

**IMPROVING OXYGEN REDUCTION REACTION CATALYSTS FOR
POLYMER ELECTROLYTE MEMBRANE FUEL CELLS**

by

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A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemical Engineering

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ABSTRACT

Polymer electrolyte membrane fuel cells include proton exchange membrane fuel cells (PEMFCs) and hydroxide exchange membrane fuel cells (HEMFCs). PEMFCs use a proton conducting electrolyte, generating an acidic environment, while HEMFCs employ a hydroxide conducting electrolyte, providing a basic environment. For both types of fuel cells, the oxygen reduction reaction (ORR) at the cathode is sluggish and controls the fuel cell performance. Therefore, this thesis focuses on improving ORR catalyst activity and durability.

PEMFCs, the more mature technology, have been commercially implemented in fuel cell cars like the Toyota Mirai and Honda Clarity. However, PEMFCs are expensive because they require a large amount of platinum (Pt) catalyst to overcome the ORR overpotential and the rapid catalyst degradation caused by the acidic operating environment. Current PEMFCs use Pt nanoparticles supported on amorphous carbon black as ORR catalysts. These catalysts have activity and durability concerns resulting from both the Pt nanoparticles and the amorphous carbon support. Strategies to improve catalyst activity and durability include generating a support-less catalyst, increasing the durability of the catalyst support, and switching to a basic environment.

A transition to unsupported catalysts with an extended surface structure improves specific activity and durability and in turn, the cost-effectiveness of the entire

fuel cell. Pt-coated copper nanowires (Pt/CuNW) exemplify these desirable catalytic traits. Improving this platform, post-synthetic processing is used to further enhance the ORR performance of the Pt/CuNW catalyst. Specifically, annealing followed by electrochemical dealloying increases activity by introducing geometric lattice tuning through Cu alloying. The resultant bimetallic PtCu-coated copper nanowire (PtCu/CuNW) catalyst yields ORR specific and mass activities of $2.65 \text{ mA cm}_{\text{Pt}}^{-2}$ and $1.24 \text{ A mg}_{\text{Pt}}^{-1}$, surpassing the respective DOE targets (SA and MA) of $0.72 \text{ mA cm}_{\text{Pt}}^{-2}$ and $0.44 \text{ A mg}_{\text{Pt}}^{-1}$. PtCu/CuNWs demonstrate enhanced durability over Pt nanoparticle catalysts by maintaining 64.1 % of its active surface area after undergoing 30,000 cycles of a potential cycling accelerated durability test (0.6 - 1.1 vs RHE). Post durability PtCu/CuNWs outperformed the DOE targets with a SA and MA of $1.50 \text{ mA cm}_{\text{Pt}}^{-2}$ and $0.477 \text{ A mg}_{\text{Pt}}^{-1}$.

Alternately, increasing catalyst support durability through the introduction of a more durable carbon support has also been accomplished. Highly graphitic and cost-effective Cup-stacked carbon nanofiber supports have the potential to address the support durability concerns. Pt supported on carbon black (Vulcan XC-72) and cup-stacked carbon nanofibers as well as each carbon support alone underwent a high potential (1.4 V vs RHE) accelerated durability test in acidic and basic environments using rotating disk electrode techniques. It was shown that in all environments the cup-stacked carbon nanofiber support demonstrated higher durability and the catalysts tested in the basic environment had better overall stability compared to their acidic counterpart.

HEMFCs have the potential for incorporating a wide variety of non-precious metal catalysts and promise to dramatically lower the fuel cell cost. One commercially available non-precious metal catalyst is Acta 4020. This carbon-based catalyst, containing 3.5 wt. % transition metals, when compared to state-of-the-art Pt/C catalysts shows comparable ORR performance and superior durability while exposed to a potential cycling (0.6 – 1.1 V vs RHE) accelerated durability test. Fuel cell testing also demonstrated the feasibility of incorporating this catalyst into the cathode electrode of a HEMFC.

Chapter 1

INTRODUCTION

1.1 Fuel Cells

It is essential to innovate efficient and cost-effective renewable-energy conversion and storage devices to meet the increasing global energy demand and reduce the world's dependency on polluting fossil fuels. Growing fields in renewable energy generation (Figure 1.1) include: wind, solar, hydroelectric, biomass, and geothermal.¹ All of these energy generating techniques have potential, but are limited by a geographic dependence, intermittent power generation, and isolation from major electric grids. Converting renewably-generated energy to a stable chemical form can allow for easier transport and use at a point of need. Hydrogen (H₂) is a good candidate for chemical storage. H₂ can be safely stored and transported at high pressure or cryogenically in liquid phase. Chemical energy stored in H₂ can then be converted into usable electricity using a H₂ fuel cell. Fuel cells are an attractive candidate for this energy conversion because of their high efficiency and near zero greenhouse gas emission.

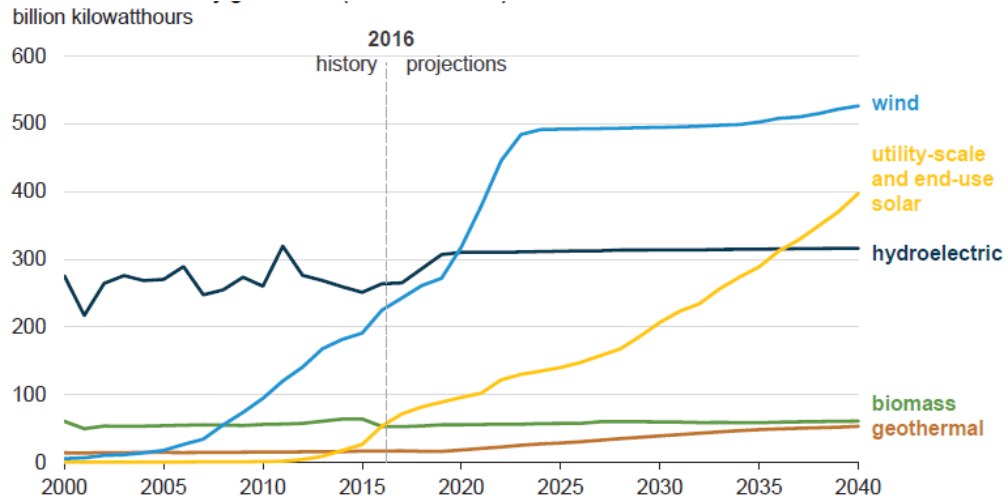


Figure 1.1 EIA Renewable electricity generation projected to 2040¹

Fuel cells are power generating electrochemical devices that combine a fuel and oxygen (O_2) to generate usable electricity. The fuel cell reaction is split into two half reactions which take place at each of the fuel cell's electrodes. The fuel is oxidized at the anode, generating electrons which are transported via an external circuit to the cathode, where the reduction of O_2 takes place. Balance ions in the fuel cell are transported through the separator in between the anode and the cathode in order to prevent a build-up of charge. The fuel cell's energy production is different from the direct combustion of fuel; therefore, is not limited by the Carnot cycle efficiency. The fuel cell can achieve efficiencies of greater than 80%. Additionally, fuel cells release less pollutants compared with internal combustion engines (ICE). H_2 used as a fuel produces zero pollutants and carbon based fuels, produced from renewable methods, result in zero or small net pollutants. Fuel cells also benefit from greater mechanical

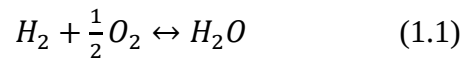
robustness compared to conventional ICEs because a fuel cell stack operates with zero moving parts.

There are five major types of fuel cells: alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), molten carbonate fuel cells (MCFCs), solid oxide fuel cells (SOFCs), and polymer electrolyte membrane fuel cells. AFCs and PAFCs are liquid based fuel cells that utilize concentrated electrolytes (potassium hydroxide for AFCs and phosphoric acid of PAFCs) immobilized in porous separators and operate at temperatures of ~ 200 °C. AFCs had broad applications in the space program for clean power generation and water production, but suffer from carbonate poisoning in terrestrial applications. PAFCs are mainly used for stationary power applications. MCFCs and SOFCs operate at much higher temperatures (650 °C for MCFCs and 600 – 1000 °C for SOFCs) and are almost entirely used for stationary power generation. These high temperature fuel cell solutions are unique because they can use methane (CH_4) or carbon monoxide (CO) as the feed fuel. The carbon based fuel can be internally reformed into hydrogen H_2 fuel or directly electrochemically oxidized.² Polymer electrolyte membrane fuel cells operate at low temperatures, typically below 100 °C, and utilize a solid ion-exchange polymer membrane. The solid-state nature combined with low temperature operation allows for the polymer electrolyte membrane fuel cell to be used in a wide variety of applications from portable electronics to automotive applications. Polymer electrolyte membrane fuel cells can operate with a variety of different fuels; however, H_2 is the most thoroughly investigated because of its high gravimetric energy density, 39.4 kWh kg^{-1} (compared to gasoline's 12.9 kWh kg^{-1}).³

There are two major sub-categories of polymer electrolyte membrane fuel cells: one which leverages the transport of an acidic proton (H^+), the proton exchange membrane fuel cell (PEMFC), and the other transports basic hydroxide (OH^-), the hydroxide exchange membrane fuel cell (HEMFC).

1.2 Hydrogen Fuel Cells

The overall chemical reaction for a hydrogen fuel cell is the combination of hydrogen and oxygen to generate water (Eq. 1.1). The hydrogen fuel cell operates with zero harmful emissions and if the hydrogen is produced from green techniques, such as the electrolysis of water using renewably generated electricity, the entire hydrogen fuel cell energy system releases zero pollution. $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$ (1.1)



The two subclasses of hydrogen fuel cells, PEMFCs and HEMFCs, have very little structural differences (Figure 1.2). The major distinction is the ion-conductive nature of the membrane. The PEMFC uses a proton exchange membrane (PEM) that transports H^+ , and the HEMFC uses a hydroxide exchange membrane (HEM) that transports OH^- . The two different ionic transport membranes cause the PEMFC to operate in an acidic environment and the HEMFC operate in a basic environment.

