1.33 electrons per each 110 and 100 site (from DFT) in the deconvolution method)) calculated with the H-UPD method, CO stripping method, and our deconvolution method.

<table>
<thead>
<tr>
<th></th>
<th>Total site density ((\mu C/cm^2_{geo}))</th>
<th>H-UPD ((\mu C/cm^2_{geo}))</th>
<th>CO stripping ((\mu C/cm^2_{geo}))</th>
<th>Deconvolution method ((\mu C/cm^2_{geo}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(pc) 0.1 M HClO(_4)</td>
<td>375</td>
<td>277</td>
<td>313</td>
<td></td>
</tr>
<tr>
<td>Pt(pc) 0.1 M NaOH</td>
<td>336</td>
<td>280</td>
<td>263</td>
<td></td>
</tr>
<tr>
<td>Pt(pc) 0.1 M KOH</td>
<td>336</td>
<td>274</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pt/C 0.1 M KOH</td>
<td>903</td>
<td>815</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table S6-13. Fraction of total sites which correspond to 111, 100 and 110 type sites, calculated from cyclic voltammograms measured on shape controlled platinum nanoparticles by Devivaraprasad et al.\(^ {66}\) in NaOH. While the absolute values differ between the method used here and the methods used by Devivaraprasad et al.\(^ {66}\), the trend in which nanoparticles show the highest relative proportion of 100 type sites matches.

<table>
<thead>
<tr>
<th>Fraction of total sites</th>
<th>111</th>
<th>100</th>
<th>110</th>
<th>111 ((^ {66}))</th>
<th>100 ((^ {66}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-NC</td>
<td>0.76</td>
<td>0.16</td>
<td>0.14</td>
<td>0.13</td>
<td>0.52</td>
</tr>
<tr>
<td>Pt-CO</td>
<td>0.76</td>
<td>0.19</td>
<td>0.05</td>
<td>0.3</td>
<td>0.45</td>
</tr>
<tr>
<td>Pt-TD</td>
<td>0.83</td>
<td>0.09</td>
<td>0.09</td>
<td>0.6</td>
<td>0.14</td>
</tr>
<tr>
<td>Pt-PC</td>
<td>0.73</td>
<td>0.12</td>
<td>0.10</td>
<td>0.02</td>
<td>0.21</td>
</tr>
</tbody>
</table>
Table S6-14. Fraction of total sites which correspond to 111, 100 and 110 type sites, calculated from cyclic voltammograms measured on shape controlled platinum nanoparticles by Vidal-Iglesias et al.\textsuperscript{67}. While the absolute values differ between the method used here and the methods used by Vidal-Iglesias et al.\textsuperscript{67}, the trend in which nanoparticles show the highest relative proportions of 111 and 100 types sites both match between the two methods.

<table>
<thead>
<tr>
<th>Fraction of total sites</th>
<th>111</th>
<th>100</th>
<th>110</th>
<th>111 (\textsuperscript{67})</th>
<th>100 (\textsuperscript{67})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-NP\textsubscript{cubic}</td>
<td>0.67</td>
<td>0.16</td>
<td>0.17</td>
<td>0.11</td>
<td>0.52</td>
</tr>
<tr>
<td>Pt-NP\textsubscript{trunc}</td>
<td>0.74</td>
<td>0.10</td>
<td>0.16</td>
<td>0.33</td>
<td>0.17</td>
</tr>
<tr>
<td>Pt-NP\textsubscript{sphe}</td>
<td>0.67</td>
<td>0.11</td>
<td>0.21</td>
<td>0.06</td>
<td>0.14</td>
</tr>
<tr>
<td>Pt-NP\textsubscript{tetra}</td>
<td>0.84</td>
<td>0.05</td>
<td>0.12</td>
<td>0.42</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Chapter 7

First Principles Calculation of Pt Surface Energies in an Electrochemical Environment: Thermodynamic Driving Forces for Surface Faceting and Nanoparticle Reconstruction

This chapter has been submitted for publication as: McCrum, I.T.; Hickner, M.A.; Janik, M.J.; First Principles Calculation of Pt Surface Energies in an Electrochemical Environment: Thermodynamic Driving Forces for Surface Faceting and Nanoparticle Reconstruction. Langmuir

Abstract

Platinum is a widely used catalyst in aqueous and electrochemical environments. The size and shape of Pt nanoparticles and the faceting (and roughness) of extended Pt surfaces change during use in these environments due to dissolution, growth, and reconstruction. Further, many Pt nanoparticle synthesis techniques are carried out in an aqueous environment. The surface structures formed are impacted by the relative surface energies of the low index facets in these environments. Density functional theory is used to calculate the surface energy of the low index facets of platinum as a function of electrochemical potential and coverage of adsorbed hydrogen, hydroxide, oxygen, and the formation of surface oxide in an aqueous environment. Whereas Pt(111) is the lowest energy bare surface in vacuum, the strong adsorption of hydrogen to Pt(100) at low potentials and of hydroxide to Pt(110) and oxygen to Pt(100) at high potentials drives these surfaces to be more stable in an electrochemical environment. We experimentally conditioned a polycrystalline platinum electrode by cycling the potential and find a growth in the total area as well as in the fraction of 110 and 100 sites, which are lower in energy at potentials where dissolved Pt is deposited or surface oxide is reduced. Further, we find the lower surface energy of Pt(100) at low potentials may play a role in the growth of tetrahedrahedral nanoparticles seen on
square wave cycling of spherical Pt nanoparticles. Wulff constructions are presented as a function of Pt electrode potential.

7.1. Introduction

Surface energy is an important material property as it dictates surface structure and stability, both of which effect catalytic activity and selectivity as well as degradation. The surface energy provides insight into how resistant a catalyst material is to sintering, ripening, and dissolution. Surface energy is not a constant material property and may depend on the environment which surrounds the surface, as adsorption of reactant or spectator species can promote the stability of a particular surface structure or facet.

The surface energy of platinum in an aqueous environment is particularly important, as it is one of the most active, well studied, and widely used catalysts in solution phase heterogeneous and electrochemical catalytic reactions. Platinum is frequently used to catalyze selective alcohol$^1$, 2 and aldehyde$^3$ oxidation as well as electrochemical hydrogen oxidation and evolution$^4$, oxygen reduction$^5$, and methanol oxidation$^6,7$. Understanding platinum electrode stability is particularly important in the development of fuel cells, as these devices require high electrode activity for thousands of hours of operation and through many start-up/shut-down cycles, which cycle the potential of the platinum electrode$^8-13$. Through these processes restructuring and dissolution/growth of platinum electrode surfaces occurs in electrochemical environments$^{14-22}$. Further, platinum catalysts can be synthesized in an aqueous environment$^{23-30}$, where the surface energy can affect the growth rate as well as nanoparticle size and shape/faceting$^{25}$.

Potential cycling can have a profound effect on platinum nanoparticle/electrode size and shape due to the generation/reduction of surface oxide and dissolution/deposition of surface Pt atoms. Shao-Horn et al. give a thorough review of the mechanisms of platinum surface area loss
and restructuring under electrochemical conditions for fuel cell applications, highlighting platinum dissolution and Ostwald ripening as the key factors in platinum surface area loss. Cherevko et al. have recently published an extensive review of bulk and nanoparticle platinum dissolution, in the context of fuel cell catalyst stability. Further, potential induced or electrochemically-driven dissolution and restructuring has been used advantageously to produce highly faceted Pt nanoparticles, including tetrahexahedral and hexoctahedral nanoparticles.

Mechanistic insight into nanoparticle restructuring processes can be gained by examining the potential dependent behavior of smooth platinum single crystal electrodes. Gómez-Marín et al. examined the restructuring of single crystal Pt(111) electrode surfaces in non-adsorbing perchloric acid using cyclic voltammetry. 110-type steps grew during repeated cycling into the oxygen adsorption and oxide formation potential region. Aberdam et al. used low energy electron diffraction (LEED) to show a Pt(111) electrode exhibits point defects and monoatomic steps on repeated cycling in perchloric acid. Wakisaka et al. used in situ scanning tunneling microscopy (STM) to examine the potential dependent restructuring of Pt(111) in hydrofluoric acid. The formation of a surface oxide at high potentials, then its subsequent reduction during cycling to low potentials, lead to the growth of steps and small islands. Surface roughening has also been examined with in-situ x-ray techniques. Similar restructuring of Pt(111) has been observed in alkaline and sulfuric acid electrolytes. The potential dependent dissolution of smooth single crystal Pt(111), Pt(100), and Pt(110) have also been investigated, with atomic force microscopy (AFM) and in-situ inductively coupled mass spectrometry (ICP-MS), where it has been found that oxide formation at high potentials hinders dissolution.

Understanding the rates and equilibrium conditions for each of these restructuring or dissolution processes requires knowledge of the surface energy of not only the bare surface, but also of the potential dependent surface energy in the presence of adsorbates in an electrochemical environment. The electrochemical environment may stabilize higher index surfaces and defects;
determination of the surface energy under aqueous electrochemical conditions can aid interpretation of these phenomena.

Density functional theory (DFT) has been used to calculate platinum surface energies, though few studies have focused on an aqueous electrochemical environment. An extensive investigation by Vitos et al. used DFT to examine the surface energies of the low index facets of 60 metals across the periodic table. Singh-Miller and Marzari and Da Silva et al. more recently evaluated surface energies of platinum (Pt(111), Pt(100), Pt(110)) and the Pt(111) surface, respectively. Barnard and Chang used DFT to examine the surface energy of the low index facets of platinum and platinum steps. These studies considered the surface energy in the absence of adsorption. Seriani and Mittendorfer used DFT to examine the stability and surface energy of platinum under oxidizing conditions where oxygen can adsorb. Zhu et al. considered oxygen adsorption as a function of electrochemical potential on the low index Pt surfaces, as well as on stepped (210), (520), and (730) surfaces. They found that the strong binding of oxygen to stepped facets may promote their growth during potential cycling, seen during the formation of tetrahexahedral Pt nanoparticles. Bonnet and Marzari used DFT to calculate the surface energy of Pt(111) and Pt(100) and resultant platinum nanoparticle shapes under electrochemical conditions, considering the effect of hydrogen adsorption and electrode potential, but limited their investigation to low potentials and did not consider hydroxide or oxygen adsorption, nor the 110 facet.

Herein, we use density functional theory to calculate the surface energy of Pt(111), Pt(100), and Pt(110) surfaces as a function of electrode potential, considering the adsorption of hydrogen, hydroxide and water, oxygen, and the formation of surface oxides. This analysis covers a wide range of electrode potential, from low potentials (below 0 V_{RHE}), where a high coverage of adsorbed hydrogen covers all of the surfaces, to high potentials (above 1 V_{RHE}) where surface oxide formation is thermodynamically favorable on all of the surfaces. We find that while Pt(111)
is the lowest energy surface in the absence of adsorption, the strong adsorption of hydrogen, hydroxide, and oxygen to Pt(100) and Pt(110) gives these facets comparable or lower surface energies than that of Pt(111) in an electrochemical environment at low and high potential. We also carry out experimental cycling of a polycrystalline platinum electrode which shows the preferential growth of 110 and 100 step sites after cycling to high oxide formation potentials. Our DFT results show that the Pt(110) surface is the most stable surface near potentials where this surface oxide is reduced (0.6-0.85 V\textsubscript{RHE}) with the Pt(100) surface most stable at slightly more positive potentials (> 0.95 V\textsubscript{RHE}), supporting the experimental measurements showing the growth of these facets.

7.2. Methods

7.2.1. Computational Methods

We previously used DFT to model the adsorption of hydrogen, potassium, and hydroxide (with co-adsorbed water) on Pt(111), Pt(100), and Pt(110) using density functional theory\textsuperscript{55}. We use these results as well as additional simulations of oxygen adsorption and surface oxide formation to calculate the potential dependent surface energy of Pt(111), Pt(100), and Pt(110). DFT calculations were performed with the Vienna ab initio Simulations Package (VASP)\textsuperscript{56-58} with a plane wave basis set and the Perdew-Wang (PW91) exchange correlation functional\textsuperscript{59}. The ion core potentials were modeled using the Projector Augmented Wave (PAW) approach\textsuperscript{60-61}. The plane wave basis set cutoff energy was 450 eV and the structural optimization was carried out until the forces on the atoms were below 0.02 eV Å\textsuperscript{-1}. Each surface was modeled with a 4 layer slab, with the bottom two layers frozen at the experimental lattice constant of platinum, 3.92 Å\textsuperscript{62}. Varying coverages were investigated using multiple adsorbates in a 2x2 or 3x3 unit cell with a
7x7x1 or a 5x5x1 Monkhorst-Pack\textsuperscript{63} mesh k-space sampling grid, respectively. Dipole corrections were included in the surface normal direction (VASP keywords: IDIPOL=3, LDIPOL=TRUE).

The same structures and relative coverage of co-adsorbed hydroxide and water that were examined previously\textsuperscript{55} were used to calculate the surface energy as a function of potential. The minimum energy co-adsorbed hydroxide and water structures on Pt(111) and Pt(100) were taken from literature (Pt(111)\textsuperscript{64-70}, Pt(100)\textsuperscript{71}). Structures with varying coverages of hydroxide and water on Pt(110) were previously investigated\textsuperscript{55}. While the minimum energy structures may be only local minima, a lower energy structure would only give more favorable hydroxide and water adsorption on Pt(110), such that the structures used here give a positive adsorption potential limit (weaker adsorption). A thorough discussion of the co-adsorbed hydroxide and water structures investigated is given in\textsuperscript{55}.

The surface oxide structures examined here were those found using DFT as the lowest energy oxide structures on Pt(111) (PtO\textsubscript{2}\textsuperscript{72-74}), on Pt(100) (PtO)\textsuperscript{74}, and on Pt(110) (PtO\textsubscript{2})\textsuperscript{75}. Images of the oxide structures can be found in the supplementary information and were rendered by VESTA\textsuperscript{76}.

Wulff constructions were generated and nanoparticle shapes rendered using Wulffmaker\textsuperscript{77}.

\textbf{7.2.2. Calculating Surface Energy}

The surface energy of Pt(111), Pt(100), and Pt(110) is calculated as a function of potential with varying coverages of specifically adsorbed hydrogen, hydroxide and co-adsorbed water, and oxygen (in the absence and presence of near surface potassium). These surface energies are calculated relative to the surface energy of the bare surface taken from the literature.
The adsorption reactions are given in equations 1, 2, and 3:

\[ H^+_{(aq)} + e^- + * \rightarrow H^* \]  \[ \text{[1]} \]

\[ H_2O_{(aq)} + * \rightarrow OH^* + H^+_{(aq)} + e^- \]  \[ \text{[2]} \]

\[ H_2O_{(aq)} + * \rightarrow O^* + 2H^+_{(aq)} + 2e^- \]  \[ \text{[3]} \]

Equation 4 shows how the surface energy is corrected for reductive adsorption of a proton:

\[ \gamma(U) = \gamma_{bare} + \frac{G_{H^*} - G_\ast - G_{H^+_{(aq)}} + |e|U}{A} \]  \[ \text{[4]} \]

where \( \gamma_{bare} \) is the surface energy of the bare surface (taken from literature), \( G_{H^*} \) is the free energy of the surface with an adsorbed hydrogen atom, \( G_\ast \) is the free energy of the bare surface, \( G_{H^+_{(aq)}} \) is the free energy of the solution phase proton, \( eU \) is the free energy of the transferred electron, and \( A \) is the surface area of the metal. For an oxidation reaction, such as those shown in equations 2 and 3, equation 5 is used to calculate the surface energy:

\[ \gamma(U) = \gamma_{bare} + \frac{G_{OH^*_x} - G_\ast - G_{H_2O_{(aq)}} + (2 - x)G_{H^+_{(aq)}} - (2 - x)|e|U}{A} \]  \[ \text{[5]} \]

where \( G_{H_2O_{(aq)}} \) is the free energy of solution phase water and \( x \) can be 0 or 1 to represent O* or OH* adsorption. For hydroxide and water co-adsorption, adsorbed water was used as the reference state instead of solution phase water (\( G_{H_2O_{(aq)}} \)). Using adsorbed water as a reference state gave hydroxide adsorption potentials which compared more favorably with experiment and also allowed for a more direct comparison to adsorption in the presence of a co-adsorbed potassium cation. In previous work\(^{55, 78-79}\) we have found that near surface alkali cations retain most of their charge on adsorption and exhibit strong interactions with near surface water. A low energy water hexamer on Pt(111)\(^{67, 80-81}\), 6 water molecule chain on Pt(100)\(^{71}\), and 4 water
molecule chain/square on Pt(110) in a 2x2 unit cell are taken as the adsorbed water structures.

The free energy of the bare surface is calculated by equation 6:

\[ G_* = E_*^{DFT} \]  \[6\]

where \( E_*^{DFT} \) is the DFT calculated bare surface energy. The free energy of the surface with an adsorbate is calculated with equation 7:

\[ G_X = E_X^{DFT} + ZPVE - TS_{vib} \]  \[7\]

where \( ZPVE \) is the zero point vibrational energy of the adsorbate on the surface and \( TS_{vib} \) is the temperature multiplied by the vibrational entropy of the adsorbate on the surface.

The free energy of the solution phase proton \((G_{H^+_{\text{aq}}})\) is calculated using the computational hydrogen electrode method. Using this method, the free energy of the aqueous phase proton is calculated from the free energy of gas phase hydrogen at the equilibrium potential of 0 V \( \text{RHE} \) following the reaction and equation shown in equations 8 and 9:

\[ \frac{1}{2} H_2(g) \leftrightarrow H^+_{\text{aq}} + e^- \]  \[8\]

\[ \Delta G = G_{H^+_{\text{aq}}} - |e|U - \frac{1}{2} G_{H_2(g)} \Delta G = 0 \ @ U = 0V_{\text{RHE}} \]  \[9\]

The free energy of the gas phase hydrogen molecule is calculated using equation 10:

\[ G_{H_2(g)} = E_{H_2}^{DFT} + ZPVE - TS_{gas} + U_{int} + PV \]  \[10\]

where \( S_{gas} \) includes the vibrational, rotational, and translational entropy of a gas phase hydrogen molecule, \( U_{int} \) is the internal energy, and \( PV \) is the pressure volume contribution to the gas phase free energy of molecular hydrogen. The free energy of aqueous phase water is calculated as the free energy of gas phase water, similarly to equation 10, but at a pressure equal to the vapor pressure of an aqueous solution at 300K (0.035 bar), where \( G_{H_2O_{\text{aq}}} = G_{H_2O_{\text{g}}} \). All other free energies are calculated at a temperature of 300 K and a pressure of 1 bar.
7.2.3. Experimental Methods

Cyclic voltammograms (CVs) were measured in argon saturated 0.1 M KOH on a polycrystalline platinum rotating disk electrode (working electrode). Measurements were conducted in a three electrode cell, with a Ag/AgCl reference electrode and platinum wire counter electrode. The working electrode was polished with a 0.05 μm alumina slurry and rinsed with DI water prior to measurement. Window opening cyclic voltammograms were measured at 100 mV/s for 10 cycles from -0.9 V to 0 V, 10 cycles to 0.2 V, and 10 cycles to 0.3 V (vs. Ag/AgCl). Electrode conditioning was then carried out by cycling between -0.9 V and 0.3 V (vs. Ag/AgCl) at 200 mV/s for 100 cycles. An additional 50 cycles from -0.9V to 0.05V (vs Ag/AgCl) at 100 mV/s were measured after conditioning.

