IN SITU DIAGNOSIS OF ELECTROLYTIC AND FUEL CELLS USING ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

A Dissertation in
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by
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ABSTRACT

In situ EIS data are presented for the CuCl/HCl electrolyzer and Liquid Metal Anode Solid Oxide Fuel Cells (LMA-SOFC) operating under different conditions. The durability of the CuCl electrolyzer operating for 168 hours while maintaining the high current density of 0.3 A cm$^{-2}$ under 0.7 V is reported for the first time. The impedance spectra of the cell, along with the polarization curves ($V$-$I$ data), show the effect of operating temperature and contact pressure at the end plates of the membrane electrode assembly (MEA).

After the durability test, the potential required to maintain the cell at 0.3 A cm$^{-2}$ increased from 630 mV of the fresh membrane electrode assembly (MEA) to 710 mV. The increase in the ohmic resistance of the membrane by 41% was observed to be the primary cause of degradation. Starting from 0.6 Ω cm$^2$, there was a small change in the ohmic resistance of the cell during the first 90 hours, followed by a significant increase of 25%, and then attained a steady value of 0.85 Ω cm$^2$. Simultaneously, a change in the decomposition potential was observed as it increased from 0.18 V in the beginning to 0.25 V at the end of testing. This is mainly due to the decrease in efficiency of the regeneration column and dilution of the anolyte solution over time. Further, the use of EIS in the through-plane conductivity cell proved to be a reliable and time-efficient method for evaluation new and existing membranes before testing in the electrolyzer.

A liquid metal anode solid oxide fuel cell (LMA-SOFC) is constructed to study the kinetics and transport properties of the system. The behavior of the system is investigated by operating the cell as a metal-air battery while operating under argon, and as a fuel cell
with hydrogen and coal as the fuel feeds. EIS signatures and OCP analysis provides insight into the reaction mechanism and indicate the formation of a SnO$_2$ layer at the electrolyte/anode interface. The OCP of 0.885 and 1.117 V was observed for the coal and hydrogen powered fuel cell, respectively. The results show the gradual increase in efficiency of the reduction of SnO$_2$ by using carbon and hydrogen as the fuels. The EIS spectra obtained for the hydrogen fed cell was a characteristic of the diffusion controlled systems and equivalent circuit modeling was used to calculate the oxygen diffusion coefficients. The effective oxygen diffusion coefficients of $1.9 \times 10^{-3}$ cm$^2$ s$^{-1}$ at 700 °C, $2.3 \times 10^{-3}$ cm$^2$ s$^{-1}$ at 800 °C and $3.5 \times 10^{-3}$ cm$^2$ s$^{-1}$ at 900 °C are similar to the published results. The resistance added by the SnO$_2$ layer was the primary cause of degradation and further improvements in performance rely heavily on minimizing losses in the liquid Sn layer.
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Chapter 1

Introduction

1.1 Research Contributions and Motivation

1.1.1 Research Contribution

This dissertation presents contribution towards \textit{in-situ} diagnosis of liquid metal anode solid oxide fuel cells (LMA-SOFCs) and the CuCl/HCl electrolyzer using Electrochemical Impedance Spectroscopy (EIS). The highlights of this dissertation are as follows:

1. State-of-Health determination using EIS as an ageing protocol to study performance degradation in the LMA-SOFC and CuCl/HCl electrolyzer.
2. Investigation of the transport mechanism of oxygen ions through the liquid tin layer in the LMA-SOFC system.
3. Evaluation of the effect of operating parameters on the performance of CuCl/HCl electrolyzer and LMA-SOFC.
4. Development of equivalent circuit models to quantify the different voltage losses during the operation of CuCl/HCl electrolyzer and LMA-SOFC.

1.1.2 Research Motivation
Liquid metal anode solid oxide fuel cells have a huge potential to reduce greenhouse emissions by efficiently utilizing coal as a source of energy production. Further, it has added advantages over the conventional Ni-based anode SOFCs as the liquid metal anode is tolerant to various impurities, has a better usage of the active surface area, and it can operate as a metal-air battery in case of fuel starvation [1-3].

Liquid Tin Anode Solid Oxide Fuel Cells have gained significant attention recently and the technology is commercialized by CellTech Power [3-7]. However, the electrochemical reactions and transport processes within the liquid tin anode are not fully understood yet [2]. Performance degradation of the LTA-SOFC due to build-up of the oxide layer is also a big challenge in achieving the desired durability.

Hydrogen has long been considered as an alternative fuel because of its ability to power fuel cells in zero-emission electric vehicles which are two to three times more efficient than internal combustion engines [8, 9]. All major automobile companies like Mercedes, Daimler AG, Honda, Hyundai and Toyota confirmed to have their fuel cell vehicles for sale by 2015. Currently, 96% of hydrogen is produced from fossil fuels resulting in CO$_2$ emissions [10]. Thus, there is a need to devise eco-friendly hydrogen generation techniques to minimize the negative impact on the environment. The CuCl/HCl thermochemical cycle is one of the most promising technologies for economic production of hydrogen because of high efficiency and moderate temperature requirements [10, 11]. However, the technology suffers from the durability issues due to physical, chemical and electrochemical processes contributing to the degradation of the system.
Electrochemical Impedance Spectroscopy (EIS) has the potential to characterize the performance of the LTA-SOFC and the CuCl/HCl electrolyzer, and more importantly, diagnose the failure modes by separating the impedance contribution from different components leading to degradation. EIS analysis, coupled with Linear Sweep Voltammetry (LSV), provides accurate estimates of the State of Health (SOH), calculates the electrochemical and transport parameters, and provides insight into the reaction mechanisms at different electrodes.

1.2 Background

1.2.1 Electrochemical Impedance Spectroscopy

EIS is a powerful characterisation technique for investigating the mechanisms of electrochemical reactions, diagnosing the failure modes, and to explore the properties of different electrode materials. It is used to characterize cell limitations and distinguish between processes occurring on different time-scales. EIS studies the voltage response when a small amplitude Alternative Current (AC) current is imposed to the system.

The EIS characterization technique has been widely employed towards the development and characterization of fuel cells [12-22]. The power of this technique lies in its ability to distinguish, in the frequency domain, the individual contributions of charge-transfer, mass-transfer and ohmic losses [23-25]. Despite its high potential and applicability to all fuel cells and electrolyzers, data interpretation is sometimes difficult. Interpretation of the EIS data requires a model representing the physically meaningful
parameters relevant to the system, and an assessment of the stochastic error structure. The
most common approach to simulate the experimental data is the development of
equivalent circuits, consisting of an arrangement of different electrical elements and
having the same frequency response than the one obtained by EIS tests. The most
commonly used equivalent circuit elements are:

1. Resistors - The impedance of a resistor is independent of frequency and
has no imaginary component. The current through a resistor stays in phase with the
voltage across the resistor.

2. Capacitors - A capacitor's impedance decreases as the frequency is raised.
Capacitors also have only an imaginary impedance component.

3. Constant Phase Elements (CPE) - It is encountered frequently in solid
state electrochemistry, however no general physical interpretation has not been
established yet. The CPE behaviour of interfaces has been ascribed to a fractal nature
(special geometry of the roughness) of the interface.

4. Warburg Element - Diffusion can create an impedance known as the
Warburg impedance. At high frequencies the Warburg impedance is small since
diffusing reactants don't have to move very far. At low frequencies the reactants have
to diffuse farther, thereby increasing the Warburg impedance. On a Nyquist plot, it
appears as a line with a slope of 0.5.

5. Gerischer Element – This form of impedance is similar to the Warburg
impedance in the high frequency region, but in the low frequency region the
dispersions are distinctly different. This transfer function is derived from Fick’s
second law by including a reaction term, thus representing the mixed kinetic and diffusion controlled systems.

1.2.1.1 Circuit Ambiguity

One of the major bottlenecks associated with the use of equivalent circuit modeling is that the equivalent circuits can be non-unique; multiple equivalent circuit models can fit the same impedance data (Figure 1-1).

![Different circuit models fitting the same EIS data](image)

Figure 1-1 Different circuit models fitting the same EIS data

The possibility of multiple models fitting the same EIS data makes it necessary for the user to understand the system physically, and then select a model which is relevant to the study.
1.2.1.2 Fitting Algorithms

The complex nonlinear least squares (CNLS) method [26] is one of the most common methods to fit the EIS data. The commercial fitting program, ZView, which was used to simulate the EIS data considered in this study uses the CNLS method. In order to minimize the CNLS fitting functions, chi-squared ($\chi^2$) algorithm [27] was used. The CNLS method is based on the assumption that the experimental EIS data is contaminated by only random errors (Gaussian in nature). The presence of errors of any other characters significantly effects the reliability of the fitting results. The convergence of the CNLS procedure depends on many factors. The algorithm may stop at a “local minimum”, characterized by a large $\chi^2$. In such cases, changing the initial value of the model’s parameter and/or an instantaneous change of its character from free to fixed could be helpful. The smaller the value of $\chi^2$, the better is the (statistical) goodness of the fit.

1.2.1.3 Initial Data Analysis: Kramers-Kronig Transformations

Before carrying out a detailed analysis of the EIS data and fitting it to an equivalent circuit model, it is necessary to validate the data internally. The Kramers-Kronig (K-K) relations are used to evaluate the data quality [28]. The K-K relations state that the real part of the EIS data can be obtained by an integration of the imaginary part and vice versa.

The K-K relations will always hold for EIS data that is linear, causal, and stable [29]. If the experimental real and imaginary data do not comply with the K-K relations, the
data violates one of the necessary conditions for EIS measurements and the experimental system should be further refined. There is no point in fitting the non K-K compliant data to a circuit model, and hence, K-K analysis of data should always be carried out before interpreting any physical meaning from it.