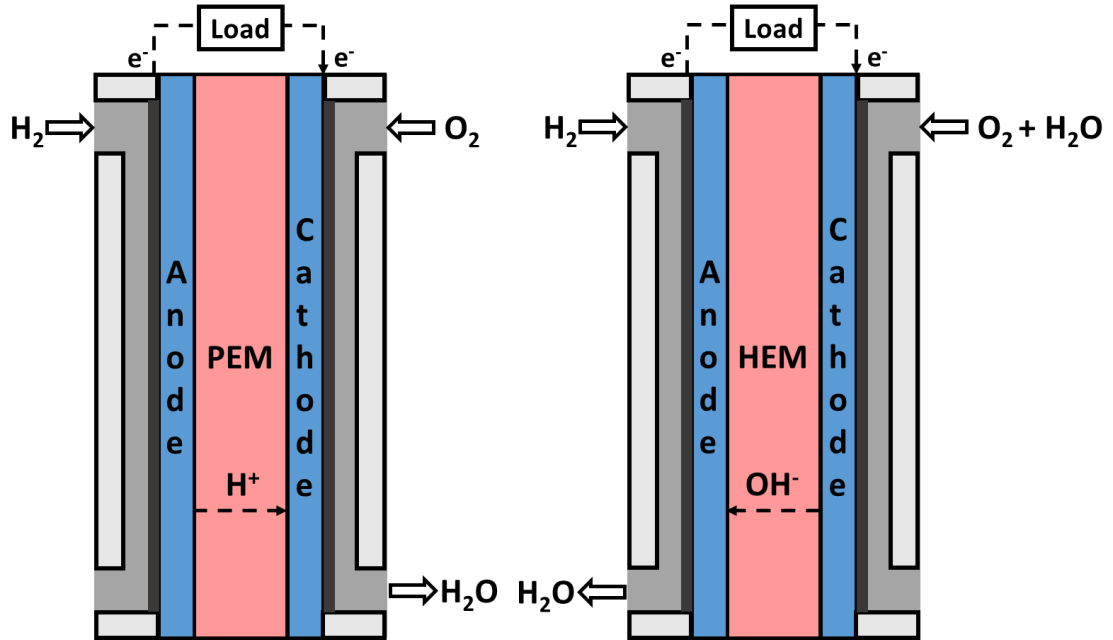
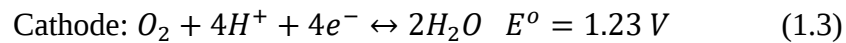
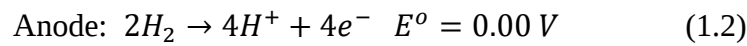


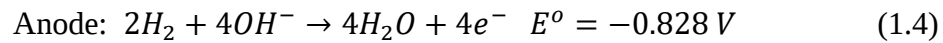
Figure 1.2 Diagram of the two subclasses of hydrogen fuel cells: the proton exchange membrane fuel cell (left) and the hydroxide exchange membrane fuel cell (right).

The operating environment of the hydrogen fuel cell determines the half-reactions of the PEMFC and HEMFC. The two sets of half-reactions are the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR)⁴:

PEMFC:



HEMFC:



Both sets of half reactions share a theoretical standard cell voltage of 1.23 V at 298 K and 1 atm P_{H_2} and P_{O_2} . At the standard operating temperature of a PEMFC, 353 K, the cell voltage is reduced to 1.18 V.⁵

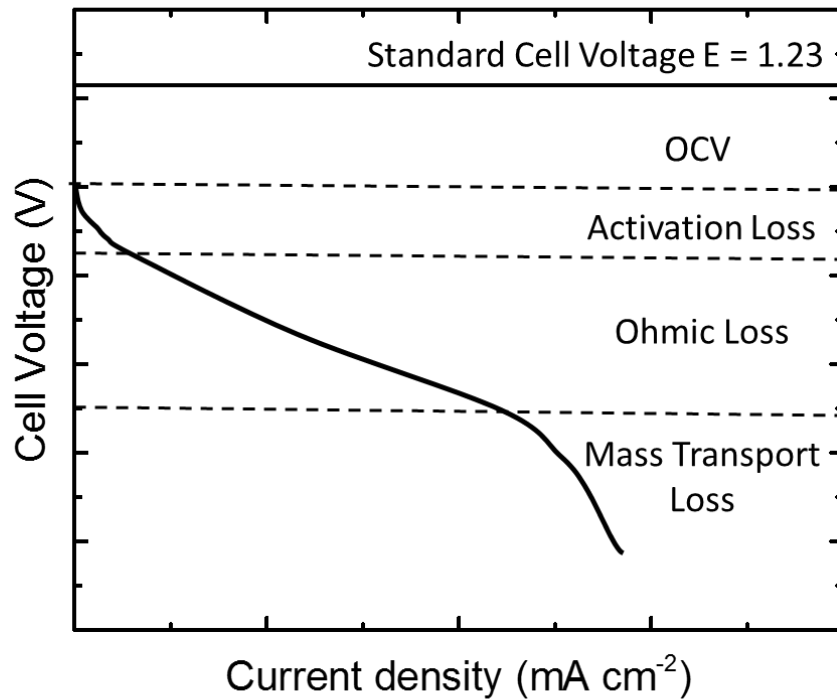


Figure 1.3 Diagram of a model hydrogen fuel cell polarization curve with the different forms of losses.

The measured open-current cell voltage (OCV) is lower than the theoretical cell voltage because of activation losses, fuel crossover/internal current losses, ohmic losses, and mass transport losses (Figure 1.3).⁵⁻⁶ Activation losses are a result of the kinetics of the fuel cell reactions. Depending on the two half-reactions' reaction rates and the operational conditions of the fuel cell a certain overpotential is necessary to overcome

the activation barrier. Improving the electrode catalyst performance will reduce the activation losses. Voltage reduction from activation losses is more dramatic at low current densities. Fuel crossover and internal current losses are caused by fuel leakage across the membrane and uneven fuel/current distributions on an electrode. Ohmic losses are related to the electric and ionic resistance of transporting electrons through the electrode and out of the fuel cell and ions from the electrodes through the membrane to the opposite electrode. This loss is directly proportional to the operational current of the fuel cell. Mass transport losses are caused by the depletion of reactants or accumulation of products in both the anode and cathode of the fuel cell. These effects occur at high operational currents and dramatically reduce cell voltage.

1.2.1 PEMFC

The PEMFC's high performance allows it to be a promising replacement for ICEs. In 2015, Toyota deployed the world's first commercial PEMFC powered vehicle, the Mirai. This hydrogen powered fuel cell car achieved comparable performance to gasoline cars in the same class, but the Mirai's fuel cell as well as all other PEMFC's are still effected by the slow kinetics of the ORR reaction and durability issues caused by the PEMFC's acidic environment.

ORR kinetics in the cathode of a PEMFC require an overpotential 300-400 mV.⁷ This has led to the investigation and development of higher performance catalysts. Much progress has been made through nanostructuring platinum (Pt) alloy catalysts, which are capable of achieving an order of magnitude increase in ORR catalyst specific

activity.⁸⁻¹⁰ Combining the high-performance ORR catalysts with the near-zero overpotential needed for the HOR at the anode has resulted in very high performing PEMFCs. However, the durability of PEMFCs is a large concern. The acidic environment in the electrodes coupled with the high biasing potential experienced by the cathode requires extremely durable Pt-based catalysts.¹¹⁻¹² Additionally, the high cost and low abundance of Pt hinders full commercial incorporation of PEMFCs in automotive applications.

1.2.2 HEMFC

HEMFCs have the potential for cost savings compared to PEMFCs. However, historically HEMFCs have been investigated to a smaller degree when compared to PEMFC because of their membrane/ionomer stability issues.¹¹⁻¹³ In the past decade, much progress has been made addressing the membrane/ionomer stability and now state-of-the-art HEMFC membranes are stable at PEMFC operating temperatures and lifetimes. HEMFC's alkaline environment allows for more cost effective and earth abundant alternatives catalysts to replace Pt. The ORR reaction in the cathode of the HEMFC still suffers from slow kinetics, but the compatible performance observed in non-precious metal catalysts makes up for these limitations. Also, non-precious metal catalysts can still be cost effective at higher loadings. The HEMFC's HOR reaction kinetics, even with Pt-group catalysts, is two orders of magnitude slower compared to the PEMFC's acidic counterpart.¹⁴⁻¹⁵ The pH dependency of HOR performance is still not fully understood, but better fundamental understanding is currently a topic of

research. This research interest is leading to the development of higher performance Pt-alloys and non-precious metal HOR catalysts for alkaline environments.

1.3 Polymer Electrolyte Membrane Fuel Cell Cost Analysis

The Department of Energy (DOE) has established a long term fuel cell cost target of $\$30 \text{ kW}^{-1}$ or approximately \$2,400 per vehicle to drive fuel cell commercialization.¹⁶⁻¹⁷ Much progress has been made, but the current state of the art PEMFCs only achieves a production cost of US $\$54 \text{ kW}^{-1}$.¹⁸⁻¹⁹ Data from the US Drive 2013 Fuel Cell Technical Team Roadmap is represented in Figure 1.4's PEMFC cost breakdown. The cost breakdown shows approximately 50 % of a fuel cells cost is in the fuel cell stack and the remainder of the cost is associated with the balance of plant. The highest contributor to the cost of a PEMFC system is the Pt catalyst with 49 % of the fuel cell stack cost. The membrane and bipolar plates also contribute with 27 % of the stack cost. This high cost is a result of the expensive materials required to survive the acidic environment of the PEMFC. The balance of plant for the PEMFC also consumes a significant portion of the overall fuel cell cost. The gas delivery and temperature control system account for 68 % of the balance of plant cost. These necessary and costly components prevent the PEMFC from achieving the DOE's commercialization cost target. Therefore, to address the high cost of PEMFC the HEMFC have been investigated.¹³

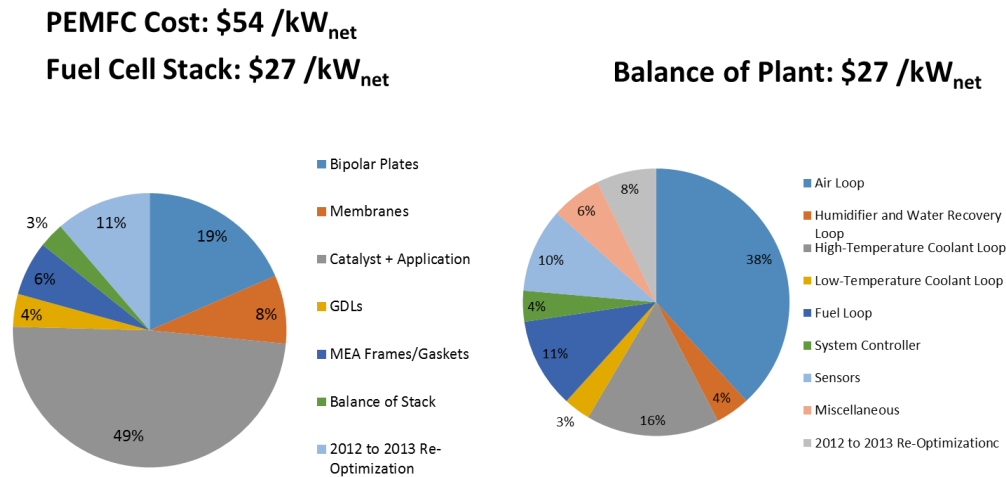


Figure 1.4 Cost breakdown for PEMFC (left) fuel cell stack and (right) balance of plant.¹⁶

HEMFC's alkaline environment has the promise to allow for significant savings for many components in the fuel cell system. Figure 1.5 is a prediction of the cost breakdown for the HEMFC system based on the USDrive's PEMFC model. First, cost-effective and earth-abundant materials can be used to replace the Pt catalyst required in PEMFCs.²⁰⁻²² This reduces the cost of the catalyst to a negligible amount assuming comparable loadings and performance. Next, the hydrocarbon based membranes allow for significant cost savings compared to their perfluorinated counterparts again reducing their cost contribution to a negligible level.²³⁻²⁴ The costly corrosive resistant bipolar plate material and/or coatings are not required in the HEMFC's basic environment.²⁵ This allows for a cost reduction of the total fuel cell stack to \$8 /kW_{net}. The HEMFC's balance of plant also allows for significant savings. Due to lower stack costs, higher performance per stack is not as essential and more low-powered cells could operate

under more cost effective operating conditions.¹⁸ This could result in a cheaper balance of plant for the HEMFC system. The optimum HEMFC's operating humidity, pressure, and temperature could allow for cost savings on the gas delivery and temperature control systems. These savings could allow for a balance of plant cost of \$19 /kW_{net} and a total system cost of \$27 /kW_{net}.