Potentials were corrected to a reversible hydrogen electrode scale (RHE) for a solution pH=13 and a Ag/AgCl potential of 0.222 V_NHE.  

7.3. Results and Discussion

7.3.1. Adsorption of Hydrogen, Hydroxide and Water, and Oxygen

Figures 7-1a, b, and c show the calculated surface energies for Pt(111), Pt(100), and Pt(110) (respectively) as a function of potential considering the adsorption of hydrogen, co-adsorption of hydroxide and water, and adsorption of oxygen. In Figures 7-1a, b, and c, the line with the lowest surface energy defines the most favorable surface coverage at that potential. The bare surface energy is potential independent, such that favorable adsorption lowers the surface energy.
Figure 7-1. Surface energy as a function of potential and hydrogen, hydroxide and water, and oxygen coverage on Pt(111) (a), Pt(100) (b), and Pt(110) (c). Bold labels and vertical lines define stability regions for the adsorbates. In the H* region, hydrogen coverage increases as potential is decreased. In the OH*+H2O* and O* region, adsorbed oxygen species coverage increases as potential is increased. Due to the strong adsorption of hydrogen and hydroxide (with co-adsorbed water) on Pt(100) and Pt(110), there is no potential where the bare 100 or 110 surfaces are most stable.
On Pt(111), hydrogen adsorbs at low potentials, below \(~ 0.4 \text{ V}_{\text{RHE}}\) with the coverage increasing as the potential decreases. Hydrogen adsorption on Pt(111) is strongly coverage dependent, with 1 ML of hydrogen not reached until the electrode potential is more negative than \(0 \text{ V}_{\text{RHE}}\). Hydroxide and water co-adsorb on Pt(111) above \(0.58 \text{ V}_{\text{RHE}}\); only one coverage, the minimum energy coverage of adsorbed hydroxide and water (\(1/3 \text{ ML OH}^*\) and \(1/3 \text{ ML H}_2\text{O}^*\)) was examined. We can see that a low coverage of adsorbed oxygen (\(1/9 \text{ ML}\)) is never more favorable than \(1/3 \text{ ML OH}^* + 1/3 \text{ ML H}_2\text{O}^*\). Oxygen adsorption at \(1/3 \text{ ML}\) is more favorable above \(1.08 \text{ V}_{\text{RHE}}\). This compares well with DFT from Holby et al. who show that low coverage oxygen adsorption is favorable between 0.76 and \(~ 1 \text{ V}_{\text{RHE}}\), though they do not compare with hydroxide adsorption (which we find to be more favorable below \(1 \text{ V}_{\text{RHE}}\))\(^{84}\). We also see general agreement with Chen et al. who performed a detailed DFT and Monte Carlo analysis of hydroxide and oxygen competitive formation on Pt(111)\(^{85}\). The results in Figure 7-1a compare well with experiment, where cyclic voltammetry on Pt(111) in non-adsorbing hydrofluoric acid\(^{39}\), perchloric acid\(^{86-88}\), methanesulfonic acid\(^{89}\), and trifluoromethanesulfonic acid\(^{90}\) indicate hydrogen adsorption below \(0.35 \text{ V}_{\text{RHE}}\), hydroxide adsorption between 0.55 and \(0.8 \text{ V}_{\text{RHE}}\), and oxygen adsorption at \(1.0-1.1 \text{ V}_{\text{RHE}}\)\(^{39}\).

Similar results are seen with adsorption on Pt(100) (Figure 7-1b) and Pt(110) (Figure 7-1c), except all species are adsorbed more strongly than on Pt(111). This stronger binding drives hydrogen adsorption to more positive potentials and hydroxide adsorption to more negative potentials (relative to Pt(111)). On Pt(100) and Pt(110), both hydrogen and hydroxide bind strongly enough that their adsorption is competitive at low potentials (\(0.41 \text{ V}_{\text{RHE}}\) on Pt(100) and \(0.28 \text{ V}_{\text{RHE}}\) on Pt(110)) and therefore there is no potential where the surface is bare. This competitive adsorption has been considered by others previously on both Pt(110) and Pt(100)\(^{91-93}\) and the results here compare well with experimentally measured voltammetric features and the potential of zero total (displaced) charge in perchloric acid (\(0.415 \text{ V}_{\text{RHE}}\)\(^{94}\) on Pt(100) and 0.22
\( \text{V}_{\text{RHE}}^{95}, 0.24 \text{ V}_{\text{RHE}}^{96} \) on Pt(110)). Only the minimum energy coverage of adsorbed hydroxide and water was considered. For Pt(110), this coverage (0.5 ML) may be larger than that calculated based on the total charge transferred at low potentials from experiment. In contrast with Pt(111), adsorption of hydrogen above 1 ML (to 1.25ML considered here) is favorable on both Pt(100) and Pt(110) near 0 V\(_{\text{RHE}}\). Adsorption near 0 V\(_{\text{RHE}}\) is difficult to observe experimentally in cyclic voltammograms, as hydrogen evolution occurs near this potential, but the onset (trailing edge) of a second H* adsorption (desorption) peak can be observed on Pt(100) below 0.1 V\(_{\text{RHE}}\) (which has seen additional experimental examination, to deconvolute adsorption from hydrogen evolution\(^97\)). Oxygen also adsorbs more strongly on Pt(100) and Pt(110) than on Pt(111), but is competitive with hydroxide adsorption on all three surfaces. On Pt(100), this stronger adsorption gives a formation potential for adsorbed oxygen (0.88 V\(_{\text{RHE}}\)) below that of Pt(111). On Pt(110), the strong adsorption of hydroxide to this surface drives oxygen adsorption/formation to potentials more positive (1.19 V\(_{\text{RHE}}\)) than that of Pt(111). These calculated potentials to convert the hydroxide and water covered surface to a partially oxygen covered surface are close to those measured experimentally, slightly above the potential measured on Pt(110)\(^90, 98\) and below that measured on Pt(100)\(^88, 90, 99\) (near 1V\(_{\text{RHE}}\) on both surfaces). Surface oxide formation is also favorable near these potentials (see following section), making it difficult to determine the state of these surfaces at high potentials.

Figures 7-1a-c label regions of most stable H*, OH*, and O* and the major transitions in coverage on each low index Pt surface. We identify and plot the lowest surface energy for each surface facet as a function of potential in Figure 7-2. While the bare Pt(111) surface is lower in energy than bare Pt(100) and Pt(110), the adsorption of hydrogen or hydroxide in an electrochemical environment drives the surface energy of Pt(100) and Pt(110) lower than that of bare Pt(111). Pt(110) and Pt(100) bind hydrogen and hydroxide so strongly that these surfaces are not bare at any potential in an electrochemical environment. Even small changes in the
relative surface energy between facets can have significant effects on equilibrium nanoparticle shapes and surface reconstruction, which are considered in a following section.

![Figure 7-2. Surface energy as a function of potential and coverage of adsorbed hydrogen, hydroxide and water, and oxygen on Pt(111) (blue), Pt(100) (red), and Pt(110) (black). The surface energy of the most stable coverage at any given potential is plotted.](image)

In basic solutions with alkali hydroxide, the peak positions associated with H*/OH*/O* adsorption shift in potential (on a relative potential scale). We have previously considered the effect of a near surface alkali metal cation (potassium) on H*/OH* adsorption to the low index platinum facets. Near surface alkali metal cations have little effect on hydrogen adsorption on platinum, but cause a significant weakening of hydroxide adsorption\(^{55,78}\). Figures S7-1, S7-2, and S7-3 show the calculated surface energies of Pt(111), Pt(100), and Pt(110) as a function of potential (similar to Figures 7-1a, b, and c) in an alkaline electrolyte, including the effect of the near surface potassium cation on hydroxide adsorption and oxygen adsorption. The surface phase diagram on Pt(111) (Figure S7-1) matches experiment very well, with hydroxide adsorption favorable above 0.69 V\(_{\text{RHE}}\) (onset ~0.60 V\(_{\text{RHE}}\), peak 0.77 V\(_{\text{RHE}}\)\(^{100}\), slightly positive to that measured in acid, and oxygen adsorption at 0.94 V\(_{\text{RHE}}\) (0.97 V\(_{\text{RHE}}\)\(^{100}\), slightly less positive to that
measured in acid. The surface phase diagrams for Pt(100) and Pt(110) in an alkaline electrolyte, Figure S2 and S3, respectively, match experiment qualitatively in capturing the shift of the competitive adsorption of hydrogen and hydroxide to more positive potentials in an alkaline electrolyte\textsuperscript{100-101}, though with a slightly larger shift than what is observed experimentally. It is difficult to experimentally determine at what potentials and to what coverage oxygen adsorbs on Pt(110) and Pt(100) in an alkaline electrolyte. There are multiple CV peaks which overlap at high potentials at high pH on Pt(100)\textsuperscript{101-103} and we find that surface oxide formation is competitive with oxygen adsorption on both of these surfaces. Our DFT results suggest oxygen adsorption at lower potentials than what is likely observed experimentally in an alkaline electrolyte. This is primarily due to an over-estimation of the weakening effect of the cation on hydroxide adsorption. We also observe that the presence of the cation strengthens oxygen adsorption, though this is likely over-predicted due to a lack of cation solvation in this model. Images of the adsorbed hydroxide and adsorbed oxygen with the co-adsorbed alkali cation are given in the supplementary information.

7.3.2. Formation of Surface Oxide

The surface energy of 1 ML of surface oxide on Pt(111) and Pt(100) and 0.5 ML on Pt(110) was also calculated. Structures of this oxide layer were taken from the literature, for PtO\textsubscript{2} on Pt(111)\textsuperscript{72-74}, PtO on Pt(100)\textsuperscript{74}, and PtO\textsubscript{2} on Pt(110)\textsuperscript{75}. Images of the structures are given in the supplementary information.

Figures S7-4, S7-5, and S7-6 compare the surface energies of adsorbed platinum oxide against that of oxygen adsorption as a function of potential on Pt(111), Pt(100), and Pt(110), respectively. On Pt(111), the formation of the surface oxide layer occurs at potentials significantly more positive of oxygen adsorption, near 1.25 V\textsubscript{RHE}. In contrast, the formation of an
oxide layer on Pt(100) and Pt(110) is at least as thermodynamically favorable as the adsorption of a low coverage of oxygen, competing with hydroxide adsorption near 0.77 V_{RHE} on Pt(100) and 0.81 V_{RHE} on Pt(110). These potentials are ~0.2-0.3 V below that where sharp oxidation peaks occur in cyclic voltammograms on these surfaces. While surface oxide formation is thermodynamically favorable at these potentials, it may be kinetically limited relative to oxygen adsorption, as it requires significant restructuring of the platinum surface and platinum incorporation into the oxide layer (or oxygen into subsurface platinum), breaking Pt-Pt bonds.

More detailed DFT investigations of oxygen adsorption and oxide formation on Pt(111) are given by Holby et al.\textsuperscript{84}, Seriani et al.\textsuperscript{74}, and Hawkins et al.\textsuperscript{73}; on Pt(100) by Gu et al.\textsuperscript{104} and Seriani et al.\textsuperscript{52}; and on Pt(110) by Seriani et al.\textsuperscript{52}, Helveg et al.\textsuperscript{105}, and Pedersen et al.\textsuperscript{75}. Fantauzzi et al. have also used a reactive force field model (ReaxFF) to examine oxygen adsorption and surface oxide formation on Pt(111)\textsuperscript{106-108}. We give our own analysis here to provide an estimate of the relative thermodynamic favorability of surface oxide formation with equivalent methods to our H\*/OH\*/O\* adsorption analysis.

7.3.3. Nanoparticle Shape and Surface Restructuring in an Aqueous Electrochemical Environment

In an aqueous environment, the relative surface energies of Pt(111), Pt(100), and Pt(110) are significantly different than that of the bare surfaces (and are 0.8 – 1 J/m\(^2\) lower at the potential extremes). Under potential control, this shift in the relative surface energies will be largest at potential extremes, at low potentials where the (100) surface has the lowest surface energy at high hydrogen coverage, and at high potentials where Pt(110) covered with adsorbed hydroxide and Pt(100) covered with adsorbed oxygen have lower surface energies than Pt(111) (Figure 7-2). These results may help guide the design of methods to develop shape controlled nanoparticles or
to better understand synthesis, growth, and stability of platinum nanoparticles in an aqueous environment. The relative surface energies dictate the thermodynamics for nanoparticle dissolution, growth, and surface restructuring. For example, the strong adsorption of hydrogen to Pt(100) surfaces has been proposed as the driving force behind the growth of truncated square cuboids and truncated octahedron Pt nanoparticles generated by reduction of dissolved Pt in an operating fuel cell\textsuperscript{109}.

Figures 7-3a and 7-b give the equilibrium nanoparticle shapes (Figure 7-3a) and relative surface area fractions (Figure 7-3b) derived by Wulff construction using the surface energies given in Figure 7-2. Significant changes in shape are seen between the bare nanoparticle surface and those in an aqueous electrolyte at varying potentials, with a greater 110 site fraction at all potentials. At low potentials, the strong binding of hydrogen to Pt(100) drives the formation of a more cubic nanoparticle, expressing a high ratio of 100 sites. At intermediate potentials, the fraction of 111 sites is maximized. At high potentials, the strong binding of hydroxide and water to Pt(110) drives the formation of a large fraction of 110 sites. Even small changes in the relative facet surface energies can result in significant changes in shape. For example, the decrease in surface energy of the Pt(110) and of the Pt(100) surface by $\sim 0.2 \text{ J/m}^2$ at 0.3 V\textsubscript{RHE} relative to the bare surface energies (in UHV) results in an increase of the 110 facet surface area fraction from 0% to 14% and of the 100 facet from 17% to 31% at this potential (relative to the bare surface shape).
Figure 7-3. a) Equilibrium nanoparticle shapes as given by Wulff constructions under the following conditions (from left to right): UHV environment, 0 V$_{RHE}$, 0.3 V$_{RHE}$, and 0.7 V$_{RHE}$. b) Fraction of total surface area of each facet (111, blue; 100, red; 110, green) of a platinum surface as a function of potential given by Wulff construction. For comparison, the UHV/bare surface energies give a Wulff construction that is 82.7% 111, 17.3% 100, and 0% 110.

The potential dependent surface energies and Wulff constructions may also help explain the changes in the shape of Pt nanoparticles and the restructuring of single or polycrystalline platinum electrodes observed on potential cycling, which typically show a growth of 110 and 100 step sites after cycling to potentials where dissolution and surface oxide formation are favorable. This cycling may be purposeful, to “condition” or “activate” the surface, where the electrode is cycled from low potential to high potential over many cycles, until reproducible cyclic voltammograms or electrocatalytic activity is obtained$^{110-114}$. This procedure also helps to oxidize organic contaminants that may be present on the surface of the electrode. Cycling may also be an undesired consequence of other experimental conditions, for example during start up and shut down of an operating fuel cell. Cycling has a significant effect on the measured cyclic
voltammograms, which change in size and shape in the low potential (0-0.5 \text{ V}_{\text{RHE}}) region\textsuperscript{110}.

The growth of step sites upon electrode cycling has seen significant study with single crystal Pt electrodes. Wakisaka et al. used in situ STM to observe changes in the surface structure of a Pt(111) single crystal electrode in 0.01 M HF and found that on reduction of a surface oxide, the surface became covered in islands and pits, increasing the number of step defects \textsuperscript{39}. Similar results were noted previously by Aberdam et al. with Pt(111) in both perchloric and sulfuric acid using a combined cyclic voltammetry, low energy electron diffraction (LEED), and auger electron spectrometry (AES) approach\textsuperscript{38}. Gómez-Marín et al.\textsuperscript{37} and Björling et al.\textsuperscript{45, 115} have performed extensive electrochemical measurements on single crystal Pt(111) and stepped Pt electrodes examining the kinetics of and anion effects on the disordering/restructuring of the electrode surface. Furuya and Shibata used cyclic voltammetry and STM to show the growth of steps and islands after cycling in a systematic study of many stepped platinum surfaces in both acid and alkaline electrolytes\textsuperscript{42}. Similar results are obtained with smooth polycrystalline electrodes, for which Shinozaki et al. found that cycling a polycrystalline platinum (or Pt/C) electrode to 1.4 \text{ V}_{\text{RHE}} (1.2 \text{ V}_{\text{RHE}}) (conditioning) increases the total surface area, changes the shape of the low potential region of the CV measured on the electrode, and results in improved ORR kinetics on the electrode\textsuperscript{110}.

These morphological changes in the surface structure of the single crystal or polycrystalline platinum electrodes under potential cycling can be explained by considering the DFT calculated surface energies shown in Figure 7-2. The formation of a surface oxide (thermodynamically favorable above \textasciitilde 0.8 \text{ V}_{\text{RHE}} on Pt(100) and Pt(110) and above 1.3 \text{ V}_{\text{RHE}} on Pt(111)) disorders the platinum surface. On reduction of this surface oxide, at potentials between 0.7 and 0.9 \text{ V}_{\text{RHE}}, the surface energy of Pt(100) with adsorbed oxygen is close to that of Pt(111) and the surface energy of Pt(110) with adsorbed hydroxide and water is lower than that of Pt(111). The lower surface energies of Pt(100) and Pt(110) creates a thermodynamic driving force
for, in particular, the growth of 110 facets upon reduction of this oxide (Figure 7-3b, at 0.7 V).
Alternatively, or in addition to oxide growth, surface platinum may dissolve (by oxidation) at high potentials and redeposit (by reduction) at low potentials. The surface energies can again predict what facets should grow during deposition; a less stable surface should be more prone to dissolution, and a more stable surface is more favorable to form upon reduction/deposition. Dissolution and deposition may be especially important for nanoparticle reconstruction, as dissolution is more favorable than for a flat surface (at similar potentials). While extended Pt(100) and Pt(110) terraces are examined here, the adsorption strength of hydrogen and hydroxide on these terraces are similar to that of 100 and 110 steps (on surfaces with 111 terraces)\textsuperscript{78}.

Beyond traditional cycling (with a symmetric triangular applied potential vs. time), more complex cycling techniques can be developed to give greater control over the reconstruction or growth of a particular facet/step site on a platinum electrode. Forming the surface oxide, then directly stepping to a lower potential (square wave) chosen to give a desired ratio of surface energies, could yield a desired surface faceting. For example, square wave potential cycling between high (above 1.2 V\textsubscript{RHE}) and low (typically between -0.2 and 0.2 V\textsubscript{RHE}) potentials restructured spherical nanoparticles into a tetrahexahedral shape\textsuperscript{33-34}. Tian et al. generated tetrahexahedral Pt NPs from spherical nanoparticles by square wave cycling in a sulfuric acid solution (containing a low concentration of ascorbic acid) from 1.2 V\textsubscript{RHE} to -0.1 to -0.2 V\textsubscript{RHE}\textsuperscript{33}. 100 terraces and steps (in particular the (730), (310), and (210) planes) grew on cycling. Figure 7-2 shows the lower surface energy of 100 sites at low potentials due to the strong high coverage adsorption of hydrogen to these sites. This lower surface energy (relative to the other facets) contributes to the selective growth of 100 sites at low potentials under these cycling conditions. Recent work from Hersbach et al. also highlights the selective formation of 100 type sites on holding a Pt wire at low potentials under cathodic corrosion/etching, though the mechanism is
different\textsuperscript{116}. Again, the formation of primarily 100 facets may be due to the strong binding of hydrogen to this surface at low potentials.

