MODELING Pt AND CATALYST LAYER DEGRADATION IN POLYMER ELECTROLYTE FUEL CELLS

A Dissertation in
Mechanical Engineering
by
Yubai Li

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Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2017
The dissertation of Yubai Li was reviewed and approved* by the following:

Chao-Yang Wang
Professor and William E. Diefenderfer Chair of Mechanical Engineering
Dissertation Advisor
Chair of Committee

Donghai Wang
Associate Professor of Mechanical Engineering

Adri van Duin
Professor of Mechanical Engineering

Michael Janik
Professor of Chemical Engineering

Karen Thole
Distinguished Professor of Mechanical Engineering
Department Head of Mechanical and Nuclear Engineering

* Signatures are on file in the Graduate School.
ABSTRACT

Cost and durability of polymer electrolyte fuel cells (PEFCs) are two most critical issues faced by commercialization of fuel cells. Cathode catalyst layer (CCL) plays an important role in PEFCs from both aspects of cost and durability. Due to the sluggish oxygen reduction reaction (ORR) at CCL, sufficient Pt-loading is needed at CCL to provide electrochemical surface area (ECA) for the ORR. Meanwhile, a micro-scale oxygen transport resistance through the ionomer film covering the Pt nanoparticles is recently found. Sufficient Pt-loading is also needed at CCL to prevent large micro-scale oxygen transport loss. The cost of the Pt metal could not be reduced by mass production and features largely in the total cost of PEFC stack. At the same time, the Pt catalysis in CCL is inevitable to degrade during the PEFC lifetime, and ECA loss and PEFC performance loss are caused consequently. So using the precious Pt wisely and reducing the Pt degradation are vital challenges to achieve long-term good performance of PEFCs. Based on this, modeling the Pt and catalyst layer degradation in PEFC is urgently needed to understand the fundamental mechanisms of CCL degradation and finding methods to mitigate the CCL degradation.

A one-dimensional model is firstly developed and validated to study Pt degradation and subsequent ECA loss through the CCL of PEFCs. The model includes two mechanisms of Pt degradation: Ostwald ripening on carbon support and Pt dissolution-re-precipitation through the ionomer phase. Impact of H$_2$ | N$_2$ or H$_2$ | Air operation, operating temperature, and relative humidity (RH) on Pt degradation during voltage cycling is explored. It is shown that ECA loss is non-uniform across the CCL with a zone of exacerbated Pt degradation and hence much lower ECA found near the membrane. This non-uniform Pt degradation is caused by consumption of Pt ions by crossover H$_2$ in both H$_2$ | N$_2$ and H$_2$ | Air systems. An important consequence is that thinning the cathode electrode in a PEFC would lead to more ECA loss as a higher fraction of the
thin CCL would fall in this exacerbated degradation zone. We have quantified the effect of thin CCLs on Pt degradation for the first time.

The micro-scale oxygen transport resistance significantly complicates the consequence of Pt degradation. It is found that this micro-scale oxygen resistance increases with ECA normalized current density. So as the ECA in CCL losses during the Pt degradation, it not only induces higher ORR kinetic losses, but also causes extra voltage loss by increasing the micro-scale transport resistance. To elucidate this complicated issue, the 1D physics-based Pt degradation submodel is coupled into the transient M2 model to study the non-uniform Pt degradation and its impacts on long-term PEFC performance. The performance loss of a low Pt-loading PEFC with Pt degradation, the interactions of Pt degradation with the micro-scale transport resistance, the cause and consequence of non-uniform Pt degradation, as well as a strategy of raising lower current density in current cycling test are quantified. This Pt degradation model is demonstrated to be an effective approach to better understand Pt degradation, performance loss caused by Pt degradation, and mitigation strategies to alleviate Pt degradation, all important for achieving excellent durability of PEFCs.

The non-uniform Pt degradation in the channel-land direction is well predicted by the transient physics based Pt degradation model. However, further application of this method is limited by computational cost. On the other hand, the along-channel non-uniform ECA distribution can cause non-negligible effect on end-of-life (EOL) performance of PEFC compared with uniform ECA distribution when the cathode Pt-loading of the PEFC is low. Thus capturing the along-channel non-uniform Pt degradation is essential to predict the EOL performance of PEFC. In this dissertation, an empirical model for Pt degradation is developed and integrated into M2 model to predict the along-channel non-uniform Pt degradation and the EOL performance of low Pt-loading PEFCs. This method is first applied on 3D single channel PEFC modeling case. The shift of current density distributions, and the critical role of micro-scale oxygen transport loss
during the degradation for low Pt loading PEFCs are also discussed with this model. Then, this modeling method is applied on a medium scale PEFC modeling case to demonstrate its future applicability to realistic industrial PEFC regarding to EOL performance.
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ACKNOWLEDGEMENTS

I would like to express my sincere appreciation and thanks to my advisor Professor Chao-Yang Wang, you have been a tremendous mentor for me. Thank you for leading me into PEFC research and leading me to grow as a researcher in mechanical engineering. Your advices on both my research and career have been priceless. Besides my advisor, I would like to thank my other committee members, Professor Donghai Wang, Professor Adri van Duin, and Professor Michael Janik, for providing insightful comments and suggestions. I would also like to thank the members at the Electrochemical Engine Center, for being great colleagues and friends. I have learned a lot from each of you. I will miss good working time with you. Finally, I would like to thank my parents, my wife Feiyan Yu and Feiyan’s parents for supporting me spiritually throughout my PhD study and my life in general.
Chapter 1

Introduction

1.1 Background and Motivation

Cost, reliability and durability of polymer electrolyte fuel cells (PEFCs) are crucial issues for the commercialization of fuel cell vehicles. U.S. DOE set the goal to develop a 60% peak-efficient, 5,000 hour durable, direct hydrogen fuel cell power system for transportation at a cost of $40/kW by 2020 in 2012 technical plan [1]. To achieve these goals, a comprehensive understanding of the degradation mechanisms and effective mitigations strategies based on the understanding of the degradation mechanisms are sorely needed. Figure 1-1 illustrated several components’ degradation mechanisms in PEFCs. Membrane degradation, carbon corrosion and catalyst degradation are all important to the lifespan of PEFCs [2]. Among them, catalyst degradation is of special importance and has received extensive attention of academic and industries recently. In an estimation of cost breakdown from Nissan, 46% of the total cost of PEFC stack comes from the catalyst and application [3]. Due to the precious nature of Pt, the cost of Pt catalyst could not be reduced by mass production [3]. At the same time, the catalyst electrode suffers from deterioration and results in performance loss during the PEFC lifetime [4]. As a result, catalyst layer degradation is among the most critical degradation mechanisms for PEFCs. Understanding and alleviating the catalyst layer degradation are the most challenging research topics in PEFC durability studies.

Fuel cell modeling plays an important role in today’s fuel cell stack design. This computer-aided engineering approach can significantly reduce the time and cost of experimental trial-and-errors [5]. Like the combustion simulation for the IC engine in conventional automobiles, the fuel cell modeling would be an essential engineering approach to fuel cell engineering. Although great
achievement has been made in the PEFC modeling in recent years [6] [7], the catalyst degradation modeling for PEFCs is still at the early stage. Developing a catalyst degradation model for PEFCs has a two-fold objective. First, a catalyst degradation model can quantitatively elucidate the underlying mechanisms of the degradation results observed in testing. Second, a catalyst degradation model can be applied to provide strategies for the mitigation of degradation. New strategies using a parametric study can be tested with the catalyst degradation modeling before initiating experimental attempts.

1.2 Literature Review on PEFC Catalyst Degradation

1.2.1 Catalyst Degradation Mechanisms

A central issue of PEFC catalyst layer durability is the loss of electrochemical surface area (ECA) over time. Much research has been carried out in the past two decades [2] to understand the fundamental mechanisms of platinum degradation and to suggest effective mitigation strategies. Four processes have been outlined as possible Pt degradation mechanisms [8]: i) Ostwald ripening on carbon support [9-13]; ii) Pt crystal migration and coalescence [14-16]; iii) detachment and agglomeration of Pt nanoparticles induced by carbon corrosion [17-20]; and iv) Pt dissolution, Pt ion transport in the ionomer phase and subsequent re-precipitation by H₂ crossover through the membrane [10, 12, 21-24]. Although the dominating degradation mechanisms under various fuel cell operating conditions are still under debate, durability test protocols [25] of electrocatalysts, such as those suggested by Fuel Cell Commercialization Conference of Japan (FCCJ), can lend some basic insight into degradation mechanisms. For start/stop durability tests, a triangular-wave potential cycle of 1.0 – 1.5 V vs. reversible hydrogen electrode (RHE) is chosen and the major degradation is carbon corrosion [25] and the ensuing Pt agglomeration and Pt detachment [26]. Suppressing carbon corrosion under such high voltage would be the first priority [27, 28]. On the other hand, a square-wave potential cycle of 0.6 – 1.0
V vs. RHE is used to simulate the load-cycle tests and Pt degradation induced by carbon corrosion is minor in this case [25, 29], and Ostwald ripening and Pt dissolution followed by re-precipitation could lead to accelerated degradation [10, 30]. The Chapter 2 and Chapter 3 in this dissertation is limited on investigating the Pt degradation behavior under the load-cycle test condition, and further study is expected to extend to actual PEFC load conditions during vehicle driving. The start-stop stability, which is determined by carbon corrosion, has not been included in this dissertation.

According to Pourbaix diagram, Pt dissolution can occur at voltages higher than 1.0 V and pH less than 0 at 25°C [31]. Mitsushima et al. [32] suggested that Pt solubility in acidic media increases with temperature and decreases with pH. It was also observed that the voltage cycling accelerates the dissolution of Pt [33-35]. Since the PEFCs used in automotive fuel cells involve an acid membrane, and the cathode potential vs. RHE at open circuit voltage is above 1.0 V, the above mentioned degradation mechanisms occur [36]. The typical operating temperature of an automotive fuel cell could be as high as 90°C, and the cathode catalyst layer (CCL) is usually subjected to voltage cycling in a realistic driving cycle [36]. Therefore, Pt dissolution is ubiquitous in automotive PEFCs and hence, ECA loss [31].

1.2.2 Impacts of Operating Conditions

Influences of operating conditions on Pt degradation have been scrutinized in the literature. It was reported that higher temperature [36-41] and higher relative humidity (RH) [38-43] conditions could induce more rapid Pt degradation. The effect of O₂ partial pressure on the dissolution of Pt nanoparticles has also been investigated [43-45]. A fundamental study of Matsumoto et al.[44] found 18 times accelerated dissolution of polycrystalline Pt under pure O₂ as compared to under pure N₂; however, this acceleration factor decreased to only 1.2 for carbon-supported Pt nanoparticles. Further weakening of the O₂ partial pressure effect was
experimentally observed in catalyst layers made of carbon-supported Pt nanoparticles [43, 45]. Indeed, Bi et al. [43] reported that the ECA loss under $\text{H}_2 | \text{N}_2$ condition is marginally higher than the loss under $\text{H}_2 | \text{Air}$ condition. This is likely due to the fact that when the O2 partial pressure increases, the Pt ion sink is pushed farther away from the CCL into the membrane, thereby lowering the Pt ion flux dissolved and transported into the membrane [46, 47]. Such a weak effect of O2 partial pressure on Pt degradation and ECA loss in a fuel cell cathode can only be explained by a one-dimensional physics model to be developed in the present work.

1.2.3 Non-uniform Nature of Catalyst Degradation Problem

The Pt degradation in CCL is spatially highly non-uniform. In the through-plane direction, an important consequence of the combined Pt Ostwald ripening and Pt dissolution-re-precipitation [48] is non-uniform distribution of degradation across the CCL. Indeed, under in-situ voltage cycling test conditions, it was observed that most of Pt mass loss occurred near the CCL-membrane interface for both $\text{H}_2 | \text{N}_2$ [10, 12] and $\text{H}_2 | \text{Air}$ [49] conditions. Moreover, Nagai et al. [50] carried out durability tests for Pt catalyst on carbon support with different catalyst loadings and hence different catalyst layer thickness, and found that a lower Pt-loading catalyst layer suffers from more rapid ECA loss but the total Pt mass dissolved remains almost the same. Such an observed trend of ECA loss versus catalyst layer thickness could be theoretically explained by the possibility that most of the Pt mass loss occurred near the membrane where the Pt ion sink created by crossover $\text{H}_2$ is located, and Pt mass near the GDL is preserved by re-deposition [50]. However, accurate measurement of ECA loss distribution across the CCL is difficult, if possible at all.

For the channel-land and the along-channel directions, the Pt degradation in the CCL is also prone to be non-uniform. As reviewed, temperature and RH are two important factors that have impacts on the Pt degradation rate in CCL. In realistic PEFCs, the temperature field [51] and
liquid saturation field [52] are highly non-uniform in CCL, hence spatially non-uniform Pt degradation commonly results. This spatially non-uniform Pt degradation distribution is hard and tedious to be determined by accurate measurement, especially for the large scale of fuel cell stack. And many issues are left untouched due to this difficulty, for example, whether the aged CCL would induce higher risk of localized flooding. CAE is playing an important role in fuel cell engineering nowadays [4], and modeling study has shed light on design and development of PEFCs with better performance [5]. Now a model including the Pt degradation distribution for CCL is urgently needed to estimate the PEFC CCL aging rate, to investigate the aged PEFC performance, and to look for mitigation strategies to reduce Pt degradation.