### 1.2.2 Liquid Metal Anode Solid Oxide Fuel Cells

High temperature Solid Oxide Fuel Cells are very efficient electrochemical energy conversion devices that convert the chemical energy stored in fuels to electrical power. Even with the capability to scale up the technology, durability and performance degradation due to impurities mixed with the fuel are a huge cause of concern [30-33].

The operation with LMA-SOFC allows a variety of carbonaceous fuels to be used as fuels, while remaining tolerant towards impurities in the fuel. A schematic of the LMA-SOFC, along with an electrical circuit model is shown in Figure 1-2.
Figure 1-2 A schematic of LMA-SOFC along with an equivalent circuit model to show various resistances.

Air or oxygen is supplied to the cathode where electrochemical reduction of oxygen takes place to form oxide ions (O²⁻) that travel through the electrolyte, to the anode, and oxidize the liquid metal anode to its oxide form. Two electrons are released that travel through an external circuit and power is generated. The metal is regenerated by the chemical reduction of the oxide species by the fuel.

Cathode: \[ \frac{1}{2} O_2 + 2e^- = O^{2-} \]
Anode:

\[ Sn + 2O^{2-} = SnO_2 + 4e^- \]

\[ 2H_2 + SnO_2 = Sn + 2H_2O \]

Being a relatively new and novel system, LMA SOFCs are still some way from being fully commercialized due to unique engineering challenges associated with the system. However, the processes happening in the liquid anode are not fully understood. There are certain inconsistencies associated with the transport mechanism in the liquid anode and little is known about the effective diffusion coefficients of oxygen. The objective of this dissertation is to better understand the transport mechanism in liquid tin anode and characterize the effect of different fuels using EIS.

### 1.2.3 CuCl/HCl Electrolytic Cell

In the CuCl/HCl electrolyzer, hydrogen is produced by the oxidation reaction of CuCl(aq), upon applying electric potential in the presence of concentrated hydrochloric acid. A schematic of the electrolyzer is shown in Figure 1-3 [34].
Figure 1-3 Conceptual schematic of CuCl electrolysis with a proton exchange membrane; adapted from [34]

At the anode, CuCl(aq) is oxidized to CuCl$_2$(aq) and produces protons which diffuse through the membrane are reduced to hydrogen at the cathode.

While the CuCl electrolyzer has obvious advantages of high efficiency and capability to recycle all the materials, performance degradation and durability are still a big cause of concern for its economic feasibility. There are little or no published data which separate different voltage in the CuCl electrolyzer and show the desired performance for long period of times. In this dissertation, the durability of the cell is demonstrated by meeting the DOE’s target of running the system for 168 hours at 0.3 A cm$^{-2}$ under 0.7 V. State-of-Health (SOH) determination of the cell is studied by using EIS at different overpotentials and key factors leading to the degradation of the system are quantified.
1.3 Overview of the dissertation

Chapter 2 presents the analysis of the CuCl/HCl electrolyzer using EIS and LSV at different operating conditions. The experimental data was collected at three different temperatures and an equivalent circuit model was developed to observe the changes in the ohmic, charge-transfer and mass transfer resistances at different temperatures. The high efficiency of the cell at 80 °C was attributed due to relatively lower ohmic and charge-transfer resistances. The effect of temperature was more pronounced at 0.4 V of applied compared to the data decomposition potential (DP). The measurements indicated a higher charge transfer rate at 80 °C and at high overpotentials. As the contact pressure at the end plates has a direct effect on the ohmic resistance, an optimum value of contact pressure was selected to minimize the ohmic losses without sacrificing on the effective diffusion length.

Chapter 3 follows with the study on the durability of the CuCl/HCl electrolyzer in long term operation after optimizing the parameters such as temperature, solutions concentrations, flow rate and contact pressure at the end plates for maximum efficiency. In-situ analysis was carried out using EIS to determine state of health of the cell and characterize degradation over time.

Following the successful implementation of EIS as a diagnostic tool to study the kinetic and mass-transfer properties in the CuCl/HCl electrolyzer, Chapter 4 deals with the electrochemical characterization of liquid metal anode solid oxide fuel cells. EIS was used to study the cell behavior at different temperatures and operating under different fuels. An equivalent circuit model consisting of Warburg element was developed to
model the mass transfer resistance and calculate effective oxygen diffusion coefficients. Further, the transport mechanism in the liquid tin layer was studied and performance degradation was attributed mainly due to build-up of the tin dioxide layer.

Chapter 5 presents the conclusions and future work.
Chapter 1 References


Chapter 2

Diagnosis and Modeling of the CuCl Electrolyzer Using Electrochemical Impedance Spectroscopy

The text for this chapter was originally published for the *Electrochemical Society Transactions* as “Diagnosis and Modeling of the CuCl Electrolyzer Using Electrochemical Impedance Spectroscopy”, Sanchit Khurana, Derek Hall, Rich Schatz, Serguei N. Lvov, ECS Transactions 53 (9), 41-50.

Preface to Chapter 2

This chapter is a study of the effect of operating parameters on the performance of the CuCl electrolyzer. Experimental EIS data analysis and equivalent circuit modeling were used to observe the change in ohmic resistance and investigate the reaction kinetics at different temperatures. The high performance observed in the $V-I$ data at 80 ºC is corroborated by the AC impedance analysis which shows the decrease in overall impedance as the temperature was increased from 40 to 80 ºC. The effect of contact pressure at the end plates of the MEA was also studied and an optimum value was found.
Abstract

A CuCl electrolytic cell was operated with a single-layer pressed Nafion 117 membrane at different temperatures to quantify the effect of temperature on the overall performance. Polarization curves and EIS data were taken at 40, 60 and 80 ºC to observe the changes in ohmic, charge-transfer and interfacial resistance. Our research showed a significant increase in the cell performance as the temperature was increased from 40 to 80 ºC. While the polarization data were used to observe the overall increase in the current density in a specific range of applied potential, the corresponding EIS data showed a decrease in the ohmic and charge transfer resistance. It was also observed that pressure applied on the end plates during cell assembly has a significant effect on the ohmic resistance. An optimum pressure of 6.3 psi (bolt torque: 20 Nm) showed the best performance. This paper demonstrates how changes in the signature of EIS spectra with temperature reflect the cell performance.

Introduction

Electrochemical Impedance Spectroscopy (EIS) is identified as one of the most promising in-situ diagnostic method to better understand and characterize the irreversible changes in the chemical and/or transport properties of an electrochemical system. It is based on the principle that a small alternating potential is applied to the cell at different frequencies, and the response in alternating current is measured. While the Cu-Cl thermochemical cycle is among the most attractive technologies proposed for hydrogen
production, its commercialization requires an insight on the main causes of degradation in the performance. EIS is getting more popular because of its potential for in-situ and quantitative analysis method for electrochemical systems (1-5). Other studies have been reported to analyze the fuel cell components individually by EIS (6-9). The application of EIS has been extended to stack-diagnosis for PEM fuel cells (10-12) starting from single-cell diagnosis. The concept of symmetric cell has also been used to separate the anode and cathode impedance by measuring anode and full cell impedance data (1, 12-14).

The Cu-Cl thermochemical cycle, a novel H₂ producing technology, has been studied because of the moderate temperature requirements and high efficiency (15-21). Significant improvement in voltage and current efficiencies of the CuCl electrolyzer, a key component of the cycle, have been obtained recently (22, 23). In spite of all the proven merits and its strong capabilities to diagnose an electrochemical system, EIS has not been reported to analyze the performance of the Cu-Cl electrolyzer operating under different conditions. There is little or no published literature to describe the effects of assembly torque on the performance of the CuCl electrolyzer. In this study, we convolute the EIS spectra of the cell using equivalent circuit modeling approach and report the optimum value of the clamping torque as 20 Nm corresponding to the lowest ohmic resistance.
Experimental

Preparation of MEA

Nafion 117 polymer membrane was used to fabricate the MEA. The membrane was pretreated by the following steps to remove the organic and inorganic contaminants before being used in the electrolyzer. First, the membrane was soaked in 3 wt % \( \text{H}_2\text{O}_2 \) solution at 80 °C, followed by soaking in 80 °C DI-water to remove traces of \( \text{H}_2\text{O}_2 \). Then, the membrane was soaked in 1 mol L\(^{-1}\) \( \text{H}_2\text{SO}_4 \) (aq). Finally, the membrane was soaked in DI-water at 80 °C to remove any residual \( \text{H}_2\text{SO}_4 \) (aq). The membrane was placed in each solution for 1 h. The membrane was dried overnight in a desiccator and hot-pressed at 93.33 °C before being allowed to cool at the room temperature. Two 5 cm\(^2\) carbon-cloth electrodes, painted with 4 mg cm\(^{-2}\) of XC-72 R catalyst with 20 % Pt (0.8 mg cm\(^{-2}\) Pt), were placed on each side of the membrane before installing in the electrolyzer.

Operation and stability of a single cell

The CuCl electrolysis can be represented by the following reaction:

\[
2 \text{CuCl (aq)} + 2 \text{HCl (aq)} \rightarrow 2 \text{CuCl}_2 (aq) + \text{H}_2 (g)
\]

The general concept of the CuCl electrolysis using a proton-conducting membrane is shown in Figure 2-1. However, it should be noted that the anodic reaction only represents
a possible mechanism and does not reflect the anolyte chemistry, which could involve various intermediate species (15).