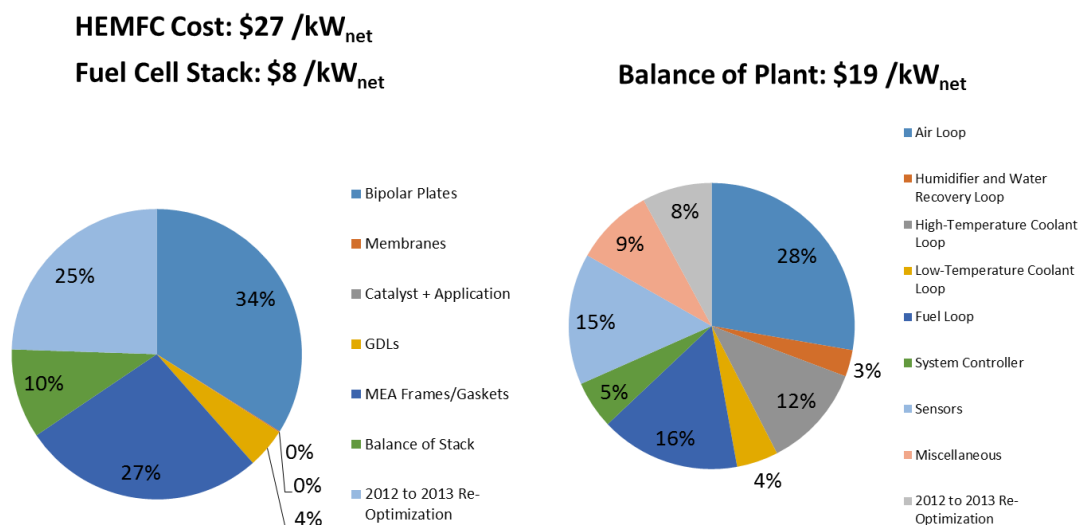


Figure 1.5 Cost breakdown for HEMFC (left) fuel cell stack and (right) balance of plant.
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1.4 Outline of Dissertation

The primary requirements of an ORR catalyst are its performance and durability. Therefore, a foundational understanding of the factors that contribute to the performance and durability of the ORR are essential. This dissertation focuses on high-performance and durable polymer electrolyte membrane fuel cell cathode catalyst development and implementation in both the acidic and basic environments.

Chapter 2 presents a summary of the ORR. This chapter highlights the accepted reaction mechanism, reaction kinetics, and introduces catalyst corrosion and methods to analyze catalyst durability.

In Chapter 3, we synthesize platinum copper supported on copper nanowire catalysts (PtCu/CuNW) for the ORR in PEMFCs. Catalyst post processing techniques were used to investigate the effect of induced lattice strain on the performance of extended structure Pt catalysts. Potential cycling accelerated durability testing was performed to demonstrate the enhanced durability of an extended structure catalyst compared to traditional Pt nanoparticles supported on carbon.

In Chapter 4, the durability of alternate catalyst support materials as well as the durability of ORR catalysts in acidic and basic environments were investigated. In this study, Pt decorated carbon nanofibers were synthesized to investigate the durability of this enhanced catalyst support and see if their enhanced durability in the acidic environment is reflected in the basic environment.

In Chapter 5, non-precious metal catalysts were investigated for their performance and durability compared to Pt/C in the basic conditions of the HEMFC. Non-precious metal cathode fuel cell performance was also shown to demonstrate the feasibility of the incorporation of these types of catalysts in the HEMFC.

Chapter 6 summarizes the previous chapters as well as provides future work for the investigated fields.

Chapter 2

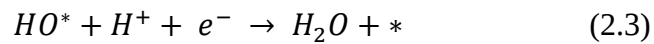
THE OXYGEN REDUCTION REACTION

Over the past 50 years of polymer electrolyte membrane fuel cell research, the ORR reaction has been a topic of major focus. Pt based materials are still the main solution to the slow kinetics and durability issues of ORR catalysts; especially in PEMFC's acidic environment. Non-precious metal catalysts have more promise in the alkaline HEMFC, but Pt based catalysts continue to be the high performing incumbent. To improve the performance and durability of ORR catalysts it is essential to understand the fundamental reaction mechanisms and the kinetics of the ORR. It is also important to identify why Pt based catalysts perform so well in order to improve the performance of other precious and non-precious metal catalysts.

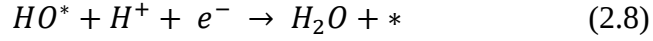
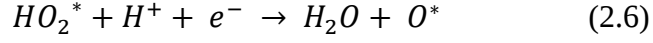
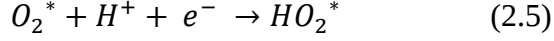
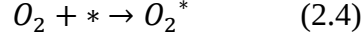
2.1 Reaction Mechanism

The fuel cell's ORR is a 4-electron process that reduces oxygen into water (hydroxide ions in HEMFC) through a variety of elementary steps. On certain catalysts, a 2-electron process occurs resulting in the formation of a peroxide, but this is not ideal in a fuel cell. There are two generally accepted ORR mechanisms: the dissociative mechanism (eq. 2.1 – 3) and the associative mechanism (eq. 2.4 – 8).²⁶

Dissociative Mechanism



Associative Mechanism

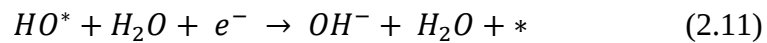
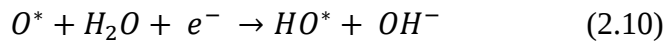
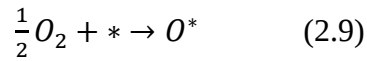


* Represents free surface site and X^* illustrates species adsorbed on the surface

In the dissociative mechanism, the oxygen molecule dissociates onto the catalyst's surface and is then hydrogenated to water before leaving the site. In the associative mechanism, the hydrogenation occurs with the oxygen molecule before the dissociation of the oxygen-oxygen bond. Eq. 2.6 can terminate the ORR process releasing hydrogen peroxide. This 2-electron process is referred to as the peroxo-mechanism.²⁶

The alkaline environment of the HEMFC shows the same mechanism for ORR, but with the hydrogenating proton coming from water instead of the acidic proton (Eq. 2.9 – 2.11). This is essentially an algebraic addition of OH^- to both sides of the chemical formula.²⁷

Dissociative Mechanism (Alkaline Environment)



The rate determining step (RDS) of the ORR mechanism depends on the magnitude of the binding energy of the catalyst to O and OH species. For strong binding energies, the initial oxygen adsorption and dissociation is very fast, but the subsequent electron transfer and protonation steps limit the reaction rate. For weak binding energy catalysts, the electron transfer and protonation are fast, but the adsorption of oxygen onto the surface is the rate determining step. ORR follows Sabatier's principle with an optimal binding energy allowing fast oxygen adsorption and dissociation as well as fast electron transfer and protonation.²⁶

2.2 Reaction Kinetics

The thermodynamic potential for the ORR is 1.23 V vs RHE, but kinetic limitations require an overpotential to drive the reaction. The current-overpotential relationship can be quantified by the following equation:

$$i_k = i_o \left[e^{\frac{\alpha z F}{RT} \eta} - e^{\frac{(1-\alpha) z F}{RT} \eta} \right] \quad (2.12)$$

where i_k is the kinetic current density [mA cm^{-2}], i_o is the exchange current density [mA cm^{-2}], α is the charge transfer coefficient, η is the overpotential [V], z is the number of electrons transferred in the RDS, F is Faraday's constant [C mol^{-1}], R is the ideal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$], and T is the temperature [K]. The exchange current density represents the rate of an electrochemical reaction at equilibrium. The magnitude of the exchange current density indicates the rate of the kinetics of the ORR as well as the effectiveness of a catalyst material.²⁸

At large overpotentials the contribution from the reverse reaction becomes negligible and equation 2.12 simplifies to

$$i_k = i_o e^{\frac{\alpha z F}{RT} \eta} \quad (2.13)$$

This current/overpotential relationship can then be linearized to

$$\eta = \frac{2.303 R T}{\alpha z F} (\log i_k - \log i_o) \quad (2.14)$$

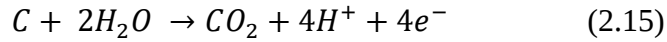
In this form the Tafel slope can be extracted. The two important parameters in the Tafel slope are the charge transfer coefficient (α) and the number of electrons involved in the RDS (z). The charge transfer coefficient is dependent on the catalyst material as well as the operating conditions of the fuel cell (i.e. Temperature, pressure, relative humidity), but under normal operating conditions and on most catalysts $\alpha \approx 0.5$. The number of electrons in the RDS is dependent of the catalyst material as well as the operating potential and has a typical value of $z = 1$ or 2 . Typical Tafel slope values for ORR are 60 mV dec^{-1} and 120 mV dec^{-1} .²⁸ In general, to increase current at a particular overpotential, the exchange current density should be increased and the Tafel slope should be reduced.