1.2.4 Mathematical Modeling of Catalyst Degradation

Mathematical modeling has been used to aid in deconvoluting Pt degradation mechanisms. Darling and Meyers [53, 54] were the first to develop kinetic rate equations for Pt electrochemical dissolution, Pt oxide film formation, and Pt oxide chemical dissolution. This model explained why under steady potential, equilibrium concentration of dissolved Pt increases monotonically from 0.65 to 1.1 V vs. SHE and decreases at potentials higher than 1.1V [55]. A protective Pt oxide layer can be formed on the surface of Pt particles at high potential and prevent Pt from directly exposure to high voltage and further dissolution [53]. Franco and Tembely [56] proposed a transient multiscale model of Pt degradation in the cathode electrode using the multi-layer model [57] of electrochemical interface. Pt degradation under galvanostatic conditions instead of potentiostatic conditions was investigated with this model [56]. Bi and Fuller [58] proposed a one dimensional (1D) bi-modal particle size model to investigate the Pt degradation processes, and the mechanism of Pt ion re-precipitation was included. As two particle size groups cannot fully represent the nature of nearly continuous PSD in reality, the predicted ECA and particle size profiles were found to be abrupt. Holby et al. [59] refined the model of Darling and Meyers [53]
by applying hundreds of particle size groups to represent the nearly continuous PSD. Rinaldo et al. [60] investigated Pt Ostwald ripening under constant Pt ion concentration condition, and in a more recent study [61] proposed the equations of coagulation and detachment in addition of dissolution and redeposition and compared the ECA loss behaviors under different degradation mechanisms. Researchers from Toyota [49, 62] developed a 1D Pt degradation model which could predict the overall ECA loss and non-uniform Pt mass distribution across the CCL, but no specific result on non-uniform Pt$^{2+}$ concentration or non-uniform ECA distribution was given. Recently, Ahluwalia et al. [41] proposed a model based on the hypothesis that Pt dissolution and subsequent particle agglomeration are responsible for Pt degradation and ECA loss. One significant advance in the work of Ahluwalia et al. [41] is that both thermodynamics and kinetics of Pt dissolution are accounted for [63], as the Pt equilibrium concentration (solubility) could play an important role in Pt dissolution.
Figure 1-1. Illustration of several important degradation mechanisms in PEFCs.
Chapter 2

One Dimensional Physics Platinum Degradation Model

2.1 Introduction

Based on the kinetic equations of Holby et al. [59], a 1D physics model that describes Pt degradation phenomenon across the CCL is developed in this chapter. This 1D Pt degradation model is focused on the non-uniform Pt degradation distribution and predicts the non-uniform ECA distribution across the CCL, which means the through-plane direction. This 1D model is used to elucidate the influence of H₂ | N₂ vs. H₂ | Air conditions on Pt degradation in CCL and is found to capture well the temperature effects on Pt degradation. Additionally, a new method is introduced to allow the model to capture the humidity effect on both ECA and PSD evolutions. The Pt degradation as consequence of reducing Pt-loading by thinning the CL is quantified by this 1D physics model.

2.2 Model Development

The modeling zone is a 1D domain as shown in Figure 2-1 where \( L \) is the thickness and \( A \) is the area of the catalyst layer. The CCL-membrane interface is at \( x = 0 \) and the CCL-GDL interface is at \( x = L \). Throughout the present study, all Pt particles are assumed to be semi-spherical.

The electrochemical reactions for Pt oxidation and Pt dissolution can be written as:

\[
Pt_{(s)} + H_2O_{(aq)} \leftrightarrow PtO_{(s)} + 2H^+ + 2e^- \tag{2.1}
\]

\[
Pt_{(s)} \leftrightarrow Pt^{2+}_{(aq)} + 2e^- \tag{2.2}
\]
Additionally, chemical dissolution of Pt oxide may be considered as shown in Equation 2.3 (Darling and Meyers [53]):

\[ \text{PtO}_x(s) + 2H^+ \leftrightarrow \text{Pt}^{2+}(_{aq}) + \text{H}_2\text{O} \]  

However, as discussed by Tang et al. [65] for Pt nanoparticles, the direct electro-oxidation denoted by Equation 2.2 is the major dissolution mechanism. Uchimura et al. [42] also suggested that the chemical dissolution of Pt oxide is negligible when compared with the electrochemical dissolution of the Pt. Therefore, chemical dissolution of Pt oxides is neglected in this study.

Equations 2.4–2.8 [59, 64] in the following are used for the current model to capture the PSD and oxide fractional coverage evolutions. The Pt oxide formation and removal is described by a thermo-kinetic rate model developed by Holby and Morgan [64]. In their model, the forward and backward reaction rates were derived from the Eyring-Polanyi equation, and the Brönsted-Evans-Polanyi approach was applied to treat the deviation from equilibrium [64]. The Pt dissolution and re-deposition was modeled with a modified Butler-Volmer rate equation developed by Holby et al. [59]. Gibbs-Thomson approximation was applied in their model derivation to capture the size dependent stability effect of Pt nanoparticles [59]. As shown in Figure 2-1, the 1D domain can be divided into \( N \) control volumes. Assume that on each of the control volume \( i \) there are \( M \) discrete particle size groups, and one particle size group is denoted by \( j \). The diameter of each particle group is \( d_{i,j} \), and the oxide coverage ratio of each particle group is \( \theta_{i,j} \). The particle number in each diameter group is \( \text{Num}_{i,j} \). The particle net oxidation rate \( r_{\text{net,oxide}} \) [mol/(cm\(^2\)·s)] [64] and the net Pt dissolution rate \( r_{\text{net,pt}} \) [mol/(cm\(^2\)·s)] [59] can be written, respectively, as:

\[
 r_{\text{net,oxide}} = v_i^* \Gamma \exp \left[ \frac{-1}{RT} \left( \tilde{H}_{2,\text{fit}} + \Lambda \theta_{i,j} \right) \right] \times \left\{ \left( \frac{\theta_{i,j}}{2} \right) \exp \left[ -\frac{n_2 F (1 - \beta_2)}{RT} \left( U_{\text{fit}} + \frac{\omega \theta_{i,j}}{n_2 F} - V \right) \right] \right\} \]  

\[
 r_{\text{net,pt}} = \frac{v_i^*}{v_1^*} \exp \left[ \frac{-n_2 F \beta_2}{RT} \left( U_{\text{fit}} + \frac{\omega \theta_{i,j}}{n_2 F} - V \right) \right] \]
where the total surface tension $\gamma_{total}$ [J/cm$^2$] can be expressed as [64]:

$$
\gamma_{total} = \gamma + \Gamma \theta_{i,j}RT \times \left[ \log \left( \frac{v_2}{v_1} \right) + \log \left(10^{-2}d_i \right) + \frac{n_i F}{RT} \left( U_{fit} - V \right) + \frac{\omega \theta_{i,j}}{2RT} \left( \frac{1}{2} \frac{\theta_{i,j}}{2} \right) \right]
$$

The specific descriptions and values of the parameters and physical properties are listed in Table 2-1. The $c_{pt^2+}$ term in Equation 2.5 denotes the Pt$^{2+}$ concentration, which can be solved from the 1D Pt$^{2+}$ diffusion equation in this study. For every particle diameter group $(i,j)$, the particle size and oxide fractional coverage evolutions can be tracked. The initial number of particles in each particle diameter group $(i,j)$ is generated by the initial PSD and the initial total particle number calculated from $d_m$, the area $A$ and Pt-loading. The initial oxide fractional coverage $\theta_{i,j}$ is assumed to be zero in each particle group. The particle diameter evolution rate [cm/s] [41] and oxide fractional coverage development rate [1/s] [59] can be expressed as:

$$
\frac{d(d_{i,j})}{dt} = -r_{net, Pt} \Omega
$$

$$
\frac{d(\theta_{i,j})}{dt} = \frac{r_{net, oxide}}{\Gamma} - \frac{2\theta_{i,j}}{d_{i,j}} \frac{d(d_{i,j})}{dt}
$$

In this chapter, because Pt degradation under voltage cycling is of primary interest, the particle diameter growth induced by surface oxides is assumed to be reversible in each potential cycle [66]. This means that the Pt oxidation and reduction under the voltage cycling does not directly affect the particle diameter evolution, as indicated by Equation 2.7. But the oxide
fractional coverage can indirectly affect the Pt dissolution rate, as the high oxide fractional coverage at high voltage prohibits Pt from dissolution, as indicated by Equation 2.5. Equations 2.7 and 2.8 are discretized and simulated with classical Runge-Kutta method.

The diffusion equation of Pt\(^{2+}\) concentration, \(c_{Pt^{2+}}(x)\) \([mol/cm^3]\), is given by:

\[
\varepsilon \frac{\partial c_{Pt^{2+}}}{\partial t} = \nabla \cdot \left( \varepsilon^{1.5} D \nabla c_{Pt^{2+}} \right) + S_{Pt^{2+}} \tag{2.9}
\]

where \(D\) is the Pt\(^{2+}\) diffusivity in the ionomer. Notice that Pt\(^{2+}\) migration occurs with electrolyte potential distribution resulting from current distribution within the electrode. However, its effect can be neglected based on the order of magnitude analysis at a high potential [58] as well as the simulated low Pt\(^{2+}\) concentration at a low potential in this study. As a result, the model is applicable to the actual PEFC undergoing voltage cycling as demonstrated in the model validation section. The diffusivity suggested by Ferreira et al. [10] is used in this study for the cases under fully humidified condition:

\[
D = D_{_{Pt^{2+},H_{2}O}} \times H_{2}O \tag{2.10}
\]

At the CL-GDL interface, there is no flux boundary condition for \(c_{Pt^{2+}}(x)\), i.e.

\[
\frac{\partial c_{Pt^{2+}}}{\partial x} \bigg|_{x=L} = 0 \tag{2.11}
\]

Under the \(H_2 \mid N_2\) (anode/cathode) condition, a Pt\(^{2+}\) sink can be assumed to be exactly at the CL-membrane interface as shown in Figure 2-1, as the crossover \(H_2\) will reach this interface without meeting \(O_2\). Thus, the boundary condition at this interface is:

\[
c_{Pt^{2+}} \bigg|_{x=0} = 0 \tag{2.12}
\]

On the other hand, under the \(H_2 \mid Air\) (anode/cathode) condition, a Pt band forms in the membrane, and the Pt\(^{2+}\) concentration can be assumed to be linear from the CCL-membrane
interface to the Pt band. Then Pt\(^{2+}\) concentration boundary condition at the CL-membrane interface is written as:

\[
\varepsilon_{\text{1.5}} \frac{\partial c_{\text{Pt}^{2+}}}{\partial x} \bigg|_{x=0} = -\frac{c_{\text{Pt}^{2+}}}{\delta_{\text{Pt}}}
\]

2.13

where \(\delta_{\text{Pt}}\) is the distance of the Pt band from the CCL-membrane interface, which can be estimated as follows [46]:

\[
\delta_{\text{Pt}} = \frac{2K_{O_{2}}p_{O_{2}}\delta_{M}}{K_{H_{2}}p_{H_{2}} + 2K_{O_{2}}p_{O_{2}}}
\]

2.14

where \(\delta_{M}\) is the thickness of the membrane, \(p_{H_{2}}\) is the partial pressure of H\(_{2}\), \(p_{O_{2}}\) is the partial pressure of O\(_{2}\), while \(K_{H_{2}}\) and \(K_{O_{2}}\) are the permeabilities of H\(_{2}\) and O\(_{2}\) through the membrane.

The initial \(c_{\text{Pt}^{2+}}(x)\) is assumed to be zero throughout the problem domain. Equation 2.9 is discretized using Implicit Euler and central difference schemes and solved by tridiagonal matrix algorithm (TDMA). In Equation 2.9, \(S_{\text{Pt}^{2+}}(x)\) is the source term due to Pt dissolution. After discretization, this source term of net Pt\(^{2+}\) dissolution in each control volume is assumed to be \(S_{i}\), which can be expressed as:

\[
S_{i} = \sum_{j=1}^{M} \frac{\pi}{2} \left( \frac{d_{i,j}}{2} \right)^{2} \frac{\text{Num}_{i,j} r_{\text{net},\text{Pt}}}{\Delta v}
\]

2.15

where \(\Delta v\) is the volume of the control volume:

\[
\Delta v = LA / N
\]

2.16

The geometric surface area (GSA) and the ECA can be calculated by:

\[
\text{GSA} = 2\pi \sum_{i=1}^{N} \sum_{j=1}^{M} \text{Num}_{i,j} \left( \frac{d_{i,j}}{2} \right)^{2}
\]

2.17

\[
\frac{ECA(t)}{GSA(t)} = \frac{ECA(0)}{GSA(0)}
\]

2.18
Equation 2.18 assumes $ECA(t) / GSA(t)$ to be constant [64] during the degradation process. After the $GSA(t)$ is calculated at each time step, the normalized electrochemical surface area $ECA(t) / ECA(0)$ can be obtained. Similarly, the normalized electrochemical surface area distribution can be calculated as $ECA(x,t) / ECA(x,0)$.

### 2.3 Results and Discussion

In this section, a comparison of model predictions with the experimental data of Ferreira et al. [10] is first made. Second, we use the model to explore the effect of $O_2$ partial pressure. The Pt$^{2+}$ concentration distribution across the CCL is found to be affected by the location of the Pt band in the membrane. Consequently, the remaining ECA after voltage cycling is affected by $O_2$ partial pressure. Third, the temperature effect on ECA evolution is investigated. In addition, an approach to introduce the humidity effect in the current model is developed and validated to capture the ECA and PSD evolutions. Finally, the consequences of lowering the Pt-loading through thinning the CCL are studied.