![Conceptual schematic of CuCl electrolysis with a proton exchange membrane; adapted from (15)](image)

Two 5-cm² graphite blocks having serpentine flow channels were obtained from Electrochem Inc. and used as the end plates. 2 mol CuCl (s) dissolved in 7 mol L⁻¹ HCl (aq), and 7 mol L⁻¹ HCl (aq), were fed into the anode and the cathode electrodes respectively. A schematic diagram of the experimental set-up is shown in Figure 2-2. The cell was maintained at 80 °C during the experiment and the solutions were pumped at a flow rate of 130 ml min⁻¹. Variable values of clamping torques –10, 15 and 20 Nm -- were applied on the end plate bolts which correspond to 3.2, 4.7 and 6.3 psi pressure values respectively. The objective was to ensure good electrical contact between the loose components of the MEA.
Electrochemical Impedance Spectroscopy

For EIS measurements, 10 mV of voltage perturbation was applied by sweeping the frequency from 0.01 Hz-50 kHz with 10 points per decade interval. The data were obtained at 0 V vs cathode, and under an applied potential of 0.4 V. A delay of 2 minutes was applied between each measurement in order to allow the cell reaching the steady-state. Consistency and quality of data were established by Kramers-Kronig validation.
Linear Sweep Voltammetry (LSV)

The LSV data were taken with a scan rate of 10 mV s\(^{-1}\) to obtain the current density values for the 0-0.7 V potential range and hydrogen measurements were carried at 0.7 V. The LSV polarization curves were obtained before and after EIS measurements to ensure that the cell characteristics were not changed.

Results and Discussions

Figure 2-3 shows steady decrease in the cell impedance at OCP as the temperature was increased from 40 to 80 ºC.

Figure 2- 3 Nyquist plots at 0 V of the CuCl electrolytic cell representing decrease in overall impedance with increase in temperature.
Figure 2-4 represents the corresponding LSV curves where an increase in the current density is observed.

![Polarization curves showing the increase in the current density as the temperature was raised from 40 to 80 ºC](image)

Figure 2- 4 Polarization curves showing the increase in the current density as the temperature was raised from 40 to 80 ºC

An equivalent circuit model (as shown in Figure 2-5) was used to simulate the experimental data and quantify the physical parameters to observe the change in system performance with temperature.
Figure 2-5. Equivalent circuit model used to simulate the experimental data: Rohm represents the ohmic resistance of the cell, Rct; charge transfer resistance, and Rm; interfacial resistance.

The model consists of $R_{ohm}$, which is the high frequency intercept of the kinetic loop with the real axis, and represents the ohmic resistance of the cell, $R_{ct}$; charge transfer resistance, which is calculated by the difference between the maximum value of the high frequency resistance ($R_{maxHF}$) and the ohmic resistance ($R_{maxHF} - R_{ohm}$), and $R_m$; interfacial resistance. The constant phase elements (CPEs) were incorporated in place of capacitors to account for the inhomogeneity in the system. The CPE is defined by two values; CPE-T and CPE-P. Mathematically, it is expressed as: $Z = 1/(T(wp)^{0.5})$, where $w$ is the angular frequency of the AC signal, $T$ (CPE-T) is capacitance and $P$ (CPE-P) is non-homogeneity constant. The circuit model precisely fits the experimental data, as shown in Figure 2-6, and the fit converged satisfactorily ($chi$-squared $< 5 \times 10^{-4}$).
Further, the model was validated by Kramers-Kronig transformation for internal consistency. As shown in Table 2-1, the ohmic resistance of the membrane decreases from 0.15 Ω to 0.137 Ω as the temperature was increased from 40 to 80 ºC.

**TABLE 2-1.** Ohmic Resistance for the EIS Data taken at 0 V

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Ohmic Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 ºC</td>
<td>0.150</td>
</tr>
<tr>
<td>60 ºC</td>
<td>0.140</td>
</tr>
<tr>
<td>80 ºC</td>
<td>0.137</td>
</tr>
</tbody>
</table>

The effect of temperature on the system was more pronounced when the cell was operating under an applied potential as this state involves contribution from all physical processes. A similar but separate test was performed when the cell was operating under
an applied potential of 0.4 V. From Figure 2-7, it was observed that there was a significant decrease in both the ohmic and charge transfer resistance as the temperature was increased from 40 to 80 ºC. The charge transfer resistance decreased from 1.2 Ω to 0.08 Ω indicating improved kinetics and higher reaction rate with increase in temperature.

Figure 2-7. EIS data at 40 and 80 ºC for the cell operating under an applied potential of 0.4 V (left) and the zoomed in section (right) to highlight the change in impedance as the temperature was increased.

Figure 2-8 represents the effect of applied pressure on the ohmic resistance of the cell and shows its gradual decrease from 0.25 to 0.22 Ω as the clamping torque was increased from 10 to 20 Nm by applying pressure from 3.2 psi to 6.3 psi.
Figure 2-8. The figure shows the decrease in ohmic resistance as the clamping torque was increased from 10 to 20 Nm by altering the applied pressure from 3.2 psi to 6.3 psi.

The corresponding polarization curves reflecting an increase in the current density are shown in Figure 2-9.
Figure 2-9. Polarization curves representing increase in the overall performance as the clamping torque was increased by altering the applied pressure.

However, it should also be noted that excessive pressure may result in reduced length of path for effective mass transfer and result in the decrease in efficiency. Thus, 6.3 PSI (20 Nm) represents the optimum value of applied pressure as the ohmic resistance did not decrease after further increasing the pressure.
Conclusions

The Cu-Cl electrolyzer was operated at different temperatures and EIS was successfully applied to monitor the system behavior with changes in temperature. An equivalent circuit model was used to fit the experimental EIS data and it was concluded that the ohmic resistance of the membrane decreased with the increase in temperature. A significant decrease in the charge transfer resistance was also observed and this was attributed to the improved kinetics at high temperatures. Experimental results demonstrated that the contact resistance between interfaces was heavily dependent on clamping torque and an optimum applied pressure of 6.3 psi (bolt torque: 20 Nm) was selected based on the ohmic resistance measurements.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy via a subcontract with Argonne National Laboratory. We thank Drs. Mark Fedkin, Michele Lewis and Shabbir Ahmed for their useful feedbacks on the obtained data.
Chapter 2 References


Chapter 3

State of Health of the CuCl electrolyzer during a 168 h test

This text for this chapter was originally prepared for the International Journal of Hydrogen Energy as “State of Health of the CuCl electrolyzer during a 168 h test”, Sanchit Khurana, Derek Hall, Rich Schatz, Mark Fedkin, Serguei N. Lvov. The paper was submitted June 2014.

Preface to Chapter 3

Chapter 3 demonstrates the ability of the electrolyzer to operate for 168 hours at the current density of 0.3 A cm$^{-2}$ under 0.7 V. In-situ EIS measurements help to track the evolution of ohmic resistance and characterize the degradation mechanisms. The effect of applied voltage on the EIS signature is presented which is followed by the theoretical calculation of the OCP of the system.
Abstract

A state-of-health test of the CuCl/HCl electrolytic cell was carried out by maintaining a constant current density of 0.3 A cm$^{-2}$ for 168 h at 80 °C and ambient pressure. While the most common method used to characterize the electrochemical performance of a CuCl electrolytic cell is to record current-voltage ($I$-$V$ curves), it is also essential to separate the electrochemical and ohmic components of the polarization curve. In our study, the AC impedance characteristics of a single cell were studied along with the DC polarization curves. After the durability test, the potential required to maintain the cell at 0.3 A cm$^{-2}$ increased from 630 mV of the fresh membrane electrode assembly (MEA) to 710 mV due to some degradation processes in the electrolytic cell. Quantitative analysis of the performance decay was carried out by Electrochemical Impedance Spectroscopy (EIS). EIS measurements showed an increase in the area specific ohmic resistance of the MEA from 0.6 Ω cm$^{-2}$ to 0.85 Ω cm$^{-2}$ and area specific charge-transfer resistance from 0.61 Ω cm$^{-2}$ to 0.8 Ω cm$^{-2}$ measured at an overpotential of 0.2 V. The degradation in the cell is attributed to the decrease in membrane conductivity and an increase in the charge-transfer resistance.

Keywords:

Hydrogen Production; Performance Degradation; Electrochemical Impedance Spectroscopy; CuCl/HCl thermochemical cycle
Introduction

There is growing interest in studying the Cu-Cl thermochemical cycle for generating hydrogen as the technology has about four times lower decomposition potential of the CuCl/HCl electrolytic cell as compared to water electrolysis [1] as well as significantly lower temperature requirements compared to other thermochemical cycles along with a better overall efficiency [2,3]. While the Cu-Cl thermochemical cycle is among the most attractive technologies proposed for hydrogen production, it is essential to study the performance degradation in order to meet the DOE’s target of producing hydrogen at the cost of $6/kg by 2015 and further reducing it to $4/kg by 2025 [4].

Electrochemical Impedance Spectroscopy (EIS) is a powerful diagnostic method that helps to better understand the degradation mechanisms in electrochemical systems as the technique can provide information on individual cell potential losses. EIS has a great prospective to quantitatively analyze electrochemical systems [5,6,7] and extract the electrochemical cell components [8,9]. Recently, few authors have applied EIS to study the characteristics of the CuCl/HCl electrolytic cell [1, 10, 11] but there is no published data to characterize and separate the components leading to degradation in the CuCl/HCl electrolytic cell. In this study, we quantify the contribution of different physical processes to the main losses in the electrolyzer and investigate the main cause of degradation over time. An in situ EIS approach has been used to monitor the evolution of both the ohmic and charge-transfer resistances with time at different applied potentials.
Experimental

Cell preparation

In the investigated membrane electrode assembly (MEA), Nafion 117 ionomer membrane was used. The pretreatment method was the same as discussed previously [12]. Two 5 cm² carbon-cloth electrodes, painted with 4 mg cm⁻² of XC-72 R catalyst (0.8 mg cm⁻² Pt), were applied to each side of the membrane without hot pressing. Two 85 cm² graphite blocks having serpentine flow channels were obtained from Electrochem Inc. and used as the end plates. A solution of 2 mol of CuCl(s) in 7 mol L⁻¹ HCl(aq) was the anolyte and 7 mol L⁻¹ HCl(aq) was the catholyte. The experimental system which was used was similar to our previous studies [12].