2.3 ORR Catalyst Durability

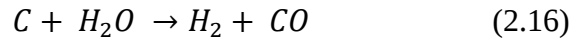
2.3.1 Corrosion of Catalyst Support

Understanding the durability issues for ORR catalysts is necessary for the development of high performance and durable catalyst materials. There are two primary modes of degradation of ORR catalysts: corrosion of the support (typically high surface

area carbon black) and the degradation of the catalyst material.²⁹⁻³⁰ The main issue caused by carbon corrosion is catalyst particle dislocation and isolation from the rest of the electrode. Carbon corrosion is mainly through the electrochemical oxidation of C to CO₂.¹² (Eq. 2.15)



This reaction is thermodynamically favorable at 0.207 V vs SHE and under normal PEMFC cathode operating conditions (0.6 – 0.8 V vs RHE) there is sufficient overpotential to drive this reaction.³¹⁻³² Carbon can also undergo the heterogeneous water-gas oxidation leading to the generation of CO.³³ (Eq. 2.16)



This process's reaction rate is lower than the direct oxidation of C to CO₂, but the CO can poison the metal catalyst's surface and decrease the overall ORR performance.³⁴ Carbon corrosion is catalyzed by the ORR catalyst the carbon is supporting.³⁵ Therefore, high catalyst loadings lead to more rapid carbon degradation. Carbon can also be partially oxidized into a variety of surface functional groups.³⁶ This can alter the surface properties of the support and lead to issues with transport inside the catalyst layer of a fuel cell.

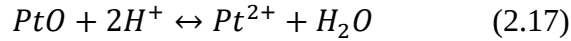
2.3.2 Corrosion of Catalytic Metals

Metal catalyst degradation is mainly gauged by the reduction of electrochemical surface area (ECSA).³⁷ This loss of ECSA occurs through metal nanoparticle coarsening, coalescence, and dissolution.^{12, 29-30} Coarsening, also known as Ostwald

ripening, is a process where catalyst dissolves from the surface of the nanoparticle, transports through the ionomer, in the solution phase, or along the carbon support, and then re-deposits onto the surface of another particle.³⁸⁻³⁹ Coalescence is when smaller nanoparticles agglomerate or sinter through particle migration along the carbon support.⁴⁰⁻⁴¹ Dissolution occurs through the oxidation of the metal catalyst particles into soluble species that are lost in the membrane/ionomer or the aqueous environment.³⁰ It is uncertain which of these methods dominate ECSA loss, but it is understood that these forms of loss depend on the fuel cell's operating conditions.³⁷ Higher operating temperature, humidity, and potential are all driving forces towards greater ECSA loss.

For Pt catalysts, the previously mentioned ECSA loss mechanisms have great impact on the durability of the ORR catalyst. Additionally, various forms of Pt oxidation also pose significant problems.¹² Two forms of Pt oxidation occur on the Pt surface: reversible Pt surface oxidation and irreversible Pt oxidation.⁴²⁻⁴³ Both forms of Pt oxides can include PtO, PtO₂, Pt(OH)₂, and Pt(OH)₄. Reversible Pt oxide is a thin monolayer of surface oxide generated under moderate oxidizing conditions and can be rapidly reduced with modest (below 0.7 - 0.8 V vs RHE) reducing potentials. Irreversible Pt oxide is a thicker bulk porous oxide layer generated under higher oxidizing potentials and requires much more driving force to reduce.⁴⁴ Both forms of Pt oxidation lower the ORR performance of the catalyst. Irreversible Pt oxides are not as easily reduced and cause a greater effect on catalyst performance. Pt oxide layers passivate the surface and reduce dissolution when operating at a constant high potential. However, cycling between Pt oxide forming and reducing potentials leads to higher rates of Pt loss. This

accelerated Pt dissolution is a product of the Pt ions that are formed during the Pt oxide reduction reaction.¹² (Eq. 2.17)



2.3.3 Accelerated Durability Testing

Over the lifetime of a PEMFC stack, the ORR catalyst will experience conditions that promote a variety degradation mechanisms. It is impractical to test catalyst durability by replicating real operating conditions in an actual PEMFC. This would require thousands of hours of operation and the results would be convoluted with all the variables that effect fuel cell operation.¹² This has led to the development of targeted accelerated durability tests (ADT) that isolate certain operating conditions to rapidly give information on a catalyst's degradation. The primary ADT methods are: thermal degradation under varying atmospheric conditions, degradation under various solution conditions, and electrochemically driven aging under constant and varied potential conditions. Thermal and solution ADTs are good initial screens for catalyst materials to investigate if they can survive the PEMFC or HEMFC's environment.^{33, 35} Electrochemical ADTs can then be used to probe different components of the catalyst (support vs catalyst particle) as well as different operating conditions (start-up/shut-down vs sustained operation).⁴⁵⁻⁴⁷ Fixed high potential tests (1.2 – 1.4 V vs RHE) are commonly used to probe support corrosion and the high potential environment that is sometimes reached during fuel cell start up and fuel starvation conditions.⁴⁸⁻⁵⁰ Cycling

potential ADTs (0.6 – 1.1 V vs RHE) are used to target catalytic material degradation as well as mimic standard fuel cell operation.⁵¹⁻⁵²

ADTs allow for quick ex-situ investigation of fuel cell catalyst durability. An ADT should be chosen based off the desired characteristics to be investigated for a particular catalyst. An inappropriate ADT can lead to wrong conclusions for a catalyst's ORR performance and durability.

Chapter 3

HIGH-PERFORMANCE DEALLOYED PtCu/CuNW OXYGEN REDUCTION REACTION CATALYST FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

One major barrier to fuel cell commercialization is the high cost of oxygen reduction reaction (ORR) catalysts. Current catalysts are predominantly supported Pt nanoparticles. These nanoparticles show high surface area but low specific activity and durability. A transition to unsupported catalysts possessing an extended surface would improve both specific activity and durability and in turn, cost-effectiveness when high surface area can be achieved. Platinum-coated copper nanowires (Pt/CuNW) exemplify these advantages. In this study, post-synthetic processing is used to further improve the performance of Pt/CuNW catalyst. Specifically, annealing followed by electrochemical dealloying enhances activity through geometric lattice tuning. The resultant bimetallic PtCu/CuNW catalyst yields specific and mass activities (SA and MA) of 2.65 mA cm^{-2} and $1.24 \text{ A mg}_{\text{Pt}}^{-1}$, surpassing the respective DOE benchmarks of 0.72 mA cm^{-2} and $0.44 \text{ A mg}_{\text{Pt}}^{-1}$. PtCu/CuNWs demonstrate enhanced durability over Pt nanoparticle catalysts by maintaining 64.1 % of its active surface area after 30,000 cycles between 0.6 - 1.1 vs. RHE at a scan rate of 50 mV s^{-1} in Ar saturated 0.1 M HClO_4 . Post durability PtCu/CuNWs outperformed the DOE benchmarks with a SA and MA of 1.50 mA cm^{-2} and $0.477 \text{ A mg}_{\text{Pt}}^{-1}$.

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Catalyst for Proton Exchange Membrane Fuel Cells. ACS Catalysis, 4(9), 3145–3151.
<http://doi.org/10.1021/cs500692y>. Copyright 2014 American Chemical Society.

3.1 Introduction

Proton exchange membrane fuel cells (PEMFCs) are clean, power generation devices that electrochemically combine hydrogen and oxygen via two half reactions: hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR). While high power densities can be achieved using PEMFCs, high loadings of expensive platinum (Pt) catalyst are required due to the slow ORR kinetics, severely limiting PEMFC commercialization.¹¹ Conventional methods to decrease Pt usage include carbon-supported nanoparticles; however, these are currently unable to meet the activity and durability requirements as set by Department of Energy (DOE) (precious metal mass activity (MA) of 0.44 A mg_{Pt}⁻¹ (2017-2020) and specific activity (SA) of 0.72 mA cm⁻² (2010-2015)).^{53,54} The durability of supported catalyst are limited by the corrosion of the carbon support and the loss of Pt surface area through: coarsening (Ostwald ripening), coalescence (Smoluchowski ripening), and dissolution of Pt nanoparticles.²⁹⁻³⁰ Consequently, new promising catalysts are required to be cheaper, more active, and more durable than the conventional carbon-supported nanoparticles.

Since breakdown of the carbon support is the main degradation pathway in carbon-supported catalysts, the use of new supports or a support-less catalyst may provide the necessary durability.^{30,55-56} Indeed, first generation support-less catalysts have shown improved durability, e.g., Pt-black, but demonstrate a low mass activity.⁵⁶

More advanced support-less Pt nanotubes (PtNT), generated from galvanic displacement of nonprecious metal-based nanowires (CuNW) have shown superior stability over Pt-black.⁵⁶⁻⁵⁷ Furthermore, the extended surface of the resulting PtNT(Cu) provides a higher SA, attributed to the bulk Pt-like structure.⁵⁶⁻⁵⁸ PtNT(Cu) met the DOE SA target,⁵⁷ but its low Pt utilization resulted in a MA below the DOE benchmark. To increase Pt utilization, a partial galvanic displacement of CuNWs was used to form Pt coated CuNWs (Pt/CuNW). An optimum Pt content of 18 wt. % was chosen, resulting in a continuous coating with a minimum amount of Pt (theoretical Pt thickness of 2 nm or 14 monolayers).⁵⁷ The continuous Pt coating enhances SA by providing a bulk Pt-like extended surface; MA by lowering the overall Pt content; and durability by preventing acid leaching of vulnerable underlying Cu.⁵⁷

While both the SA and MA are improved, bimetallic systems such as the Pt/CuNW have the potential for even further enhancement in activity. Density functional theory (DFT) calculations showed that ORR activity can be improved by reducing the Pt-O binding energy.²⁶ The three primary mechanisms that bimetallic systems utilize to improve ORR activity are ensemble, ligand, and geometric effects.^{56, 59-61} The ensemble effect occurs when discrete surface atoms take on distinctive mechanistic functionalities.^{61,62} Ligand effects are brought on by dissimilar atoms in a neighboring atomic position inducing electronic charge transfer and altering the d-band structure.⁶³ Geometric effects are caused by the change in electronic structure that results from surface strain (compression or expansion) brought on by atoms of different atomic sizes in a crystal lattice.⁶³⁻⁶⁵ Ensemble and ligand effects are only applicable in

a bimetallic coordination of less than a few monolayers.⁶¹ Therefore, the only feasible mechanism applicable in the Pt/CuNW system would be geometric tuning. Strasser et al. has demonstrated that an optimal strain exists to boost Pt activity with Cu.⁶¹ Specifically, Cu introduces a compressive lattice strain which shifts the d-band center down causing a decrease in the adsorption energy between Pt and oxygen.^{61, 63-64}

In this study, we explored compressive strain's effects on the ORR activity of Pt/CuNWs. We used post-synthetic annealing and electrochemical dealloying to generate a PtCu alloy on the surface of the CuNWs (PtCu/CuNW). Low (150 °C), medium (250 °C), and high (350 °C) annealing temperatures were chosen to control of the degree of diffusion between surface Pt atoms and the underlying Cu, consequently varying the amount of compressive strain in each system. Afterwards, electrochemical dealloying of the PtCu/CuNW removed surface Cu, increasing the amount of active Pt surface exposed on the nanowire, while maintaining the strain induced from the alloy. It has been shown previously for nanoparticles that the strain induced by the alloying is retained due to the rapid progression of the dealloying process. This does not allow the Pt surface to relax from its strained state.^{61, 65-67} The dealloying can also act to increase the surface roughness and thus the electrochemical surface area (ECSA) depending on the underlying alloy structure and composition.^{65, 68}

3.2 Materials and Methods

3.2.1 Synthesis of CuNW and Pt/CuNW

CuNWs were synthesized through the reduction of precursor copper (Cu) nitrate by hydrazine (N_2H_4 , 35 wt %) in the presence of shape directing ethylenediamine (EDA) and sodium hydroxide (NaOH).⁶⁹⁻⁷⁰ A Cu nitrate solution (241.6 mg in 10 mL water) was added to 200 mL of 10 M NaOH in a 500 mL reaction vessel. Next, 1.5 mL of EDA and 0.25 mL hydrazine were added sequentially. After each addition, the vessel was capped and vigorously shaken to ensure the even distribution of the reactants. The reaction vessel was placed in a 65 °C water bath for 45 min. The resulting product was then cooled in an ice bath and filtered. Filtering continued until the effluent showed a neutral pH. The product was collected off the filter cake and stored in a vacuum desiccator.