7.3.4. Experimental Polycrystalline Platinum Surface Restructuring

To compare our DFT results more directly with experiments, we experimentally cycled and restructured a polycrystalline platinum electrode in an alkaline electrolyte. This experiment allowed us to compare specific changes in the cyclic voltammogram to the potential dependent relative surface energies. Prior to conditioning, the electrode was cleaned\textsuperscript{114} by cycling for 10 cycles from 0.09 V\textsubscript{RHE} to 1 V\textsubscript{RHE}, 10 cycles to 1.2 V\textsubscript{RHE}, and 10 cycles to 1.3 V\textsubscript{RHE} (CVs shown in Figure S7-7). Figure 7-4 shows experimentally measured cyclic voltammograms during the “conditioning” of a polycrystalline platinum electrode in 0.1 M KOH. This conditioning was carried out by cycling for 100 cycles at 200 mV/s from 0.09 V\textsubscript{RHE} to 1.3 V\textsubscript{RHE}. On increasing the positive scan limit (and prolonged cycling at the highest positive 1.3 V\textsubscript{RHE} limit), there are three major changes to the measured cyclic voltammogram. The entire low potential region (0.09 V\textsubscript{RHE} to 0.6 V\textsubscript{RHE}) of the CV increases in total charge, the maximum current in the peaks corresponding to adsorption of H*/OH* on 110 steps (0.29 V\textsubscript{RHE}) and 100 steps (0.39 V\textsubscript{RHE}) grows significantly, and the total charge measured at high potentials increases. These changes are consistent with the growth in the total surface area of the electrode and with an increase in the relative area of the 110 and 100 facet or step sites. CVs were also measured after conditioning for 50 cycles at 100 mV/s from 0.09 V\textsubscript{RHE} to 1.05 V\textsubscript{RHE}. A representative CV (after conditioning) is shown in Figure S7-8 and compares well with that measured by Rheinländer et al. on polycrystalline platinum in NaOH\textsuperscript{117}. The changes in the cyclic voltammogram on conditioning the electrode are similar to those reported with polycrystalline Pt in an acidic electrolyte\textsuperscript{110}. 
Figure 7-4. Cyclic voltammograms measured at 200 mV/s during conditioning of a polycrystalline platinum electrode in argon saturated 0.1 M KOH. 100 cycles from -0.9 to 0.3V vs Ag/AgCl are shown, with the first (black) and last (red) highlighted. These cyclic voltammograms were measured after window opening cyclic voltammograms (shown in Figure S7-7).

The change in the low potential region of the CV can be quantified by deconvoluting the CV into contributions from hydrogen adsorption on 111-like terraces and hydrogen and hydroxide competitive adsorption on 110 steps/terraces and on 100 steps/terraces\textsuperscript{118}. The results of this deconvolution are shown in Figure 7-5, which plots the individual contributions to the total adsorption charge density (directly proportional to surface area) on the last cycle of each step in the conditioning protocol. On increasing the positive potential limit, the total active surface area grows, with a greater increase in the 110 and 100 step site contribution to the total surface area. The calculated surface area and relative fraction of step sites are intended only as an estimate of the relative growth in the number/fraction of these sites, as the deconvolution method used was only validated for surfaces comprised primarily of 111 terraces (with 110 or 100 steps).
Figure 7-5. Total site density (for 1 electron transferred per 111 site and 1.3 per 100 and per 110 site, µC/cm$_{geo}^2$, or nanomole Pt/cm$_{geo}^2$) of 111 terrace (blue), 110 step/terrace (grey), and 100 (orange) step/terrace sites calculated by deconvoluting the experimentally measured cyclic voltammograms shown in Figure S7-7. Also shown is the total site density calculated from a CV measured after 200 cycles from 0.1 to 1.3 V$_{RHE}$ (after electrode conditioning) (AC – 1.05V) and that calculated after an additional 50 cycles to 1.05 V$_{RHE}$ (50th).

The observed surface restructuring is similar to that reported for single crystal electrodes in acidic electrolyte solutions, where the number of 111 sites and to a lesser extent 100 sites grows upon cycling. As described in the previous section, this surface restructuring can be explained by considering the potential dependent surfaces energies at potentials where the surface oxide is reduced. The relative surface energies near potentials where this oxide is reduced (0.7 V$_{RHE}$ to 1 V$_{RHE}$) will dictate the facets formed on oxide reduction. The weakening of hydroxide and promotion of oxygen adsorption in an alkaline electrolyte relative to an acidic electrolyte (Figures S7-1, S7-2, and S7-3 relative to Figures 7-1a, b, and c calculated for an acidic electrolyte) has only a minor effect on the relative surface energies at the potentials of interest. The predicted relative site fractions calculated at each potential in both acid and base are given in Table S7-1 in the supplementary information (those in base are also plotted in Figure S7-9).
Figure S7-10 shows a positive correlation between a lower surface energy at 0.7 \( V_{RHE} \) and growth of a specific facet experimentally. While kinetics plays a role in dictating the degree of restructuring, the calculated driving force for reconstruction correlates with the degree of measured restructuring upon cycling.

The lower surface energy of 110 and 100 at potentials above 0.7 \( V_{RHE} \) drives the formation of these facets or step sites on reduction of surface oxide, supporting the observation of their growth on repetitive cycling through the surface oxide formation region. Fewer structural changes are observed on cycling to potentials below that where a surface oxide is formed or where dissolution occurs, even though this thermodynamic driving force still exists (cycling to ~ 0.8 \( V_{RHE} \) or below). The lack of significant structural changes within this potential region may be due to a kinetic limitation in the restructuring of the ordered facets, which may be lowered after surface oxide formation.

Surface atom dissolution/deposition may also affect the faceting of an extended surface. The rate of dissolution or deposition on both nanoparticles and extended surfaces may be surface structure dependent as the activation barrier for dissolution might be expected to correlate with surface energy, where a more stable surface would be expected to give a higher barrier to dissolution.

### 7.4. Conclusions

Density functional theory (DFT) was used to calculate the surface energy of Pt(111), Pt(100), and Pt(110) in an aqueous environment as a function of electrode potential, under conditions where hydrogen, hydroxide, and oxygen can adsorb. The favorable adsorption of hydrogen at low potentials and of hydroxide and oxygen at high potentials reduces the surface energy below that of the bare surfaces. While the Pt(111) surface is the most stable
(thermodynamically favorable) low index platinum facet when all three surfaces are bare, the strong adsorption of hydrogen and hydroxide to Pt(100) and Pt(110) drives these surfaces to be more stable than Pt(111) at low potentials (hydrogen adsorbed) and high potentials (hydroxide and oxygen adsorbed). Experimental measurements show that cycling a polycrystalline platinum electrode through increasingly positive potentials (where surface oxide formation is favorable) grows the relative proportion of these (Pt(110) and Pt(100)) step sites. While kinetics of surface oxidation and reduction may certainly play a role in surface area growth and electrode restructuring, our thermodynamic analysis may explain the driving force behind the growth of these 110 and 100 sites upon surface oxide/dissolved Pt ion reduction (where hydroxide covered Pt(110) and oxygen covered Pt(100) are more favorable than hydroxide covered Pt(111)). Similarly, the strong binding of hydrogen at low potentials to Pt(100) provides a driving force for the growth of 100 sites on oxide/Pt ion reduction at low potentials during square wave cycling.

These results highlight the importance of considering the catalyst environment and the adsorption of reactive or spectator species when determining the stability of a catalyst surface. Further, understanding the surface energy of platinum as a function of potential may be useful in designing or improving aqueous platinum nanoparticle synthesis or restructuring/shape control techniques.

7.5. Acknowledgements

I.T. McCrum gratefully acknowledges support from The Pennsylvania State University Diefenderfer Graduate Fellowship and the National Science Foundation NRT #1449785. This work used the Extreme Science and Engineering Discovery Environment (XSEDE), supported by National Science Foundation grant number ACI – 1053575.
7.6. References


93. Garcia-Araez, N.; Climent, V.; Feliu, J. M. Analysis of Temperature Effects on Hydrogen and OH Adsorption on Pt(1 1 1), Pt(1 0 0) and Pt(1 1 0) by Means of Gibbs Thermodynamics. J. Electroanal. Chem. 2010, 649, 69-82.
96. Gómez, R.; Climent, V.; Feliu, J. M.; Weaver, M. J. Dependence of the Potential of Zero Charge of Stepped Platinum (111) Electrodes on the Oriented Step-Edge Density:


114. Conway, B. E.; Angerstein-Kozlowska, H.; Sharp, W. B. A.; Criddle, E. E.
   Ultrapurification of Water for Electrochemical and Surface Chemical Work by Catalytic
115. Björling, A.; Ahlberg, E.; Feliu, J. M. Kinetics of Surface Modification Induced by
116. Hersbach, T. J. P.; Yanson, A. I.; Koper, M. T. M. Anisotropic Etching of Platinum
   Oxidation/Evolution Reaction on Polycrystalline Platinum in Alkaline Electrolyte Reaction
118. McCrum, I. T.; Janik, M. J. Deconvoluting Cyclic Voltammograms to Accurately
7.7. Supplementary Information

Figure S7-1. Pt(111) surface energy as a function of potential and coverage of adsorbed hydrogen, hydroxide and water, and oxygen in an alkaline electrolyte (in the presence of near-surface K*). Bold labels and vertical lines define regions of stability for the different adsorbates. At low potentials, hydrogen coverage increases with decreasing potential. At high potentials, adsorbed oxygen species coverage increases with increasing potential.

Figure S7-2. Pt(100) surface energy as a function of potential and coverage of adsorbed hydrogen, hydroxide and water, and oxygen in an alkaline electrolyte (in the presence of near-surface K*). Bold labels and vertical lines define regions of stability for the different adsorbates. At low potentials, hydrogen coverage increases with decreasing potential. At high potentials, adsorbed oxygen species coverage increases with increasing potential.
Figure S7-3. Pt(110) surface energy as a function of potential and coverage of adsorbed hydrogen, hydroxide and water, and oxygen in an alkaline electrolyte (in the presence of near-surface K⁺). Bold labels and vertical lines define regions of stability for the different adsorbates. At low potentials, hydrogen coverage increases with decreasing potential. At high potentials, adsorbed oxygen species coverage increases with increasing potential.

Figure S7-4. Pt(111) surface energy as a function of potential and hydroxide and water, oxygen, and platinum surface oxide coverage (identical to Figure 7-1 in main paper but showing only the high potential region and including formation of a surface oxide).
Figure S7-5. Pt(100) surface energy as a function of potential and hydroxide and water, oxygen, and platinum surface oxide coverage (identical to Figure 7-2 in main paper but showing only the high potential region and including formation of a surface oxide).

Figure S7-6. Pt(110) surface energy as a function of potential and hydroxide and water, oxygen, and platinum surface oxide coverage (identical to Figure 7-3 in main paper but showing only the high potential region and including formation of a surface oxide).
Figure S7-7. Cyclic voltammograms measured at 100 mV/s on polycrystalline Pt in argon saturated 0.1 M KOH. 10 cycles to a positive potential limit of 0V, 10 cycles to 0.2V, and 10 cycles to 0.3V vs Ag/AgCl are shown.

Figure S7-8. Representative steady state cyclic voltammogram measured after electrode conditioning. The cyclic voltammogram was measured on a Pt(pc) electrode at 100 mV/s in 0.1 M KOH.
Table S7-1. Fraction of 111, 100, and 110 surface sites calculated by Wulff construction as a function of potential in a non-adsorbing acid electrolyte and in an alkaline electrolyte containing potassium cations. The surface fractions calculated in an alkaline electrolyte only consider the effect of potassium on hydroxide adsorption (as the effect on hydrogen adsorption is small). Fraction of sites also shown for bare nanoparticle surfaces (in UHV).

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base (K*)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Potential (V&lt;sub&gt;RHE&lt;/sub&gt;)</strong></td>
<td>111</td>
</tr>
<tr>
<td>0.0</td>
<td>0.247</td>
</tr>
<tr>
<td>0.1</td>
<td>0.281</td>
</tr>
<tr>
<td>0.2</td>
<td>0.382</td>
</tr>
<tr>
<td>0.3</td>
<td>0.549</td>
</tr>
<tr>
<td>0.4</td>
<td>0.466</td>
</tr>
<tr>
<td>0.5</td>
<td>0.325</td>
</tr>
<tr>
<td>0.6</td>
<td>0.229</td>
</tr>
<tr>
<td>0.7</td>
<td>0.238</td>
</tr>
<tr>
<td>Bare (UHV)</td>
<td>0.827</td>
</tr>
</tbody>
</table>

Figure S7-9. Fraction of 111 (blue), 100 (red), and 110 (green) surface sites calculated by Wulff construction from the potential dependent surface energies in an alkaline electrolyte (including the effect of an alkali cation, potassium, on hydroxide adsorption, shown in Figures S7-1, S7-2, and S7-3). The presence of a near surface cation weakens hydroxide adsorption, which yields a wider potential range over which bare Pt(111) is stable and increases the surface energy of Pt(100) and Pt(110) at high potentials. This results in a greater fraction of 111 sites at potentials equal to and greater than 0.4V<sub>RHE</sub>, relative to those calculated in an acid electrolyte (Figure 7-3b).
Figure S7-10. Ratio of the surface site density (SA) after conditioning to that measured before conditioning plotted against the ratio of the bare surface energies (SE) to that of the surface energies calculated at 0.7 \( V_{\text{RHE}} \) in the presence of a near-surface potassium cation. The x-axis represents a thermodynamic driving force for reconstruction calculated using DFT and the y-axis the experimentally measured extent of reconstruction.

Figure S7-11. Pt(111) 1/3 ML OH* + 1/3 ML H\(_2\)O* + 1/9 ML K*
Figure S7-12. Pt(111) 1/3 ML O$^*$ + 1/9 ML K$^*$

Figure S7-13. Pt(100) 1/3 ML OH$^*$ + 1/3 ML H$_2$O$^*$ + 1/9 ML K$^*$

Figure S7-14. Pt(110) 1/2 ML OH$^*$ + 1/2 ML H$_2$O$^*$ + 1/4 ML K$^*$
Figure S7-15. Pt(110) 1/2 ML O* + 1/4 ML K*

Figure S7-16. Pt(111) 1ML PtO₂*, top view (left) and side view (right).
Figure S7-17. Pt(100) 1 ML PtO\(^*\), top view (left) and side view (right).

Figure S7-18. Pt(110) 1 ML PtO\(_2\)\(^*\) (0.5 ML Pt\(_2\)O\(_4\)\(^*\)), top view (left) and side view (right).
Chapter 8

Quaternary Ammonium Specific Adsorption on Platinum Electrodes: A Combined Experimental and Density Functional Theory Study

Abstract

Quaternary ammonium cations are commonly used to provide ionic conductivity in anion conducting polymer ionomers and membranes for use in electrochemical systems. While significant study has been devoted to their alkaline stability and to improving hydroxide anion conductivity, there are limited studies on the electrode/polymer interface. We use density functional theory as well as experiment to examine the adsorption of tetramethyl-, tetraethyl-, tetrapropyl-, and benzyltrimethyl-ammonium cations to platinum electrode surfaces. Using DFT we find that adsorption of these cations to Pt(111), Pt(100), and Pt(110) is favorable at low potentials in an alkaline electrolyte and that van der Waals interactions contribute significantly to adsorption. The strong van der Waals attraction drives adsorption to be more favorable with increasing alkyl chain length. Near-surface solvation weakens the adsorption of the long alkyl chain cations, and promotes the adsorption of the shorter chain cations, suggesting adsorption of these cations may be possible at low potentials even in acidic electrolytes. We further find that the cations retain most of their charge on adsorption, which contributes to repulsive interactions between adsorbates. Steric hindrance further contributes to a strong coverage dependence, with only low coverage adsorption (~1/9-1/4 monolayer) stable within the electrochemical window of an aqueous electrolyte. Our experimental results show that all of the quaternary ammonium cations examined blocked surface sites, hindering the adsorption of hydrogen and hydroxide. This matches our DFT results, showing these organic cations favorably adsorb at low potentials in
alkaline electrolytes, even though significant electron transfer to the organic cations is not seen experimentally.

8.1. Introduction

Hydrogen fuel cells directly convert the chemical energy stored in hydrogen into electrical energy. While the traditional proton exchange membrane (PEM) fuel cell gives great performance, with high efficiency and power density, its high cost has limited its use\textsuperscript{1-3}. This has motivated the development of potentially lower cost alkaline exchange membrane (AEM) fuel cells\textsuperscript{4-7}. However, the commercialization of these AEM fuel cells has been hindered by the typically lower overall ionic conductivity of hydroxide conducting membranes\textsuperscript{4-5, 8-9} and their poor stability\textsuperscript{4-5, 8}. Recent research has been focused on improving both conductivity and stability\textsuperscript{10-16}, but little is known about the interaction between the hydroxide conducting membrane/ionomers and catalyst electrode surfaces, which may affect both the fuel cell performance and operating lifetime. To understand the mechanism and magnitude of the interaction between the organic cation component of the ionomer and the electrode surface, we use both experiment and density functional theory to examine the specific adsorption of quaternary ammonium cations to platinum electrodes.

Quaternary ammonium cations have commonly been used to impart anionic conductivity to polymer backbones, forming polymer alkaline/hydroxide conducting membranes (AEM, alkaline exchange membranes)\textsuperscript{5, 8, 11}. Significant effort has been put into studying their typically poor stability in alkaline solutions, both experimentally\textsuperscript{17-24} and computationally\textsuperscript{25-28}. Little work has been performed identifying their structure and stability near the electrode/electrolyte interface, and how that may affect electrocatalytic reactions such as hydrogen oxidation and oxygen reduction. Ünlü et al. investigated the electrode/electrolyte interface (in both an operating
AEM fuel cell and aqueous liquid electrolyte) and found that quaternary ammonium cations specifically adsorb to platinum electrodes and can lower the rate of methanol oxidation. Xu et al. suggested from cyclic voltammetry that cetyltrimethylammonium cations irreversibly adsorb to Pt(100) in acidic electrolytes. Ong et al. found that quaternary ammonium cations at 1 mM in an alkaline electrolyte blocked adsorption of hydrogen onto platinum at low potentials and reduced the rate of the oxygen reduction reaction (relative to a pure potassium hydroxide electrolyte) on polycrystalline Pt and Pt/C electrodes. Yim et al. showed the rate of hydrogen oxidation is significantly limited in the presence of tetramethyl- and benzyltrimethyl- ammonium, when in solution or bound in an ionomer. Chung et al. showed similar results, with additional spectroscopic data to suggest these cations can adsorb onto the surface, and inhibit hydrogen diffusion to/near the electrode surface. These experimental results suggest many organic cations can block ion (hydrogen and hydroxide) adsorption at low potentials, interact with surface bound adsorbates, and effect various electrocatalytic reactions on platinum electrodes, but atomic scale detail of quaternary ammonium adsorption is not available.