The cell was maintained at 80 °C during the experiment and the solutions were pumped at a flow rate of 130 ml min⁻¹. For stable operation, a constant current density of 0.3 A cm⁻² was maintained for 168 h. The test was semi-continuous, as the solutions were replaced every night to avoid any possible precipitation of CuCl(s) resulting from the increase in concentration of CuCl(aq), and the experiment was paused every night for 6-8 hours. However, it should be noted that the cell was maintained at a temperature of 80 °C for the whole test period and the effective duration for which the membrane was soaked in the HCl(aq) at 80 °C was over 400 h.

Electrochemical characterization

Electrochemical characterization of the cell was performed by EIS in the frequency range from 10 mHz to 50 kHz with 15 points per decade interval. EIS was used to keep a
periodic track of degradation with time and observe the effect of applied potential. The data were obtained at the decomposition potential (DP) and at overpotentials of 0.2, 0.4 and 0.5 V. Before starting each EIS measurement, the cell was pre-polarized for at least 3 minutes at the measured potential to reach a steady state. The current densities before and after measurement were recorded to prove stability of the cell during the test time. For continuous monitoring of the ohmic resistance with time, measurements were taken periodically after every 4 h. Consistency and quality of data were established by Kramers-Kronig validation [13]. The Kramers-Kronig transformation constrains the real and imaginary components of the impedance for systems that satisfy the conditions of causality, linearity and stability. Polarization curves, using linear sweep voltammetry (LSV) were obtained after every 4 h to observe the cell behavior over a potential range from 0 to 0.7 V and observe the maximum current density at 0.7 V.

Membrane conductivity

The conductivity of the pretreated, Nafion 117 membrane was obtained using a through-plane glass clip conductivity cell [12] with the active area of 0.74 cm$^2$. The cell consists of parallel disk electrodes and measurements were performed in a 7 mol L$^{-1}$ HCl(aq) solution. The membrane was equilibrated with a [2 mol L$^{-1}$ CuCl(aq) + 7 mol L$^{-1}$ HCl(aq)] for 20 h and the cell conductance was measured at atmospheric pressure and ambient temperature of 25 °C. EIS was used to calculate the conductivity using Gamry electrochemical system and data were taken in a frequency range of 30 - 500 kHz. The resistance of the pre-pressed Nafion 117 membrane was obtained as the difference between the high frequency intercept obtained with and without the membrane.
Results and Discussions

AC impedance analysis and polarization curves

LSV measurements were carried out periodically and Figure 3-1. shows the steady decrease in the current density of the cell over time from 0.46 A cm\(^{-2}\) at the beginning, to 0.31 A cm\(^{-2}\) at the end of the test at the applied potential of 0.7 V.

![Graph showing decrease in current density](image)

Figure 3- 1. Decrease in the current density during the 168 h test.

Since the electrolyzer was operated in daily cycles and the anolyte solution was diluted every night, it is important to observe the daily trend in the system performance to reflect the DP changes as well as in the consumption of Cu (I). Figure 3-2 represents the gradual decrease in the total impedance of the cell (left) at DP over 16 hours of operation on the first day, and a corresponding increase in the current density was observed (right).
Figure 3-2. Gradual change in the EIS spectra at DP during a 16 h daily cycle (left) and I-V curve showing the corresponding increase in the current density with time (right) as the cell impedance decreased.

However, as shown in Figure 3-3, in the end of testing there was no significant decrease in the total impedance, and correspondingly, the current density did not improve over time. This is attributed to the fact that the DP decreased during every 16 h of daily cycles in the first 6 days of testing and reached a stable value in the concluding phases (Figure 3-4). The lower value of the DP and the dynamic behavior of the system in the initial phases is believed due to a freshly packed regeneration column and freshly prepared anolyte solution resulting in more efficient conversion of Cu\(^{2+}\) aqueous species to Cu\(^{+}\) aqueous species.
Figure 3-3. EIS spectra obtained at DP in the concluding phase of the test representing the degraded nature of the CuCl/HCl electrolyzer (left) and I-V curve representing the stable current density (right).

Figure 3-4. Variation of experimentally obtained DP as a function of operational time.
The obtained impedance spectra were described by an equivalent circuit model of the elementary impedance elements. The circuit represents various impedance elements as physical representation of the membrane, charge-transfer and mass-transfer resistances. Figure 3-5 represents the equivalent circuit model along with the simulation results for the experimental EIS data obtained at 0.2 V overpotential.

The model consists of $R_{\text{ohm}}$, which is the high frequency intercept of the impedance semi-cycle with the real axis and represents the ohmic resistance of the cell, $R_{\text{ct}}$, which is the charge transfer resistance calculated by the difference between the maximum value of the high frequency resistance ($R_{\text{maxHF}}$) and the ohmic resistance ($R_{\text{maxHF}} - R_{\text{ohm}}$), and $R_m$, which is the mass transfer resistance observed in the low-frequency region. The constant phase elements (CPEs) were incorporated in place of capacitors to account for the inhomogeneity in the system. The CPE is defined by two values, $CPE-T$ and $CPE-P$. Mathematically, it is expressed as $Z = \frac{1}{(T \sqrt{wP})}$, where $w$ is the angular frequency of the AC signal. In the above abbreviations, $CPE-T$ and $CPE-P$, $T$ is capacitance and $P$ is non-homogeneity constant. The circuit model precisely fits the experimental data and the fit converged satisfactorily. The chi-squared parameter [14], which quantifies the goodness of fit, was $< 8 \times 10^{-4}$. 
Figure 3-5. Equivalent circuit model with the simulation of the experimental data obtained at the overpotential of 0.2 V.

Figure 3-6 compares the EIS data taken at the overpotential of 0.2 V after 15, 90 and 156 h of operation and as shown in Table 3-1, the area specific ohmic resistance of the membrane increased from 0.60 to 0.85 Ω cm$^2$ over a period of 168 hours, while the increase in the area specific charge-transfer area specific resistance was more pronounced as it increased from 0.51 Ω cm$^2$ to 0.80 Ω cm$^2$. The change in the mass-transfer area specific resistance was not so significant as it only increased from 0.15 Ω cm$^2$ to 0.18 Ω cm$^2$. 
Figure 3-6. EIS spectra at 0.2 V overpotential representing the degradation of the CuCl/HCl electrolyzer with time.

Table 3-1. Parameters of equivalent circuit model shown in Figure 5 used in simulating the CuCl/HCl electrolyzer individual reaction process related to the ohmic, charge-transfer and mass-transfer resistances.

<table>
<thead>
<tr>
<th>Equivalent circuit element</th>
<th>Fresh cell (Ω cm²)</th>
<th>Degraded cell (after 168 h of testing)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area specific ohmic resistance</td>
<td>0.60</td>
<td>0.85</td>
</tr>
<tr>
<td>Area specific charge-transfer resistance</td>
<td>0.51</td>
<td>0.70</td>
</tr>
<tr>
<td>Area specific mass-transfer resistance</td>
<td>0.15</td>
<td>0.18</td>
</tr>
</tbody>
</table>

One can see from the EIS results that the contribution of each component on the performance degradation was as follows: ohmic resistance (41 %, 0.25 Ω cm²) > charge-transfer resistance (37 %, 0.19 Ω cm²) > mass-transfer resistance (20 %, 0.03 Ω cm²).
While the increase in the charge-transfer resistance is primarily related to the available active surface area and an improvement in this regard has already been discussed elsewhere [11], the possible reasons of the increase in ohmic resistance are decrease of conductivity by chemical degradation and delamination between catalyst layer and membrane. The mass transfer resistance is not a dominant parameter in degradation due to the high flow rate and high concentrations of solutions.

Figure 3-7 represents the evolution of the ohmic resistance with time and the test can be divided into three phases: (1) 0-90 h - where the ohmic resistance is relatively constant and no significant degradation was observed, (2) 90-130 h – representing the progressive membrane degradation where the ohmic resistance increased by 25 % in 40 h, and (3) 130-168 h – slow degradation, where the ohmic resistance showed a moderate decline and the current density reached a stable value of 0.31 A cm\(^{-2}\) at the applied potential of 0.7 V.
While the continuous monitoring of the system over time helps to identify any possible degradation, it is also essential to observe the cell behavior at different applied potentials to find out the contribution of different parameters while the cell is operating on-line. Figure 3-8 represents the EIS data at DP and at overpotentials of 0.2 and 0.4 V after 90 h of testing.
As expected, the charge transfer resistance decreases from 0.6 to 0.35 Ω cm$^2$ upon increasing the overpotential from 0.2 to 0.4 V, while the mass-transfer resistance remains same at 0.17 Ω cm$^2$. This characteristic decrease in the charge-transfer resistance with increasing applied potentials is attributed to the higher reaction rate at high overpotentials. As shown in Figure Table 3-2, the mass-transfer resistance has a relatively higher contribution towards total impedance at 0.4 V overpotential whereas the cell was charge-transfer controlled at low overpotentials.