Pt/CuNWs were synthesized through a partial galvanic displacement with CuNWs.⁵⁷ A solution of dispersed CuNW (8.4 mg in 200 mL of water) was placed in a magnetically stirred 500 mL round-bottom flask with an attached drop funnel containing a chloroplatinic acid solution (3.5 mg in 100 mL of water). The whole system was flushed with argon (Ar) for 10 min prior to the start and throughout the reaction. Chloroplatinic acid was added dropwise at a rate of approximately 1 drop per 3 seconds. Following the addition, the flask was allowed to sit for 30 min to ensure completion. The generated Pt/CuNWs were filter collected with a 1 M hydrochloric acid wash and excess water washes.

3.2.2 Post-Processing for Pt/CuNW

Pt/CuNWs were directly placed into a tube furnace to generate the corresponding post-synthetic annealed PtCu/CuNW samples. The annealing was performed under flowing Ar. The temperature was ramped to the desired temperature over a 30 min time period and maintained there for 2 h. The furnace was naturally cooled overnight under Ar before the product was collected.

Dealloying and rotating disk electrode (RDE) experiments were both conducted in a 3-electrode cell equipped with a saturated calomel reference electrode (SCE), Pt wire counter electrode, and a 5 mm glassy carbon working electrode (Pine Instruments). The cell was controlled by a multichannel potentiostat (VMP2, Princeton Applied Research). The working electrode was connected to a modulated speed rotator (Pine Instruments). All tests were performed in 0.1 M HClO₄ (diluted from 70 % HClO₄, EMD Millipore)

3.2.3 Electrochemical Measurements

Catalyst ink solutions were generated from 0.261 mg mL⁻¹ water dispersions of nanowire materials. A thin film catalyst layer was deposited on the working electrode by pipetting three additions of 15 μ L of catalyst ink. A final catalyst loading of 60 μ g cm⁻² (10.8 μ g_{Pt} cm⁻²) was achieved.

Dealloying consisted of a series of cyclic voltammetry (CV) scans in saturated Ar.^{30, 61, 65} Five initial scans were performed at a slow scan rate of 50 mV s⁻¹, to analyze initial Cu stripping characteristics. The following 200 scans were carried out at an

accelerated rate of 200 mV s⁻¹ to insure all surface copper was leached out and a stable CV was obtained.

The ECSA was determined from the double layer corrected average charge of the Pt-hydrogen adsorption and desorption regions between 0.05 V and ~0.4 V (the onset of the double layer region), assuming a Pt surface charge density of 210 $\mu\text{C cm}_{\text{Pt}}^{-2}$.⁷¹ The measurement was taken at a scan rate of 50 mV s⁻¹ in saturated Ar.

ORR measurements were performed by cycling from 0.05 – 1.1 V vs RHE at 20 mV s⁻¹ in saturated O₂ at a rotation rate of 1600 rpm. The ORRs SA and MA were determined from extracting anodic scan's kinetic current (i_k) at 0.9 V vs. RHE and normalizing that value to the active surface area of the catalyst and the weight of Pt in the catalyst, respectively.⁷¹⁻⁷² The kinetic current was calculated with the Koutecky-Levich equation (Eq. 3.1),

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (3.1)$$

where i_d is the diffusion limiting current and i is the measured current. The diffusion limiting current was determined experimentally by measuring the current at high ORR overpotentials where the current has reached a constant value. This value was verified against the calculated diffusion limited current calculated from Eq. 3.2.

$$i_d = 0.62zFD^{2/3}\omega^{1/2}\nu^{-1/6}c_o \quad (5.2)$$

Where z is the number of electrons involved in the reaction, F is Faraday's constant, D is the diameter of the RDE electrode, ω is the rotation rate, ν is the kinematic viscosity,

and c_o is the concentration of the reactant in the bulk of the solution. For the ORR at 1600 RPM the theoretical i_d is 5.8 mA cm^{-2} .

3.2.4 Microscopy

Scanning electron microscopy (SEM) images and energy-dispersive X-ray spectroscopy (EDS) were taken at 9 kV with a JSM-7400F microscope. Transmission electron microscopy (TEM) images were taken at 200 kV with a JEM-2010F microscope. The TEM samples were prepared by adding a drop of the catalyst suspensions on lacey carbon Cu grids (Ted Pella, Inc.).

3.3 Results and Discussion

3.3.1 Characterization of PtCu/CuNWs

The unannealed Pt/CuNWs, low, medium, and high temperature annealed PtCu/CuNWs, PtCu-(0, 150, 250, 350) respectively, express a diameter of 100 nm and a length of 25-40 μm (Figure 3.1 a-h). The diameter is maintained during the galvanic displacement reaction, but the wire length is reduced from the precursor CuNW's length of 40-50 μm . All of the coated structures contained 18 wt. % Pt (remainder: Cu and O), as determined by EDS (Figure 3.2). EDS has been validated as an adequate tool for measuring chemical composition in alloyed nanomaterials by ICP in various previous studies.^{67, 73}

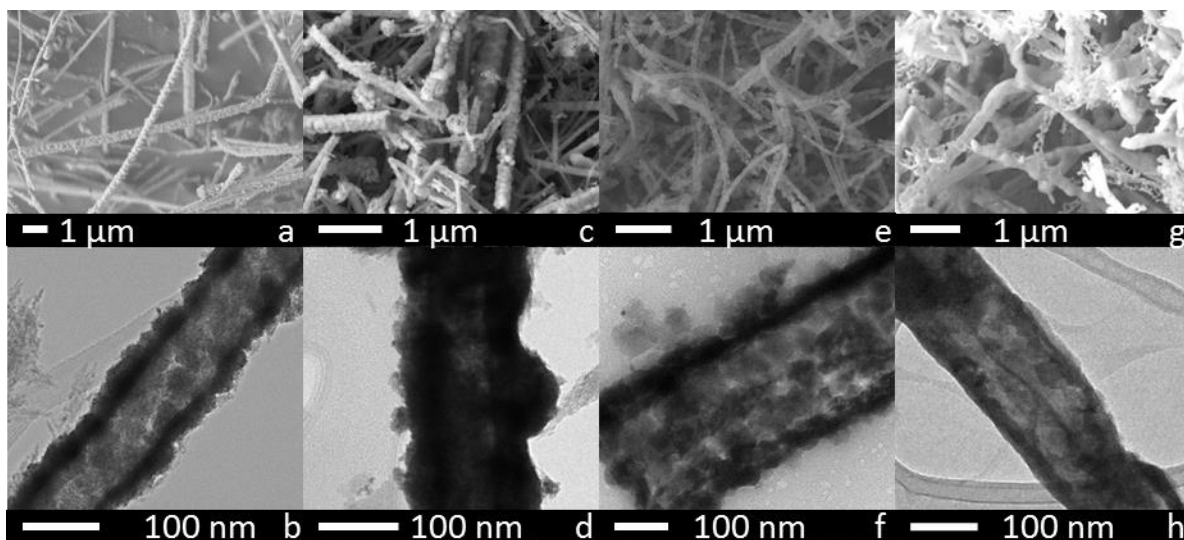


Figure 3.1 SEM and TEM images of PtCu/CuNWs: PtCu-0 (a-b), PtCu-150 (c-d), PtCu-250 (e-f), and PtCu-350 (g-h).

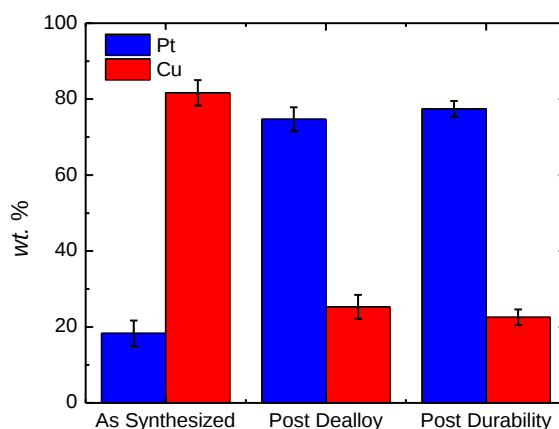


Figure 3.2 Composition of PtCu-250 catalyst determined by EDS for as-synthesized, post dealloying, and post durability testing. Pt composition was 18.3 ± 3.35 wt. % for the as-synthesized catalyst, 74.7 ± 3.15 wt. % for post dealloying, and 77.4 ± 2.05 wt. % for the post durability test. A change of 2.7 wt. % was observed for the elemental composition from post dealloying to post durability. This indicates a minor amount of Cu was leached out during testing, this would correlate to a minimal effect on overall fuel cell performance.⁵³

3.3.2 Electrochemical Characterization

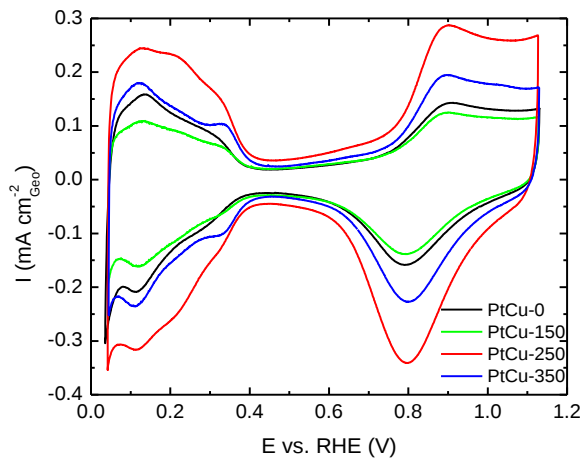


Figure 3.3 Post dealloying cyclic voltammetry (CV) scan for PtCu-(0, 150, 250, 350). CV scans were taken at 50 mV s^{-1} in Ar saturated 0.1 M HClO_4 . Currents were normalized to the geometric area of glassy carbon disk electrode.