#### 2.3.1 Model Validation and Effects of $H_2 | Air$ Condition

The equilibrium Pt$^{2+}$ concentration is crucial to the understanding of Pt dissolution behavior [8], and the modeling of Pt Ostwald ripening behavior [59] in PEFC. In the Holby et al. [59] model, the equilibrium concentration data of Bindra et al. [67] are used. The Pt$^{2+}$ solubility from Bindra et al.’s measurement is with Pt foil [67] and there exists a strong dependence of Pt equilibrium concentration on the particle size [8]. Therefore, in this chapter, we refitted the value $c_{ref}^{Pt^{2+}}$ with the equilibrium concentration data of Ferreira et al. [10]. Following the approach of
Holby and Morgan [64], the net dissolution rate should be zero at equilibrium, which means for a nanoparticle of 2.5 nm, the equilibrium concentration at 80°C and 0.95 V is about $1 \times 10^{-6}$ M [10]. A major adjusting parameter in this chapter is the Pt dissolution activation enthalpy $\overline{H}_{1,\text{fit}}$. $\overline{H}_{1,\text{fit}}$ is adjusted to fit the ECA evolution and PSD distribution from experimental results of Ferreira et al. under 80°C, H$_2$ | N$_2$ condition, and the voltage cycles from 0.6 to 1.0 V vs. RHE with sweeping rate of 20 mV/s [10]. The initial PSD follows a Gauss distribution with mean diameter of $d_m = 3$ nm and variance of $\sigma^2 = 0.22$, and the Pt-loading is assumed to be 0.4 mg/cm$^2$ [10]. This case is regarded as a baseline in the present chapter.

The temporal evolutions of Pt$^{2+}$ concentration near GDL and oxide fractional coverage on a particle of 3 nm near GDL in one (the first) voltage cycle are shown in Figure 2-2. In this cycle, the Pt$^{2+}$ concentration reaches about 1.24 μM when the voltage reaches 1.0 V, which is a reasonable value considering the Pt$^{2+}$ solubility limit at 80°C and 1.0 V (about 0.8 – 1.5 μM) [10]. Another finding from this calculation is that the Pt$^{2+}$ concentration is only large under high voltage and is negligible when the voltage is lower than 0.85 V in this voltage cycle. On the other hand, the current density is small at voltage higher than 0.85 V [58]. So the Pt$^{2+}$ electro-osmotic migration effect driven by potential drop is neglected in this chapter, as shown in Equation 2.9. Then, $\overline{H}_{1,\text{fit}}$ is adjusted and a test of 10,000 voltage cycles is performed. As this calculation is under fully humidified condition, this value of $\overline{H}_{1,\text{fit}}$ is defined as $\overline{H}_{1,\text{fit,100\%RH}}$ and is used in the following sections. The predicted ECA evolution is in good agreement with the experimental result [10] as shown in Figure 2-3. The remaining Pt mass distribution on carbon support after cycling is compared in Figure 2-4. Both experimental and predicted results show non-uniform Pt mass loss, and the highest Pt mass losses are near the CCL-membrane interface. A Pt mass depletion region could be found near the CCL-membrane interface, as the soluble Pt$^{2+}$ ion meets
H$_2$, then re-precipitates and nucleates on the large Pt particles in the ionomer phase near this interface [10]. In our model, the Pt mass depletion region is narrower than that seen in the experiments of Ferreira et al. [10] where a lot of large Pt particles off carbon support could be found deep within the CCL. On the contrary, the current study assumed Pt re-precipitation to occur only at the CCL-membrane interface. These large Pt particles off carbon support could induce Pt re-precipitation in the CCL, which is neglected in the current study. There could be one possible implication. If the CCL is so thin as to be totally under the Pt mass loss region, much faster Pt degradation and overall ECA loss could be found. This is a possible limitation for very thin CCLs and will be discussed in detail later. For the PSD, the comparison is only made near the CL-GDL interface, as Pt particles off carbon support can be found at other places across the CCL [10] and our model could only account for Pt particles on carbon support. This comparison of PSD is shown in Figure 2-5.

The Pt$^{2+}$ sink created by crossover H$_2$ will lead to non-uniform Pt$^{2+}$ concentration across the CCL and non-uniform ECA loss. The Pt$^{2+}$ concentration distribution in one voltage cycle is shown in Figure 2-6a. As crossover H$_2$ could reach the CCL-membrane interface under H$_2$|N$_2$ condition, the Pt$^{2+}$ sink described by Equation 2.12 causes a region of lower Pt$^{2+}$ region near membrane. Under H$_2$|Air condition described by Equation 2.13, the Pt$^{2+}$ sink is in the membrane and the corresponding Pt$^{2+}$ concentration distributions in one voltage cycle are shown in Figure 2-6b. Consequently, another case study to investigate the effect of H$_2$|Air condition is performed and compared with the baseline. The overall ECA loss is compared in Figure 2-7, and it can be found that the overall remaining ECA under H$_2$|Air condition is slightly higher than under H$_2$|N$_2$ condition. This finding is in accordance with experimental results of Bi et al. [43]. Further, our model revealed that Pt mass lost into the ionomer/membrane occurs through dissolution into Pt$^{2+}$, diffusion and subsequent re-precipitation inside the membrane under the H$_2$ | Air condition, whereas the dissolved Pt ions re-precipitate immediately at the CCL-membrane interface in the
H$_2$ | N$_2$ case. Consequently, Pt mass loss into the ionomer/membrane is stronger under H$_2$ | N$_2$ condition than that under the H$_2$ | Air, with the former calculated at 10.2% after 10,000 cycles versus 0.8% for the latter.

The effect of O$_2$ partial pressure on Pt degradation and ECA loss is clearly explained through the present modeling study. The different boundary conditions at the CCL-membrane interface under H$_2$ | N$_2$ and H$_2$ | Air conditions, respectively, lead to differing Pt$^{2+}$ concentration distributions shown in Figure 2-6, leading to different remaining ECA distributions shown in Figure 2-8. For both cases, faster ECA loss can be found near the CCL-membrane interface. The ECA distribution across the CCL is difficult to measure experimentally, so the current model offers an alternative to investigate the through-plane non-uniform distribution of ECA loss in the CCL.

### 2.3.2 Temperature and Humidity Effects

Several series of experimental data are used to demonstrate the predictability of this model under different temperatures and relative humidity (RH). First, a series of experimental results are used to test whether this model could capture temperature effects on Pt degradation quantitatively. In these tests, square wave potentials are applied on all cycling experiments (25 cm$^2$ subscale cells, catalyst loading of 0.35 mg/cm$^2$) under fully humidified H$_2$ | N$_2$ condition with voltage hold time of 10 s at 0.95 V and 2.5 s at 0.6 V vs. RHE [36]. The only variable in these experiments is the cell temperature, i.e. 40°C, 60°C, and 80°C. The CCL thickness and initial PSD are assumed to be identical to those used in the last section. As shown in Figure 2-9, the ECA evolutions predicted by the model are in good accordance with the experimental results, indicating that temperature effects are quantitatively captured by this model. The temperature impact on the diffusion coefficient of Pt$^{2+}$ has been neglected in the current stage of study.
Up to this point, all the work deals with Pt degradation under fully humidified condition. This part of study further concerns Pt degradation at low humidity condition. As the proton diffusivity in the ionomer phase is a strong function of RH, the current study assumes that the Pt$^{2+}$ diffusivity follows the same function of proton conductivity with RH [68]:

$$D = D_{\text{Pt}^{2+/H_2O}}^{xH_2O}RH^{2.84}$$ \hspace{1cm} 2.19

Then, as suggested by Ahluwalia et al. [41], the Pt dissolution rate can be written as a function of RH. One hypothesis is that the lower RH restricts the solvation of Pt$^{2+}$ by H$_2$O and therefore suppresses Pt dissolution [40]. Assume a linear correlation as follows:

$$\bar{H}_{1,fit} = \bar{H}_{1,fit,100\%RH} [C(1 - RH) + 1]$$ \hspace{1cm} 2.20

where the coefficient $C$ is fitted from experimental data. Uchimura et al. [42] performed a series of experimental tests (25 cm$^2$ subscale cells, catalyst loading of 0.35 mg/cm$^2$) to investigate the RH effects on the ECA evolutions. The temperature is held constant at 80 °C, the upper potential is held for 10 s at 0.95 V vs. RHE and the lower potential is held for 2.5 s at 0.6 V vs. RHE. In addition to the test under 100% RH, two other tests are conducted under 30% and 70% RH. Thus, $\bar{H}_{1,fit,30\%RH}$ and $\bar{H}_{1,fit,70\%RH}$ can be found by fitting the 30% and 70% RH results as shown in Figure 2-10. Using the least square fitting method, we find $C = 0.3$. The following correlation is thus developed to account for the humidity effect on Pt degradation:

$$\bar{H}_{1,fit} = \bar{H}_{1,fit,100\%RH} [0.3(1 - RH) + 1] \quad 0.3 \leq RH \leq 1.0$$ \hspace{1cm} 2.21

Finally, to demonstrate the effectiveness of the above correlation and the current model, a series of parametric studies are performed and compared with the experimental results from Yang et al. [40] who did a series of tests to investigate parametric impacts on CCL degradation. The electrode thickness is estimated to be about 10 μm from their post-test microscopy images. Their base case uses square wave potential cycle which holds 10 s at 0.95 V and holds 10 s at 0.4 V vs.
RHE. The cell temperature is 80°C and the RH is 100%. Three other experiments are conducted in their study. The low-humidity test only lowers the RH to 30%, the high temperature test only raises the operating temperature to 90°C and the higher upper potential test only raises the higher upper potential to 1.05 V compared with the base study. The Pt-loading of the cathode is 0.2 mg/cm², and the PSD of the pristine sample for these cases is measured with TEM and reported [41]. As a result, the PSD from TEM measurement [41] is applied as the initial PSD in the present model. The correlation expressed by Equation 2.21 is used to determine \( \tilde{H}_{1,fit} \). The overall ECA evolutions are compared with experimental results [40] in Figure 2-11. And the remaining PSDs at the middle of the cathode electrode are compared with TEM measurement [69] as shown in Figure 2-12. The current model is found to reasonably capture the impact of RH on both ECA and PSD evolutions. It is worthwhile to note that only a rough estimation of Pt\(^{2+}\) diffusivity with RH is used in this study. It would be helpful to establish a correlation of Pt\(^{2+}\) diffusivity with both temperature and RH for further understanding of the Pt degradation in CCL.

2.3.3 Thinning the Cathode Catalyst Layer Effect

In the last decade, significant advances have been made in reducing Pt-loading in PEFC. Gasteiger et al. [70] demonstrated that in state-of-the-art MEAs operated with H\(_2\) and air, the anode Pt-loading can be reduced to 0.05 mg/cm\(^2\) and the cathode loading can be reduced to 0.20 mg/cm\(^2\) with a voltage loss of only 20 mV. Researchers then applied advanced Pt dispersion techniques to develop catalyst layers with thickness of several microns [71] to less than 1 micron [72] to reduce Pt-loading. Reducing Pt-loading is vital to the PEFC cost reduction [73], however, it is found that there is large performance decay for low Pt-loading CCLs caused by the O\(_2\) transport resistance at the ionomer thin film near the Pt surface [74-77]. Besides the increase of O\(_2\) transport loss, more rapid Pt degradation and ECA loss has also been found for thin CCLs in a
recent experimental study [78]. The present study attempts to explain and quantify how the CCL thinning would affect the degradation.

A case under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 60°C, fully humidified H₂ | N₂ condition is chosen as the starting point for this part of the study, as it is found to experience moderate Pt degradation during the 10,000 cycle period. For this case, the cathode electrode has Pt-loading of 0.4 mg/cm², and thickness of 10 μm. Then a series of thinner CCLs are modeled. These thinner CCLs have thicknesses of 5 μm, 2.5 μm, and 1.25 μm, consequently, the corresponding Pt-loadings are 0.2 mg/cm², 0.1 mg/cm², and 0.05 mg/cm². The ECA evolutions are compared in Figure 2-13 and a clear trend that thinning the CCL leads more rapid ECA loss can be seen. The acceleration of degradation is not significant when thinning the CCL from 10 μm to 5 μm, however, it becomes important when thinning the CCL further to 2.5 μm and 1.25 μm. If 50% of the overall ECA loss is chosen as a failure criterion, the electrode with 0.4 mg/cm² Pt-loading could last 7,000 cycles, however, the electrode with 0.05 mg/cm² Pt-loading could only last 5,200 cycles – a 26% reduction in durability.

In the previous modeling cases, an exacerbated degradation region is found near the membrane, which is caused by the lower Pt²⁺ concentration in this region due to Pt²⁺ sink, as seen in Figure 2-14 which shows the ECA distributions under normalized CCL thicknesses. For the thinned CCL, a larger fraction of the CCL thickness is under the exacerbated degradation region and faster ECA loss can be found throughout the CCL. The present study clearly suggests that the faster Pt degradation is a limitation for lowering the cathode Pt-loading by thinning the CCL.

The uneven variation in ECA across the catalyst layer can be comprehended by comparing PSDs across the CCL. Figure 2-15 shows the PSDs at four different locations for the electrode with 0.05 mg/cm² Pt-loading and 1.25 μm thickness. Although the initial PSD at each position is identical, the variation in PSD along the CCL thickness could be clearly seen in Figure 2-15 after
10,000 voltage cycles. The model calculates that larger Pt particles will be near CCL-GDL interface due to less impact from Pt$^{2+}$ diffusion into the membrane. Therefore particles grow more at the CCL-GDL interface primarily due to re-deposition from available Pt$^{2+}$. To sum up, the current 1D Pt degradation model offers a quantitative approach to investigate non-uniform Pt degradation across the CCL.