Table 3-2. Percentage contribution of each resistance at overpotentials of 0.2 and 0.4 V.

<table>
<thead>
<tr>
<th>Equivalent circuit element</th>
<th>Overpotential = 0.2 V</th>
<th>Overpotential = 0.4 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ohmic resistance contribution (%)</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>Charge-transfer resistance contribution (%)</td>
<td>41</td>
<td>30</td>
</tr>
<tr>
<td>Mass-transfer resistance contribution (%)</td>
<td>12</td>
<td>23</td>
</tr>
</tbody>
</table>
Membrane Conductivity

The membrane conductivity, if properly measured, should be directly related to the ohmic resistance \( R_{\text{ohm}} \), and it is given by equation:

\[
k = \frac{\delta}{R_{\text{ohm}} \times A}
\]  

(1)

where the membrane thickness, \( \delta \), in our studies was 0.0195 cm for the tested Nafion 117 membrane, and the exposed surface area \( (A) \) of the membrane was 5 cm\(^2\) in the electrolyzer. The ohmic resistance of the membrane was also determined separately by the single through-plane conductivity cell \( (R_{\text{con}}) \) and was found to be 0.89 \( \Omega \). The active area in the single conductivity cell was 0.74 cm\(^2\). Putting these values in (1), the conductivity of the membrane is calculated as 0.029 S cm\(^{-1}\). The ohmic resistance calculated from the equivalent circuit model used to simulate the electrolyzer is 0.12 \( \Omega \). Thus, the membrane conductivity in the electrolyzer using equation (1) comes out to be 0.032 S cm\(^{-1}\). Therefore, we conclude that the ohmic resistance of the cell is the resistance of the membrane and an increase in the ohmic resistance represents degradation of the membrane. The small difference in the conductivities obtained using two independent methods could be due to the contact resistance between the flow field and the carbon cloth or other reasons.


**Electrolysis efficiency**

The current efficiency, $\eta_c$ in $\%$, of the CuCl electrolyzer can be estimated from the comparison between the experimentally produced amount of hydrogen, $m[H_2(\text{exp})]$, per unit of time and the theoretical rate of hydrogen gas generation at a particular current density, $m[H_2(\text{theor})]$, as calculated from Faraday’s law:

$$\eta_c = 100 \times \frac{m[H_2(\text{exp})]}{m[H_2(\text{theor})]}$$

The average current efficiency calculated for all experimental points obtained from the CuCl/HCl electrolyzer was always above 95 $\%$ (Figure 3-9), which indicates that the hydrogen production reaction $2 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{gas})$ was the only process taking place at the electrolyzer cathode and, therefore, no parasitic reactions were apparent at the cathode.
Figure 3-9. H2(g) production in CuCl/HCl electrolyzer using [2 mol/L CuCl(aq) + 7 mol•L⁻¹ HCl(aq)] anolyte and 7 mol•L⁻¹ HCl (aq) catholyte at 80 ºC.

The voltage efficiency, $\eta_v$, was estimated in this study as the percent ratio of the experimentally obtained decomposition potential, $-E_D$ (exp) which was 0.18 V, to the applied voltage, $E_{app}$. The variation of voltage efficiency with increasing current density is shown in Figure 3-10.
Figure 3-10. Voltage efficiency of the CuCl/HCl electrolytic cell. The dotted line represents the extrapolation to the theoretical efficiency at DP.

The voltage efficiency decreases from 47.5% at 0.1 A cm\(^{-2}\) to 32% at 0.3 A cm\(^{-2}\) due to the increased overall losses in the system at higher current densities. Consequently, more efficient electrolysis is needed to overcome the voltage losses and increase the voltage efficiency.

**Experimental and Theoretical Decomposition Potential for the CuCl Electrolyzer**

One of the significant sources of degradation in the cell performance during the durability test was from rising the decomposition potential magnitude as the test proceeded. One possible explanation for this increase is an increase in the permeation of copper and copper chloride aqueous species through the membrane throughout the
duration of the test. Further testing is needed to determine the possible origin of this problem. Another explanation is an increase of Cu(II)(aq) species in the anolyte during the electrolysis. To address this second possibility, the effect of the change in Cu(II) concentration needed to change the decomposition potential was quantified. Predicting trends of the decomposition potential for the CuCl/HCl electrolytic reaction requires thermodynamic properties of the aqueous species present in the anolyte and catholyte solutions. Using the Gibbs energy minimization approach described previously [1], equilibrium activities of the CuCl₅ complexes involved in the electrolytic reaction were evaluated. Helgeson-Kirkham-Flowers (HFK) [1, 15] model values for calculating apparent standard Gibbs energy values for aqueous species were collected from literature for the following ionic species; Cl⁻(aq), Cu⁺(aq), Cu(OH)₂⁻(aq), CuCl₂⁻(aq), CuCl₃²⁻(aq), Cu²⁺(aq), CuOH⁺(aq), HCUO₂⁻(aq), CuO₂⁻(aq), CuCl⁺(aq), CuClδ⁻(aq) and CuCl₄²⁻(aq) [15–17]. Neutral species considered were HClₒ(aq), CuOHₒ(aq), CuClₒ(aq), CuOₒ(aq) and CuCl₂ₒ(aq) [18–20]. As the actual reaction for this electrolytic cell is not known, an assumed reaction was selected. All decomposition potentials were calculated for the following reaction:

\[
\text{CuCl}_3^{2-}(aq) + H^+(aq) = \text{CuCl}_3^-(aq) + 0.5 H_2(g) \quad (2)
\]

This reaction was selected because of its simplicity, i.e. least number of active species, and the concentration of CuCl₃²⁻(aq) is the dominant Cu(I) species in high concentrations of HCl(aq) [21]. Though the actual reaction(s) may differ slightly, after accounting for activity effects, all possible electrolytic reactions within this cell will have
the same potential at equilibrium [22]. The apparent Gibbs energy values used for the species in the reaction at 80 °C and 1 bar are summarized in the Table 3-3.

Table 3-3. Apparent Gibbs energy values of Reaction (2) species at 80 °C and 1 bar [20].

<table>
<thead>
<tr>
<th>Species</th>
<th>ΔG° / (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl_2 (aq)</td>
<td>-382.70</td>
</tr>
<tr>
<td>CuCl_3 (aq)</td>
<td>-315.98</td>
</tr>
<tr>
<td>H_2 (g)</td>
<td>-7.33</td>
</tr>
<tr>
<td>H^+ (aq)</td>
<td>0</td>
</tr>
</tbody>
</table>

Using the values in Table 3, the Gibbs energy of reaction at unit activity in the infinitely dilute solutions (molal standard state) is 68.056 kJ/mol with a standard cell potential of -0.654 V, which is very different from the experimentally measured cell potential of -0.12 V.

As demonstrated previously [21,23], highly concentrated HCl(aq) solutions have activity coefficients considerably larger than unity. Therefore, in addition to the values of the standard Gibbs free energy of reaction, the activity coefficients should be considered for the catholyte and anolyte solutions composed of highly concentrated HCl(aq). To account for the non-ideality of the charged species within the aqueous phase, the mean activity coefficients of HCl(aq) solution can be used because HCl(aq) is the dominating electrolyte. The activity coefficients, γ±, for a wide range of concentrations from 1 to 11 mol kg⁻¹ HCl(aq) solutions are available from 25 to 80 °C [22].

Table 3-4. The activity coefficients of HCl(aq) at 80 °C and 1 bar as a function of molality b [21]

<table>
<thead>
<tr>
<th>b / (mol/kg)</th>
<th>γ±</th>
</tr>
</thead>
</table>
The equation used to model the mean activity coefficient of the dominant electrolyte using experimental data was the third approximation of the Debye-Hückel theory \[24\]

\[
\log_{10}(\gamma_\pm) = \frac{A|z_+z_-|\sqrt{I_m}}{1+B\hat{a}\sqrt{I_m}} + CI_m - \log_{10}\left(1 + \frac{b_t}{55.51}\right)
\] (3)

Here 55.51 is the number of moles of water in one kilogram of water, \(b_t = \sum b_i\) refers to the sum of molalities for all of the solute species, \(A\) and \(B\) are the Debye-Huckel parameters \[25\], \(z_+\) and \(z_-\) are the charge of the anion and cation, respectively, in the dominant electrolyte, \(\hat{a}\) is the empirical radius of the aqueous component, \(C\) is the empirical parameter of the supporting electrolyte \([\text{HCl(aq)}]\) and \(I_m\) is the ionic strength of the solution on the molal scale. For these calculations, 0.45 nm was used for the \(\hat{a}\) parameter of each species considered.