Catalyst ECSAs are calculated from CV curves obtained for all dealloyed structures immediately following the dealloying process (Figure 3.3). ECSAs for PtCu-(0, 150, 250, 350) are 6.72 , 3.84 , 8.40 , and $7.35 \text{ m}^2 \text{ g}^{-1}$ based on total metal and 37.3 ± 3.5 , 21.4 ± 4.5 , 46.7 ± 2.6 , and $40.8 \pm 3.7 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ based on Pt. PtCu-0, which underwent no post-synthesis annealing processing, demonstrates a moderate ECSA. This is explained by the intrinsic surface roughness produced by the galvanic displacement reaction. The ECSA value agrees with the previously reported value for Pt/CuNWs.⁵⁷ PtCu-150 shows a decrease in the ECSA from the unprocessed wire, likely due to a reduction of surface roughness caused during the low temperature annealing. PtCu-250 demonstrates the highest ECSA owing to the formation of surface pores and roughness introduced during the annealing and dealloying process.⁶⁸ This enhanced surface roughness can also be observed in TEM micrographs of the PtCu-250 sample (Figure

3.1f). The ECSA of PtCu-350 still benefits from the surface roughening, but the agglomeration of the nanowires during the high temperature annealing slightly decreases it from that of the PtCu-250 sample. Due to this reason, higher annealing temperatures were not preferred.

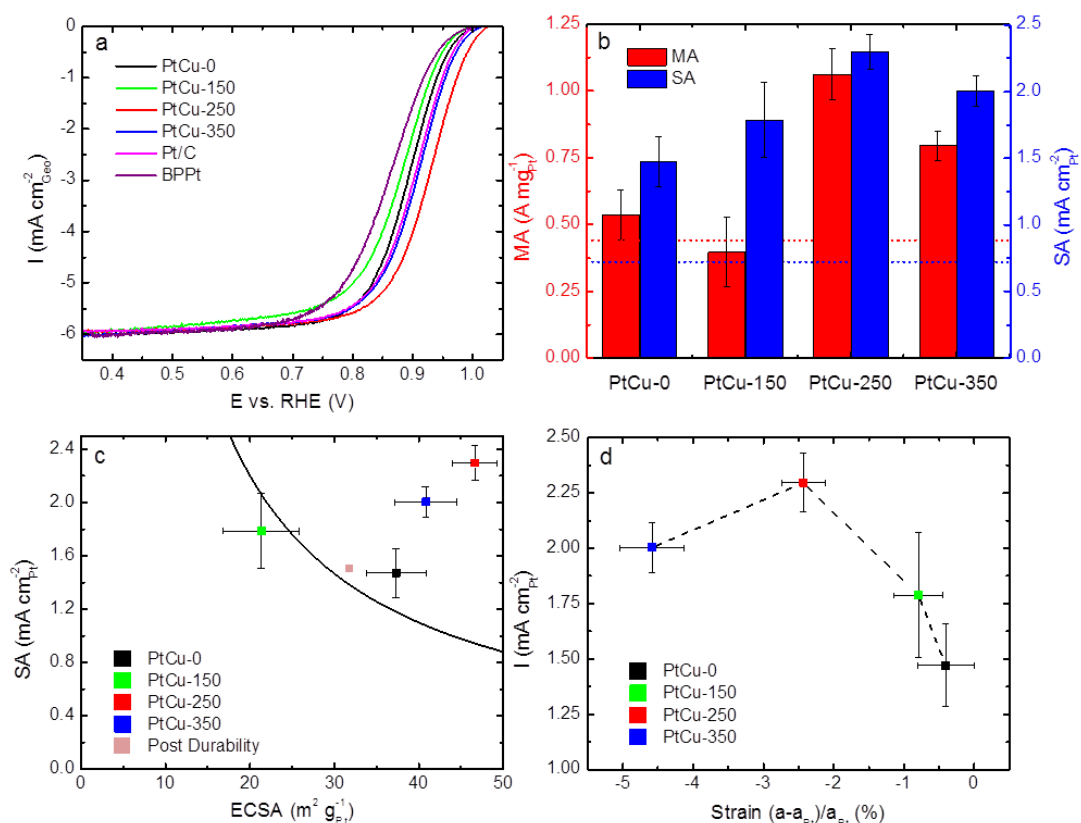


Figure 3.4 (a) Anodic ORR polarization curves PtCu-(0, 150, 250, 350) as well as Pt/C and bulk polycrystalline Pt (BPt). ORR scans were taken at 20 mV s⁻¹ and 1600 rpm in O₂ saturated 0.1 M HClO₄. Currents were normalized to the geometric area of glassy carbon disk electrode. (b) ORR activities for PtCu-(0, 150, 250, 350) normalized to Pt mass and Pt ECSA. DOE targets for MA and SA are denoted by dashed lines. Activities were calculated at 0.9 V vs. RHE for the ORR anodic polarization scans at 20 mV s⁻¹ and 1600 rpm in O₂ saturated 0.1 M HClO₄. (c) SA vs. ECSA plot for PtCu-(0, 150, 250, 350) as well as post durability testing PtCu-250. Determined at 0.9 V vs. RHE for the ORR anodic polarization scans at 20 mV s⁻¹ and 1600 rpm in O₂ saturated 0.1 M HClO₄. Solid line represents

the iso-MA line of the DOE MA target of 0.44 A/mg_{Pt}. (d) SA plotted as a function of percentage strain for PtCu-(0, 150, 250, 350). Percent strain was determined by the percent change between the lattice parameters of PtCu samples and the known Pt lattice parameter (3.925 Å). The negative values indicate compressive lattice strain. PtCu lattice parameters were determined from an average of lattice fringe measurements made on TEM micrographs. Cu lattice parameter is 3.619

Anodic ORR polarization curves are obtained for PtCu-(0, 150, 250, 350) (Figure 3.4a) from which MA (Pt mass) and SA (surface area of Pt) were determined (Figure 3.4b). PtCu-250 demonstrated the highest performance with a SA of 2.30 mA cm⁻² and MA of 1.06 A mg⁻¹, which enhanced the ORR activity of PtCu-0 SA by 64% (1.47 mA cm⁻²) and MA by 50% (0.535 A mg⁻¹). This catalyst also outperforms the DOE SA and MA target by a factor of 3.2 and 2.4, respectively.

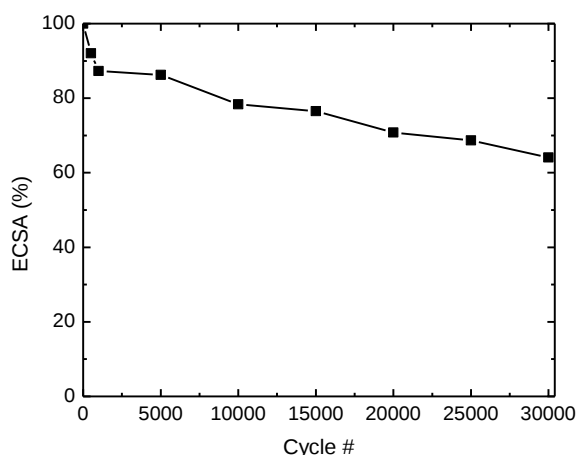


Figure 3.5 ECSA retention relative to initial ECSA (49.61 m² g_{Pt}⁻¹) for PtCu-250 vs. number of durability cycles. Durability was tested by cycling 30,000 times between 0.6 - 1.1 vs. RHE at a scan rate of 50 mV s⁻¹ in Ar saturated 0.1 M HClO₄.

3.3.3 PtCu/CuNW Durability Analysis

Accelerated durability tests are conducted via potential cycling at 50 mV s^{-1} between 0.6 and 1.1 V vs. RHE. ECSA measurements are taken after 500; 1,000; and 5,000 cycles and afterward, at every 5,000 cycles until 30,000 cycles are reached (Figure 3.5). PtCu-250 maintained 64.1 % of its surface area compared to PtCu-0's 62.3% retention.⁵⁷ The ECSA loss is due to the reduction of surface roughness through Pt surface atom migration and Pt dissolution. Post durability SEM demonstrates that the wire morphology is maintained (Figure 3.6). A 2.7 wt. % decrease of Cu in the post durability sample is observed for PtCu-250 (Figure 3.2). Therefore, Cu dissolution is not expected to cause major performance loss for the membrane and ionomer during fuel cell operation. Supportless PtCu-250 catalyst shows a higher durability than Pt/C, which demonstrates lower ECSA retention, 54.1 %.⁵⁷ The enhanced robustness is credited to the elimination of carbon support and the resistance to Pt degradation caused by the extended Pt structure. PtCu-250 also exhibits an enhanced stability over dealloyed PtCu/C nanoparticles, allowing it to maintain performance in an ink state for 9 months (Figure 3.7).⁶⁶

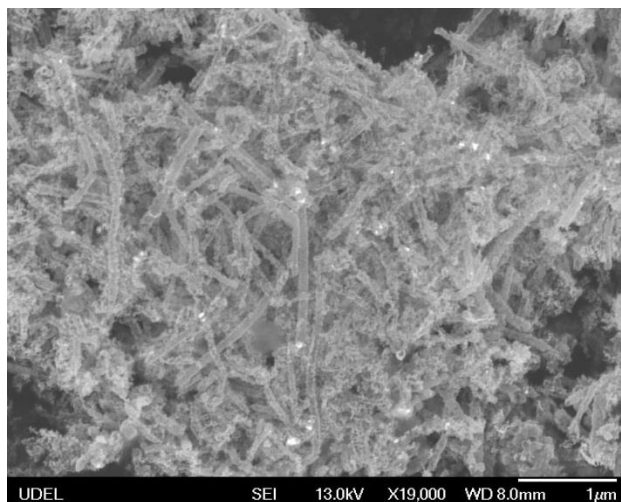


Figure 3.6 SEM of PtCu-250 following durability testing (30,000 cycles between 0.6 - 1.1 vs. RHE at a scan rate of 50 mV s^{-1} in Ar saturated 0.1 M HClO_4). Wire structure is still maintained.