### 2.4 Conclusion

In this chapter, a 1D Pt degradation model is developed and validated. Slightly faster degradation is found for the CCL under $H_2 | N_2$ than under $H_2 | Air$ condition, as the Pt$^{2+}$ sink moves into the membrane under $H_2 | Air$ condition instead of at the CCL-membrane interface under $H_2 | N_2$ condition. The temperature effect on ECA evolution is well captured by the current model. In addition, a new approach to capture RH effect on Pt degradation is developed and compared with experimental results. Thus, the current model of Pt degradation is extended to work under low-humidity conditions. Due to the non-uniform Pt$^{2+}$ concentration distribution across a CCL, the ECA loss is found to be non-uniform across the CCL as predicted by the current model. Exacerbated degradation could be found near the CCL-membrane interface. One important consequence is that thinning the CCL would induce more rapid ECA loss. This new physical insight is quantitatively explored with the current model. When the cathode thickness is reduced from 10 $\mu$m to 5 $\mu$m, the accelerated degradation is insignificant. However, when the cathode thickness is further reduced to 2.5 $\mu$m and 1.25 $\mu$m, the apparent accelerated ECA loss is predicted, suggesting that worsen Pt degradation could be a limitation in thinning the cathode catalyst layer to achieve low or ultra-low Pt-loading.
Table 2-1. Physical properties and parameters.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
<th>Reference</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_1 )</td>
<td>( 1 \times 10^4 )</td>
<td>Hz</td>
<td>Ref. 64</td>
<td>Forward Pt oxide formation rate constant</td>
</tr>
<tr>
<td>( v_2^* )</td>
<td>( 2 \times 10^{-2} )</td>
<td>Hz</td>
<td>Ref. 64</td>
<td>Backward Pt oxide formation rate constant</td>
</tr>
<tr>
<td>( \Gamma )</td>
<td>( 2.2 \times 10^{-9} )</td>
<td>mol/cm²</td>
<td>Ref. 64</td>
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<tr>
<td>( \bar{H}_{2,fit} )</td>
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<td>J/mol</td>
<td>Ref. 64</td>
<td>Partial molar oxide formation activation enthalpy (zero coverage)</td>
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<td>( \beta_2 )</td>
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<td></td>
<td>Ref. 64</td>
<td>Butler-Volmer transfer coefficient for Pt oxide formation</td>
</tr>
<tr>
<td>( n_2 )</td>
<td>2</td>
<td></td>
<td>Ref. 64</td>
<td>Electrons transferred during Pt oxide formation</td>
</tr>
<tr>
<td>( U_{fit} )</td>
<td>1.03</td>
<td>V</td>
<td>Ref. 64</td>
<td>Pt oxide formation bulk equilibrium voltage</td>
</tr>
<tr>
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<td>J/mol</td>
<td>Ref. 64</td>
<td>Pt oxide dependent kinetic barrier constant</td>
</tr>
<tr>
<td>( \omega )</td>
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<td>Pt oxide-oxide interaction energy</td>
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<tr>
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<td>Dissolution attempt frequency</td>
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<td>Butler-Volmer transfer coefficient for Pt dissolution</td>
</tr>
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<td>( n )</td>
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<td>Pt dissolution bulk equilibrium voltage</td>
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<td>cm³/mol</td>
<td>Ref. 64</td>
<td>Molar volume of Pt</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( 2.4 \times 10^{-4} )</td>
<td>J/cm²</td>
<td>Ref. 64</td>
<td>Pt [1 1 1] surface tension</td>
</tr>
<tr>
<td>( c_{Pt^{2+}}^{ref} )</td>
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<td>mol/L</td>
<td>Fit</td>
<td>Reference Pt²⁺ concentration</td>
</tr>
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<td>J/mol</td>
<td>Fit</td>
<td>Pt dissolution activation enthalpy under fully humidified condition</td>
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<tr>
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<td>( 3.3 \times 10^{-13} )</td>
<td>mol/(cm²·s·kPa)</td>
<td>Ref. 46</td>
<td>H₂ permeability at 100% RH and 80°C</td>
</tr>
<tr>
<td>( K_{O_2} )</td>
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<td>mol/(cm²·s·kPa)</td>
<td>Ref. 46</td>
<td>O₂ permeability at 100% RH and 80°C</td>
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<td>kPa</td>
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<td>kPa</td>
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<td>Partial pressure of O₂</td>
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<td>cm²/s</td>
<td>Ref. 10</td>
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<td></td>
<td>Ref. 10</td>
<td>Volume fraction of the ionomer increment in cathode electrode</td>
</tr>
<tr>
<td>( L )</td>
<td>( 1.0 \times 10^{-3} )</td>
<td>cm</td>
<td>Assumed</td>
<td>Thickness of CCL if not specified</td>
</tr>
</tbody>
</table>
| \( \delta_M \) | \( 1.8 \times 10^{-3} \) | cm            | Assumed  | Thickness of membrane (used for H₂ | Air condition)
Figure 2-1. Schematic of 1D Pt degradation model in a PEFC cathode.
Figure 2-2. Voltage, Pt$^{2+}$ concentration and PtO fractional coverage evolutions in one voltage cycle.
Figure 2-3. Comparison of predicted and experimental (46 wt% Pt/Vulcan, 0.4 mg/cm$^2$ cathode) [10] ECA evolution under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 80°C, fully humidified $\text{H}_2$ | $\text{N}_2$ (anode/cathode) condition.
Figure 2-4. Comparison of predicted and measured (46 wt% Pt/Vulcan, 0.4 mg/cm$^2$ cathode) [10] Pt mass remaining on carbon support under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 80°C, fully humidified H$_2$ | N$_2$ (anode/cathode) condition.
Figure 2-5. Comparison of predicted and measured (46 wt% Pt/Vulcan, 0.4 mg/cm² cathode) [10] Pt PSD remaining on carbon support near CL-GDL interface under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 80°C, fully humidified H₂ | N₂ (anode/cathode) condition.
Figure 2-6. Pt$^{2+}$ concentration distributions in one voltage cycle under: (a) H$_2$ | N$_2$ (anode/cathode) and (b) H$_2$ | Air (anode/cathode) condition.
Figure 2-7. Comparison of ECA evolutions under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 80°C, fully humidified H$_2$ | N$_2$ (anode/cathode) and H$_2$ | Air (anode/cathode) condition.
Figure 2-8. ECA distributions through voltage cycling test under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 80°C, fully humidified (a) H₂ | N₂ (anode/cathode) and (b) H₂ | Air (anode/cathode) condition.
Figure 2-9. Comparison of predicted and measured (46 wt%, Pt/C, 0.35 mg/cm$^2$ cathode) [36] ECA evolutions under 10 s hold at 0.95 V, 2.5 s hold at 0.6 V vs. RHE, fully humidified H$_2$ | N$_2$ (anode/cathode) condition at various temperatures.
Figure 2-10. Comparison of predicted and measured (46 wt%, Pt/C, 0.35 mg/cm² cathode) [42] ECA evolutions under 10 s hold at 0.95 V, 2.5 s hold at 0.6 V vs. RHE, 80 °C, H₂ | N₂ (anode/cathode) condition at various RH.
Figure 2-11. Comparison of predicted and measured (40 wt%, Pt/C, 0.2 mg/cm² cathode) [40] ECA evolutions.
Figure 2-12. Comparison of analytical carbon-supported PSDs (near CCL-GDL interface) with TEM measurements (40 wt%, Pt/C, 0.2 mg/cm² cathode) [69] after 10,000 voltage cycles.
Figure 2-13. Comparison of ECA evolutions with thinner CCLs under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 60°C, fully humidified H₂ | N₂ (anode/cathode) condition.
Figure 2-14. Comparison of ECA distributions after cycling with thinner CCLs under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 60°C, fully humidified H₂ | N₂ (anode/cathode) condition.
Figure 2-15. Analytical carbon-supported PSDs across a CCL after 10,000 cycles under 0.6 V – 1.0 V vs. RHE, 20 mV/s, 60°C, fully humidified H₂ | N₂ (anode/cathode) condition.
Chapter 3

Modeling of Transient Platinum Degradation in a Low Pt-Loading PEFC under Current Cycling

3.1 Introduction

Pt catalysts in the form of nanoparticles inevitably degrade under dynamic load condition of automotive PEFCs [25, 42, 45]. Pt nanoparticles are prone to dissolution when the CCL is subjected to high voltage, as their small diameter results in higher Gibbs-Thomson energy [59]. The Pt dissolution phenomenon is the driving force of Pt Ostwald ripening and Pt dissolution and re-precipitation in non-conductive ionomer phase [10]. This Pt degradation is found to be significantly enhanced under voltage cycling condition [50, 79-82]. For automotive PEFCs, the load ramps up and down at acceleration and deceleration, which means the PEFCs work under dynamic voltage condition. The dynamic load induced Pt degradation is found to be one of the most important degradation mechanisms for automotive PEFCs [25]. The consequence of Pt degradation is the loss of valuable ECA in CCL. For the low Pt-loading CCL especially, the loss of ECA will not only induce ORR kinetic losses, but also cause extra voltage loss by increasing the micro-scale transport resistance. Clearly, modeling the Pt degradation in PEFC CCLs and the performance of PEFCs after degradation is sorely needed to estimate long-term performance and to find methods to mitigate Pt degradation.

Due to the vital role of PEFC CCL, extensive modeling studies have been performed from macroscale to pore scale regarding the transport phenomenon and performance of CCL [7, 83]. The homogeneous model [84, 85] and agglomerate model [74, 86-91] are two prevalent macroscale models established for PEFC CCL. In the agglomerate model, the CCL is assumed to be composed by agglomerates which are clusters of carbon particles with Pt catalysts on their
surface, ionomer and pores. Typically the macroscale PEFC CCL modeling is a part of macroscale PEFC dynamic modeling [5, 92-95], which has become an essential approach in current PEFC design [96-99]. On the other hand, Wang et al. [100] developed a pore scale modeling method for PEFC electrodes by using direct numerical simulation (DNS) method. With this pore scale model, the morphology effects on CCL performance were investigated and optimal volume fractions of the void and electrolyte phases were predicted in a subsequent study [101]. Lange et al. [102] developed pore scale modeling and performed modeling with stochastically reconstructed microstructures. The impacts of the carbon particle radius on Knudsen diffusion, proton conductivity and oxygen consumption were investigated with this model. The effects of water vapor transport and thermal transport were then studied with this pore scale CCL modeling method [103]. The up-to-date understanding of PEFC CCL and parameters adjusted by experimental measurement or the pore scale CCL modeling study [104] could provide valuable input into macroscale PEFC CCL modeling. For example, Hao et al. [105] integrated the micro-scale oxygen transport resistance model [77] into a comprehensive PEFC model, M2 model, to capture the low CCL Pt-loading effect on PEFC performance, and extended the M2 model capability to model low Pt-loading PEFCs. The agglomeration effect is specifically discussed in their study and this low Pt-loading PEFC model was systematically validated with experimental data under a wide range of Pt-loading [105]. One important assumption for the micro-scale oxygen transport resistance model is that this resistance is proportional to ECA normalized current density [77, 106]. It is worthwhile the ECA here is the geometric active area which has unit of (m$^2$/m$^2$) and is equal to the Pt-loading (mg/cm$^2$) multiplies the Pt surface area per gram of Pt (m$^2$/g). It means no matter the Pt-loading is reduced by lowering the Pt weight percentage or by bare carbon dilution, higher micro-scale transport resistance is triggered. While assuming Ostwald ripening as the major Pt degradation mechanisms, the Pt-loading is conserved but the Pt
surface area per gram of Pt (m$^2$/g) lowers during the degradation. Thus stronger micro-scale resistance and corresponding stronger voltage loss is also triggered.

The non-uniform Pt degradation causes non-uniform ECA across the PEFC CCL in the through-plane direction as introduced. This non-uniform ECA distribution of the degraded PEFC CCL could reshape the current density distributions in PEFC CCLs. Jomori et al. [76] established a 1D PEFC model with the micro-scale oxygen transport submodel implemented to investigate PEFCs with low Pt-loadings. A 1D non-uniform ECA profile across the CCL was assumed and incorporated into their model to reveal how the non-uniform Pt degradation reshapes the current density distribution in the through-plane direction across CCL and to evaluate the performance of the non-uniform degraded low Pt-loading PEFCs [76]. The non-uniform Pt degradation phenomenon is not limited to the through-plane direction, as Pt degradation is faster under higher temperature and higher relative humidity (RH) [36]. Due to the complex water and thermal transport phenomenon in PEFCs, the humidity and temperature are highly non-uniform in PEFC CCLs, in the channel-land dimension for example [107]. In this chapter, a transient PEFC model coupling the Pt degradation modeling and the Pt performance modeling is established by implementing the 1D physics-based Pt degradation model into the M2 model with low Pt-loading CCL effects considered [105]. Our primary objective of this chapter is to numerically evaluate the in-plane distribution of Pt degradation between land and channel areas such that one can assess how much effect the land-to-channel width ratio is on not only fuel cell performance but also durability.
3.2 Numerical Modeling

The schematic of coupling Pt degradation model as a submodel in the CCL domain into the M2 model in all PEFC domains is shown in Figure 3-1. With this model, the impacts of the Pt degradation on the low Pt-loading PEFC performance and on the reaction current distribution in PEFC CCLs are investigated. Although the current stage of study considers Pt nanoparticles as catalyst for PEFCs, the methodology used in this study could be extended to explore degradation and performance of PEFC CCL with Pt alloys or alternative metal content as catalysts, which both receive much research to date [108-111].