Ab-initio computational modeling, such as density functional theory (DFT), can examine organic cations at the electrode/electrolyte interface, and determine if and under what conditions these cations will specifically adsorb to electrode surfaces. While DFT has been used to study the adsorption of some organic cations, including imidazolium and pyridinium, to metal surfaces, it has seen limited use in modeling the adsorption of quaternary ammonium cations. Chung et al. used DFT to calculate the adsorption energetics of quaternary ammonium cations onto platinum surfaces, but did not solvate the solution phase cation or examine the effects of solvation near the
electrode surface (giving a binding energy instead of an adsorption free energy)\textsuperscript{35}. We have previously examined alkali cation specific adsorption onto Pt(111)\textsuperscript{39}, Pt(100) and Pt(110)\textsuperscript{40} as well as the effect of adsorbed/near surface alkali cations on the adsorption of hydrogen and hydroxide onto the low index\textsuperscript{40} as well as stepped\textsuperscript{41} platinum surfaces.

The effect of near surface solvation is important to consider when modeling the electrode/electrolyte interface, but is difficult to capture using DFT due to the long length and time scales of water motion and hydrogen bonding and the computational intensity of DFT. Many methods have been developed to approximate the effects of near-surface solvation, including implicit continuum solvation models \textsuperscript{42-51}, and explicit solvent models \textsuperscript{52-58} with explicit water molecules added near the electrode surface. Each method has its own benefits and limitations. The use of a continuum solvent model requires knowledge of the solvent dielectric constant near the electrode surface, which may differ from the bulk constant. Explicit methods require reasonable sampling of solvent structures near the electrode surface. To approximate the effects of surface solvation, we place a small number of static, explicit water molecules near the surface adsorbate (micro-solvation) and approximate the change in entropy between the solvated bare surface and the solvated adsorbate covered surface to be minor. Prior work with alkali cation specific adsorption showed that a small number of water molecules (5-6 H\textsubscript{2}O) placed near the surface adsorbate gave similar adsorption energetics as fully solvating the region above the surface with an ice-like water structure\textsuperscript{39}. This method is computationally tractable, but gives only an approximation to the effect of near surface solvation.

Using DFT (with dispersion corrections, DFT-D\textsuperscript{2} \textsuperscript{59-61}), we find that it is favorable for ammonium and quaternary ammonium cations to specifically adsorb to Pt(111), Pt(100), and Pt(110) to low coverages (1/9 ML) at low potentials (near 0 V\textsubscript{RHE}). We examine the effect of alkyl chain length, solvation, and coverage on the favorability of adsorption. Our experimental results support adsorption of these quaternary ammonium cations and their competition with or
blocking of hydrogen and hydroxide adsorption on platinum electrode surface sites. These results are important for the design of high performance alkaline fuel cells, which require stable organic cations which do not block active sites or hinder electrocatalytic reactions.

8.2. Methods

8.2.1. Computational Details

Density functional theory was used to examine the adsorption of ammonium, tetramethyl-, tetraethyl-, tetrapropyl-, and benzyltrimethyl- ammonium cations on to Pt(111), Pt(100), and Pt(110). Electronic structure calculations were performed using the Vienna ab initio Simulation Package (VASP)\textsuperscript{62-64}. A plane wave basis set was used, with the projector augmented wave (PAW) approach used to model the core potentials\textsuperscript{65-66}. The basis set cut off energy was 450 eV. Exchange and correlation were described with the PBE functional\textsuperscript{67-68}. Dispersion corrections were performed using the DFT-D2 method\textsuperscript{59}. The dispersion coefficient and van der Waals radius used for Pt were those calculated by Ramos-Sanchez and Balbuena (C\textsubscript{6} = 42.44 nm\textsuperscript{6} and R\textsubscript{0} = 1.75 Å, respectively)\textsuperscript{61}. Structural optimization was performed until the forces on atoms were less than 0.02 eVÅ\textsuperscript{-1}.

The Pt surfaces were represented with a 4 layer slab, the bottom two layers frozen at the experimental lattice constant, 3.92 Å\textsuperscript{69}. Dipole corrections were included in the surface normal direction. Adsorbate coverages of 1/16 ML, 1/9 ML, 1/6 ML, and 1/4 ML were modeled in 4x4, 3x3, 3x2, and 2x2 unit cells, respectively. Coverage is defined as the number of ammonium adsorbates per surface Pt atom. A 5x5x1 Monkhorst-Pack mesh\textsuperscript{70} was used to sample k-space for the 4x4, 3x3, and 3x2 unit cells and a 7x7x1 mesh was used for the 2x2 unit cell.

Images of the adsorbate structures were rendered using VESTA\textsuperscript{71}.
8.2.2. Calculating Adsorption potentials

The method for calculating cation equilibrium adsorption potentials has been described previously\textsuperscript{39}, and is detailed in full here. Equilibrium adsorption potentials are calculated following the reaction described in equation 1:

\[ QA^+_{(aq)} + e^- + * \rightarrow QA^* \]  \[1\]

where \( QA^+_{(aq)} \) is an aqueous phase cation, \( e^- \) an electron, \( * \) is a bare surface site, and \( QA^* \) is the adsorbed quaternary ammonium. The Gibbs free energy for adsorption is calculated with equation 2:

\[ \Delta G_{ads}(U_{abs}) = G_{QA^*} - G_{QA^+_{(aq)}} + |e^-|U_{abs} - G_* \]  \[2\]

where \( G_{QA^*} \) is the free energy of the quaternary ammonium species adsorbed on the surface, \( G_{QA^+_{(aq)}} \) is the free energy of the aqueous phase cation, \( G_* \) is the free energy of the bare surface, and \( |e^-|U_{abs} \) is the energy of the electron at a potential relative to an absolute (vacuum) electrode.

The free energy of the adsorbed state is calculated using the DFT calculated energy and the vibrational energy and entropy of the surface-adsorbate. It is assumed that the phonon modes of the surface are relatively unperturbed by adsorption (such that the difference in surface vibrational energy/entropy between the reactant and product states is negligible). The bare surface free energy and adsorbed state free energy are calculated as shown in equations 3 and 4.

\[ G_* = E^{DFT}_* \]  \[3\]

\[ G_{QA^*} = E^{DFT}_{QA^*} + ZPVE + U_{int,vib} - TS_{vib} \]  \[4\]

In equation 3 \( E^{DFT}_* \) is the DFT calculated energy of the bare surface. In equation 4, \( E^{DFT}_{QA^*} \) is the DFT calculated energy of the adsorbed state, \( ZPVE \) the zero point vibrational energy, \( U_{int,vib} \) the vibrational energy at the temperature of interest, and \( TS_{vib} \) the product of temperature...
and the vibrational entropy.

The free energy of the aqueous phase cation is calculated by calculating the free energy of the cation in the gas phase (including all gas phase energy/entropy contributions) and then correcting this to the aqueous phase by using the solvation free energy calculated using the COSMO\textsuperscript{72} continuum solvation model in DMol3\textsuperscript{73}. Equation 5 gives the free energy of the aqueous phase cation:

\[
G_{QA}^{\text{aq}} = E_{QA}^{\text{FT}} + ZPVE + U_{\text{int}} - TS_{\text{gas}} + G_{\text{solv}} + pV
\]  \[5\]

where \(S_{\text{gas}}\) is the gas phase entropy of the cation including translational, rotational, and vibrational entropy, \(U_{\text{int}}\) the translational, rotational, and vibrational energy, \(G_{\text{solv}}\) is the solvation free energy, and \(pV\) is the pressure-volume contribution to the free energy. To calculate the adsorption potential, the potential dependent free energy of adsorption is solved for the potential that gives a free energy change equal to zero. This yields equation 6:

\[
U_{\text{abs}} = \frac{G_{QA} - G_{QA}^{\text{aq}} - G_{\ast}}{-|e^{|}}.
\]  \[6\]

To convert to the normal/standard hydrogen electrode potential scale (NHE, SHE), the potential of the standard hydrogen electrode reaction on an absolute scale (4.6 V was used here, but estimates vary from 4.4-4.8 V\textsuperscript{74-76}) is added to the absolute potential. To account for the effect of the interaction of the near surface electric field with the surface normal dipole moment, an additional term is added, as shown in equation 7:

\[
U_{\text{abs}} = \frac{G_{QA} - G_{QA}^{\text{aq}} - G_{\ast} - |e^-|4.6}{-|e^-| - |e^-| \left(\frac{\mu_{QA} - \mu_{\ast}}{d}\right)}.
\]  \[7\]

where \(\mu_{QA}\) is the surface normal dipole moment of the adsorbed state, \(\mu_{\ast}\) is the dipole moment of the bare surface, and \(d\) is the thickness of the double layer, taken to be 5Å\textsuperscript{77}.

Unless otherwise noted, all free energies are calculated at T=300K and a pressure of 1 bar.
8.2.3. Surface Solvation

To consider the effects of solvent near the electrode surface, equilibrium adsorption potentials were calculated with both the bare surface and the adsorbed product state solvated with a varying number of explicit water molecules (1-6 H$_2$O) placed near the surface adsorbate bond. These potentials were calculated for adsorption on the Pt(111) surface, but this method can be applied to any surface. We have previously used this method to examine the specific adsorption of alkali metal cations$^{39}$ and halide anions$^{78}$ to metal surfaces. While only a few water structures are considered (and DFT is not guaranteed to find the global minimum energy water structure), we previously noted when modeling the solvation of adsorbed alkali metal cations that the adsorption potential calculated using a small number of water molecules converged to that calculated with a much larger number optimized in the minimum energy ice-like structure (on Pt(111)) beyond about 5-6 water molecules$^{39}$. For the potentials calculated with 6 water molecules, the reactant state is the minimum energy water bilayer. Further, we consider only the change in vibrational entropy/energy and assume the change in translational, rotational, or configurational entropy is small between the bare surface and adsorbed ($G_{Q,A^+}$) states. This approach represents a computationally tractable way to estimate the effects of near-surface solvation on the adsorption of ionic species.

8.2.4. Experimental details

Cyclic voltammograms (CVs) were measured in 0.1 M tetramethyl-, tetraethyl-, and benzyltrimethyl- ammonium hydroxide, as well as in 0.1 M KOH on a polycrystalline platinum disk (0.5 cm diameter) electrode. A three electrode cell was used, with a Ag/AgCl reference electrode and platinum wire counter electrode. The platinum disk working electrode was polished
with 0.05 μm alumina slurry before use in each electrolyte. CVs were measured at scan rates of 25 mV/s, 50 mV/s, and 100 mV/s between -0.9 and 0.3 V vs Ag/AgCl (only those measured at 100 mV/s are shown) in argon saturated electrolytes. Potentials were corrected to the reversible hydrogen electrode scale (RHE) for a solution pH = 13 and a Ag/AgCl potential of 0.222 V_{NHE}^{79}.

8.3. Results

8.3.1. Adsorption at Low Coverage

Figure 8-1 shows the equilibrium adsorption potential for the low coverage (1/9 ML) adsorption of ammonium, tetramethylammonium, tetraethylammonium, tetrapropylammonium, and benzyltrimethylammonium cations on Pt(111), Pt(100), and Pt(110) surfaces. Adsorption of these cations is more favorable at any potential more negative of the equilibrium adsorption potential (as cation adsorption is a reduction reaction). The adsorption potentials of these cations on Pt(111) calculated without van der Waals correction are given in the supplementary information (Figure S8-1). van der Waals forces drive a strong interaction between quaternary ammonium cations and platinum surfaces, which increase with increasing alkyl chain length. Without van der Waals interactions, the cations all show similar, weak adsorption that is independent of alkyl chain length. There is little effect of the van der Waals contribution on the adsorption favorability of the ammonium ion.
Figure 8-1. Equilibrium adsorption potentials of ammonium, tetramethyl-, tetraethyl-, tetrapropyl-, and benzyltrimethyl- ammonium at 1/9 ML on Pt(111), Pt(100), and Pt(110). Potentials are calculated at a cation concentration of 1M and a temperature of 300K. van der Waals corrections are included. *The adsorption potential for benzyltrimethylammonium on Pt(110) is 1.75 V\textsubscript{NHE}.

With the exception of benzyltrimethylammonium, there is not a significant difference in the adsorption favorability across the three low index platinum surfaces (Figure 8-1). In general, the quaternary ammonium cations absorb more favorably on Pt(100) and Pt(110) surfaces, though this trend is less clear with the larger tetraethyl- and tetrapropyl-ammonium cations. Adsorption of benzyltrimethylammonium is significantly more favorable (by ~2.5 eV) on Pt(110) than on Pt(111) or Pt(100). Images of adsorbed benzyltrimethylammonium on all three low index Pt facets are shown in Figure S8-2. The trimethylammonium group prevents the ring from sitting flat/parallel with the surface on Pt(111) and Pt(100), where it remains tilted. At 1/9 ML coverage, the more open and corrugated Pt(110) surface allows the aromatic ring in benzyltrimethylammonium to sit flat on the surface, giving much stronger adsorption than on Pt(111) and Pt(100). The strong interaction between the benzyl group and the surface also contributes to a significant thermodynamic driving force for benzyltrimethylammonium to decompose. On Pt(100), a flat adsorbed benzyl and adsorbed trimethylamine are more stable by ~2.6 eV than the tilted, adsorbed benzyltrimethylammonium. The presence of ions and solvent
near the electrode surface may affect the preferred orientation of the benzyl group (parallel vs. perpendicular to the electrode surface), but this was not considered. Table S8-1 gives the difference in adsorption energy for benzyltrimethylammonium on the three surfaces for parallel vs. perpendicular benzyl group adsorption.

Given the results in Figure 8-1, we would expect all of the quaternary ammonium (as well as ammonium) cations investigated here to specifically adsorb to any platinum electrode surface to low coverages near the equilibrium potential for hydrogen evolution/oxidation in an alkaline electrolyte, \(-0.826 \text{ V}_{\text{NHE}}\). This suggests they could compete with hydrogen adsorption on Pt(111) and competitive hydrogen and hydroxide adsorption on Pt(100) and Pt(110)\(^{40}\). Their presence on the electrode surface under these conditions could also affect the rate of electrocatalytic reactions occurring at low potentials, such as hydrogen oxidation and hydrogen evolution, in an alkaline electrolyte.

**8.3.2. Effect of Near Surface Solvation**

Figure 8-2 illustrates the effect of near surface solvation on the adsorption of quaternary ammonium cations on Pt(111) at 1/9 ML coverage. Adsorption of sodium is also shown for comparison\(^{39}\). A small number of explicit water molecules (1-6 H\(_2\)O molecules) are added near the surface-adsorbate. Our prior work with the alkali metal cations showed that the adsorption potential had converged after about 5-6 water molecules, and that this adsorption potential matched that calculated using the double reference method where the entire surface region is filled with 24 H\(_2\)O molecules in an ice-like minimum energy structure at an appropriate density\(^{39}\).
Figure 8-2. Equilibrium adsorption potential of ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium at 1/9 ML on Pt(111) without and with six water molecules added near the surface adsorbate. van der Waals corrections are included. Adsorption of sodium is also shown for comparison, from Mills et al. (without vDW corrections)\textsuperscript{39}.

An interesting trend is observed in the effect of solvation with increasing quaternary ammonium alkyl chain length, shown in Figure 8-2. For small cations (ammonium and tetramethylammonium) surface solvation promotes adsorption, whereas for larger cations surface solvation weakens adsorption. This is a result of two competing effects. The first is water promoting adsorption due to strong interaction with the partially charged cation. Similar to the alkali metal cations\textsuperscript{39}, the organic cations retain some of their charge on adsorption. The surface normal dipole moments are given in Table S8-2 of the supplementary information. The presence of water near the surface acts to screen and stabilize this charge, creating an attractive interaction relative to adsorption in vacuum, promoting adsorption. A competing effect is the cation disruption of the water-water hydrogen bonding. As the cations become larger, the hydrophobic alkyl chains interrupt hydrogen bonding between neighboring water molecules. The alkyl chains also block the water molecules access to the locally charged nitrogen atom. The larger cations delocalize the positive charge somewhat, weakening its interactions with water. Larger cations
also decrease the favorable interaction of the near surface water with the platinum surface, as the water molecules are hydrogen bonded and bound/adsorbed to the surface in the reactant state in the absence of the adsorbed cation. The disruption of hydrogen bonding and blocking of the interaction of water with the surface (by the adsorbed cation) may explain why the adsorption potential continues to decrease with an increasing number of water molecules (and doesn’t seem to converge) for the larger alkyl chain cations (Figure S8-3). This highlights a limitation in using a microsolvation model with a small number of explicit water molecules. A significantly larger number of water molecules may be needed to accurately capture the magnitude of the effect of near surface solvation on the adsorption of the larger quaternary ammonium cations. Aside from this limitation, Figure 8-2 does suggest that tetaethyl- and tetrapropyl- ammonium adsorption may be weaker than that shown in Figure 8-1 (calculated without surface solvation).

The promotion of the adsorption of ammonium and the smaller quaternary ammonium cations by near surface water suggests that these cations may be adsorbed to a low coverage near 0 V\text{RHE} even under acidic conditions (near 0 V\text{NHE}). Given the limitations in capturing the effects of near surface solvation using a small number of static, explicit water molecules, we would not expect the calculated adsorption potentials to be exact, but could be within ± 0.5 eV of the true adsorption potential, with the potential calculated referencing the water bilayer (6 H\text{2O}) representing an under-estimate (weaker adsorption) of the true adsorption potential.

### 8.3.3. Coverage Dependence of Adsorption

Figures 8-3, 8-4, and 8-5 give the adsorption potential for the quaternary ammonium cations as a function of coverage on Pt(111), Pt(100), and Pt(110), respectively (without surface solvation). Coverage here is defined as the number of nitrogen atoms (or number of ammonium adsorbates) per platinum atom. Higher coverages of the longer alkyl chain cations (above ~1/9
ML) were not examined, as the alkyl chains showed strong van der Waals interaction with the surface, blocking available surface sites and crowding the surface. In general, the adsorption favorability decreases with increasing coverage. This is most likely due to both a coulombic repulsion (as the cations retain some of their positive charge) and a steric repulsion between the alkyl chains with increasing coverage. Highlighting the role of the stearic repulsion is the fact that the coverage dependence is larger (more negative slope) with increasing length of the alkyl chain (following the trend ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium). Given that the repulsive interactions at these coverages for adsorbed ammonium are relatively small, steric repulsion between the alkyl chains dominates the interaction between larger adsorbates.

Due to the strong repulsive interactions between the adsorbates, it seems un-likely that any quaternary ammonium cation would be adsorbed above ~ 0.25 ML within the electrochemical window of water (at any pH). Higher coverages may be reached at significantly more negative potentials (well below -1 V_{NHE}). While the number of adsorbates (or nitrogen atoms) per platinum atom may be limited to less than 0.25 ML, the strong van der Waals attraction between the alkyl chain and the surface may allow an adsorbed quaternary ammonium cation to block multiple surface sites, with the number of blocked sites increasing with increasing length of the alkyl chain.

![Figure 8-3. Equilibrium adsorption potentials for ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium on Pt(111) as a function of cation coverage. van der Waal corrections are included.](image-url)
Figure 8-4. Equilibrium adsorption potentials for ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium on Pt(100) as a function of cation coverage. van der Waal corrections are included.