The SAs of PtCu-(0, 150, 250, 350) as well as post durability PtCu-250 are plotted as a function of ECSA (Figure 3.4c), with the iso-MA line representing the DOE 2017-2020 MA target. Points to the upper right of the iso-MA line surpass the DOE MA target. All but the PtCu-150 exceed the DOE MA target; this is due to the low ECSA of PtCu-150. PtCu-250 allows for the best utilization of Pt enabling it to achieve both a high SA and MA. PtCu-250, even after the durability test, maintains a SA (1.50 mA cm^{-2}), exceeding the DOE SA target, and this combined with its high retention of ECSA leads to a post durability MA (0.477 A mg^{-1}) above the DOE target. Post durability PtCu-250 shows a MA and SA similar to fresh PtCu-0's results. The SA loss is attributed to the slow dissolution of Cu from the Pt lattice.

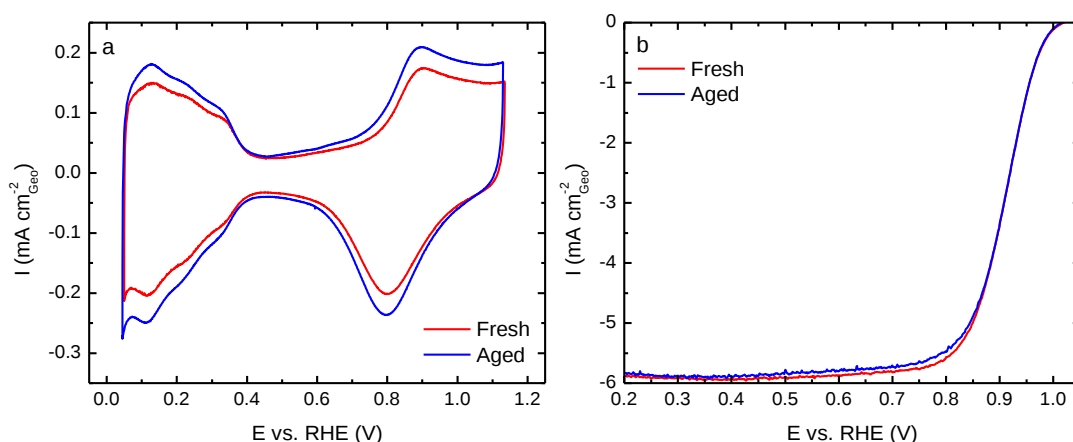


Figure 3.7 Stability analysis of PtCu-250. Fresh sample (blue) were tested soon after synthesis and aged samples (red) were tested after 9 months of storage in an ink state. (a) Post dealloying cyclic voltammetry (CV) scan for PtCu-250 for fresh and aged samples. CV scans were taken at 50 mV s^{-1} in Ar saturated 0.1 M HClO_4 . Comparable ECSA was observed. (b) Anodic ORR polarization curves for PtCu-250 fresh and aged. ORR scans were taken at 20 mV s^{-1} and 1600 rpm in O_2 saturated 0.1 M HClO_4 . Specific activity is maintained over the timeframe tested. Fresh: $2.2 \text{ mA cm}_{\text{Pt}}^{-2}$; Aged: $2.1 \text{ mA cm}_{\text{Pt}}^{-2}$. All currents were normalized to the geometric area of glassy carbon disk electrode.

3.3.4 Effects of Compressive Lattice Strain

DFT predicted that Pt ORR activity can be improved through the shifting of d-band center. By increasing compressive strain, the d-band shifts away from the Fermi level, resulting in improvements in ORR kinetics. This ORR improvement was previously observed in dealloyed PtCu nanoparticles,^{30, 61, 65} theoretical Pt overlayers on Cu and alloys;⁷⁴ unannealed nanowire and nanotube configurations.⁵⁷ Consequently, compressive strain was examined as an indicator for d-band center. The compressive strain was defined using the percent change in lattice parameter of PtCu samples

compared to that of pure Pt (3.925 Å). The lattice parameter was determined from the following equation (Eq. 3.2):

$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + l^2 + k^2)}{a^2} \quad (3.2)$$

Where a is the lattice parameter, d_{hkl} is the lattice spacing, and hkl represent the crystal facet.

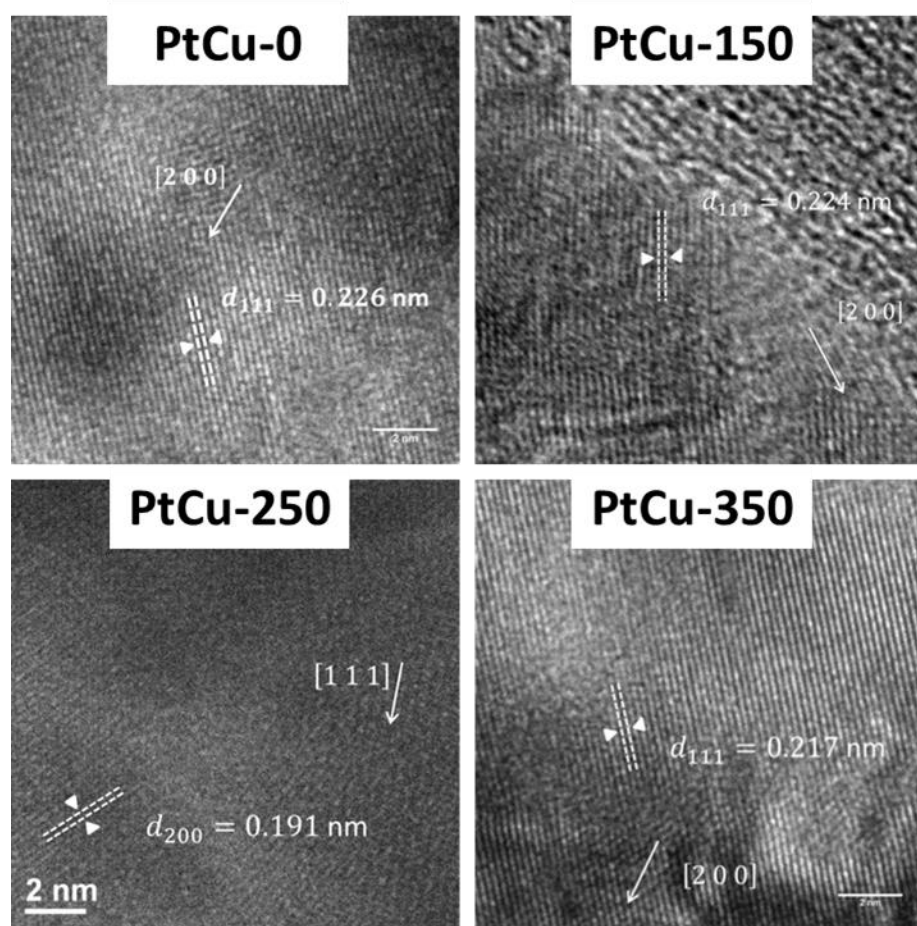


Figure 3.8 Representative HRTEM images showing the lattice spacing for PtCu-(0, 150, 250, 350) samples.

Based on the lattice parameters determined from HRTEM (Figure 3.8), we observed an increase in strain with annealing temperature (Figure 3.4d). PtCu-0

demonstrated a strain and lattice parameter of -0.38% and $3.91 \pm 0.02 \text{ \AA}$, respectively; PtCu-150 showed a higher strain of -0.89% and smaller lattice parameter of $3.89 \pm 0.01 \text{ \AA}$; PtCu-250 demonstrated a much higher strain and smaller lattice parameter (-2.67% and $3.82 \pm 0.02 \text{ \AA}$); and PtCu-350 possessed the highest strain and smallest lattice parameter of -4.97% and $3.73 \pm 0.03 \text{ \AA}$. As the Cu-induced compressive strain increased from PtCu-0 to PtCu-250, ORR activity increased as expected.⁶¹ This is due to the weakening of the Pt-O binding energy, which increases the ease of product formation and desorption.^{26, 53} However, for PtCu-350, the Pt-O binding energy becomes too weak, limiting reactant binding and resulting in a decrease in ORR activity compared to that of PtCu-250.

3.3.5 Understanding Post Processing Annealing and Dealloying

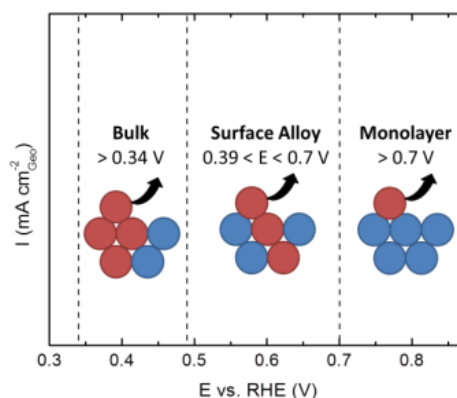


Figure 3.9 Schematic illustrating the three different Cu dissolution types and the potentials at which they become thermodynamically favorable. Bulk dissolution involves Cu stripped from Cu underlayers. Surface alloy dissolution is Cu removed from a blended PtCu layer. Monolayer dissolution is Cu removed from a pure Pt underlayer.

Details of the actual surface alloy structure were deduced from the initial dealloying CV scans.⁶⁵ Since stripping of Cu occurs at a potential dependent on its coordination with other elements such as Pt, CV scans provided an estimate of the degree of alloying between Cu and Pt at each PtCu surface. For example, onset of bulk Cu dissolution occurs at 0.34 V vs. RHE.⁷⁵⁻⁷⁷ In contrast, the Cu in PtCu surface alloys experiences a stabilizing effect provided by the Pt, which results in an onset Cu dissolution potential between $0.39 < E < 0.49$ V vs. RHE,⁷⁵ depending on the specific Pt:Cu ratio. The stabilizing effect is maximized for a Cu monolayer with a Pt subsurface, giving an onset dissolution potential of 0.7 vs. RHE.⁷⁶⁻⁷⁷ Thus, surface structural information was inferred by examining the potentials of the Cu dealloying against the known Cu stripping potentials. Figure 3.9 shows a schematic representation of the dissolution potentials for the different surface structures of Cu.