In this study, a 1D physics-based Pt degradation model is integrated into the transient M2 model with the low Pt-loading effects in consideration. For the transient M2 model, conservation equations of mass, momentum, species and charge are solved and these equations can be expressed as:

Continuity equation:
\[ \nabla \cdot (\rho \vec{u}) = 0 \]  

Momentum conservation:
\[ \frac{\rho}{\varepsilon} \left[ \frac{\partial \vec{u}}{\partial t} + \frac{1}{\varepsilon} \nabla \cdot (\rho \vec{u}) \right] = -\nabla p + \nabla \cdot \tau + S_u \]  

Energy conservation:
\[ \frac{\partial (\rho c_p T)}{\partial t} + \nabla \cdot (\gamma T \rho c_p \vec{u} T) = \nabla \cdot (k_{\text{eff}} \nabla T) + S_T \]  

Species conservation:
\[ e^{\text{eff}} \frac{\partial C^K}{\partial t} + \nabla \cdot (\gamma_e \vec{u} C^K) = \nabla \cdot \left( D^K \nabla C^K \right) - \nabla \cdot \left[ \left( \frac{m f^k_{11}}{M^k} - \frac{C^K}{\rho_g} \right) \vec{j}_l \right] + S_k \]  

Charge conservation (electrons):
\[ 0 = \nabla \cdot \left( \sigma^{\text{eff}} \nabla \Phi_e \right) + S_{\Phi_e} \]  

Charge conservation (protons):
\[ 0 = \nabla \cdot \left( \kappa^{\text{eff}} \nabla \Phi_p \right) + S_{\Phi_p} \]  

where \( \rho \), \( \vec{u} \), \( P \), \( T \), \( C^K \), \( \Phi_e \) and \( \Phi_p \) are the density, superficial velocity, pressure, temperature, species molar concentration, electronic and electrolyte phase potential. The source terms for these conservation equations may be found in reference [112]. To reduce the computational time and
the mesh for this full physic based transient modeling, a 2D differential cell is used in the present study as illustrated in Figure 3-2. As shown in Figure 3-2, the 1D physics-based Pt degradation model is implemented at the nodes of CCL in transient M2 model. The geometry parameters as well physical parameters for the modeling can be found in Table 3-1.

In the physics-based Pt degradation model, the electrochemical reactions of Pt nanoparticle oxidation and dissolution are modeled. In the 1D Pt degradation model, at each control volume i, a certain number of discrete particle size groups are assigned. The particle size group number at each control volume is denoted by j. The Pt nanoparticle diameter $d_{ij}$ and the Pt oxide coverage $\theta_{ij}$ in each particle size group at every control volume are tracked in the 1D degradation model by solving Equation 2.7 and 2.8. While the Pt particle net oxidation rate $r_{net, oxide}$ and the net Pt dissolution rate $r_{net, Pt}$ can be expressed as Equation 2.4 and 2.5.

In these equations, $V$ is the local difference of the electronic potential and ionomer phase potential $\Phi_s - \Phi_e$ from transient M2 modeling. $c_{Pt^+}$ is solved from 1D Pt ion diffusion equation at each time step of the transient Pt degradation modeling. The temperature $T$ is the temperature field in CCL solved by M2 model. A correlation of $H_{1,fit}$ with the water activity in CCL as expressed by Equation 2.21 is used in this model to capture the humidity effect on Pt degradation. The physical parameters used in Pt degradation model can be found in Table 2-1. By tracking the evolution of $d_{ij}$ in every particle size group, the ECA at every time step during the degradation process is calculated for each computational node in CCL. This local ECA is used as input for the kinetic equation for ORR and for calculating the effective diffusion length [105] in the micro-scale oxygen transport resistance at each node in CCL for the M2 model.

Intensive computation of physics-based comprehensive PEFC model, transient M2 model, is a great challenge. The time step to perform Pt degradation modeling is quite small compared with
the time step of the M2 model. Thus, a dual-time-step approach is used in the current study as
shown in Figure 3-3. The dual-time-step approach means a larger time step, $\Delta t$, is used for M2
model to accelerate the speed of computation and a smaller time step, $\delta t$, is used for Pt
degradation submodel to capture the fast transients of Pt dissolution from small nanoparticles and
Pt$^{2+}$ redeposition to large nanoparticles under various voltage conditions. The transient M2 model
provides the temperature, humidity, electronic- and ionic-phase potential fields for the Pt
degradation model, and the Pt degradation model returns the ECA at every time step for the
transient M2 model. The current study models a total time of 5000 current cycles with 6s of each
cycle. The current density profile in each voltage cycle is shown in Figure 3-3.

The steady state operation tests are also performed to characterize the performance of the
pristine and cycled PEFCs. The steady state operations of the initial PEFC are first performed
under a series of current density conditions. The current densities from 0.05 A/cm$^2$ to 2.0 A/cm$^2$
with step of 0.05 A/cm$^2$ are applied sequentially. Thus the polarization curve for the PEFC at the
beginning-of-life can be generated. Then, after every 1000 current cycles until the end of current
cycle test, the same parametric sweep of current densities is performed to generate the
polarization curve for this degraded PEFC. At the same time, the remaining ECA distributions
and reaction current density distributions in the pristine and cycled CCLs under those steady state
operation testing conditions can be generated to specifically investigate the non-uniform Pt
degradation and the shift of reaction current density in CCLs through degradation.

3.3 Results and Discussion

3.3.1 Overall Performance Loss Due to Pt Degradation

For both the current cycling test and the steady characterization test, the PEFC is operated
under 80°C and 150 kPa. The stoichiometry flow rate ratio is 1.5 for anode and 2.0 for cathode
corresponding to 2.0 A/cm$^2$ in the cycling test, and the inlet humidity is kept at 65% at both anode and cathode inlet. For the PEFC catalyst electrodes, the anode Pt-loading is 0.05 mg/cm$^2$, while the cathode Pt-loading is 0.10 mg/cm$^2$ which corresponds to Pt weight percentage of 20% in this study. This low cathode loading is chosen to better investigate the interactions of the Pt degradation with the micro-scale oxygen transport resistance. Figure 3-4 shows the dynamic voltage response of the PEFC during the current density cycling test. It can be seen that the current cycling between high and low current densities causes a voltage cycling between low and high. This voltage cycling condition is similar to the potential cycle durability test condition which will accelerate Pt degradation. For the cycled PEFC, the loss of ECA causes loss of voltage as indicated in Figure 3-4, and this voltage deficiency is much larger under high current density condition.

The underlying reason can be clearly explained with the polarization curves of the cycled PEFC as shown in Figure 3-5. The current model predicts that the average ECA remaining in CCL after the 5000 cycle test is 66.2 % of the ECA at beginning-of-life. Assuming Tafel kinetics for a simplified analysis [106], the ORR kinetic voltage loss is roughly 12.5 mV. As indicated in Figure 3-5, the total voltage loss after 5000 cycle test is 28.1 mV under 1.0 A/cm$^2$. This demonstrates that the ORR kinetic loss and the micro-scale transport loss both contribute to the total voltage loss under moderate current condition. On the other hand, under the high current density condition, the micro-scale oxygen transport resistance is triggered by high ECA normalized current density and poses an additional interfacial concentration overpotential. Also, this micro-scale oxygen transport resistance is amplified by the ECA loss during Pt degradation process and causes larger interfacial concentration overpotential for the cycled PEFC. From Figure 3-5, it can be observed that the total voltage loss after 5000 cycle test is 70.6 mV under 2.0 A/cm$^2$, which is several times larger than the voltage loss predicted by ORR kinetics. This result suggests that the micro-scale transport resistance dominates the voltage loss for the degraded
CCL under high current density, as the ECA loss substantially amplifies the micro-scale transport resistance. The voltage deficiency under large current density implies power deficiency for cycled PEFC when the power demand is high, which is highly undesirable. Therefore, quantitative estimation of the Pt degradation and the voltage loss of cycled PEFC is necessary and mitigation strategies to depress Pt degradation under dynamic load condition is warranted.

3.3.2 Non-Uniform Pt Degradation and Ensuing Current Distributions

The Pt degradation in CCL is indeed highly non-uniform and the non-uniform ECA distribution after degradation is hard to estimate experimentally. The current study provides an effective method to estimate this non-uniform degradation and the consequence thereof. The remaining ECA distributions during the current cycling test are shown in Figure 3-6. The most significant non-uniform degradation is found in the through-plane direction and exacerbated Pt degradation can clearly be found near the CCL and membrane interface. In the CCL, the temperature is lower under the land due to shorter path of heat transfer, while the RH is higher under the land due to longer path of water transport. Lower temperature would cause slower Pt degradation and higher RH would cause faster Pt degradation. Thus, without appropriate method, it is hard to quantify the non-uniform Pt degradation in the channel-land direction. With the present modeling method, it is found that the degradation is faster under the land as shown in Figure 3-6. The non-uniformity of Pt degradation in the channel-land direction is observed to be slightly smaller than the non-uniformity of Pt degradation in the through-plane direction for this case. It is worthwhile to mention that the land and channel width in this study are both 0.5 mm, which is chosen to mimic the recent trend to reduce land width for oxygen transport enhancement and better water removal under the land. If the land width was 1.0 mm, the non-uniformity of Pt degradation in the channel-land direction would be higher due to longer path of water transport under the land. As shown in Figure 3-6, the difference of remained ECA under channel and land
areas is less than 3%, indicating that the non-uniform Pt degradation along the in-plane direction is insignificant and hence there is little need to experimentally separate Pt degradation under land from channel areas, respectively.

Much attention has been paid on the local current density distributions in the PEFC CCLs in recent years [76, 105, 113]. The non-uniform Pt degradation would induce shift in the current density distributions in the cycled CCLs. Without a proper modeling method, estimation of the current density distribution in the CCL is hard. Figure 3-7 shows the local current density distribution in the initial and cycled CCL under the average current density of 1.0 A/cm$^2$, which represents a moderate current density condition. It can be found that the shift of current density distribution caused by the non-uniform ECA loss is mainly in the through-plane direction. This means that the non-uniform ECA loss in through-plane direction clearly shifts the current density distribution under moderate current density. However, as the magnitude of non-uniformity of ECA loss is relatively small in the channel-land direction, the shift of the current density distribution is not significant in this direction under moderate current density. On the other hand, as shown in Figure 3-8, the shift of current density distributions can be found in both through-plane and channel-land directions as the micro-scale oxygen transport resistance comes into effect under high current density PEFC operation. Lower ECA remains under the land in the cycled CCL and triggers higher micro-transport resistance. Thus, the reaction current density under the land is lower for the cycled CCL under high current density condition. It is worth noticing that the current study investigates the CCL with Pt-loading of 0.1 mg/cm$^2$. When the CCL Pt-loading is further lowered, this micro-scale resistance induced current density non-uniformity would be further amplified as this micro-scale resistance is inversely proportional to ECA.
3.3.3 Effects of Raising Lower Current Density and Operating Temperature

Lowering the upper voltage is an effective approach to alleviate the aggressive Pt degradation in PEFC CCLs. As for the realistic automotive PEFCs working under highly dynamic load condition, raising the lower current density the PEFCs provide should be an effective mitigation approach for Pt degradation. This limitation of lower current density can be achieved by cooperation of PEFC with another power source, for example, a battery. The PEFC could work under more steady condition by depositing energy into the battery when the power need is low and using the deposited energy when the power need is high. The current study specifically investigates the effect of raising the lower current density under current density cycling condition. The $I_{upper}$ is fixed at 2.0 A/cm$^2$, and the $I_{lower}$ is raised from 0.05 A/cm$^2$ to 0.10 A/cm$^2$, while other operating conditions are kept to be identical.

The dynamic voltage response profiles during the 5000 cycle test are shown in Figure 3-9. It could be found that the upper voltage is effectively reduced by raising the lower current density in the cycling. The overall ECA evolutions are shown and compared in Figure 3-10. The overall ECA remaining after 5000 cycle test is improved from 66.2% to 78.9% with lower current density raised from 0.05 A/cm$^2$ to 0.10 A/cm$^2$. Clearly, raising the lower current density could depress ECA loss through lowering the upper voltage. Figure 3-11 compares the polarization curves after 5000 cycles under different $I_{lower}$. It is observed that by increasing the $I_{lower}$, the performance loss of PEFC is clearly reduced. The voltage loss at 1.0 A/cm$^2$ is reduced from 28.1 mV to 16.0 mV, while the voltage loss at 2.0 A/cm$^2$ is reduced from 70.6 mV to 41.4 mV by raising the lower current density from 0.05 A/cm$^2$ to 0.10 A/cm$^2$. The non-uniform Pt degradation with $I_{lower}$ of 0.10 A/cm$^2$ is shown in Figure 3-12. Although the non-uniformity of ECA loss in both through-plane and channel-land directions can still be seen, the remaining ECA in CCL is higher than the ECA left under $I_{lower}$ of 0.05 A/cm$^2$ at every position. The implication is that raising the lower current density the PEFC supplies could alleviate the ECA loss at every position.
in the entire CCL. This means for realistic automotive PEFCs, limiting the lower current under dynamic load condition has significant benefit in extending the lifetime of PEFCs.