Figure 8-5. Equilibrium adsorption potentials for ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium on Pt(110) as a function of cation coverage. van der Waal corrections are included.

8.3.4. Experimentally Measured Cyclic Voltammograms in Aqueous Alkaline Quaternary Ammonium Solutions on Pt(pc)

Figure 8-6 shows cyclic voltammograms (CV) measured in 0.1 M KOH and in 0.1 M tetramethyl-, tetraethyl-, and benzyltrimethyl- ammonium hydroxide on a polycrystalline platinum electrode (measured at a scan rate of 100 mV/s). The CVs measured in all but the benzyltrimethylammonium electrolyte show sharp peaks in current near -0.68 V and -0.56 V vs
Ag/AgCl (0.31 V_{RHE} and 0.43 V_{RHE}), corresponding to competitive hydrogen and hydroxide adsorption on 110 and 100 sites\textsuperscript{40-41, 80-82}. A broad peak from the lower potential limit to ~ 0.4 V_{RHE} corresponds to hydrogen adsorption on 111 terraces, and some contribution from hydrogen and hydroxide adsorption on 110 and 100 terraces\textsuperscript{83}). A sharp reduction peak at the low potential CV limit is due to hydrogen evolution. The broad and complex high potential region corresponds to the adsorption/desorption of hydroxide and oxygen on 111-like terraces and oxygen on the steps, as well as surface oxide formation beyond ~0.9-1.0 V_{RHE} (Chapter 7). Each of these features undergo changes in the quaternary ammonium alkaline electrolytes, relative to the potassium hydroxide electrolyte.

There are two significant changes to the CV that are observed in quaternary ammonium hydroxide electrolytes. At low potentials (0 – 0.6 V_{RHE}), the total charge transferred decreases relative to the CV measured in the potassium hydroxide solution, further decreasing with increasing alkyl chain length or addition of a benzyl group. At higher potentials, there is a decrease in the peak measured near 0.85 V_{RHE} in the positive going scan and there is an increase in the oxidative current at the highest potentials. A similar increase is not seen at the same potentials on the reductive current, suggesting the high potential oxidative process is irreversible.
Figure 8-6. Cyclic voltammmograms measured on Pt(pc) in 0.1 M KOH (red), 0.1 M tetramethylammonium hydroxide (TMAOH, blue), 0.1 M tetraethylammonium hydroxide (TEAOH, green), and 0.1 M benzyltrimethylammonium hydroxide (BTMAOH, teal) at 100 mV/s.

Considering first the effects of the quaternary ammonium cations on the low potential region of the CV, the decrease in the total charge transferred in this region is consistent with the specific adsorption of these quaternary ammonium cations and their subsequent blocking of platinum sites. The total charge transferred in this region decreases with increasing alkyl chain length. These effects match those predicted by our DFT results, which show adsorption of all of these quaternary ammonium cations is favorable at low potentials in a high pH electrolyte. Further, while the DFT simulations suggest the adsorption favorability of these cations are similar, the strong van der Waals interactions between the alkyl chains and the electrode surface cause the larger cations (with longer alkyl chains) to block more surface sites, matching the experimentally measured trend.

Further support for quaternary ammonium cation specific adsorption can be derived from spectroscopic measurements. Recent work from Chung et al. used in situ infrared reflection
absorption spectroscopy (IRRAS) on a platinum electrode in aqueous tetramethylammonium solutions to identify a redshift of the $v_{as}(\text{CH}_3)$ and $v_s(\text{CH}_3)$ vibration peaks relative to the solution phase vibrational peaks$^{34}$. This redshift is consistent with the adsorption of the cation onto the electrode surface weakening the internal bonds of the molecule, as a favorable interaction is gained with the surface.

The effect of the quaternary ammonium cations on the high potential region of the CV (relative to that measured in potassium hydroxide) is consistent with the oxidation of the adsorbed cation. Though DFT results suggest desorption may occur at higher potentials, oxidation of these species is likely favorable. This would explain the increase in the oxidative current at high potentials measured in the cyclic voltammograms without a subsequent increase in the reductive current (as the organic cations are oxidized to other species which then desorb from the surface).

To further quantify the effects of the quaternary ammonium cations at low potentials, we deconvoluted the experimentally measured cyclic voltammograms measured in 0.1 M KOH, 0.1 M tetramethylammonium hydroxide (TMAOH), and 0.1 M tetraethylammonium hydroxide (TEAOH), using a method we have described previously$^{83}$. This method involves fitting three separate functions to the measured cyclic voltammograms to capture the total charge due to hydrogen adsorption on 111-like terraces, hydrogen and hydroxide competitive adsorption on 110 steps and terraces, and the same on 100 steps and terraces. Given that some of these contributions to the total CV overlap and there are contributions from other types of sites, this method gives only an estimate of the total electrochemically active surface area and the relative fraction of 111, 100, and 110 sites. These site densities (given as total charge per square centimeter of geometric electrode area) are given in Figure 8-7. It is clear that the total charge or total open surface area decreases in the organic cation containing electrolytes and with increasing alkyl chain length (in the order KOH > TMAOH > TEAOH). Further, a greater fraction of the 110 and 100 sites are
blocked in TMAOH and TEAOH, relative to 111 sites, suggesting stronger adsorption on those sites (either 110, 100 steps or terraces, or both).

Figure 8-7. Total electrochemically active surface area and relative site density of 111 (blue), 100 (red), and 110 (green) sites calculated by deconvoluting cyclic voltammograms measured on Pt(pc) in 0.1 M KOH, 0.1 M tetramethylammonium hydroxide (TMAOH), and 0.1 M tetraethylammonium hydroxide (TEAOH) (CVs shown in Figure 8-6). CVs measured in 0.1 M benzyltrimethylammonium hydroxide could not be deconvoluted, given the lack of discernable contributions from 111, 110, and 100 sites. Surface area is given in units of total charge per square centimeter of geometric electrode area, assuming one electron is transferred per 111 site and 1.33 electrons transferred per every 110 and 100 site.

Using both the experimental and DFT results, the coverage of the adsorbed cation can be estimated. The DFT results suggest that the strong van der Waals attraction between the alkyl chains of the quarternary ammonium cations and the surface drives three of the four alkyl chains to adsorb to the surface, which could then potentially block active surface sites. This suggests the number of sites blocked by each adsorbed cation may be proportional to three-fourths of the number of carbon atoms (or CH₃ groups) present in the organic cation. Figure 8-8 plots the fractional decrease in total charge (surface area) calculated from experiment (relative to that measured in KOH) against the estimated number of sites blocked per adsorbate. The linear relationship seen in Figure 8-8 for the 110 and 100 sites, shows that the total number of sites blocked is directly related to the size of the organic cation; the slope gives the organic cation coverage. This suggests that tetramethylammonium and tetraethylammonium cations adsorb to
nearly the same coverage (0.12 ML), but tetraethylammonium blocks more surface sites simply because the alkyl chains are longer. While this estimated coverage is subject to the limitations of the deconvolution method, it is within what we would expect from the DFT simulations. Additionally, though adsorption on 110 and 100 steps were not considered with DFT, we would still expect the fraction of step sites blocked to be dependent on cation size, however a different dependence on cation size (on the 2D step as opposed to the 3D flat terrace) would yield a different calculated coverage.

Further study of organic cation specific adsorption using single crystal electrodes, electrochemical quartz crystal microbalance measurements, or in-situ radiotracer measurements may be able to further refine this estimated surface coverage.

![Figure 8-8. Fraction of 111 (blue diamond), 100 (red square), and 110 (green triangle) sites blocked by tetramethylammonium or tetraethylammonium adsorption as a function of the number of surface sites blocked per adsorbate (calculated assuming 3 of the 4 alkyl chains adsorb and block 1 surface site for every CH₄ unit). The fraction of sites blocked are calculated from the changes in total surface area (relative to that measured in 0.1 M KOH) calculated by deconvoluting experimentally measured cyclic voltammograms (Figure 8-7). Linear regressions are shown with a slope of 0.12 for 111, 0.12 for 100, and 0.01 for 120.](image)
8.4. Conclusion

Using density functional theory modeling of the electrode/electrolyte interface, we show that it is favorable for quaternary ammonium cations to specifically adsorb to low coverage on Pt(111), Pt(100), and Pt(110) electrode surfaces. A strong van der Waals interaction with the metal surface drives adsorption to be favorable at low potentials in an alkaline electrolyte (near 0 $V_{RHE}$, -0.83$V_{NHE}$), with adsorption becoming more favorable with increasing length of the alkyl chain. The effects of near surface solvation may drive adsorption of the smaller cations to be favorable at low potentials even in an acid electrolyte (near 0 $V_{NHE}$). For the quaternary ammonium cations with small alkyl chains, the presence of near surface water promotes adsorption, as water stabilizes the retained positive charge on the nitrogen atom. As the alkyl chain grows, near surface water weakens adsorption, as the hydrophobic alkyl chains block the favorable interaction of water with the metal surface and screen the positive charge on the nitrogen atom. Electrostatic repulsion between the positively charged adsorbates and the steric hindrance between alkyl chains makes adsorption strongly coverage dependent, with adsorption becoming significantly less favorable with increasing coverage. The coverage dependence is greater with larger alkyl chains.

Experimentally measured cyclic voltammograms show that the presence of quaternary ammonium cations in solution (0.1 M) blocks electrode surface sites on a polycrystalline platinum electrode, showing a smaller total charge transferred at low potentials than that measured in an organic cation-free electrolyte (0.1 M KOH). The decrease in total charge (blocking of surface sites) becomes more significant as the alkyl chain increases (tetramethyl<<tetraethyl<<benzyltrimethyl). This supports that these cations are adsorbed onto the electrode surface, blocking hydrogen/hydroxide adsorption at low potentials and matching our DFT results. Further, comparing cyclic voltammograms in tetramethyl- and tetraethyl-
ammonium hydroxide solutions suggests that the cations may be adsorbed to similar coverages, but the longer alkyl chain of the tetraethylammonium blocks more surface sites. DFT results suggest this is due to the strong van der Waals attraction between the alkyl chain and the electrode surface, such that a longer alkyl chain blocks more surface sites. Benzyltrimethylammonium shows the greatest site blocking effect and our DFT results suggest this is due to the strong interaction of the benzyl group with the electrode surface. Lastly, the experimental results suggest that these cations may be oxidized on the platinum electrode surface at high potentials.

This work highlights the importance of considering the interaction of the cationic group with the electrode surface, when designing anion conducting ionomers. The cation composition impacts blocking of active sites, and likely their stability on or near the electrode surface (against catalytic oxidation). Designing organic cations that minimize their van der Waals interaction with the surface (short and/or bulky alkyl groups) and are free from or hinder aromatic group adsorption should yield cations which adsorb less strongly and block fewer surface sites.

8.5. References


302


8.6. Supplementary Information

![Graph](image)

Figure S8-1. Equilibrium adsorption potentials calculated for adsorption of ammonium, tetramethylammonium, tetraethylammonium, and tetrapropylammonium at 1/9 ML on Pt(111) calculated without (red) and with (blue) DFT+D2 van der Waals corrections.
Figure S8-2. Structure of adsorbed benzyltrimethylammonium at 1/9 ML on (from top to bottom) Pt(111), Pt(100), and Pt(110) (showing the top down view on the left and a view from the side on the right).
Table S8-1. Difference in DFT energy for benzytrimethylammonium adsorbed at 1/9 ML on Pt(111), Pt(100), and Pt(110) with the benzyl ring parallel or perpendicular to the electrode surface. A negative difference in energy means the parallel configuration (ring adsorbed) is more stable.

*Difference in energy on Pt(111) calculated without van der Waals correction.

<table>
<thead>
<tr>
<th></th>
<th>Pt(111)</th>
<th>Pt(100)</th>
<th>Pt(110)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE (eV)</td>
<td>-0.28*</td>
<td>-0.75</td>
<td>-1.86</td>
</tr>
</tbody>
</table>

Table S8-2. Surface normal dipole moments for the quaternary ammonium organic cations adsorbed on Pt(111) at 1/9 ML without and with explicit water molecules.

<table>
<thead>
<tr>
<th>Surface normal dipole moment (eÅ)</th>
<th>0 H₂O*</th>
<th>6 H₂O*</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>-0.872</td>
<td>-0.704</td>
</tr>
<tr>
<td>N(CH₃)₄⁺</td>
<td>-1.433</td>
<td>-0.502</td>
</tr>
<tr>
<td>N(CH₂CH₃)₄⁺</td>
<td>-1.296</td>
<td>-1.311</td>
</tr>
<tr>
<td>N(propyl)₄⁺</td>
<td>-1.239</td>
<td>-1.436</td>
</tr>
<tr>
<td>Benzyl(NCH₃)₃⁺</td>
<td>-1.214</td>
<td></td>
</tr>
</tbody>
</table>

Figure S8-3. Equilibrium adsorption potential of ammonium, tetramethyl-, tetraethyl-, and tetrapropyl- ammonium at 1/9 ML as a function of the number of water molecules added near the surface adsorbate. van der Waals corrections are included. Adsorption of sodium is also shown for comparison, from Mills et al. (without vdW corrections) Equilibrium adsorption potentials calculated for adsorption of ammonium, tetramethylammonium, tetraethylammonium, and tetrapropylammonium at 1/9 ML on Pt(111) calculated without (red) and with (blue) DFT+D2 van der Waals corrections.⁵⁹
Chapter 9
Effect of pH and Alkali Metal Cations on the Rate of the Hydrogen Oxidation Reaction on Polycrystalline Pt

Abstract

The rate of the hydrogen oxidation reaction on Pt is 2-3 orders of magnitude slower in an alkaline electrolyte than in an acid electrolyte, and the rate of this reaction is correlated with a shift in the sharp, low potential (0-0.4 V_{RHE}) peaks in current measured by cyclic voltammetry on polycrystalline platinum electrodes. In our prior work, we used density functional theory to support that these sharp features correspond to competitive hydrogen and hydroxide adsorption, and found that the adsorption of an increasing coverage of alkali metal cation onto the electrode surface with increasing pH weakened hydroxide adsorption, explaining the pH dependence of these features. Herein, we experimentally measure the rate of the hydrogen oxidation reaction on polycrystalline Pt in 0.1 M LiOH, NaOH, KOH, and CsOH, and find that the rate also depends on the identity of the cation present in the electrolyte, with the activity following Li > Na > K > Cs. Using density functional theory we investigate the thermodynamics of adsorption of Li, Na, K, and Cs onto the low index facets of platinum, Pt(111), Pt(100), and Pt(110), as well as their subsequent interaction with co-adsorbed hydrogen or hydroxide and water. We find only a small interaction between the adsorbed cations and adsorbed hydrogen but a significant weakening of adsorbed hydroxide. The trend in hydroxide adsorption with the co-adsorbed cations on Pt(110), the most active facet for hydrogen oxidation, matches the trend in experimentally measured rate, with Li showing the smallest weakening of hydroxide adsorption and the highest rate, and Cs the largest weakening and lowest rate. On comparing hydroxide adsorption energy on various
transition metal surfaces with their activity for hydrogen oxidation, a volcano type relationship is found. We consider reaction mechanisms consistent with these results; while we cannot determine the exact mechanism for the hydrogen oxidation reaction in an alkaline electrolyte, we conclude that the effect of the alkali metal cation cannot be explained by solely considering the hydrogen binding/adsorption strength.

9.1. Introduction

The rising cost and depletion of non-renewable fuels\(^1\) has led to the exploration of more efficient energy conversion and energy storage technologies\(^2\)\(^\,\)\(^3\). Hydrogen use in fuel cells provides a means for storing, transporting, and efficiently utilizing both fossil and renewable energy\(^3\). Although the performance of proton exchange membrane (PEM) fuel cells is excellent, the need for platinum catalysts that can withstand the corrosive acidic environment and for long-lived perfluorinated membranes lead to high cost, which is the primary challenge to widespread PEM fuel cell (PEMFC) deployment\(^4\). Anion exchange membranes (AEM), which conduct hydroxide ions instead of protons, would allow the use of a broad array of lower-cost metals that are more stable in an alkaline environment. Although high pH fuel cells may present a low cost alternative to PEMFCs, the hydrogen oxidation reaction (HOR) rate, even on platinum electrodes, can be significantly slower in aqueous alkaline electrolytes than in acid electrolytes\(^5\). The mechanistic cause for this decreased rate is not known. The interaction between alkali metal cations (present in an alkaline electrolyte) near or adsorbed on the electrode surface and reactive intermediates adsorbed on the electrode surface, may lead to the loss of HOR activity on increasing the electrolyte pH. Herein, we experimentally measure variations in HOR rate with the alkali cation present in a basic electrolyte (Li, Na, K, Cs) on a polycrystalline Pt electrode. We further apply density functional theory calculations to provide a plausible mechanistic
explanation of the role of cation.

Anionic species such as (bi)sulfate, organic sulfonate, and halides are well known to specifically adsorb to platinum electrode surfaces. Anion specific adsorption has been observed electrochemically as well as with STM and spectroscopy. The rate of the oxygen reduction reaction (ORR) at high potentials in fuel cells is affected by these anions, likely through their specific adsorption onto the electrode surface and subsequent blocking of active sites. Recent studies have shown alkali metal cations effect the rate of the ORR, methanol oxidation, CO oxidation/stripping, and hydrogen oxidation at high electrode potentials on platinum electrodes in alkaline electrolytes. However, there is only limited experimental evidence to suggest alkali cation specific adsorption onto platinum; non-covalent interactions between alkali cations in the double layer and specifically adsorbed hydroxide species have been proposed to account for the effects of the alkali cation. Our recent density functional theory (DFT) results suggest that alkali metal cation specific adsorption is possible and can compete with hydrogen adsorption at potentials where the HOR occurs in alkaline electrolytes on Pt(111) and Pd(111) electrode surfaces. We have further shown that alkali metal cations adsorbed on or near the electrode surface weaken the adsorption of hydroxide and water on Pt(110), Pt(100), and on stepped platinum surfaces. As adsorbed hydroxide is an intermediate in many of these reactions (in which alkali cations have an effect), the interaction between adsorbed hydroxide and near surface alkali cations may explain the mechanism for this effect. The development of lower cost fuel cells that minimize the use of platinum in alkaline environments necessitates an understanding of how the HOR rate varies with both pH and cation identity.

We experimentally measure the rate of the hydrogen oxidation and evolution reactions (HOR/HER) in 0.1 M LiOH, NaOH, KOH, and CsOH on polycrystalline platinum and demonstrate a dependence of the exchange current on alkali cation identity. Density functional theory (DFT) calculations are used to evaluate a proposed mechanism for the cation effect on the
HOR rate and the exchange current. DFT calculations show that alkali cation specific adsorption occurs on the Pt(110) surface, the most active low index Pt surface facet\textsuperscript{21,22}, and that these adsorbed cations show an almost negligible interaction with adsorbed hydrogen, but a strong weakening of adsorbed hydroxide. The DFT calculated trend in the degree of weakening of hydroxide binding on Pt(110) between Li, Na, K, and Cs matches the experimentally measured trend in exchange current density, with Li showing the strongest hydroxide adsorption and highest rate, and Cs showing the weakest hydroxide adsorption and lowest rate.