In order to predict trends with the decomposition potential, cell conditions and species activities were needed for calculations. Cell temperature was held constant at 80 °C and pressure was 1 bar. The solution in contact with the anode was 2.49 mol of CuCl(s) in 8.71 mol kg\(^{-1}\) HCl(aq) anolyte. The cathode was in contact with 7.75 mol kg\(^{-1}\) of HCl(aq) catholyte with a gas blanket of H\(_2\)(g) at 1 bar of pressure. Using Gibbs energy minimization \[26\], the [2.49 mol of CuCl(s) + 8.71 mol kg\(^{-1}\) HCl(aq)] anolyte should have CuCl\(_3^2\)\(^-\)(aq) and CuCl\(_5\)\(^-\)(aq) concentrations of 2.47 mol kg\(^{-1}\) and 5.53 \(10^8\) mol kg\(^{-1}\), respectively. Furthermore, the resulting ionic strength of the solution was determined to

\[
\begin{array}{cc}
7.93 & 3.225 \\
9.251 & 4.197 \\
10.092 & 4.860 \\
11.102 & 5.650 \\
\end{array}
\]
be 11.18 mol/kg. With these operating conditions, the Nernst equation of the CuCl/HCl electrolytic cell expressed by the following electrochemical diagram:

(Cathode,−) Cu|Pt|HCl(aq, 7.75 mol kg$^{-1}$), H$_2$(g, 1 bar) || CuCl$_2^-$ (aq, 2.47 mol/kg), CuCl$_3^-$ (aq, 5.53 $10^{-8}$ mol/kg), HCl(aq, 8.71 mol/kg)|Cu (Anode,+)

(4)

can be given as:

$$E = -\frac{\Delta_r G}{nF} = -\frac{\Delta_r G^o}{nF} + \frac{RT}{nF} \ln \left( \frac{\Pi(b_i^{v_i} \gamma_i^{v_i})_R}{\Pi(b_i^{v_i} \gamma_i^{v_i})_P} \right)$$  \hspace{1cm} (5)$$

where $\Delta_r G^o$ is the standard Gibbs energy of reaction, $n$ is the electron number in the reaction, $F$ is Faraday’s constant of 96485 C/mol, $R$ the molar gas constant of 8.3145 J/(mol K), $T$ is the thermodynamic temperature in K, $b_i$ is the molality of the $i$-th species, $v_i$ is the stoichiometric coefficient of the $i$-th species, $\gamma_i$ is the activity coefficient of the $i$-th species, $\Pi(b_i^{v_i} \gamma_i^{v_i})_R$ is the product of the reactant activities and $\Pi(b_i^{v_i} \gamma_i^{v_i})_P$ is the product of the product activities taking into account the stoichiometric coefficient $v_i$. Using Eq. (5), apparent Gibbs energy values from Table 3, the mean activity coefficients from Table 4, and composition of anolyte and catholyte given in Diagram (4), the Gibbs energy of reaction (2), $\Delta_r G$, was calculated to be 8.39 kJ/mol and, therefore, the theoretical DP is -0.087 V.

When compared to the experimental values measured, the theoretical DP was slightly lower. One reason for the deviation between the theoretical and experimental DP was that the concentration of the Cu(II)Cl$_x$(aq) species in the anolyte was not readily known
throughout the test. Furthermore, the presence of the regeneration column ensures the values of the Cu(II)Cl\(_2\) (aq) species were very low (\(b < 1 \text{ mmol kg}^{-1}\)). This was justified by the clear to faint yellow fluid leaving the electrolytic cell. Still, this presented an issue for predicting the decomposition potential of the electrolytic cell. Therefore, we used the experimental DP measurements to estimate the CuCl\(_3\) (aq) concentrations. Experimental DP measurements, \(E_{(\text{cell})}\), were measured for a series of points during the test. As pH and hydrogen gas pressure was constant throughout the test, the cathode potential, \(E_{(\text{cathode})}\), could be considered relatively constant. By calculating the cathode potential, \(E_{(\text{anode})}\) was determined from the conditions outlined above and the \(E_{(\text{cell})}\) values measured. Potential values for the anode, cathode and cell are displayed in Table 3-4.

Using the Gibbs free energy values and the activities obtained from literature values, it is possible to estimate the CuCl\(_3\) (aq) concentrations needed to obtain the \(E_{(\text{anode})}\) values displayed in Figure Table 3-5. Table 3-5 displays the estimated CuCl\(_3\) (aq) values expected throughout the duration of the test, assuming the deviation in the cell potential is due entirely to the presence of additional copper concentration.

Table 3-5: Estimations of CuCl\(_3\) (aq) concentrations for the 168 hour test using measured DP

<table>
<thead>
<tr>
<th>Duration/h</th>
<th>(E_{(\text{cell})} = \frac{E_{(\text{cell})} - E_{(\text{cathode})}}{V})</th>
<th>(E_{(\text{cathode})}/V)</th>
<th>(E_{(\text{anode})}/V)</th>
<th>(b_{\text{CuCl}_3\text{-(aq)}}/\text{μmol kg}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.180</td>
<td>-0.096</td>
<td>-0.276</td>
<td>1.15±0.05</td>
</tr>
<tr>
<td>90</td>
<td>-0.190</td>
<td>-0.096</td>
<td>-0.286</td>
<td>1.60±0.05</td>
</tr>
</tbody>
</table>
Results from these calculations indicate that the decomposition potential could depend strongly on fluctuations in the Cu(II) species due to an increased permeation through membrane.

### Conclusions

The Cu-Cl electrolyzer was operated for 168 h and a goal to maintain the cell at 0.3 A cm$^{-2}$ under 0.7 V was successfully met. EIS was applied to monitor the system behavior over time and an equivalent circuit model was used to quantify the physical parameters contributing to the overall impedance of the cell. It was concluded that the primary cause of degradation during the 168 h of operation was the increase in the ohmic and charge-transfer resistances. The through-plane conductivity cell proved to be a reliable and time-efficient set up to calculate the membrane conductivity and screen new and existing membranes before testing in the electrolyzer. Electrochemical kinetics was improved at higher overpotentials, as the first loop shows in the EIS spectrum, which is related to the charge-transfer resistance, decreased with increasing the applied potential. A rise in the DP was observed with an increase in the total impedance over time and a thermodynamic analysis was carried out to estimate the parameters effecting the DP. A current efficiency of greater than 95 % was maintained throughout the experiment which confirms that there were no side reactions taking place in the cell. The test summarizes the
effectiveness of EIS as an aging protocol and it is recommended that it should be more widely employed towards the development of the CuCl electrolyzer to characterize the degradation mechanisms.

Acknowledgement

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Chapter 4

Performance analysis and characterization of a liquid tin anode solid oxide fuel cell

This text for this chapter was originally prepared for the Journal of Power Sources as “Performance analysis and characterization of a liquid tin anode solid oxide fuel cell”, S. Khurana, M. LaBarbera, M. Fedkin, S. Lvov, H. Abernathy, and K. Gerdes. This paper was submitted July 2014.

Preface to Chapter 4

Chapter 4 details the operation of a liquid tin anode solid oxide fuel cell in the battery mode and as a fuel cell utilizing hydrogen and coal as fuels. The experimental design of the novel LMA SOFC system is followed by the EIS data analysis to study the transport and electrochemical properties of the reactions in the liquid anode. The development of a cathode symmetry cell helps in separating the impedance contributions from the two electrodes. Equivalent circuit modeling of the data provides quantitative information on the oxygen diffusivity in the liquid anode.
Abstract

A liquid tin anode solid oxide fuel cell is constructed and investigated under different operating conditions. Electrochemical Impedance Spectroscopy (EIS) is used to reflect the effect of fuel feed as the EIS spectra changes significantly on switching the fuel from argon to hydrogen. A cathode symmetric cell is used to separate the impedance from the two electrodes, and the results indicate that a major contribution to the charge-transfer and mass-transfer impedance arises from the anode. The OCP of 0.841 V for the cell operating under argon as a metal-air battery indicates the formation of a SnO$_2$ layer at the electrolyte/anode interface. The increase in the OCP to 1.1 V for the hydrogen fueled cell shows that H$_2$ reduces the SnO$_2$ film effectively. The effective oxygen diffusion coefficients are calculated using the Warburg element in the equivalent circuit model for the experimental EIS data, and the values of $1.9 \times 10^{-3} \text{ cm}^2 \text{s}^{-1}$ at 700 °C, $2.3 \times 10^{-3} \text{ cm}^2 \text{s}^{-1}$ at 800 °C and $3.5 \times 10^{-3} \text{ cm}^2 \text{s}^{-1}$ at 900 °C are similar to the previously obtained experimental results. Further, the performance degradation over time is attributed to the irreversible conversion of Sn to SnO$_2$ resulting from galvanic polarization.

Keywords:
Solid Oxide Fuel Cell; Liquid Metal Anode; Electrochemical Impedance Spectroscopy; Equivalent Circuit Modeling, Warburg Impedance, Metal-Air Battery

Introduction

With the continuous increase in the world’s energy demands, it has been predicted that fossil fuels will remain the primary source of energy for the next two decades [1, 2].
Higher process efficiency systems are required to better utilize coal as a power source while minimizing CO$_2$ release to the environment. Solid Oxide Fuel Cells (SOFCs) are capable of generating electrical power from the oxidation of a variety of gaseous and liquid hydrocarbons [3-5]. However, the performance degradation due to impurities is still a cause of concern. Also, carbon deposition on the anode remarkably degrades the cell performance by reducing the effective surface area in conventional SOFCs [3-7].

There is growing interest in the development of Liquid Metal Anode Solid Oxide Fuel Cells (LMA-SOFCs) [8-22], as the technology is tolerant to fuel contaminants, has a better usage of the active surface area, and is capable of operating in a battery mode in case of fuel starvation [8, 9]. While significant efforts have been made to study the kinetics and thermodynamics of an LMA-SOFC system [8], and various anode materials have been tested [12, 15], the mechanism of transport of oxygen ions through the liquid tin anode under the presence of different fuels has not been conclusive so far.