Then, the effect of higher temperature operation on the PEFC Pt degradation is investigated. The operating temperature during the current cycling test (0.05 – 2.0 A/cm²) and voltage characterization is raised from 80 to 85°C while the other conditions are kept the same. As shown in Figure 3-10, the overall ECA loss increases slightly with the increasing temperature. Figure 3-13 shows the polarization curves of the pristine and cycled cells under the higher operating temperature and it is found that the ohmic losses for both initial and aged cells increase as the operating temperature is raised. The higher operating temperature of PEFC causes higher temperature in CCL which accelerates Pt degradation while reduces the humidity in CCL which decelerates Pt degradation. These opposite effects [62] are both captured by the physics-based Pt degradation model in combination with M2 performance model and the net effect on Pt degradation is given.

3.4 Conclusion

The interactions of Pt degradation and the performance loss of a low Pt-loading PEFC are investigated with a transient Pt degradation model developed in this work. First, the overall performance loss through a 5000 current cycling test is quantitatively predicted and analyzed. It is found for the cycled PEFC under high current density, the micro-scale transport resistance is amplified by Pt degradation induced ECA loss and dominates the total voltage loss. Second, the present model predicts that Pt degradation is non-uniform in both through-plane and channel-land directions in PEFC CCL. Under high current density, a shift of the local current density in the channel-land direction is observed as the low ECA left under the land caused by high humidity amplifies the micro-scale oxygen transport resistance at this region. Nonetheless, the in-plane non-uniformity of Pt degradation between land and channel areas remains less than 3%,
suggesting little need to experimentally look into the separate characterization of Pt degradation along the channel-land direction. Third, the strategy of raising the lower current density is tested with the Pt degradation model. The performance loss, overall ECA loss and local ECA loss are all found to be effectively alleviated by this method. To sum up, the transient Pt degradation modeling offers a useful method to analyze the cause of Pt degradation distribution and forecast its significance, which is valuable to achieve the goal of longer lifespan and better lifetime performance for low Pt-loading PEFCs.
Table 3-1. Physical properties and parameters.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas channel depth/width</td>
<td>0.7/0.5 mm</td>
</tr>
<tr>
<td>Shoulder width</td>
<td>0.5 mm</td>
</tr>
<tr>
<td>GDL thickness</td>
<td>160 μm</td>
</tr>
<tr>
<td>MPL thickness</td>
<td>30 μm</td>
</tr>
<tr>
<td>ACL/CCL thickness</td>
<td>6/11 μm</td>
</tr>
<tr>
<td>Membrane thickness</td>
<td>18 μm</td>
</tr>
<tr>
<td>Porosity of GDLs/ MPLs</td>
<td>0.625/0.5</td>
</tr>
<tr>
<td>Weight ratio of ionomer to carbon in ACL/CCL</td>
<td>0.6/0.95</td>
</tr>
<tr>
<td>Equivalent weight of dry membrane</td>
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</tr>
<tr>
<td>Dry density of membrane</td>
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</tr>
<tr>
<td>Carbon support density</td>
<td>1.95 g/cm³</td>
</tr>
<tr>
<td>Thermal conductivity of the membrane</td>
<td>0.95 W/m K</td>
</tr>
<tr>
<td>Thermal conductivity of the catalyst layer</td>
<td>1.0 W/m K</td>
</tr>
<tr>
<td>Thermal conductivity of the GDLs/MPLs through plane direction</td>
<td>0.5/0.3 W/m K</td>
</tr>
<tr>
<td>Thermal conductivity of GDLs/MPLs in plane direction</td>
<td>20.0/5.0 W/m K</td>
</tr>
<tr>
<td>Hydraulic permeability of MPLs /CLs</td>
<td>$8.0 \times 10^{-14}$ / $8.0 \times 10^{-14}$ m$^2$</td>
</tr>
<tr>
<td>Hydraulic permeability of GDLs through plane direction</td>
<td>1.5$ \times 10^{-11}$ m$^2$</td>
</tr>
<tr>
<td>Hydraulic permeability of GDLs in plane direction</td>
<td>8.0$ \times 10^{-12}$ m$^2$</td>
</tr>
<tr>
<td>Surface tension, liquid-water-air (80°C)</td>
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<td>Contact angle in GDLs/ MPLs/CLs</td>
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</tr>
<tr>
<td>Initial average Pt particle diameter</td>
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</tr>
<tr>
<td>Variance of initial Pt particle diameter distribution (Gauss)</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Figure 3-1. Schematic of coupling Pt degradation model into M2 model.
Figure 3-2. Geometry, computational mesh and 1D Pt degradation coupling scheme.
Figure 3-3. Illustration of current density profile and dual-time-step method.
Figure 3-4. Voltage responses during current density cycling test between 0.05 and 2.0 A/cm².
Figure 3-5. Polarization curves through current cycling test of 5000 cycles between 0.05 A/cm$^2$ – 2.0 A/cm$^2$. 
Figure 3-6. Normalized ECA remaining in CCL during 5000 cycles between 0.05 A/cm$^2$ – 2.0 A/cm$^2$. 
Figure 3-7. Local current density distribution in cycled CCL under average current density of 1.0 A/cm².
Figure 3-8. Local current density distribution in cycled CCL under average current density of 2.0 A/cm$^2$. 
Figure 3-9. Voltage responses during current density cycling test between 0.10 and 2.0 A/cm².
Figure 3-10. Overall normalized ECA evolutions during current density cycling test.
Figure 3-11. Polarization curves comparison after whole cycling tests under various current cycling profiles.
Figure 3-12. Normalized ECA remaining in CCL during 5000 cycles between 0.10 A/cm² – 2.0 A/cm².
Figure 3-13. Polarization curves in current cycling tests under higher operating temperature.
Chapter 4

In-Plane Pt Degradation and Its Impact on End-of-Life Performance of PEFC

4.1 Introduction

Over the last few decades, computational modeling has contributed significant understanding of fundamental mechanisms, design and study of PEFC performances [5-7]. Numerical modeling has been used to study the low-humidity operation of PEFCs, which is an operation strategy widely accepted in industrial PEFC applications. Ju et al. [114] performed non-isothermal PEFC modeling to explore the characteristics of low-humidity PEFC operation and investigated effects of CL ionomer fraction, membrane thickness, and coflow and countercflow effects on current density distributions in PEFCs. Wang and Wang [97] performed ultra-large scale modeling study to investigate the cooling scheme suitable for low-humidity operation of automotive PEFCs. Cold start is another crucial issue for automotive PEFCs. Mao et al. [115] set up a multiphase model to investigate PEFC cold start process and to examine the transport, electrochemical reactions, and ice formation during PEFC cold start. The effects of the start-up current density and membrane thickness on the cold start performance were explored. To achieve successful PEFC cold start, lowering the membrane hydration is necessary when the PEFC shuts down and gas purge is applied to minimize the residual water. Sinha and Wang [116] modeled the two phase transport in PEFCs during the gas purge process and effects of various parameters on gas purge were elucidated by their modeling study.

Although a lot of modeling studies have been performed on the beginning-of-life (BOL) performance of PEFCs, numerical modeling regarding to the EOL performance of PEFCs is limited. This chapter investigates the performance of the PEFC aged through Pt degradation. The
consequence of Pt degradation is loss of ECA, which will cause higher ORR voltage loss and the micro-scale oxygen transport voltage loss. The Pt degradation in CCL is highly non-uniform, thus the remaining ECA in aged CCL is highly non-uniform. By one-dimensional Pt degradation modeling in Chapter 2 and experimental observations [10, 49], the through-plane Pt degradation can be estimated and lower ECA is found to be near the CCL and membrane interface in the aged CCL. In a recent study, Jomori et al. [76] established a 1D PEFC model and puts an assumed non-uniform ECA profile across CCL thickness to evaluate the effects of the through-plane non-uniform ECA distribution on the low Pt-loading PEFC performance. They found that an additional ohmic loss comes into effect when the PEFC operates under low humidity condition, of the same order of magnitude as the ORR loss and micro-scale transport loss. This additional ohmic loss exists even when the remaining ECA is uniform and it is significantly enlarged by the through-plane non-uniform ECA distribution.

The Pt degradation is also highly non-uniform in the in-plane direction across the CCL due to the non-uniform temperature, humidity, electronic and electrolyte phase potential distributions in CCL. The non-uniform in-plane Pt degradation can be caused in the channel-land dimension and the along-channel dimension. In Chapter 3, the non-uniformity of ECA distribution in the channel-land dimension is found to be small due to the current engineering trends to reduce the cathode land width for better oxygen transport and water removal. However, the along-channel non-uniformity of ECA and its impact have not been explored by any previous work. An important question is how the non-uniform along-channel Pt degradation affects the current density distribution in the PEFC and whether the non-uniform along-channel ECA causes different cell voltage loss compared with uniform remaining ECA. If this difference is negligible, considering the small ECA non-uniformity in channel-land dimension, a simplified Pt degradation modeling can be carried out separately and the estimated remaining ECA can be used as a constant to put into PEFC modeling. Thus, the EOL PEFC performance can be estimated by
parameter adjusting of ECA without modifying the PEFC model. On the other hand, if this
difference is large, it is essential to develop a modeling method to predict the non-uniform along-
channel ECA in aged CCL and its impacts on EOL PEFC performance. The current work finds
that non-uniform along-channel ECA distribution can cause large difference in voltage loss when
the micro-scale oxygen transport resistance is large. In Chapter 3, effort is made to couple the
physics based transient Pt degradation model into transient M2 model on a 2D differential cell
case study, which requires substantial time to solve. To investigate the along-channel non-
uniform Pt degradation in 3D single channel PEFC and to further explore non-uniform Pt
degradation in medium scale or large scale PEFC modeling studies, a computationally efficient
method is needed.

This chapter summarizes the mathematical derivation of the theoretical solution of general
Ostwald ripening problem by previous researchers. Then, starting from this theoretical solution, a
simple empirical correlation is established to capture effects of temperature, humidity and voltage
on Pt degradation under constant voltage condition. Then as illustrated in Figure 4-1, the current
study combines this Pt degradation model with a comprehensive PEFC performance model, M2
model, to predict the non-uniform ECA distributions in CCL and the EOL PEFC performance.
This approach is demonstrated by a simulation study on a counter-flow, single channel PEFC
case. For a single channel PEFC, there is a clear along-channel dimension and clear co-flow or
counter-flow arrangement. However, for industrial PEFCs, the channel arrangement can be
complex. Anode and cathode channels may not follow the same pattern so there may not be a
clear along-channel dimension. The current modeling method is still applicable to study the in-
plane non-uniform Pt degradation and its impacts when the channel arrangement is complex. To
further demonstrate the applicability of the present model, Pt degradation modeling is performed
on a medium scale industrial PEFC case. It indicates that this Pt degradation modeling approach
is applicable for large scale PEFCs in the future and is a simple but meaningful tool to develop industrial PEFCs.

4.2 Importance of Modeling Along-Channel Non-Uniform Pt Degradation

Figure 4-2 shows the geometry and mesh of a single channel PEFC. The geometry parameters and operation conditions for this single channel PEFC are listed in Table 4-1. It is worthwhile to evaluate the importance of the channel-land and along-channel non-uniform ECA distribution regarding PEFC EOL performance. Thus, a series of modeling studies are designed to answer this question first. In Chapter 3, the non-uniformity of the ECA under channel and land is found to be within 3%, given the current trend of applying narrow cathode land width. One important question is whether this small channel-land ECA non-uniformity can cause large difference in PEFC performance compared with uniform ECA distribution. Assume that 32% ECA remains in a cycled PEFC CCL. The remaining ECA is assumed to be either uniform or follows the made cosine distribution with 2%, 3%, 4%, 5% differences (from channel to land) in the channel-land direction, as shown in Figure 4-3. Those ECA profiles were brought into modeling study of single channel PEFCs under average current density of 2.0 A/cm² with cathode loadings of 0.07 mg/cm², 0.06 mg/cm², and 0.05 mg/cm². Through this chapter, the thickness of CCL remains identical. So the 0.07 mg/cm², 0.06 mg/cm², 0.05 mg/cm² cathode loadings correspond to Pt weight percentage of 14%, 12% and 10%. The PEFC voltages are summarized in Table 4-2. It is found that for these low Pt-loading PEFCs, the non-uniformity of ECA in the channel-land direction cannot cause large variation (all within 2 mV) in PEFC performance. This means given the cathode land width of 0.5 mm, the non-uniformity of ECA distribution in the channel-land direction does not cause large difference in PEFC voltage responses compared with uniform ECA distribution, even considering the degradation of low Pt-loading PEFCs.
On the other hand, the along-channel ECA distributions is assumed to be either uniform or follows the made parabolic distribution as introduced in Figure 4-4, while the average remaining ECA is kept to be 32%. Modeling study is performed to see whether the along-channel non-uniform ECA distributions can cause difference in cell voltage. As shown in Figure 4-5, the along-channel non-uniform ECA distributions cause large difference in cell voltage for the PEFC with 0.05 mg/cm² cathode loading. When the Pt-loading is 0.06 mg/cm² and 0.07 mg/cm², the non-uniform along-channel ECA distribution will not induce large difference compared with uniform ECA distribution. This indicates that the non-uniform along-channel ECA affects the PEFC voltage loss only when the micro-scale oxygen transport loss is large. The non-uniform along channel ECA distribution during degradation is not important for normal Pt-loading PEFC, but can be very important for low Pt-loading PEFC based upon this study. As reducing Pt-loading in PEFC CCL is important to reduce the cost of PEFC, estimating the lifetime and EOL performance of low Pt-loading PEFC is needed. Therefore, a method to predict the along-channel non-uniform ECA distribution in PEFC CCL and its impact on the PEFC performance is essential.