9.2. Methods

9.2.1. Experimental Methods

HOR experiments were carried out in a three electrode glass voltammetry cell (Pine Instruments, Durham, NC) with a polycrystalline platinum rotating disk working electrode mounted to a rotator (MSR Electrode Rotator, Pine Instruments), a platinum counter electrode, and a Ag/AgCl reference electrode. The polycrystalline platinum 0.5 cm diameter rotating disk electrode (Pine Instruments) was polished with 0.05 μm alumina slurry and rinsed with DI water before each use. Fresh electrolyte was prepared for each measurement using 0.1 M lithium hydroxide (99.995%, monohydrate, Sigma-Aldrich), 0.1 M sodium hydroxide (99.99%, Sigma-Aldrich), 0.1 M potassium hydroxide (99.99%, Sigma-Aldrich), and 0.1 M cesium hydroxide (99.95%, monohydrate, Sigma-Aldrich). The electrochemical cell was sealed to a slight overpressure using a flexible septa and the electrolyte saturated with pure hydrogen gas for 2 hours before HOR rate data were collected. The electrochemical cell was kept at a constant 22 °C. Triplicate runs were performed for each cation. For HOR/HER rate measurements, the potential was scanned from -0.2 to 1.2 V\textsubscript{RHE} at 10 mV/s for each rotational speed of 400, 700, 900, 1200,
1600, and 2500 rpm. Measured current densities were corrected for hydrogen mass transport using the reversible Koutecky-Levich equation\textsuperscript{23}. The Butler-Volmer equation was fit to the mass transport corrected HOR/HER current densities near 0 V\text{RHE} (-0.10 to 0.20 V\text{RHE}) to calculate the exchange current density and transfer coefficient ($\alpha$) in each electrolyte. Tafel slopes (and intercepts) calculated from the same data are given in the Supplementary Information. Cyclic voltammograms were measured using the same experimental setup in an argon saturated electrolyte.

9.2.2. Computational Methods

The thermodynamics of adsorption of alkali metal cations (Li, Na, K, Cs), hydrogen, hydroxide, and water were evaluated as a function of coverage on Pt(111), Pt(100), and Pt(110). The computational details, including the functional used and a description of the surface slab models, are given in Chapter 2 (Section 2.2.) and Chapter 4 (Section 4.2.1.). The same computational techniques were also used to consider adsorption of hydrogen, hydroxide (in the absence and presence of co-adsorbed potassium), and water to Ru(0001), Ir(111), and Au(111) surfaces in a 3x3 unit cell using a 4-layer surface slab, with the bottom two layers frozen at the experimentally measured lattice constant for these metals\textsuperscript{24}.

Alkali cation specific adsorption potentials are calculated following the procedure outlined in Chapter 2 (Section 2.2.1.). Adsorption potentials for hydrogen, hydroxide, and water in the absence and presence of alkali cations are calculated in the same manner as shown in Chapter 4 (4.2.2).
9.3. Results and Discussion

9.3.1. Experimentally Measured Rate of the HOR/HER on Pt(pc) in 0.1 M (Li, Na, K, Cs)OH

Figure 9-1 shows the experimentally measured rate of the hydrogen oxidation reaction over a polycrystalline platinum working electrode (RDE) measured in 0.1 M LiOH, NaOH, KOH, and CsOH, at a rotational speed of 2500 rpm. The rate follows the trend Li > Na > K > Cs. To further examine the trend, the rate was corrected for mass transport limitations and exchange current densities were calculated in each electrolyte. These exchange current densities are shown in Table 9-1. These data are not corrected for iR-loss, however, the trend in electrolyte resistance between the alkali metal hydroxide solutions, which at low concentrations depends on solvated ion size (Li > Na > K > Cs, with a larger solvated size giving slower diffusion), matches the trend in the measured rate (Li > Na > K > Cs). Therefore correcting for electrolyte resistance should increase the absolute exchange current densities calculated and will only reinforce the trend in activity between the alkali metal cations.

Table 9-1 also shows exchange current densities measured by Sheng et al. for hydrogen oxidation and hydrogen evolution on polycrystalline platinum as well as on the low index, single crystal platinum electrodes in a potassium hydroxide electrolyte. The measured exchange current density in potassium hydroxide compares well with that measured by others previously; a slight difference is expected as iR corrections were not performed (which would increase the exchange current density relative to that shown in Table 9-1). The exchange current densities are also calculated on the basis of geometric electrode surface area; normalizing by the electrode roughness would decrease the measured exchange current densities and may also decrease the deviation between triplicate measurements. Neither correction should effect the trend between the alkali metal cations, which is the focus of the work described here.
Figure 9-1. HOR/HER polarization curves measured on a polycrystalline platinum rotating disk electrode at 2500 rpm in H₂ saturated 0.1 M LiOH, 0.1 NaOH, 0.1 M KOH, and 0.1 M CsOH at 22°C.

Table 9-1. HOR/HER exchange current densities (i₀) measured on platinum in 0.1 M alkaline electrolytes.

<table>
<thead>
<tr>
<th>i₀ (mA/cm²)</th>
<th>HOR/HER Pt(pc)</th>
<th>HOR/HER Pt(110)</th>
<th>HOR Pt(111)</th>
<th>HOR Pt(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH</td>
<td>1.06 ± 0.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>0.88 ± 0.13</td>
<td>0.79 ± 0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>0.69⁵</td>
<td>0.72¹</td>
<td>0.04²¹</td>
<td>0.05²¹</td>
</tr>
<tr>
<td>CsOH</td>
<td>0.66 ± 0.26</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The effect of alkali metal cation on the rate of hydrogen oxidation on a Pt(111) single crystal electrode has been examined previously by Strmcnik et al.¹⁴. The authors found that there was no difference in rate between the alkali metal cations at low potentials, but a small difference in rate at high potentials near where hydroxide adsorbs on Pt(111)¹⁴. The rates of oxygen reduction and methanol oxidation¹⁴ as well as CO stripping¹⁵ are also affected by the cation
identity at intermediate-high potentials. Strmcnik et al. suggest that alkali metal cations in the double-layer exhibited non-covalent interactions with specifically adsorbed hydroxide\(^{14}\).

In our prior work, we used density functional theory to find that alkali metal cation specific adsorption on to the low index platinum facets\(^{18-19}\) as well as stepped platinum surfaces\(^{20}\) is favorable at low potentials in alkaline electrolytes. Further, partially solvated sodium or potassium cations adsorbed on or near the electrode surface exhibited a small interaction with adsorbed hydrogen and a significant weakening of adsorbed hydroxide\(^{19-20}\). This weakening effect was used to explain the experimentally observed shift of the competitive hydrogen and hydroxide adsorption peak in current measured by cyclic voltammetry on Pt(110)\(^{15,25}\) as well as on stepped Pt surfaces\(^{20}\) to more positive potentials with increasing electrolyte pH (and per our results, increasing cation coverage on the surface)\(^{19-20}\). Given that hydroxide adsorbs at much lower potentials on Pt(110) and on Pt steps than on the low index Pt(111) surface\(^{19,25}\), interactions between the alkali cations and adsorbed hydroxide on these sites may explain the dependence of the hydrogen oxidation rate observed here on polycrystalline platinum on alkali cation identity at low potentials.

To better understand why the rate of the hydrogen oxidation reaction on polycrystalline platinum is dependent on the identity of the alkali metal cation present in an alkaline electrolyte, we performed density functional theory calculations, similar to those described previously\(^{19-20}\), to understand how the interaction between an alkali metal cation and adsorbed hydrogen, hydroxide, and water vary with cation identity.

### 9.3.2. Alkali Metal Cation Adsorption

Equilibrium adsorption potentials for Li, Na, K, and Cs cations on Pt(111), Pt(100), and Pt(110) were calculated using density functional theory as a function of cation coverage; results
are shown in Figures S9-1a, b, and c. As cation adsorption is a reduction process, a more positive equilibrium adsorption potential indicates more favorable adsorption. It is readily apparent that adsorption becomes less favorable with increasing cation coverage on all three surfaces and with all of the alkali cations. This indicates repulsive interactions between the alkali cations. As the alkali cations retain some of their charge on adsorption, given by the large surface normal dipole moments generated on adsorption (Table S9-1), this repulsive interaction is comprised at least in part by an electrostatic interaction between the adsorbed cations.

Adsorption of Li, Na, K, and Cs are favorable at low potentials to low coverage on all three low index Pt facets. In an alkaline electrolyte, all of these cations would favorably adsorb near the equilibrium potential for hydrogen oxidation and hydrogen evolution (−0.83 V_NHE at pH=14). The presence of solvent near the electrode surface (not considered in Figures S9-1a, b, and c) would act to promote low coverage adsorption of these cations\textsuperscript{18-19}, such that adsorption may occur at low potentials to low coverage even in intermediate or low pH electrolytes. Figure S9-2 gives the equilibrium adsorption potentials for Li, Na, K, and Cs on Pt(111) at 1/9 ML coverage solvated by a water bi-layer (6H\textsubscript{2}O\textsuperscript{+}). The presence of solvent near the electrode surface drives cation adsorption to be significantly more favorable (by 0.8 – 1 eV), making adsorption favorable near 0 V\textsubscript{NHE} (the equilibrium potential for HOR/HER at pH=0). The presence of solvent near the electrode surface also weakens the difference in adsorption favorability between the cations, spanning ~0.5 V on Pt(111) in vacuum and only ~0.1 V when the surface is solvated.

Adsorption of any alkali cation above ~ 1/3 ML on Pt(111) is probably not possible within the electrochemical window of water (due to the strong repulsion between the adsorbates). Similarly, adsorption of Li, Na above 0.5 ML and K, Cs above 0.25 ML on Pt(100) and of any of the alkali cations above 0.5 ML on Pt(110) is probably not possible within the electrochemical window of water. At high coverages (near 1 ML), the equilibrium adsorption potentials calculated for adsorption of the larger cations (K, Cs) approaches that of the equilibrium potential for K or
Cs bulk deposition/dissolution in water. At low coverage, the trend in adsorption favorability follows Cs > Na > K > Li on all three platinum surfaces. The trend in surface normal dipole moment, which indicates the degree to which the cations retain their positive charge, generated on adsorption at low coverage (Table S9-1), follows the trend Cs > K > Na > Li, which matches the trend in electronegativity between the cations, with Cs having the lowest electronegativity and Li the largest. At high coverages, the trend in adsorption favorability reverses (Li > Na > K > Cs), following the trend of increasing ion size. The trend in the coverage dependence also roughly follows the ion size, with Li showing the smallest coverage dependence (least repulsion) and Cs the largest (greatest repulsion).

9.3.3. Interaction Between Adsorbed Alkali Cation and Hydrogen

Figures 9-2a, b, and c show the equilibrium adsorption potentials for hydrogen adsorption at 1 ML onto Pt(111), Pt(100), and Pt(110) (respectively) as a function of the coverage of the alkali metal cations co-adsorbed on the surface. On all three surfaces, the favorability of hydrogen co-adsorption with a low coverage of alkali cation follows the trend Li > Na > K > Cs. On Pt(111) and Pt(100), the presence of alkali cations adsorbed on the electrode surface weakens hydrogen adsorption, with the weakening effect increasing with increasing cation coverage. While the magnitude of the effect seems large on Pt(111) (weakening H* adsorption by ~ 0.1 V at a cation coverage of 1/9 ML and by 0.2 V at 1/4 ML), this effect is smaller at a lower H* coverage (not shown). As adsorption of hydrogen above ~0.7 ML on Pt(111) is known experimentally to be convoluted with hydrogen evolution (as configurational entropy drives the calculated adsorption potential of high coverage adsorption to more negative potentials than shown in Figures 9-2a, b, and c), the small effect of the cation on low coverage hydrogen adsorption may not be observable experimentally. Cyclic voltammograms measured on Pt(111)
indicate the hydrogen adsorption region (0-0.4 V_RHE) is relatively unaffected by cation identity\textsuperscript{14}, though a small shift to more negative potentials (on an RHE scale) is seen with increasing pH\textsuperscript{20}.

The effect of the alkali metal cation on hydrogen adsorption on Pt(100) and Pt(110) (Figures 9-2b and c, respectively) is much smaller than that on Pt(111). On Pt(100), even at a cation coverage of 1/4 ML, adsorbed hydrogen is weakened only by ~0.1 V. Interestingly, the presence of an adsorbed cation on Pt(110) has only a very weak effect on hydrogen adsorption (~0.05 V) and some cations, namely Li and Na, promote hydrogen adsorption while others, K and Cs, weaken adsorption. As hydrogen adsorption on Pt(100) and Pt(110) is competitive with hydroxide adsorption\textsuperscript{19, 25, 30}, the effect of the alkali cation on hydroxide adsorption must also be considered before these results can be appropriately compared to experiment.
Figure 9-2. Equilibrium adsorption potentials calculated for hydrogen adsorption at 1 ML on Pt(111) (a), Pt(100) (b), and Pt(110) (c) as a function of the coverage of co-adsorbed Li, Na, K, Cs.
9.3.4. Interaction of Adsorbed Alkali Cation with Hydroxide and Water

Figures 9-3a and b give the equilibrium adsorption potential for co-adsorbed hydroxide and water (1/3 ML OH* and 1/3 ML H₂O*) on Pt(100) and Pt(110) as a function of cation coverage (calculated referencing surface adsorbed water in the reactant state, to partially solvate the adsorbed alkali cation). On both surfaces, the effect of the cation is to significantly weaken hydroxide adsorption, with a greater weakening with increasing cation coverage (as found previously with potassium\(^1\)). The effect of the co-adsorbed cation on the hydroxide adsorption potential is significantly larger on both Pt(100) and Pt(110) (~ 0.3 eV on Pt(100) and 0.5 eV on Pt(110)) than the effect on hydrogen adsorption. We previously identified the mechanism of this weakening effect; as the adsorbed cations retain some of their positive charge, they interact strongly with co-adsorbed hydroxide and water, and disrupt the OH*+H₂O* hydrogen bonding network\(^1\).

On Pt(100) (Figure 9-3a), the effect of the alkali cation on hydroxide adsorption follows the following trend: Li > Na > K > Cs, with Li showing the largest weakening of hydroxide (and Cs the smallest). While hydrogen and hydroxide adsorb competitively on Pt(100) in an acid electrolyte (near 0.4 V\(_{\text{RHE}}\))\(^{30,31}\), Figure 9-3a suggests that the adsorption of a cation in an alkaline electrolyte will weaken hydroxide adsorption such that it may then separate from hydrogen adsorption. van der Vliet and Koper suggest from experimentally measured cyclic voltammograms on Pt(100) that a double layer region may exist (suggesting hydroxide adsorption separates from hydrogen adsorption) in an alkaline Li containing electrolyte\(^3\) (which shows the greatest weakening of OH*, Figure 9-3a). Our DFT calculated OH* adsorption potentials at a low cation coverage (~0.11 ML) compare favorably with the location of the sharp peak measured experimentally near 0.48 V\(_{\text{RHE}}\) and with the trend between the alkali cations\(^3\).
Figure 9-3. Equilibrium adsorption potentials calculated for hydroxide (and water) adsorption at 1/3 ML (3OH*+3H_2O*) from an adsorbed water bilayer (6H_2O*) on Pt(100) (a) and Pt(110) (b) as a function of the coverage of alkali metal cation co-adsorbed on the surface.

On Pt(110) (Figure 9-3b) the trend between the cations is opposite of that seen on Pt(100), with Cs weakening hydroxide to the greatest extent and Li the least (Cs > K > Na > Li). While the weakening effect appears larger on Pt(110) (than with Pt(100)), hydroxide adsorption at low cation coverages is favorable at low enough potentials to still be competitive with hydrogen adsorption\(^{19}\). As hydrogen adsorbs to a higher coverage than hydroxide, and the effect of the cation on hydrogen adsorption is small on Pt(110), this would act to both decrease the observed shift in the H*/OH* adsorption peak (measured by cyclic voltammetry) and the difference between the various cations, relative to that shown in Figure 9-3b. Taking a weighted
average of the hydroxide adsorption potential and the hydrogen adsorption potential (based on total coverage, 1 ML for H* and, in this case 1/3 ML OH*) for adsorption near Li* and near Na* (at a cation coverage of 0.22 ML) gives a difference in potential for H*/OH* adsorption between these two cations of 22 mV, close to the 20 mV measured experimentally\textsuperscript{15} (though the absolute values are shifted positive of what is measured experimentally, with 0.366 $V_{\text{RHE}}$ for H*/OH* near Li* and 0.389 $V_{\text{RHE}}$ near Na* predicted here, compared to 0.23 $V_{\text{RHE}}$ for Li and 0.25 $V_{\text{RHE}}$ for Na\textsuperscript{15}).

9.3.5. Comparing the Experimentally Measured Hydrogen Oxidation Rate to the Effect of Cations on H*/OH* adsorption

There are three primary ways in which alkali metal cations can affect the rate of the hydrogen oxidation reaction (or any electrocatalytic reaction). First, the alkali cations could adsorb onto the electrode surface and simply block active sites, reducing the hydrogen oxidation rate with increasing cation coverage. Next, adsorbed or near-surface alkali metal cations could promote or weaken the adsorption of a reactive intermediate, which would then effect the reaction rate. Lastly, adsorbed or near surface alkali cations could directly affect the stability of the transition state of a rate limiting step, thereby directly altering the activation energy and the rate of the reaction. While the trend in alkali cation adsorption favorability across all three of the low index Pt facets roughly matches the expected trend if a site blocking effect determined the hydrogen oxidation rate, this cannot explain the 2-3 order of magnitude drop in the rate of the hydrogen oxidation reaction seen on increasing the pH from an acid to an alkaline electrolyte\textsuperscript{5, 33-34}. Additionally, while it is clear that the presence of adsorbed or near-surface alkali cations affect the thermodynamics of hydrogen and hydroxide adsorption, there is little experimental evidence to suggest the alkali cations significantly block adsorption of these species.
To better understand why the rate of the hydrogen oxidation reaction is dependent on the identity of the alkali cation present in an alkaline electrolyte, we compare the trend in rate of the hydrogen oxidation reaction with the binding strength (adsorption favorability) of hydrogen and hydroxide on the Pt(110) low index facet, as it is the most active facet for hydrogen oxidation in an alkaline electrolyte\textsuperscript{21} (Table 9-1), and may therefore dictate the rate observed on polycrystalline Pt. It is well known that the rate of the hydrogen oxidation/evolution reaction depends on the binding strength of hydrogen. A catalyst which binds hydrogen too strongly gives a low rate, as it is difficult to get adsorbed hydrogen off the surface, and a catalyst which binds hydrogen too weakly also gives a low rate, as it is difficult to get hydrogen on to the surface in the first place. This results in a “volcano” type relationship between the hydrogen oxidation rate and the hydrogen binding energy, with the optimum catalyst giving the highest rate at an intermediate binding strength\textsuperscript{35-36}. We find however, that the trend in the effect of the cations on hydrogen adsorption on Pt(110) is opposite to that expected for the rate to match the volcano trend. Pt sits on the “too strong” binding side of the volcano\textsuperscript{37-38}; therefore, if this were the only factor determining the rate, Li would be expected to give the lowest rate (as it makes hydrogen adsorption even stronger, Figure 9-2c) and Cs would give the highest rate (as it makes hydrogen adsorption weaker, Figure 9-2c), opposite of the trend we measure experimentally. Therefore some other property of the electrode-electrolyte interface must be responsible for the effect of cation on the hydrogen oxidation rate.