Electrochemical Impedance Spectroscopy (EIS) is a powerful tool that can be used to characterize the cell performance and distinguish between processes occurring on different time scales [23-25]. Numerous efforts have been made to study the different arcs observed in the EIS spectra and relate them to the physical processes. The low frequency arc is attributed to the diffusion or mass-transfer controlled processes [26-29], while the first arc in the high frequency region is believed to be arising from the charge-transfer processes [30, 31]. Despite the large number of results available for EIS analysis of conventional SOFCs, there are no published records of a detailed interpretation of EIS data for the LTA-SOFC system. As an extension to our previous work where preliminary EIS data analysis was presented [15], this study is focused on the quantitative analysis of
the effect of fuel feed and separating the impedance contributed by the liquid anode. The Open Circuit Potential (OCP) analysis of the cell operating under different fuels provides insight into the reaction mechanisms and indicates the efficiency of the reduction of SnO$_2$ to Sn under different conditions. The *effective* oxygen diffusion coefficients calculated from the Warburg impedance observed in the EIS data are in close agreement with the previous results [9], and confirm that the performance improvements in the LTA-SOFC rely heavily on minimizing the transport losses in the liquid Sn layer.

**Experimental**

**Cell preparation**

The primary goal of this study was to analyze the impedance and transport properties in the liquid tin and not to develop a prototype for maximum performance. Accordingly, a relatively thick electrolyte was used in order to have a robust system that could support variable tin loadings. The experimental system in this study was similar to the one previously used in our work [15], and utilized a YSZ crucible as the electrolyte. The thickness and base diameter of the crucible were 2.54 cm and 0.15 cm, respectively. Lanthanum strontium manganite (LSM) paste, which consists of La$_{0.8}$Sr$_{0.2}$MnO$_3$ suspended in terpenol (Fuel Cell Materials, LSM20-I), was used as the cathode and painted at the outer surface of the crucible base. The cathode was then sintered onto the crucible by heating from 25 to 1150 °C at a rate of 10 °C min$^{-1}$. The cell was maintained at 1150 °C for 12 hours and then cooled at the same rate. Two gold leads (current collector and voltage sensor) were attached to the LSM.
The total volume of the crucible was 12.9 cm³ and it was partially filled with solid tin shot (99.999 % Sigma Aldrich). For current collection, two rhenium wires were dipped into the anode with an alumina-sheathed thermocouple after tin attained its melting during heat-up. Rhenium was specifically chosen as a current collector as it does not form an alloy with Sn. An alumina feed tube was supported above the anode for injection of the additional anode material.

The LMA-SOFC described above was inserted into the top of a vertically oriented Barnstead Thermolyne tubular furnace. A constant flow rate of 50 cm³ min⁻¹ was used for both hydrogen and argon feeds at the anode. The measurements were performed using Solartron Analytical 1470-E Potentiostat with a Solartron Analytical 1252-A frequency response analyzer for EIS measurements.

**Electrochemical testing**

The liquid tin anode solid oxide fuel cell fueled by humidified hydrogen (3% H₂O) was heated from 25 to 900 °C at a rate of 10 °C min⁻¹. With the liquid anode and air-fed cathode, the OCP of the cell was monitored for 3 hours and EIS measurements were carried out periodically after every 30 min in the frequency range of 300 kHz - 50 mHz with 15 points per decade interval. Following OCP measurements, the cell was subjected to a series of 10 LSV measurements between OCP-0.4V during a ten-hour period. Finally, impedance measurements were done at the OCP following the ten polarization cycles. Kramers-Kronig transformations [32, 33] were used to validate the experimental data and fitting was done using the complex nonlinear least squares (CNLS) method [32].
**Cathode symmetry cell**

The difficulties involved in separating the impedance response using reference electrodes for SOFCs are already documented [34-37], and hence, a cathode symmetric cell was used to determine the impedance contributions from the membrane and cathode. The base of a YSZ crucible was cut from the full crucible and both sides were painted with LSM paste. The electrodes were sintered in a similar manner as described before. Silver paste was used to attach two gold wires on both sides to permit four electrode measurements.

The cathode symmetric cell was then put in an air fed furnace at 900 °C to monitor OCP in order to ensure identical chemical activities at each electrode. EIS measurements were carried out in the frequency range of 300 kHz to 50 mHz.

**Results and discussion**

**AC impedance and OCP analysis**

The LMA-SOFC was operated under hydrogen, argon and coal as the anode feeds. The impedance spectra collected from the LMA-SOFC under hydrogen and argon at the OCP are shown in Figure 4-1. The EIS data for the coal powered cell are shown separately in Figure 4-2 due to heavy overlapping with the results from the cell maintained under argon. The coal used in this study was high volatility A-bituminous coal.
Figure 4-1. Impedance spectra generated by liquid tin anode SOFC at 900 °C under argon and hydrogen anode feeds. A 10 mV alternating potential is applied at a range of frequencies 10 kHz to 50 mHz plotted (left) and high frequency close-up (right).
Figure 4-2. Impedance spectra generated by the liquid tin anode SOFC at 900 °C under coal.

Figure 4-3 represents the equivalent circuit models used to simulate the experimental data and the fit converged satisfactorily. The chi-squared ($\chi^2$) parameter, representing the goodness of the fit [38], was $5 \times 10^{-4}$.

![Equivalent circuit models](image)

Figure 4-3. Equivalent circuit models used in fitting LMA-SOFC: Argon and coal fed LMA-SOFC model (top); Equivalent circuit model used to fit hydrogen fueled LMA-SOFC (bottom).

The models consist of $R_{\text{ohm}}$, which is the high frequency intercept with the real axis corresponding to the ohmic resistance of the cell, and the two nonohmic impedance components. The nonohmic impedance consists of: $R_{\text{ct}}$, which is the charge transfer resistance calculated by the difference between the maximum value of the high frequency
resistance ($R_{\text{maxHF}}$) and the ohmic resistance ($R_{\text{maxHF}} - R_{\text{ohm}}$), and $R_m$, which is the mass transfer resistance observed in the low-frequency region. The constant phase elements (CPEs), first introduced by Cole and Cole [39], were incorporated to adjust the ideal capacitive elements under realistic conditions. Mathematically, the impedance of a CPE is defined as $Z = 1/(Q(j\omega)^p)$, where $\omega$ is the angular frequency of the AC signal, $Q$ is the admittance constant, and $p$ is an adjustment parameter whose typical value is between 0.5 and 1.0.

Table 4-1. shows the equivalent circuit modeling results for the cell operated under different fuels along with their corresponding OCP.

Table 4-1. Area specific ohmic, charge transfer and mass transfer resistance values for the cell operated under different fuels with the corresponding OCP.

<table>
<thead>
<tr>
<th></th>
<th>Open Circuit Potential (V)</th>
<th>$R_{\text{ohm}}$ (Ω cm$^2$)</th>
<th>$R_{\text{ct}}$ (Ω cm$^2$)</th>
<th>$R_m$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>1.1</td>
<td>4.33</td>
<td>9.1</td>
<td>162.1</td>
</tr>
<tr>
<td>Coal</td>
<td>0.885</td>
<td>3.02</td>
<td>1.98</td>
<td>-</td>
</tr>
<tr>
<td>Argon</td>
<td>0.841</td>
<td>2.85</td>
<td>1.86</td>
<td>-</td>
</tr>
</tbody>
</table>

The area specific charge transfer resistance increased from 1.86 to 9.1 Ω cm$^2$ as the anode feed was switched from argon to hydrogen, while the mass transfer was absent for the cell operated under argon. This is mainly attributed to the fact that under an inert atmosphere, the only electrochemical reaction would be the oxidation of tin at the electrolyte/anode interface. The hydrogen-fed cell showed an additional mass transfer resistance of 163.1 Ω cm$^2$. The hydrogen fueled LMA-SOFC maintained an OCP of 1.1 V, and while under argon the OCP observed was 0.841 V. The OCP of 0.841 V generated
by the cell under argon results from the oxidation of liquid tin to solid tin dioxide and is nearly equal to the theoretical standard potential of 0.85 V for this reaction at 900 °C. On the other hand, the OCP of 1.1 V generated by the hydrogen fueled cell is similar to the hydrogen Nernst potential at 900 °C, indicating that the OCP was governed by the oxidation of fuel. The area specific ohmic resistance of the cell also increased from 2.83 to 4.33 Ω cm$^2$. Since hydrogen reduces SnO$_2$ to Sn, one would expect to see a decline in the ohmic resistance upon introducing hydrogen. However, this counterintuitive increase in the ohmic resistance for the hydrogen fueled cell stems from the fact that the effective diffusion length is reduced in the case of hydrogen fueled cell [8]. This leads to a higher percentage of SnO$_2$ which has a very low conductivity of 0.3 S cm$^{-1}$ at 1000 °C [40]. The higher ohmic resistance of the hydrogen fueled cell also indicates the possibility of some dissolved hydrogen.

It is interesting to note that OCP of the cell following coal injection was 0.885 V, which is lower than the hydrogen fueled cell and higher that the cell operated under argon. This indicates that the addition of carbon resulted in only a partial reduction of SnO$_2$, and while the LMA –SOFC system could utilize carbonaceous fuels, the most efficient fuel remains hydrogen.

The results from the cathode symmetric cell are shown in Figure 4-4, and the model shown in Figure 4-3 was used to fit the experimental data.
The charge-transfer resistance of $6.55 \, \Omega \, \text{cm}^2$ was calculated by the model, and taking half of electrode response, the nonohmic (or purely charge transfer) cathodic resistance was found to be $3.27 \, \Omega \, \text{cm}^2$. On comparing it with the charge transfer resistance of the full cell ($9.1 \, \Omega \, \text{cm}^2$), it is concluded that 63% of the charge transfer resistance is contributed by the liquid tin anode.

While the data presented so far was useful to characterize the performance of an LMA-SOFC, it was also essential to observe the cell behavior at different temperatures and calculate the *effective* oxygen diffusion coefficient in liquid tin.
Warburg impedance for the hydrogen fueled LMA-SOFC

Figure 4-5, shows the EIS data for the cell operating at 700, 800 and 900 ºC using hydrogen as the anode feed.