4.3 Model Development

Wagner [117] obtained the “asymptotic” solution [118] of the Ostwald ripening equations both under the kinetics controlled condition and under the diffusion controlled condition. Ferreira et al. [10] has analyzed the Pt dissolution behavior in PEFC CCL and suggested that the Pt dissolution in CCL is controlled by kinetics instead of by diffusion. Gibbs-Thompson effect is regarded as the driving force of Ostwald ripening and results in the Ostwald’s equation [117]:

\[ c_{P_t^{2+}, r} = c_{P_t^{2+}, 0} \exp \left( \frac{2 \gamma \Omega}{rRT} \right) \]  

4.1
where \( c_{Pt_r^+} \) is the saturation concentration for particles of radius \( r \). \( c_{Pt_0^+} \) is the saturation concentration for the infinitely coarse Pt particles. \( \gamma \) is the Pt surface tension and \( \Omega \) is the molar volume of Pt. For the kinetic controlled Ostwald ripening process, the particle growth is governed by the following equation:

\[
r = -k\Omega \left( c_{Pt_r^+} - c_{Pt_0^+} \right)
\]

4.2

where \( c_{Pt_r^+} \) is the mean concentration in a system of particles with different radius.

Wagner [117] derived that the radius of a particle in equilibrium with the surrounding of the solution denoted by \( r^* \) would follow the equation over time:

\[
r^* (t) = r^* (t = 0) \left[ 1 + t / \tau_D \right]^{-1/2}
\]

4.3

\[
\tau_D = \frac{3\nu \gamma_K \left[ r^* (t = 0) \right]^2 RT}{4\gamma_k c_{Pt_0^+} \Omega^2}
\]

4.4

Following their derivation, it is easy to derive the \( ECA(t) \) evolution over time as:

\[
ECA(t) = ECA(0) \left[ 1 + t / \tau_D \right]^{-1/2}
\]

4.5

Now, an analysis of the characteristic time \( \tau_D \) is useful for understanding of the kinetics controlled Ostwald ripening process. \( \nu \) is a stoichiometry factor for dissociating substances, and for the elementary substance Pt in our problem, \( \nu \) is assumed to be 1. \( \gamma_K \) is an auxiliary parameter and it is found to be 4/3 by Wagner. \( \gamma \) and \( \Omega \) are Pt surface tension and Pt molar volume and they are constants. And \( r^* \) has the following expression:

\[
r^* = \frac{\int_0^\infty f(r,t) r^2 dr}{\int_0^\infty f(r,t) rdr}
\]

4.6

So Equation 4.4 could be reformed into:
It can be found from Equation 4.7 that when the initial radius of the Pt particles is smaller, the characteristic time \( \tau_D \) is shorter. This trend is in accordance with the fact that faster Ostwald ripening and faster Ostwald ripening induced Pt degradation are caused when the initial Pt particles are smaller [59]. From Equation 4.7, one can find that fundamentally, the kinetic constant \( k \) and the saturation concentration of infinitely coarse Pt particle \( c_{Pt^{2+},0} \) determine the rate of Pt Ostwald ripening. A simple correlation of \( c_{Pt^{2+},0} \) [mol/m\(^3\)] with the voltage (lower than 1.1 V) is established with experimental results from Wang et al. [55]. In their experimental measurements, the polycrystalline platinum wires were used and the equilibrium concentrations were measured after 72 h of voltage holdings. Polycrystalline platinum wire could be regarded as infinite coarse Pt particle. And a linear fit is used for correlating \( \log(c_{Pt^{2+},0}) \) with voltage \( V \) and result is shown in Figure 4-6. The fitting result is:

\[
\log(c_{Pt^{2+},0}) = 15.783V - 38.7781
\]

Assume the reaction rate \( k \) follows the Arrhenius equation, then \( k \) has a form of:

\[
k = k_{vp}A_mE^{-E_a/RT}
\]
physics model. Now bring Equation 4.8, 4.9, and 2.21 into Equation 4.7, then $\tau_D$ has the following form:

$$
\tau_D = \frac{r'(t = 0)^2 T}{k_v \exp\left(-\frac{H_{L,100\%RH}}{RT} \left[\frac{0.3(1-a)+1}{\exp(15.783V - 38.778)}\right] \right)^2} \frac{R}{x^2}
$$

The first demonstration of using Equation 4.5 and 4.10 is on determining the value of $k_v$ under constant voltage hold condition and modeling the ECA loss under constant voltage hold condition. Ferreira et al. [10] performed long-term Pt degradation test under voltage hold at 0.75 V and 0.95 V, so their experimental results are used to determine $k_v$ to be 3.5 m/s under the voltage hold condition. The fitting results are shown in Figure 4-7. The ECA evolutions under other voltage hold conditions with this $k_v$ are also shown in Figure 4-7.

Taking the voltage at 0.7 V as an example, the ECA evolutions predicted by Equation 4.5 and 4.10 under various temperatures, under various water activities, and for the various particle radiiuses are plotted in Figure 4-8. Up to this point, the Pt degradation under voltage hold condition could be fully captured by Equation 4.5 and 4.10. Then this Pt degradation is coupled into a comprehensive PEFC model, M2 model. The micro-scale oxygen transport resistance is considered in this model to capture low Pt-loading effect [105], which is necessary to predict the performance of the aged PEFCs. This PEFC model has been validated with various experimental data thus it is demonstrated to give good prediction of PEFC voltage performance and water transport in PEFCs [99, 105, 119]. The specific conservation equations, properties and parameters used in the modeling can be found in reference [105]. The constant current operation of the PEFC is investigated. In each time step, which is in order of magnitude of 1000 h, the steady state solution of the last time step is used to provide local $\Phi_s - \Phi_e$, temperature, and humidity in CCL as inputs $V$, $T$, $a$ into Equation 4.10. In each time step, the PEFC can be regarded as to work
under constant voltage condition and Equation 4.5 is used to update the ECA distribution. Then the predicted new ECA distribution is used as inputs into the PEFC model to calculate the next steady state solution.

4.4 Results and Discussion

4.4.1 Non-Uniform Pt Degradation in Single Channel PEFC under Long Time Constant Current Operation

The modeling study is first performed with a single channel PEFC case as shown in Figure 4-2. The operational conditions are the same as in the previous case studies. The average ECA evolutions and voltage evolutions are shown in Figure 4-9 for PEFCs with three different cathode Pt-loadings. As constant current condition is applied, the voltage output for high loading PEFC is higher than the low loading PEFC. Thus the higher voltage causes faster ECA loss for the high Pt-loading PEFC. However, as for the voltage loss, the low Pt-loading PEFC suffers significantly faster voltage loss. The underlying reason is that although the slower ECA loss can cause lower ORR voltage loss for low Pt-loading CCL, the low Pt-loading CCL suffers much more aggressive micro-scale oxygen transport loss when it degrades and the micro-scale oxygen transport loss largely damages the performance of PEFC. This is demonstrated in Figure 4-10. The implication is that besides considering the BOL performance, engineers who try to reduce Pt-loading should definitely consider degradation and EOL PEFC performance after degradation. As predicted by the current model, when the Pt-loading is reduced from 0.075 mg/cm² to 0.05 mg/cm² which means a reduction of 1/3 CCL Pt-loading, the EOL voltage output reduces from about 0.49 V to 0.45 V after 90000 h constant current operation. If a further 1/4 reduction of the CCL Pt-loading from 0.05 mg/cm² is made, the EOL voltage outputs is only about 0.39 V after 90000 h constant current operation. And for this 0.0375 mg/cm² CCL loading PEFC, although its BOL performance seems tolerable, it provides insufficient voltage output for most of its lifetime.
Figure 4-11 and Figure 4-12 show the in-plane ECA distributions and current density distributions for PEFC with different cathode Pt-loadings. Similar to a recent physics-based Pt degradation modeling, Figure 4-11 indicates that the non-uniformity of ECA in the channel-land dimension is small given the narrow channel and land width. However, the non-uniformity of ECA in the along-channel direction is found to be between 10% and 20%. As shown in Figure 4-11 (a), the ECA loss is high under the land compared with under the channel, and high in the middle compared with two ends. This ECA distribution is majorly governed by humidity distribution in CCL. For the low humidity counter-flow arrangement of PEFCs, the humidity is higher under land than under channel, and is higher in the middle than at the two ends. As shown in Figure 4-11 (b), when the Pt-loading is reduced to 0.0375 mg/cm², the ECA loss pattern is similar to the high loading case during the first 40000 h of its lifetime. However, when this low Pt-loading CCL further degrades, the non-uniform ECA distribution changes its pattern. This is because when the ECA is extremely low, the micro-scale oxygen transport loss dominates total voltage loss and reshapess humidity distribution in CCL by reshaping the current density distribution. As shown in Figure 4-12 (a), the current density distribution follows a typical pattern at the beginning, and this pattern is governed by ohmic voltage loss. Then as the ECA decreases due to degradation, the micro-scale transport resistance comes into play and reshapes the current density distribution. After 80000 h, it can be found the ohmic voltage loss and micro-scale transport resistance loss shape the current density distribution together. On the other hand, as indicated in Figure 4-12 (b), the current density distribution of the 0.0375 mg/cm² Pt-loading is totally reshaped and governed by the micro-scale oxygen transport loss after 40000 h, as the micro-scale oxygen transport loss is significantly higher than the ohmic loss due to very low ECA in CCL.
4.4.2 Non-Uniform Pt Degradation in a Medium Scale PEFC under Long Time Constant Current Operation

Next, the modeling method is applied to one medium scale industrial PEFC case to demonstrate its applicability. For the recent industrial PEFC design, the channel arrangement can be more complex than the co-flow or counter-flow arrangement. As shown in Figure 4-13 for example, the cathode side of this medium scale PEFC is straight channels for easier water removal. On the anode side, parallel serpentine channels are applied to preserve water on the anode side under low-humidity operating conditions. The geometry parameters are same as listed in Table 4-1 except the serpentine channels instead of a straight single channel is applied on anode side for this PEFC with a 18 mm by 18 mm MEA. The CCL Pt-loading is 0.05 mg/cm². The overall performance of this medium scale PEFC under long time current holding at 1.5 A/cm² and 2.0 A/cm² is shown in Figure 4-14. The non-uniform ECA distributions in CCL after 40000 h and 80000 h of constant current operation of 2.0 A/cm² are shown in Figure 4-15. It is clear that the non-uniformity of ECA between channel and land is relatively small, while the current model predicts that a non-negligible in-plane ECA non-uniformity exists corresponding to the channel arrangements. The initial and final current density distributions (2.0 A/cm² current holding) are shown in Figure 4-16. It could be found that a significant difference exists between the initial current density and the final current density distributions. As discussed, this significant difference in current density distribution is actually a shift of current density pattern. For the initial PEFC, the voltage loss is majorly governed by ohmic loss thus governed by water content distribution in the membrane. For the PEFC suffering severe Pt degradation, large micro-scale oxygen transport loss is triggered. As a result, the voltage loss is governed by oxygen transport loss and governed by oxygen concentration distribution as shown in Figure 4-16(b).
4.5 Conclusion

The EOL performance of PEFC regarding Pt degradation is investigated in the current chapter. For the aged PEFC CCL, the non-uniform ECA distribution in the channel-land direction is not prone to cause PEFC voltage difference compared with uniform ECA. On the other hand, the ECA non-uniformity in the along-channel direction causes voltage difference compared with uniform ECA when the PEFC cathode loading is low. So, the study in this chapter indicates that the along-channel non-uniform Pt degradation is non-negligible when considering the low Pt-loading PEFCs. Then the current chapter develops an empirical Pt degradation model and couples it into M2 model to predict long term PEFC Pt degradation when it works under constant current condition. For low Pt-loading PEFCs, the micro-scale oxygen transport loss governs the EOL PEFC performance. The micro-scale oxygen transport loss is triggered as the cathode Pt-loading is low. For the pristine low Pt-loading PEFC, the micro-scale oxygen transport loss is not the governing voltage loss yet. But as the PEFC degrades, the loss of ECA significantly amplified the micro-scale oxygen transport loss and this exacerbated micro-scale oxygen transport loss is found to govern the EOL PEFC performance. The current density distribution is also significantly shifted in the aged low Pt-loading PEFC compared with the BOL current density distribution.

Next, this modeling method is performed on a medium scale PEFC case to demonstrate its applicability. Although industrial scale PEFC modeling is not performed in this chapter due to limited time, this modeling method is applicable for industrial scale PEFC modeling. The modeling method developed herein is a valuable tool to design industrial PEFCs considering the EOL performance.
Table 4-1. Geometry parameters and operating conditions.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane thickness (μm)</td>
<td>10</td>
</tr>
<tr>
<td>CCL thickness (μm)</td>
<td>10</td>
</tr>
<tr>
<td>ACL thickness (μm)</td>
<td>6</td>
</tr>
<tr>
<td>MPL thickness (μm)</td>
<td>30</td>
</tr>
<tr>
<td>GDL thickness (μm)</td>
<td>160</td>
</tr>
<tr>
<td>Channel width (mm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Channel height (mm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Land width (mm)</td>
<td>0.5</td>
</tr>
<tr>
<td>Channel length (cm)</td>
<td>10</td>
</tr>
<tr>
<td>Anode/cathode pressure (atm)</td>
<td>1.5/1.5</td>
</tr>
<tr>
<td>Average current density (A/cm²)</td>
<td>2.0</td>
</tr>
<tr>
<td>Stoichiometric ratio in the anode/cathode</td>
<td>1.5/2.0</td>
</tr>
<tr>
<td>RH of anode/cathode inlet @ 80°C</td>
<td>20%/20%</td>
</tr>
</tbody>
</table>
Table 4-2. Single channel PEFC voltages with non-uniform channel-land ECA distributions.