It has been proposed recently that adsorbed hydroxide may play a role in the hydrogen oxidation reaction, at least in alkaline electrolytes, where it has been shown that stronger hydroxide binding yields a higher hydrogen oxidation rate\textsuperscript{39}. If we consider the effect of the alkali metal cations on hydroxide adsorption on Pt(110) (Figure 9-3c) we see that Li gives the strongest hydroxide binding and the highest hydrogen oxidation rate and Cs the weakest hydroxide binding and lowest reaction rate (following the trend Li > Na > K > Cs for both hydroxide binding and
reaction rate). This supports the idea that the reaction rate correlates with the hydroxide adsorption energy. Figure 9-4 plots the logarithm of our experimentally measured exchange current densities against the DFT predicted hydroxide adsorption energy as a function of alkali cation identity, showing a linear relationship.

![Figure 9-4](image)

Figure 9-4. Experimentally measured exchange current densities plotted against the DFT predicted hydroxide adsorption potential in the presence of 0.22 ML of co-adsorbed Li, Na, K, and Cs.

To further consider the role of adsorbed hydroxide in the hydrogen oxidation reaction, we also plot experimentally measured rates of hydrogen oxidation on Ru(0001), Au(111), Pt(111) as well as on Pt(111), Pt(100), and Pt(110) single crystal electrodes against our DFT predicted hydroxide adsorption potentials. The results are shown in Figure 9-5, where a “volcano” type relationship is apparent between the reaction rate and the hydroxide adsorption favorability. Figure S9-3 plots the hydrogen adsorption energy against the hydroxide adsorption energy on these same surfaces, showing only a very weak correlation, suggesting Figure 9-5 is not a reflection of a hydrogen binding volcano. While this further supports the idea that adsorbed hydroxide (or adsorbed water, as hydroxide adsorption is always considered with co-adsorbed water molecules) plays a role in the hydrogen oxidation reaction, significant study is needed to
identify the exact mechanism by which this occurs. Additionally, recent studies have added doubt to the importance of adsorbed hydroxide\textsuperscript{40-42}. Though our results cannot conclusively support the role of adsorbed hydroxide, we can say that the binding strength of hydrogen cannot be the sole descriptor, as the effect of the alkali metal cations on hydrogen adsorption does not match the experimentally measured trend in the rate of hydrogen oxidation.

The effect of alkali metal cations on the activation barrier for the rate limiting step of the hydrogen oxidation reaction should additionally be examined; this is outside the scope of the work presented here.

Figure 9-5. Volcano plot of the experimentally measured rate of the hydrogen oxidation reaction and the DFT calculated hydroxide adsorption potential on Ru(0001), Ir(111), Au(111), Pt(111), and Pt(100) in the presence of co-adsorbed potassium, as well as Pt(110) in the presence of co-adsorbed Li, Na, K, and Cs (with the experimentally measured rate on Pt(pc)). Hydroxide adsorption is considered with co-adsorbed water, at 1/3 ML OH*, 1/3 ML H\textsubscript{2}O*. Cation coverage is 1/9 ML on all surfaces except Pt(110), where the cation coverage is 2/9 ML. Red lines are drawn to highlight the volcano shape. Rate of the HOR/HER measured on Ru, Ir, Au, and Pt(111) single crystal electrodes are from Strmcnik et al.\textsuperscript{39} and on Pt(111), Pt(100), and Pt(110) single crystal electrodes from Markovic et al.\textsuperscript{21}.
9.3.6. Possible Hydrogen Oxidation Mechanisms

To evaluate the role adsorbed hydroxide may play in the hydrogen oxidation reaction, we consider possible reaction mechanisms. Our experimentally measured Tafel slopes fall within 100-120 mV/dec (Table S9-2), suggesting that the rate limiting step involves electron transfer (either a Heyrovsky Step or Volmer step); similar to that found recently by others on polycrystalline platinum in alkaline electrolytes. For the direct involvement of adsorbed hydrogen and adsorbed hydroxide, a Langmuir-Hinshelwood type mechanism can be written, following a Tafel step, as shown in Equations 1-3:

\[
H_2 + 2 \ast \rightarrow 2H^* \quad (\text{Tafel step}) \quad [1] \\
OH^{-}_{(aq)} + \ast \rightarrow OH^* + e^- \quad [2] \\
H^* + OH^* \rightarrow H_2O_{(aq)} + \ast \quad [3]
\]

where \(\ast\) indicates an empty surface site. Equation 3 can be similarly written for a Heyrovsky type mechanism. A rate determining step involving electron transfer suggests either Equation 2 is rate limiting or Equation 3 is rate limiting with only partial electron transfer to the adsorbed hydroxide in Equation 2 (and partial electron transfer in Equation 3). The rate of hydroxide adsorption on Pt(111) has been measured experimentally and is fast in both acid and base, while proton adsorption is fast only in acid and is slow in base, suggesting that hydroxide adsorption may not be rate limiting. Additionally, Equation 2 as the rate limiting step would yield a reaction rate with no explicit dependence on the hydrogen binding strength, which shows a volcano type relationship with the HER rate in an alkaline electrolyte. Equation 3 as the rate limiting step (with partial electron transfer) yields a reaction rate dependent on both the hydrogen adsorption strength and hydroxide adsorption strength.

Another possible mechanism involves an interaction between near surface hydroxide or water with the electrode surface only at the transition state for hydrogen (proton) desorption. The
overall reaction rate would be written in the same manner as the traditional Volmer (or similarly for the Heyrovsky) step, only the rate constant would exhibit an apparent dependence on the hydroxide/water adsorption energy. This mechanism is detailed schematically in Figure 9-6. This step, as the rate limiting step in hydrogen oxidation or evolution, involves explicit electron transfer, as expected from the experimentally measured Tafel slopes, and explains the dependence of the rate on hydrogen binding energy, hydroxide binding energy, and alkali metal cation (through its interaction with hydroxide and water).

It has been proposed previously that the structure of the electrolyte near the electrode surface effects the rate of proton adsorption/desorption\textsuperscript{29} and hydrogen oxidation/evolution\textsuperscript{44} and changes with pH, to explain the effect of pH on the HOR/HER. We take this further by adding three additional hypotheses (as given by Figure 9-6), 1) the presence of an alkali metal cation near the electrode surface contributes to or mediates the effect of pH on the structure of the electrode-electrolyte interface (with the presence of the cation near the surface increasing with increasing pH), 2) the identity of the alkali metal cation therefore also effects the structure of the electrode-electrolyte interface, and 3) the structure of this interface has some dependence on the metal electrode surface (identity and facet/structure), to explain the apparent dependence of the hydrogen oxidation and evolution reaction rates on hydroxide/water adsorption strength.

Future work should examine the rate of hydrogen adsorption/desorption as a function of electrode-electrolyte structure using density functional theory, as well as the rate of proton adsorption/desorption and hydrogen oxidation/evolution on various transition metal single crystal electrodes, such that the DFT results can be directly compared to experiment.
Figure 9-6. Schematic diagram for a proposed hydrogen (proton) desorption mechanism in acid and alkaline electrolytes which proceed through an intermediate state (TS) where a partially solvated water molecule (acid) or hydroxide anion (alkaline) interacts directly with the electrode surface. IS indicates the initial state, TS the transition state, and FS the final state.

9.4. Conclusions

We find that the rate of the hydrogen oxidation reaction in an alkaline electrolyte on polycrystalline platinum is dependent on the alkali cation present in the alkaline electrolyte, with the rate following the trend Li > Na > K > Cs. Using density functional theory, we examine the specific adsorption of these alkali cations to the low index facets of platinum, Pt(111), Pt(100), and Pt(110), as well as the interaction of these adsorbed alkali cations with co-adsorbed hydrogen, hydroxide, and water. Adsorption of these cations is favorable at low potentials in alkaline electrolytes, to low coverages. Near-surface water promotes the adsorption of the cations such that adsorption to low coverage may be possible even in intermediate or low pH electrolytes. Once on the surface, the cations weaken hydrogen adsorption on Pt(111) and Pt(100), while Li
and Na promote hydrogen adsorption and K and Cs weaken hydrogen adsorption on Pt(110). On all three surfaces, the effect on hydrogen adsorption is small.

In agreement with what we have found previously with potassium, the alkali metal cations have a larger effect on hydroxide adsorption, weakening hydroxide adsorption on both Pt(100) and Pt(110). The cations retain some of their charge on adsorption and act to disrupt the hydrogen bonding network between adsorbed hydroxide and co-adsorbed water. On Pt(110), the most active low index facet for hydrogen oxidation/evolution in an alkaline electrolyte, the trend in the weakening of hydroxide adsorption with the alkali cations matches the trend in the measured rate of hydrogen oxidation, with Li weakening hydroxide adsorption the least and giving the highest rate, and Cs weakening hydroxide the most and giving the lowest rate. This correlation supports an argument proposed recently by others that the rate of hydrogen oxidation depends on the hydroxide binding strength (in addition to the hydrogen binding strength).

While we cannot assign a definite mechanism to the hydrogen oxidation reaction in alkaline electrolytes, we can conclude that the effect of the alkali metal cation on hydrogen oxidation cannot be explained by considering only the hydrogen binding strength as the sole descriptor of HOR/HER activity, as the trend with alkali cation is opposite to that expected given the location of Pt on the hydrogen binding volcano.

9.5. References


Figure S9-1. Equilibrium adsorption potentials calculated for Li, Na, K, and Cs adsorption on to Pt(111) (a), Pt(100) (b), and Pt(110) (c) as a function of coverage from a solution cation concentration of 1 M at 300K. Horizontal lines (black) indicate the equilibrium potential for the HOR/HER at pH = 14.
Table S9-2. Surface normal dipole moment generated on adsorption of Li, Na, K, and Cs on Pt(111), Pt(100), Pt(110) at a coverage of 1/9 ML.

<table>
<thead>
<tr>
<th>1/9 ML</th>
<th>Pt(111) (eÅ)</th>
<th>Pt(100) (eÅ)</th>
<th>Pt(110) (eÅ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare</td>
<td>0.012</td>
<td>0.003</td>
<td>-0.033</td>
</tr>
<tr>
<td>Li*</td>
<td>-0.559</td>
<td>-0.454</td>
<td>-0.336</td>
</tr>
<tr>
<td>Na*</td>
<td>-0.816</td>
<td>-0.731</td>
<td>-0.594</td>
</tr>
<tr>
<td>K*</td>
<td>-1.06</td>
<td>-1.027</td>
<td>-0.926</td>
</tr>
<tr>
<td>Cs*</td>
<td>-1.10</td>
<td>-1.112</td>
<td>-1.066</td>
</tr>
</tbody>
</table>

Figure S9-2. Equilibrium adsorption potentials calculated for adsorption of Li, Na, K, and Cs at 1/9 ML onto a bare (red) and solvated (blue) Pt(111) surface. The surface is solvated with a water bilayer (6 H₂O*). The solid black line corresponds to the equilibrium potential for the HOR/HER in an acid electrolyte (pH = 0) and the dashed black line to the equilibrium potential for the HOR/HER in a basic electrolyte (pH = 14). The presence of solvent (water) near the electrode surface significantly promotes alkali metal cation adsorption (by 0.8 - 1 V).
Figure S9-3. Hydroxide adsorption potentials plotted against the hydrogen adsorption potential on Ru(0001), Ir(111), Au(111), Pt(111), Pt(100), and Pt(110). The hydroxide adsorption potential is calculated in the presence of adsorbed/near-surface potassium. The hydroxide adsorption potential on Pt(110) is calculated in the presence of Li, Na, K, and Cs.

Table S9-3. Tafel slopes and transfer coefficients ($\alpha$) calculated from the experimentally measured mass transport corrected (using the irreversible Koutecky-Levich equation) HOR/HER current densities near 0 V$_{\text{RHE}}$ (-0.10 to 0.20 V$_{\text{RHE}}$).

<table>
<thead>
<tr>
<th></th>
<th>TS (mV/dec) HOR</th>
<th>TS (mV/dec) HER</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>119</td>
<td>146</td>
<td>0.49</td>
</tr>
<tr>
<td>Na</td>
<td>118</td>
<td>129</td>
<td>0.50</td>
</tr>
<tr>
<td>K</td>
<td>111</td>
<td>123</td>
<td>0.53</td>
</tr>
<tr>
<td>Cs</td>
<td>102</td>
<td>108</td>
<td>0.57</td>
</tr>
</tbody>
</table>
Table S9-4. HOR/HER exchange current densities ($i_0$) measured on platinum in 0.1 M alkaline electrolytes, calculated from a linear fit to a plot of log($i_k$) vs. overpotential for the HOR and for the HER (mass transport corrected using the irreversible Koutecky-Levich equation$^1$).

<table>
<thead>
<tr>
<th></th>
<th>$i_0$ (mA/cm$^2$) (HOR) Pt(pc)</th>
<th>$i_0$ (mA/cm$^2$) (HER) Pt(pc)</th>
<th>HOR/HER Pt(110)</th>
<th>HOR Pt(111)</th>
<th>HOR Pt(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH</td>
<td>0.79 ± 0.07</td>
<td>1.30 ± 0.12</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaOH</td>
<td>0.60 ± 0.07</td>
<td>0.98 ± 0.11</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KOH</td>
<td>0.49 ± 0.08</td>
<td>0.87 ± 0.11</td>
<td>0.7$^4$</td>
<td>0.04$^4$</td>
<td>0.05$^4$</td>
</tr>
<tr>
<td></td>
<td>0.69$^2$</td>
<td>0.63$^4$, 0.69$^2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsOH</td>
<td>0.31 ± 0.07</td>
<td>0.60 ± 0.10</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 10

Conclusions and Recommendations for Future Research

In this dissertation, both experiment and atomistic scale modeling of the electrode-electrolyte interface were used to better understand the mechanisms by which electrolyte pH and spectator ions (in particular the alkali metal cations) effect the rates and mechanisms of electrocatalytic reactions.

Section 10.1 provides a summary of and conclusions from each chapter. Section 10.2 gives answers to the research questions proposed in Chapter 1. Section 10.3 provides recommendations for future research, in particular, for better understanding the mechanism of the hydrogen oxidation/evolution reactions.

10.1. Summary

In Chapters 2 and 3, density functional theory is used to examine alkali metal cation specific adsorption to a variety of fcc transition metal surfaces (Chapter 2) and halide specific adsorption on Cu(111), Cu(100), and Cu(211). The results in Chapter 2 show that alkali metal cation specific adsorption is favorable at low potentials in alkaline electrolytes on Pt(111) and Pd(111). The alkali metal cations retain some of their charge on adsorption, and therefore interact strongly with near-surface water. Chapter 2 additionally shows that the use of a small cluster of hydrogen bonded water molecules accurately reproduces the effects of solvation calculated with a much larger, minimum energy, ice-like water structure, reducing the computational intensity of approximating the effects of solvation. The results in Chapter 3 show that the halide ions, in particular, Br and I, remain adsorbed even at low potentials on copper surfaces, and could
therefore effect electrocatalytic reactions occurring at low potentials on copper. The near-surface solvation method examined in Chapter 2 is applied to halide adsorption on Chapter 3. These anions adsorb neutrally to the surface, and therefore interact only relatively weakly with near-surface water, suggesting that the effects of near-surface solvation can be neglected in this case.

In Chapters 4 and 5, density functional theory is used to examine alkali metal cation, hydrogen, hydroxide, and water adsorption to Pt(110) and Pt(100) (Chapter 4), as well to stepped Pt surfaces Pt(553) and Pt(533) (Chapter 5). The DFT results show that competitive hydrogen and hydroxide adsorption occurs on the Pt(553) and Pt(533) step sites at low potentials, similar to what is seen on Pt(110) and Pt(100). This competitive adsorption is only captured with DFT if the effects of solvation on the adsorbed hydroxide are considered. The co-adsorption of water significantly promotes hydroxide adsorption by hydrogen bonding with the adsorbed hydroxide. Alkali metal cation specific adsorption is found to be favorable to all of these platinum surfaces. Once on the surface, the alkali metal cation interacts only weakly with adsorbed hydrogen, but shows a significant weakening of adsorbed hydroxide, disrupting the hydroxide and water hydrogen bonded network. The magnitude of this effect increases with cation coverage (Chapter 4), which is expected to increase with increasing pH, as the adsorption of hydrogen and hydroxide are shifted to more negative potentials on an absolute scale with increasing pH. These results were used to explain the experimentally observed anomalous shift in the low potential peaks measured by cyclic voltammetry on a relative potential scale on Pt(110) and Pt(100) as well as in the sharp, step associated peaks on Pt(553) and Pt(533), with increasing pH. In Chapter 5, cyclic voltammograms were simulated using density functional theory and were found to match experiment. The anomalous shift of these peaks has been previously found to correlate with the pH dependence of the hydrogen oxidation reaction, suggesting the presence of an adsorbed alkali metal cation and its weakening of hydroxide may play a role in the hydrogen oxidation reaction.
The better understanding of hydrogen and hydroxide adsorption on the low index and stepped Pt surfaces developed in Chapters 4 and 5 was additionally useful in defining a method to deconvolute experimentally measured cyclic voltammograms on polycrystalline Pt, given in Chapter 6. These cyclic voltammograms exhibit similar features to those seen on the single crystal low index Pt facets and stepped Pt surfaces. Functions were defined to fit the 110 step, 100 step, and 111-like terrace contributions of the total voltammogram, and were validated using cyclic voltammograms measured on single crystal stepped surfaces. The functions were found to reproduce the voltammograms, as well as the expected total charge due to hydrogen adsorption on the terrace and competitive hydrogen and hydroxide adsorption on the step (calculated by integrating the fit functions). This method was then applied to deconvolute voltammograms measured on polycrystalline platinum, where the total number of each type of site is unknown. Comparisons were made between the total electrochemically active surface area calculated using this method and the traditional H-UPD method, which is found to overestimate surface area. An accurate measure of the active surface area is important in electrocatalysis, where the intrinsic activity of a catalyst can only be determined if the real surface area is known.

The adsorption energetics calculated in Chapter 4 were used to examine the surface energy of the low index facets of platinum in Chapter 7. DFT was used to additionally examine high coverage hydrogen adsorption, oxygen adsorption, and surface oxide formation. This allows the relative surface energies for each facet to be compared at any potential in an aqueous electrolyte. Including the presence of a co-adsorbed potassium cation allows the surface energies to be compared at any pH. These surface energies define the stability of a platinum nanoparticle or a particular platinum surface faceting in an electrochemical environment, and for example, dictate how platinum nanoparticles may undergo Ostwald ripening. The strong binding of hydrogen and hydroxide to Pt(110) and Pt(100) drives these surfaces to be significantly more stable in an electrochemical environment than Pt(111), which is the most stable surface in the
absence of adsorption. The minimum energy nanoparticle shapes as a function of electrode potential were calculated. Additionally, a polycrystalline platinum electrode was experimentally cycled into the high potential region where oxide formation is favorable, and using the voltammogram deconvolution method described in Chapter 6, the number of 110 steps sites was found to increase. The calculated surface energies support this observation, as the 110 surface is the most stable surface at potentials where surface oxide is reduced.