Figure 4-5. Impedance spectra generated by liquid tin anode SOFC at different temperatures under hydrogen anode feed. A 10 mV alternating potential is applied at a range of frequencies 10 kHz to 50 mHz plotted (left) and high frequency close-up (right).

The equivalent circuit model shown in Figure 4-3, which was used to simulate the hydrogen fueled EIS data was adopted because of its simplistic approach to interpret the results, and more importantly, to maintain consistency in models while analyzing the effect of fuel on the cell. However, the fitting was slightly improved ($\chi^2$ was $8 \times 10^{-4}$) upon introducing the Warburg element, as a characteristic straight line is observed in the low frequency region of the Nyquist plot for the hydrogen fueled cell. Figure 4-6 represents
the modified equivalent circuit model and it was used to calculate the effective oxygen diffusion coefficient.

![Equivalent circuit model with Warburg element](image.jpg)

**Figure 4-6.** Equivalent circuit model with the addition of Warburg element (W) to calculate the diffusion coefficient.

Mathematically, the impedance of the Warburg element is described by:

$$W_1(s) = \frac{R_{w1} \tanh((s.T_{w1})^{P_{w1}})}{(s.T_{w1})^{P_{w1}}}$$

where $s$ is the Laplace complex frequency, $R_{w1}$ is the finite resistance at low frequencies, and $P_{w1}$ is an exponent related with the roughness of the diffusion media. $T_{w1}$ is a time constant related the diffusion effects [41, 42] as:

$$T_{w1} = \frac{L^2}{D}$$

where $L$ is the diffusion thickness, and $D$ is the effective diffusion coefficient. The diffusion thickness was measured experimentally to be 0.35 cm. The time constant, $T_{w1}$, was calculated from the Warburg element. Table 4-2 shows the values of time constant and the calculated effective diffusion coefficients at different temperatures.
Table 4-2. Time constants with the calculated values of diffusion coefficients at different temperatures.

<table>
<thead>
<tr>
<th>Operating temperature (°C)</th>
<th>Time constant (s)</th>
<th>Diffusion coefficient (10⁻³ cm² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>63</td>
<td>1.9</td>
</tr>
<tr>
<td>800</td>
<td>42</td>
<td>2.91</td>
</tr>
<tr>
<td>900</td>
<td>35</td>
<td>3.5</td>
</tr>
</tbody>
</table>

As expected, the diffusion coefficients increase with temperature. Also, it is important to note that the effective diffusion coefficients are an order of magnitude higher than the previously obtained experimental values [8], but are similar to the numbers obtained by Gemmen et al.[9], where the diffusion coefficients were measured in the presence of hydrogen. As corroborated from the fuel dependence EIS data, the effect of fuel has a significant effect on the transport properties in liquid tin and greatly contributes to the non-ohmic resistance of the cell.

**Performance degradation in LMA-SOFC**

*In-situ* EIS and LSV measurements were used to study the transient state and performance degradation of the hydrogen fueled cell at 900 °C. Figure 4-7 shows the decline in current at 0.4 V over 10 polarization cycles from OCP-0.4 V.
Figure 4-7. Decline in current at 0.4 V over 10 polarization cycles.

Figure 4-8 compares the EIS response of the fresh cell with the cycled cell. A huge increase in the overall impedance was observed after operation.
Figure 4-8. EIS spectra for the LMA-SOFC at OCP operating under hydrogen at 900 °C representing the degradation over time.

The decline in the current observed from Figure 74 stems from the significant increase in the overall impedance over time. The increase in the ohmic resistance of the cell from 4.33 to 42.1 Ω cm² indicates the formation of a SnO₂ layer which has a much lower conductivity compared to Sn. The transient characteristics and an increase in impedance upon cycling further demonstrates that the SnO₂ layer formed by oxidation of liquid Sn covered the electrolyte/anode interface and blocked the diffusion of oxygen ions for further oxidation of molten tin. This results in the reduction of the usage of available anode, thereby decreasing the overall efficiency.
Summary

A liquid tin anode solid oxide fuel cell was developed and characterized to highlight its capabilities operating under different fuels and at different temperatures. The cell operating under hydrogen showed a unique EIS spectra, which was characteristic of a diffusion controlled system. On the other hand, the EIS data for the cell maintained under argon and operating as a metal-air battery confirms the absence of any significant mass-transfer and the OCP of 0.841 V indicated the formation of SnO\(_2\). Consequently, this oxide layer accumulated over the electrolyte surface and blocked the diffusional path of oxygen ions resulting in the reduced active area. The cathode symmetry cell proved to be a useful and reliable method to separate the impedance contributions from the two electrodes. A comparison of the equivalent circuit parameters obtained from the full cell and the symmetric cell revealed that the anode was the primary source of the nonohmic resistance when the cell was operated under hydrogen feed. The effective oxygen diffusion coefficients were calculated at different temperatures, and on comparing the values with the previously established results, it was concluded that the higher diffusion coefficient was due to the presence of hydrogen.

An OCP of 0.885 V obtained for the cell powered with coal suggests that the OCP was governed by both Sn and C oxidation, and reduced only part of SnO\(_2\) formed in the battery mode. The effective oxygen diffusion coefficients for the hydrogen fueled cell were higher than the values reported in literature (where measurements were carried out in the absence of hydrogen), and indicate reduction in the effective diffusion path length. This leads to a relatively higher ratio of SnO\(_2\)/Sn than compared to the argon or coal fed
cell where the fuel diffusion was absent or insignificant. Consequently, the ohmic resistance of the hydrogen fueled cell is highest and it decreases as the anode feed is switched to argon. The performance degradation confirms that while the LTA-SOFC system does have the capability to utilize a wide range of fuels and has a clear advantage to operate in a battery mode, the resistance added by the formed SnO$_2$ layer is the primary cause of degradation and future work should be directed to minimize the losses due to the oxide layer.

Acknowledgement

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Chapter 4 References


Chapter 5

Summary

This dissertation details the author’s contribution towards the development on in-situ diagnostics methods to characterize the performance of CuCl electrolyzer and liquid metal anode solid oxide fuel cells. EIS measurements provide insight into the reaction mechanisms and also used to diagnose failure modes impeding the long term durability goals.

Chapter 1 presents the basic principles of CuCl electrolyzer and LMA SOFC along with the fundamentals of EIS. The current requirements to develop the electrolyzer and novel liquid metal anode fuel cells were discussed and the methodology of analyzing EIS data using equivalent circuit models was studied.

Chapter 2 and 3 outline the operation, efficiency and durability of the CuCl electrolyzer along with the engineering challenges involved with it. EIS analysis of the electrolyzer for different operating conditions is presented and the optimized parameters found from this study were used to test the system for durability. As confirmed by EIS and LSV measurements, the degradation in performance was attributed to the decrease in membrane conductivity. A detailed thermodynamic analysis of the CuCl electrolyzer was done to estimate the OCP of the cell.

Chapter 4 presents the analysis of a liquid tin anode solid oxide fuel cell operating under argon as a metal-air battery, and also operating as a fuel cell with hydrogen and
coal as the fuels. The results from this study were used to understand the reaction mechanism in the liquid anode layer while also studying the transport properties under different conditions.
Chapter 6

Conclusions and Future Work

The results presented in this dissertation proved that the performance efficiency of the CuCl electrolyzer is optimized at 80 °C with 2 mol of CuCl(s) in 7 mol L⁻¹ HCl(aq) as the anolyte and 7 mol L⁻¹ HCl(aq) as the catholyte. Further the contact pressure of 6.3 psi should be used at the end plates while preparing the MEA. EIS analysis of the continuous operation of the cell confirmed that degradation in the cell is mainly due to the decrease in membrane conductivity. The results strongly encourage the use of a through-plane conductivity cell as an independent set-up con screen different membranes for their use in the electrolyzer. The successful operation of the electrolyzer for 168 hours also met the DOE’s long term goal in order to further invest in this technology. However, we still believe that there is a scope of improvement to increase the longevity and performance of the electrolyzer, with both mechanical and chemical modifications. Following points should be considered and further investigated:

1. Development of new membranes with higher conductivity and lowe permeation of Cu ions.

2. Optimization of the flow-field design would result in better distribution of the current density and more efficient utilization of the active area.
3. Designing a crystallizer to avoid precipitation of CuCl(s), which is necessary for long term operation.

4. From the standpoint of cost efficiency, new catalyst materials should be explored along with the techniques to apply on the electrodes aimed at reduced catalyst loadings.

The results from the LTA-SOFC provide insight into the reaction mechanism and the show the effect of different fuels. While the cell operated as a metal-air battery under argon, introduction of coal in the anode feed slightly increased the OCP of the cell resulting from the reduction of SnO$_2$ to Sn. Upon introducing hydrogen as the fuel, the OCP was further increased and maximum efficiency was observed. The results in this dissertation proved that the nonohmic contributions in the total impedance of an LTA SOFC are mainly due to the liquid tin anode. Further, the system was diffusion controlled while the cell was operating under hydrogen and the effective oxygen diffusion coefficients were in close agreement with the previously published results. This study highlights the potential of EIS to study the degradation mechanisms as well as investigating the mass transport and kinetics of the liquid tin anode solid oxide fuel cell.

The future work towards the development of liquid metal anode solid oxide fuel cell systems should be directed on:

1. Improvement of oxygen transport within the liquid metal anode by increasing oxygen solubility.

2. Analysis of surface tension, contact angle and vapor pressure of the liquid metal.
3. Obtaining better contact between liquid metal anode and the electrolyte to optimize the contact area.
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