<table>
<thead>
<tr>
<th></th>
<th>Uniform ECA</th>
<th>2% Difference</th>
<th>3% Difference</th>
<th>4% Difference</th>
<th>5% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07 mg/cm²</td>
<td>0.48240 V</td>
<td>0.48207 V</td>
<td>0.48189 V</td>
<td>0.48168 V</td>
<td>0.48146 V</td>
</tr>
<tr>
<td>0.06 mg/cm²</td>
<td>0.45932 V</td>
<td>0.45898 V</td>
<td>0.45877 V</td>
<td>0.45854 V</td>
<td>0.45827 V</td>
</tr>
<tr>
<td>0.05 mg/cm²</td>
<td>0.38458 V</td>
<td>0.38525 V</td>
<td>0.38545 V</td>
<td>0.38557 V</td>
<td>0.38560 V</td>
</tr>
</tbody>
</table>
Figure 4-1. Illustration of coupling Pt degradation model into PEFC performance model.
Figure 4-2. Geometry and computational mesh (compressed 1/10 length in along-channel direction).
Figure 4-3. The uniform and made up non-uniform channel-land ECA distributions.
Figure 4.4. The uniform and made up non-uniform along-channel ECA distributions.
Figure 4-5. Along-channel non-uniform ECA distribution effect on PEFC voltage performance under various cathode Pt-loading.
Figure 4-6. Fitting the experimental results of equilibrium Pt$^{2+}$ concentration from polycrystalline platinum wires dissolution [55] under various potentials.
Figure 4-7. Compare the modeled and the experimental ECA evolutions [10] at various voltage holding conditions.
Figure 4-8. Comparison of ECA evolutions under various temperatures, water activities and with various radius.
Figure 4-9. Modeling predicted ECA and voltage evolutions under long time constant current operation for single channel PEFC with various cathode Pt-loadings.
Figure 4-10. Voltage loss caused by ORR and micro-scale oxygen transport under long time constant current operation for single channel PEFC with various cathode Pt-loadings.
Figure 4-11. Modeling predicted normalized ECA (%) distributions (middle of CCL, compressed 1/10 length in along-channel direction) under long time constant current operation for PEFC with cathode Pt-loading of (a) 0.075 mg/cm², (b) 0.0375 mg/cm².
Figure 4-12. Modeling predicted current density (A/cm²) distributions (middle of membrane, compressed 1/10 length in along-channel direction) under long time constant current operation for PEFC with cathode Pt-loading of (a) 0.075 mg/cm², (b) 0.0375 mg/cm².
Figure 4-13. Mesh of a medium scale PEFC with straight cathode channels and parallel serpentine anode channels (a) view from cathode side (b) serpentine anode channels.
Figure 4-14. Modeling predicted ECA and voltage evolutions under long time constant current operation for medium scale PEFC.
Figure 4-15. Modeling predicted ECA distributions (middle of CCL) after (a) 40000 h and (b) 80000 h constant current (2.0 A/cm²) operation for a medium scale PEFC.
Figure 4-16. Modeling predicted current density distributions (middle of membrane) (a) before and (b) after long time constant current (2.0 A/cm²) operation for a medium scale PEFC.
Chapter 5

Conclusions and Future Work

5.1 Conclusions

Full commercialization of PEFCs is limited by two factors: cost and durability. Pt catalyst is important from both cost and durability point of view. In this dissertation, Pt catalyst degradation in PEFC CCL has been studied by numerical modeling. Prior to this dissertation, Pt degradation modeling is generally fundamental electrochemical modeling and the non-uniform Pt degradation in CCL is not discussed. This dissertation sheds light on spatially non-uniform Pt degradation in CCL and its effects on the overall degradation speed, and on the EOL performance of aged PEFCs.

In order to study the non-uniform Pt degradation across CCL in the thickness direction caused by the interactions of Pt Ostwald ripening and Pt dissolution-re-precipitation mechanisms, a 1D Pt degradation model based on previous researchers’ fundamental electrochemical Pt degradation model is developed in Chapter 2. This model is validated against experimental measured overall ECA evolutions as well as PSDs, generating good agreement. The non-uniform Pt degradation distribution across the CCL is revealed by this model. An exacerbated Pt degradation region is found near the CCL and membrane interface caused by the Pt$^{2+}$ sink posed by crossover $\text{H}_2$. This exacerbated Pt degradation region is narrow compared with the regular CCL thickness of 10 $\mu$m. But when the thickness of CCL is further reduced, a larger fraction of CCL is exposed under the exacerbated Pt degradation region and faster overall ECA loss is caused. This clearly implies that thinning the CCL can cause faster Pt degradation. In addition, an approach to capture RH effects on Pt degradation is developed in Chapter 2 and corresponding validation by comparing experimental measurements is performed.
The Pt degradation for automotive PEFCs is tested under so-called load cycle durability test condition in industry, which means the voltage cycle between a low to a very high value. The corresponding realistic PEFC condition is the current load cycles between a very low to full load condition. Thus, modeling the Pt degradation for a PEFC under current cycling condition assists understanding of Pt degradation for automotive PEFCs under dynamic load condition. Transient M2 model is a well validated and computational efficient model which is widely used to study dynamic behavior of PEFCs. By coupling the transient 1D Pt degradation model into transient M2 model, Chapter 3 investigates the transient Pt degradation phenomenon for a low Pt-loading PEFC under current cycling condition. Taking the advantage of computationally efficient transient M2 model, this coupled model is computationally executable and it is demonstrated on a 2D differential cell. The polarization curves for the initial and cycled PEFC are generated. The performance loss of the PEFC through the current cycling test is quantified by the current study. One important finding is that increasing the lower current in the current cycling slows Pt degradation and slows Pt degradation induced PEFC performance loss. This finding leads a direct suggestion to design automotive PEFCs systems, which is to limit the lowest current density under dynamic load condition. Nowadays, FCEVs uses batteries to take the highly dynamic load and enables the PEFCs to work under relatively steady load. This FCEV strategy is beneficial to the lifetime performance of PEFC regarding Pt degradation.

In addition, the non-uniform Pt degradation in the channel-land direction is quantified in Chapter 3. The in-plane distribution of Pt degradation between land and channel is an important issue as it determines whether the land-to-channel width ratio has important impact on PEFC durability. To mimic the recent trend of reducing cathode land width, 0.5 mm width land is studied and the difference of remaining ECA under channel and land is within 3%. The implication is that the non-uniformity of Pt degradation in the channel-land direction is small.
Although extensive modeling study has been performed on the BOL performance of PEFC, modeling study on the EOL performance of PEFC is lacking. Chapter 4 considers the EOL performance of PEFC regarding to Pt degradation. One important issue before initiating model development is whether the non-uniform ECA distribution in the cycled CCL causes differences in EOL PEFC performance compared with uniform ECA distribution. If this difference is negligible, then EOL performance of PEFC can be modeled straightforwardly by changing the ECA value as a parameter. It is found that the non-uniform ECA distribution in the channel-land direction has negligible effect on EOL PEFC performance compared with uniform ECA distribution. On the other hand, the non-uniform ECA distribution in the along-channel direction has a large effect on EOL performance for the low Pt-loading PEFCs. Thus, prediction of the in-plane non-uniform Pt degradation is needed to evaluate the EOL performance of low Pt-loading PEFCs.

In Chapter 4, based on mathematical solution of the general Ostwald ripening equations by previous researchers, an empirical correlation is developed and integrated into M2 model to predict the non-uniform in-plane Pt degradation and its consequence. This approach is firstly applied to modeling single channel PEFCs with different low Pt loadings. The EOL performance, the ORR and micro-scale oxygen transport loss, and the ECA and current density distributions during long term current hold conditions are discussed with this approach. It is found although those low Pt loading PEFCs have similar BOL performance, their EOL performance differs greatly. One important implication is that when reducing the loading of PEFC CCL, the EOL performance of PEFC must be considered. For example, the 0.0375 mg/cm$^2$ loading PEFC has initial tolerable performance, but it suffers strong micro-scale transport loss and provides insufficient voltage supply during most of its lifetime. For the low Pt loading PEFCs, even though their initial current density distributions is governed by ohmic loss, the micro-scale transport loss comes into play and reshapes the EOL current density distributions. For the PEFC with 0.075
mg/cm² Pt loading, the EOL current density distribution is governed by both ohmic loss and micro-scale oxygen transport loss. And for the PEFC with 0.0375 mg/cm² Pt loading, the EOL is governed by micro-scale oxygen transport loss. Then, this model is demonstrated by modeling the Pt degradation of medium scale PEFCs with complex flow channel arrangements. This indicates that the current model has future potential for use in large scale industrial PEFC EOL modeling with focus on Pt degradation.

5.2 Future Work

In the present work, modeling of Pt and corresponding CCL degradation in PEFCs is conducted. A number of critical issues have been addressed regarding the non-uniform Pt degradation phenomenon in the CCL thickness direction, the channel-land direction, the along-channel direction, as well as the general in-plane direction with complex channel arrangement. There is still much possible future work to be done on modeling Pt degradation for PEFC engineering.

Through Equation 2.21, the speed of Pt degradation is correlated with humidity in CCL. This equation only describes the RH up to 1 because no existing experimental results can be found describing the Pt degradation rates under different CCL liquid saturations. As concluded by many recent studies, liquid water does indeed exist in CCLs under realistic PEFC working conditions. So experiments on Pt degradation rate under different CCL liquid saturation are needed. If the correlation of Pt degradation rate with CCL liquid saturation can be established, then the advantage of M2 model can be fully exploited, as M2 model has significant advantage on predicting liquid distribution in PEFCs.

For automotive PEFC CCLs, the two durability issues receiving the most attention are start-stop durability and load durability. For the start-stop durability, the rule of thumb degradation mechanism is carbon corrosion, while the rule of thumb degradation mechanisms for the load
durability is Pt dissolution induced Pt catalyst degradation, as modeled in Chapter 2 and Chapter 3. The start-stop durability can be improved by suppressing carbon corrosion. Practical method includes high flow rate purge when the PEFC shut down, using graphitized carbon support, and decreasing the start-up and shut-down temperature, to 25°C for example [120]. Pt dissolution induced Pt catalyst degradation can also happen under PEFC start-stop condition. But as the carbon corrosion is much stronger, this mechanism was a minor issue and was overlooked. In the near future, when the carbon corrosion as the major degradation mechanisms for PEFC start-stop is suppressed to a certain level, the Pt dissolution induced Pt catalyst degradation under start-stop condition becomes an issue to be addressed. One possible study is to model Pt degradation at a low temperature, 25°C for example. Quantification of Pt degradation at low temperature by modeling and experiment is helpful to compare the importance of Pt dissolution induced degradation and the suppressed carbon corrosion.

The physics based Pt degradation considers two electrochemical reactions and is a simplification of the complex nature of the Pt dissolution issue. The empirical Pt degradation model in Chapter 4 is also a highly simplified method, which is feasible for EOL PEFC performance estimation. The goal of these modeling methods is to help understand certain problems and to provide effective instructions for PEFC engineering. To investigate the deep underlying physics of Pt dissolution, modeling methods should go to the bottom of the phenomenon. Thanks to development of molecular dynamics simulation software, molecular dynamic simulation becomes an available approach for more researchers to study fundamental problems. For PEFC CCLs, much molecular dynamics simulation work has been performed on ORR mechanisms, and on O₂ permeation through Nafion ionomer on Pt surface. Molecular level modeling study on Pt degradation phenomenon is a possible future direction.
Bibliography


VITA

Yubai Li

EDUCATION

08/2013-08/2017 The Pennsylvania State University, State College, PA
  • Ph.D. in Mechanical Engineering
  • GPA: 3.95/4.0

08/2011-05/2013 Carnegie Mellon University, Pittsburgh, PA
  • M.S. in Mechanical Engineering
  • GPA: 4.0/4.0

09/2007-07/2011 Peking University, Beijing, China
  • B.E. in Engineering Structure Analysis
  • GPA: 3.4/4.0

RESEARCH EXPERIENCE

09/2013- Present Research assistant at Electrochemical Engine Center, Department of Mechanical and Nuclear Engineering, The Pennsylvania State University
(Supervised by Prof. Chao-Yang Wang)
Dissertation: Modeling Pt and Catalyst Layer Degradation in PEFCs
• Develop and validate a one-dimensional electrochemistry Pt degradation and subsequent electrochemically active surface area (ECA) loss through the cathode catalyst layer (CCL) of PEFCs.
• Investigate the impacts of H2|N2 or H2|Air operation, operating temperature and relative humidity (RH) on Pt degradation under voltage cycling with this model.
• ECA loss is found to be non-uniform across the cathode with a zone of exacerbated Pt degradation and hence much lower ECA found near the membrane for the aged CCL.
• Propose the consequence of the non-uniform Pt degradation across the CCL. Suggest that thinning the cathode electrode in a fuel cell would lead to more ECA loss.
• Coupling the Pt degradation modeling into 3D PEFC CFD modeling to generate Pt degradation distribution information for mitigating the spatially non-uniform Pt degradation.

PUBLICATIONS

• Yubai Li, Dongzhi Guo, S.C. Yao, Thermal-Aware Micro-Channel Cooling of Multicore Processors: A Three-Stage Design Approach, 2013, ASME IMECE.