Chapter 8 uses both experiment and density functional theory to examine quaternary ammonium cation specific adsorption, as these organic cations are used in alkaline polymer membrane electrochemical devices. The experimental results in Chapter 8 show that many quaternary ammonium cations block the adsorption of hydrogen and hydroxide at low potentials on a polycrystalline platinum electrode surface in an alkaline electrolyte. Using the voltammogram deconvolution method described in Chapter 6, it was found that these organic cations block more 110 and 100 sites than 111 sites. Using density functional theory, it was found that these organic cations favorably adsorb to Pt surfaces at low potentials in alkaline electrolytes, similar to the alkali metal cations (Chapter 2), but with stronger adsorption due to van der Waals interactions between the cation and the surface, which increases with increasing alkyl chain length. This explains the experimentally measured site blocking to be a result of the specific adsorption of these cations, even if explicit charge transfer to the cations is not seen experimentally. The experimental results also indicate these organic cations may oxidize at high potentials before desorbing from the surface, which could decrease their stability in an operating alkaline fuel cell.

Finally, in Chapter 9, both experiment and density functional theory were used to directly examine the effects of the alkali metal cations on the rate of the hydrogen oxidation reaction. The rate is found to depend on the alkali metal cation present in the electrolyte solution, following the trend \( \text{Li} > \text{Na} > \text{K} > \text{Cs} \). The density functional theory results show that the trend in the
weakening of hydroxide adsorption between the cations on the Pt(110) surface, the most active low index facet for hydrogen oxidation, matches the trend in the experimentally measured rate. This supports that adsorbed hydroxide may play a role in the hydrogen oxidation reaction, which others have proposed previously. While the exact role of hydroxide cannot be determined from these results alone, it suggests that the development of highly active electrocatalysts for the hydrogen oxidation reaction in alkaline electrolytes requires optimizing the adsorption strength of both hydrogen and hydroxide.

**10.2. Conclusions and Evaluation of Hypotheses**

1) Under what conditions (ion concentration, pH, electrochemical potential) is the specific adsorption of alkali metal cations to metal electrodes favorable? *Hypothesis: At low potentials and high electrolyte pH, alkali metal cations will specifically adsorb to some transition metal electrodes (within the electrochemical window of water).*

**Conclusion:** In Chapter 2, alkali metal cation specific adsorption was shown to be favorable to Pt(111) and Pd(111) electrode surfaces to low coverages at low potentials and competitive with hydrogen adsorption in an alkaline electrolyte. In Chapters 4 and 5, sodium and potassium adsorption were found to be favorable under similar conditions on the other low index Pt facets, Pt(110) and Pt(100), as well as on stepped Pt surfaces. In Chapter 9, the adsorption of Li, Na, K, and Cs are found to be favorable to all of the low index facets of platinum at low coverage and competitive with hydrogen adsorption in an alkaline electrolyte. The results in Chapter 9 also show adsorption of the cations is strongly coverage dependent and that they retain some of their charge on adsorption; this may explain why their adsorption is difficult to observe.
experimentally with cyclic voltammetry, as the total current due to their adsorption would be small and convoluted with the double layer charging current.

2) If specific adsorption of alkali metal cations is favorable, does the specifically adsorbed cation interact with common reaction intermediates, such as adsorbed hydrogen or adsorbed hydroxide? Does this explain the experimentally observed effects of pH on cyclic voltammograms measured on Pt(110) and Pt(100) electrodes? **Hypothesis:** The specifically adsorbed cation either weakens hydroxide adsorption or strengthens hydrogen adsorption, which would explain the experimentally observed effects of pH on the cyclic voltammograms.

**Conclusion:** The DFT results in Chapter 4 show that an adsorbed alkali metal cation (potassium) has only a small interaction with adsorbed hydrogen, but significantly weakens hydroxide adsorption on all three low index facets. The increasing weakening of hydroxide adsorption seen on increasing cation coverage, which is expected with increasing pH, explains the experimentally observed effects of pH on the cyclic voltammograms.

3) Does hydroxide competitively adsorb with hydrogen on along the steps of stepped platinum surfaces, similar to that seen/suggested on Pt(100) and Pt(110)? **Hypothesis:** The stronger binding of both hydrogen and hydroxide to Pt steps due to their lower coordination relative to surface atoms on Pt(111) drives adsorption of both species to be competitive and favorable at low potentials.

**Conclusion:** The DFT results in Chapter 5 show that when the effects of near-surface solvation are properly included, competitive hydrogen and hydroxide adsorption occurs on the steps of Pt(553) and Pt(533). Water near the surface can favorably adsorb and form strong hydrogen bonds with adsorbed hydroxide, promoting its adsorption along the step. Cyclic
voltammograms were simulated considering hydrogen adsorption on the terrace and competitive hydrogen and hydroxide adsorption on the steps of Pt(553) and Pt(533), and compared well with experiment; both in an acid electrolyte, and in a basic electrolyte where the competitive adsorption was modeled in the presence of co-adsorbed sodium along the step.

4) How does adsorption of hydrogen, hydroxide, oxygen, and alkali cations on the low index platinum facets effect platinum electrode stability as a function of pH and electrochemical potential? Hypothesis: The strong binding of hydrogen and hydroxide on to Pt(110) and Pt(100) surfaces drives these surfaces to be comparable in stability/surface energy to that of the Pt(111) surface (which has the lowest surface energy in the absence of adsorption).

Conclusion: The DFT results in Chapter 7 illustrate that the strong binding of hydrogen and hydroxide, as well as oxygen, drive Pt(100) and Pt(110) to be more stable than Pt(111) at low potentials (hydrogen adsorbed) and at high potentials (hydroxide/oxygen adsorbed). While the Pt(111) surface is most stable in vacuum (free from adsorbates), in an electrochemical environment, the Pt(111) surface is only the most stable surface over a very narrow range of potentials (0.2 to 0.5 V_RHE).

5) If the alkali metal cation mediates the effect of pH, is the rate of the hydrogen oxidation reaction dependent on the identity of the alkali metal cation present in an alkaline electrolyte? Hypothesis: As the adsorption of H* and OH* appear to be both pH and alkali cation dependent, and may be reactive intermediates in the hydrogen oxidation reaction, the rate of the hydrogen oxidation reaction is dependent on the alkali metal cation present in an alkaline electrolyte.
**Conclusion:** The experimental measurements in Chapter 9 show that the rate of the hydrogen oxidation and evolution reactions in an alkaline electrolyte are dependent on the identity of the alkali metal cation present, following the trend Li > Na > K > Cs. The density functional theory results show that adsorption of all of these cations is favorable to low coverages near the equilibrium potential for the HOR/HER in an alkaline electrolyte on the low index facets of platinum. The effect of the cations on the reaction rate is explained by their weakening of hydroxide adsorption; the trend between the cations in weakening hydroxide adsorption on Pt(110) matches the experimentally measured trend in the HOR/HER rate.

**10.3. Recommendations for Future Investigations**

In this dissertation, density functional theory was used to examine the effects of pH and alkali metal cations on the thermodynamics of hydrogen and hydroxide adsorption, and it was found that the rate of the hydrogen oxidation reaction varied with alkali metal cation, which is correlated with the thermodynamics of hydroxide adsorption. The mechanism of the hydrogen oxidation and evolution reactions and the role of adsorbed hydroxide however, remain unclear. Further, both pH and alkali metal cations may more directly affect the activation barriers of the elementary steps in the HOR/HER, by stabilizing or de-stabilizing the transition states, which was not examined here. Density functional theory kinetics modeling can be used to calculate the activation barriers of the possible elementary steps, to both elucidate the HOR/HER reaction mechanism as well as better understand the effects of pH and alkali metal cation.

Additional insight can be provided by experimentally measuring the rate of the HOR/HER on single crystal electrode surfaces, where the surface structure is known and the behavior can be directly compared with density functional theory results. The rate of the HOR/HER can be measured across transition metal surfaces and compared with hydrogen and
hydroxide binding strengths calculated by DFT, building on the volcano plot shown in Chapter 9 (which was limited to examining a few metals where single crystal rates had been measured in an alkaline electrolyte). To further investigate the dual site mechanism (involving both hydrogen and hydroxide) the rate can also be measured on single crystal stepped Pt surfaces and/or metal alloys, which may offer two different sites on the electrode surface with different hydrogen and hydroxide adsorption strengths.

10.3.1. Density Functional Theory Modeling of HOR/HER Mechanisms

The activation barriers for a set of possible elementary steps in a reaction mechanism will determine not only which path from reactants to products is preferred (the mechanism with the lowest activation barriers relative to the competing mechanisms), but also which step may be rate limiting, and therefore exert the largest effect on the overall rate of the reaction. For hydrogen oxidation and evolution, many possible mechanisms have been considered, with Chapter 9 providing density functional theory and experimental evidence supporting the role of adsorbed hydroxide and water in the hydrogen oxidation/evolution mechanism. In Chapter 9, it is proposed that either a dual site mechanism is involved in the rate limiting step, where both hydrogen and hydroxide react and desorb together as water, or near-surface hydroxide or water interact with the electrode surface at the transition state during hydrogen desorption, giving a dependence of the rate constant (activation barrier) on the hydroxide or water binding strength.

Density functional theory can be used to calculate the barrier for each of these possible hydrogen desorption mechanisms. This could include, for example, hydrogen desorption to a near-surface water molecule to form a solvated proton, hydrogen desorption to a near-surface hydroxide anion to form water, and hydrogen desorption through specifically adsorbed water or hydroxide (a Langmuir-Hinshelwood, dual site type mechanism). Each of these possible
elementary hydrogen desorption, or Volmer, steps could also be examined as Heyrovsky steps, involving simultaneous splitting of the H-H bond in H₂ concurrent with electron transfer and adsorption of one of the hydrogen atoms. Comparing these various elementary steps would allow for the dominant hydrogen oxidation (or evolution) mechanism to be identified as a function of electrolyte conditions.

To investigate the effects of electrolyte (pH and alkali cation) on the preferred mechanism, each activation barrier can be calculated in the presence of an applied electric field (which changes with changing pH) and an alkali metal cation adsorbed on the surface (which contributes to the experimentally observed effects of pH and of alkali metal cation (Chapters 4, 5, and 9)). The presence of a strong electric field or of an alkali metal cation adsorbed near the surface may reorient solvent near the electrode surface and alter the activation energies for each of the possible elementary steps, which may change which step is preferred (at low vs high pH, for example). This work would determine not only the mechanism of the HOR/HER in acid and alkaline electrolytes, but also how pH and alkali metal cations might directly affect the activation barriers present in the HOR/HER reaction, beyond their effects on hydrogen and hydroxide adsorption thermodynamics evaluated here.

While it has traditionally been difficult to calculate activation barriers and examine transition states of electrocatalytic reactions with density functional theory, a variety of methods have been recently developed which allow for the effects of near surface electric field and solvation to be investigated. To further simplify the problem, identification of the real hydrogen oxidation or evolution reaction mechanism as a function of pH does not require activation energies that perfectly match experiment, only activation energies which reflect a real trend between each of the possible mechanisms, so that the most favorable mechanism can be determined. This means the near-surface electrolyte structure does not need to be perfectly captured, only comparable between each of the possible elementary electron-transfer steps.
10.3.2. Experimental Measurements of the HOR/HER Rate

To gain further insight into how the binding strength of hydrogen, hydroxide, and water effect the rate of the HOR/HER, the rate of this reaction can be experimentally measured across various transition metal surfaces in an alkaline electrolyte (with the same alkali metal cation). To promote the most un-ambiguous comparison with density functional theory calculations, the HOR/HER rate should be measured on single crystal electrodes, where the surface structure is known. As the rate of hydrogen oxidation has been measured previously on the low index facets of platinum\(^4\), as well as on Ir(111), Au(111), and Ru(0001)\(^5\), the rate should be measured on the low index surfaces of other highly active electrocatalysts, such as Rh and Ir and stepped single crystal surface of Pt. If adsorbed hydroxide and/or water is actually involved in the hydrogen oxidation/evolution reaction mechanism, then the rate of this reaction over even only the most active catalysts should show a correlation (volcano type trend) with the binding strength of hydroxide or water onto these same surfaces. Experimental measurement of the activation energy for the HOR/HER across transition metal surfaces would also allow for direct comparison to density functional theory predicted kinetics.

Studying the rate of the HOR/HER on single crystal stepped platinum surfaces may be particularly useful for understanding the importance of adsorbed hydroxide or water. If the reaction does involve both adsorbed hydrogen and adsorbed hydroxide/water, then a surface which provides the optimum binding of both species will yield the highest rate. Stepped platinum surfaces offer two different types of sites, step sites, and terrace sites, which bind hydrogen and hydroxide/water very differently. As shown in Chapter 5, the 110 steps and 100 steps of Pt(553) and Pt(533) (respectively) bind hydrogen much more strongly than the 111-like terraces of these two surfaces. It is expected that hydroxide also binds much more strongly to the steps than to the terraces of these surfaces (certainly much more strongly than Pt(111), as shown in Chapter 5). If
the HOR/HER does follow a dual site mechanism (involving adsorbed hydrogen and adsorbed hydroxide/water), then a stepped surface, which offers weak binding on the terraces and strong binding on the steps, may yield a higher rate than a surface containing only weak binding sites (Pt(111)) and a surface containing only strong binding sites (Pt(110) or Pt(100) for example).

This idea is illustrated for Pt surfaces with 110 type steps in Figure 10-1, plotting the hypothetical HOR/HER reaction rate versus the fraction of step sites. The extremes are represented by Pt(111), which has no step sites, and Pt(110), which has no terrace sites. The rate of the HOR/HER is known to be faster on Pt(110) than on Pt(111) in an alkaline electrolyte. If the rate of the HOR/HER is only dependent on the adsorption strength of hydrogen, then given that Pt(110) binds hydrogen more strongly than Pt(111) (Chapter 4) and shows a higher rate than Pt(111), the rate of the HOR/HER should decrease from that on Pt(110) to that on Pt(111) with decreasing step density, as the number of these strong binding sites decreases. However, if the rate measured on various stepped Pt surfaces shows a maximum rate at an intermediate step density, then that may suggest a dual site mechanism, with strong binding of an adsorbate on the step and weak binding of an adsorbate on the terrace giving a higher rate. This also highlights the usefulness of studying the HOR/HER with both experiment and density functional theory, where the thermodynamics of hydrogen and hydroxide adsorption can be explicitly evaluated.
Figure 10-1. Hypothetical dependence of the HOR/HER reaction rate in an alkaline electrolyte on
the surface step density as expected for a single site or dual site HOR mechanism, for reaction
rates measured on stepped single crystal Pt surfaces. The rates measured on Pt(110) and Pt(111)
are known.

Additionally, studying the rate and activation energy for the HOR/HER on metal alloys
with both experiment and density functional theory provides another means to test the dual site
mechanism, where the combination of multiple metal sites may span a larger range of hydrogen
and hydroxide adsorption strengths or allow for the thermodynamics of hydrogen and hydroxide
adsorption to be de-coupled to a greater extent, yielding surfaces which bind one species strongly
and the other weakly.

10.3.3. Preliminary Results: Comparing Experimentally Measured Rates of the HOR/HER
with DFT Calculated Hydroxide Adsorption Strength Across Transition Metal Surfaces

If the weakening effect of a specifically adsorbed cation on the adsorption of hydroxide
does explain the effect of the cation identity on the rate of the hydrogen oxidation reaction in
alkaline electrolytes (Chapter 9), and the weakening of hydroxide by the cation is responsible for
the effects of pH on the thermodynamics of hydroxide adsorption (Chapters 4 and 5), then it is
reasonable to conclude the effect of the cation on the thermodynamics of hydroxide adsorption is also responsible for the effect of pH on the hydrogen oxidation reaction (where it is 2-3 orders of magnitude slower in an alkaline electrolyte than acid). This would also suggest that adsorbed hydroxide may be an intermediate in the hydrogen oxidation reaction at any pH, not just in alkaline electrolytes. To test this, Figure 10-2 plots the experimentally measured rate of the HOR/HER on many transition metal surfaces in both acidic and basic electrolytes as a function of the adsorption strength of hydroxide, calculated with DFT, on these same transition metals. This adsorption strength is given as the hydroxide adsorption potential, where a lower potential indicates stronger adsorption, and is calculated following the methods outlined in Chapters 4 and 5. While the rate of the HOR/HER has been measured on only a limited number of single crystal surfaces, a comparison between the rate on a polycrystalline surface and the hydroxide bonding strength on a single facet can still be made (assuming the difference in binding strength between the facets of a particular surface is small, such that any single facet can be chosen for the comparison). For the metals where the experimentally measured rates were measured on supported nanoparticle (metal/C) or polycrystalline electrodes, the hydroxide adsorption potential is calculated for adsorption on the fcc(111) and hcp(0001) surfaces of each fcc and hcp metal (with the bottom two layers of a four layer slab frozen at the experimentally measured lattice constants of these metals). For Pt/C and Pt(pc), the Pt(110) surface was used.

From Figure 10-2, it is clear that there is a volcano type relationship between the experimentally measured rate and the hydroxide adsorption strength. When the effects of pH are considered, it is found that hydrogen and hydroxide adsorption do not strongly correlate (as the cation weakens OH* but has a smaller effect on H*), suggesting this is not simply a reflection of the traditional hydrogen binding volcano. While most metals show a decrease in HOR/HER activity with increasing pH, the relationship in Figure 10-2 correctly captures the opposite trend on Ru(0001), where increasing the pH weakens hydroxide adsorption, increasing the hydrogen
oxidation rate, as Ru sits on the “too strong” binding side of the volcano. Figure 10-2 also captures the effect of pH and alkali cation on the HOR/HER on Pt/C and Pt(pc), where the presence of a cation with increasing pH weakens hydroxide adsorption, decreasing the rate, with the magnitude of this effect dependent on the alkali cation identity.

While this continues to support the involvement of adsorbed hydroxide or water in the HOR/HER, further study is needed to determine what the reaction mechanism is, and whether the apparent volcano plot in Figure 10-2 is merely a reflection of some other effect of the alkali metal cation and pH, for example, in destabilizing the transition state of the rate limiting step, leading to lower rates in high pH electrolytes. Experimental measurements of the rate of the HOR/HER on single crystal electrodes are needed, as the choice of modeling adsorption of hydroxide on the 111 or 0001 surfaces to compare with rates measured on polycrystalline surfaces is somewhat arbitrary.

Figure 10-2. The experimentally measured rate of the hydrogen oxidation reaction as a function of the DFT calculated hydroxide adsorption potential (a more positive potential indicates weaker adsorption). Patterned blue circles correspond to rates measured in acid, solid red circles are measured in base (with the OH\(^+\) adsorption potential calculated in the presence of K\(^+\)), and patterned red circles are the experimentally measured rates on Pt(pc) in the presence of various alkali metal cations, given in Chapter 9. The solid black lines are added as a guide to highlight the volcano trend.
10.4. References

VITA

Ian T. McCrum

Education

The Pennsylvania State University, University Park, PA
Doctor of Philosophy – Chemical Engineering
Clarkson University, Potsdam, NY
Bachelor of Science – Chemical Engineering

Publications