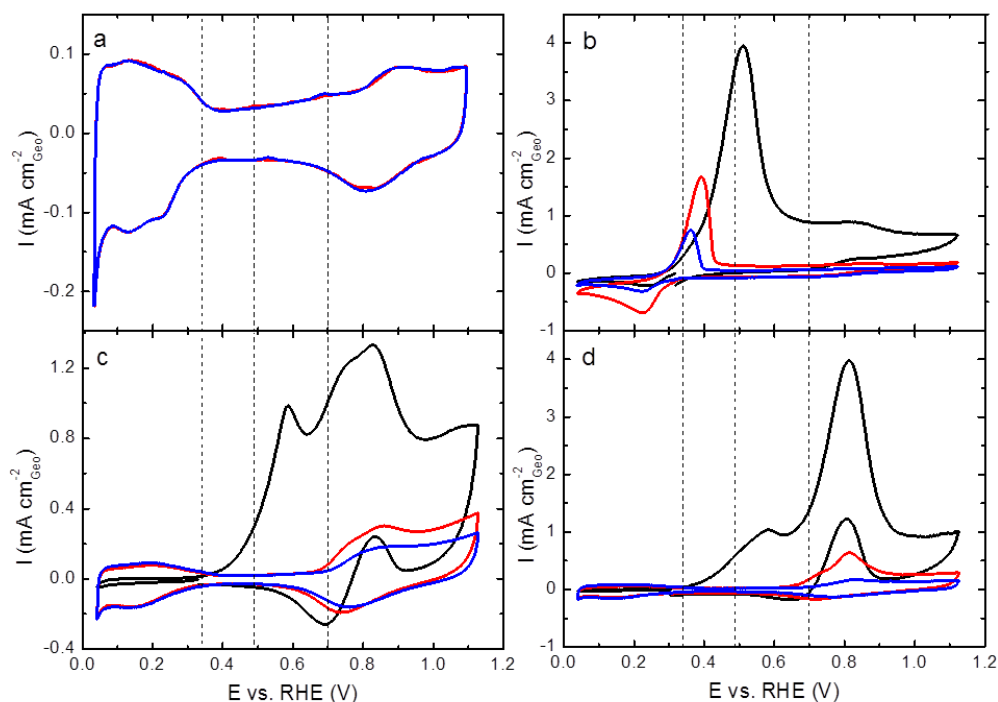


Figure 3.10 The first (black), third (red), and fifth (blue) CV scan for the dealloying process of PtCu-0 (a) and PtCu-150(b), PtCu-250 (c), and PtCu-350 (d). The vertical dashed lines are the thermodynamic minimums for the three model Cu dissolutions (bulk, surface alloy, and monolayer). The current densities are based on the electrode area.

Figure 3.10 shows the first, third, and fifth CV scans for PtCu(0, 150, 250, 350). PtCu-0 showed no sign of Cu dissolution in the initial scans, instead showing dissolution peaks indicative of pure platinum. This behavior suggested that no PtCu alloying is present at the surface of the sample.

The CV scan for PtCu-150, however, showed a large onset dissolution peak in the bulk Cu stripping regime and a minor peak in the monolayer Cu stripping zone. The existence of monolayer Cu in this sample was attributed to the migration of the bulk Cu onto Pt during the annealing process.^{65, 76-77} Over the first 5 scans of PtCu-150, the bulk

Cu dissolution peak decreased in magnitude, also showing a negative shift in potential. This behavior indicated a pure bulk Cu phase being stripped until only a Pt skin remains, also suggesting a low amount of PtCu alloying at the surface.

For PtCu-250, dissolution peaks were observed in the bulk regime followed by peaks in both the surface alloy and monolayer region. The twin peaks in the monolayer section implies the presence of a range of PtCu compositions in the surface structure. In addition, the broad overall peak pattern, with peaks shifted toward higher potentials, indicated a higher degree of mixing between Pt and Cu during annealing, compared to that seen in PtCu-150.^{65, 75} The subsequent scans showed the Cu monolayer being stripped off, leaving a pure Pt surface.

PtCu-350 expressed a minor peak in the surface alloy section with a primary peak in the monolayer sector. This indicated the highest degree of Cu migration in the samples prepared, suggesting extensive monolayer formation at the surface.⁶⁵ The succeeding 5 scans showed a decrease of the Cu monolayer peak, as expected.

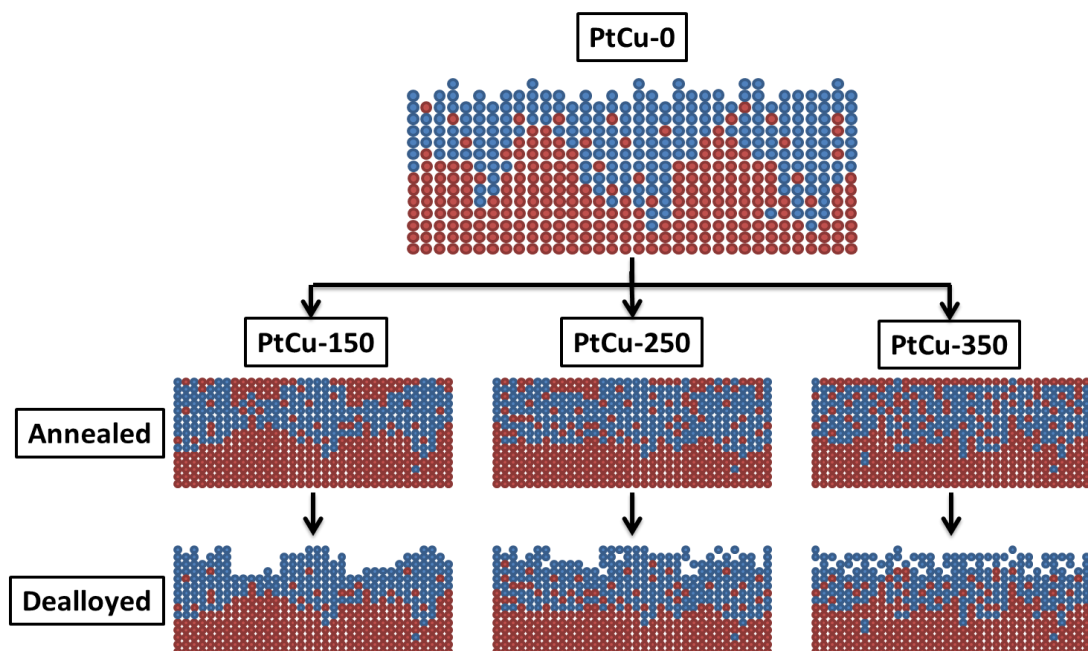


Figure 3.11 Schematic of the synthesis progression of PtCu/CuNWs from post synthetic Pt/CuNWs (PtCu-0) through the three model strain regimes, low (PtCu-150), medium (PtCu-250), and high (PtCu-350); and the respective dealloyed products. (Red circles – Cu; blue circles –Pt)

Based on the HRTEM and CV analysis of the PtCu-(0, 150, 250, 350), a schematic drawing was developed to represent the surface structures of the post-synthesis, annealed, and dealloyed samples (Figure 3.11). PtCu-0 demonstrates a rough surface covered by Pt bulk with little Cu alloying. After the sample is annealed at 150 °C, e.g., PtCu-150, the Pt expressed on the surface begins to settle into the Cu core, exposing bulk Cu to the surface. The increased annealing temperature of PtCu-250 resulted in higher mixing degrees of Cu and Pt bulk phases. The resulting product shows a stronger alloy formation, supported by the initial CV scans as well as the increased lattice compression. This trend continues as the annealing temperature is further

increased. PtCu-350 shows a fully alloyed PtCu surface partially encapsulated by monolayer Cu.

The dealloying for all three annealed samples strips away any surface Cu, leaving only an exposed Pt surface. For PtCu-150, a reduction in ECSA is observed because the Pt surface unearthed after bulk Cu stripping is smoother. Meanwhile, the PtCu-(250,350) showed an enhanced roughness due to the greater amount of surface-alloyed Cu stripped, leaving behind surface pores.

3.4 Conclusions

By incorporating post-synthesis processing (annealing and dealloying) into the synthesis of Pt/CuNWs (PtCu-0), a high-performance ORR catalyst with the ability to control induced lattice compression was obtained. These results show that tuning compressive strain in a Pt catalyst can optimize the Pt-O binding energy. Of the samples tested, PtCu-250 possessed the highest performance. Its compressive strain and low Pt content displayed a SA and MA of 2.30 mA cm^{-2} and 1.06 A mg^{-1} , respectively, surpassing the previously reported Pt/CuNWs and DOE activity targets. In addition, PtCu-250 maintained a high SA and ECSA, outperforming the DOE MA goals even after post-durability testing.

Analysis of lattice parameters and dealloying CVs showed that Pt/Cu mixing scaled with annealing temperature. Using this knowledge, surface structures were proposed for each PtCu sample, with PtCu-0 having the least Pt/Cu mixing and PtCu-350 displaying the most.

Ultimately, the simple, solution-based CuNW synthesis, coupled with the rapid Pt partial galvanic displacement and facile post-synthesis processing enhances prospects of the PtCu/CuNW catalyst for large scale commercial use in PEMFCs. However, application of these PtCu/CuNW catalysts is not limited to PEMFCs and may prove useful in other reactions, including the methanol oxidation reaction (MOR) and HOR in both acid and base. Furthermore, the concept of controlling compressive strain to tune the binding energy is quite general, and may prove insightful for future bimetallic catalysts.

Chapter 4

INVESTIGATION OF ALTERNATIVE CARBON SUPPORT DURABILITY FOR OXYGEN REDUCTION REACTION IN ACIDIC AND BASIC ENVIRONMENTS

Cathode catalyst durability issues are a major barrier to the commercialization of proton exchange membrane fuel cells, specifically carbon black supported Pt for the oxygen reduction reaction. Cup-stacked carbon nanofiber supports are a highly graphitic and cost effective alternative with the potential to solve these durability concerns. An alternative fuel cell design, the hydroxide exchange membrane fuel cell, transports hydroxide ions instead of protons, which generates a basic environment and has the potential to increase overall catalyst durability. Pt supported on carbon black (Vulcan XC-72) and cup-stacked carbon nanofibers as well as each isolated carbon support underwent a high potential accelerated durability test in acidic and basic environments using rotating disk electrode experiments. It was shown that in all environments the cup-stacked carbon nanofiber support demonstrated higher durability and the catalysts tested in the basic environment had better overall stability compared to their acidic counterpart.

4.1 Introduction

Polymer electrolyte membrane fuel cells are a clean and efficient power generation device that electrochemically combines hydrogen and oxygen through two half reactions: the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode. The conventional polymer electrolyte

membrane fuel cell, proton exchange membrane fuel cell (PEMFC), can reach high peak power densities of 2 W cm^{-2} or higher.⁷⁸⁻⁷⁹ In order to achieve these high power densities, platinum catalysts supported on carbon black are used.⁵³⁻⁵⁴ While high power is achievable, the acidic conditions of this fuel cell, as well as the high potential environment of the cathode, generate considerable durability concerns. Durability combined with the high cost of materials creates a significant commercialization barrier for these electrochemical devices.¹¹

Supported catalyst durability is limited by the corrosion of the carbon support and the loss of Pt electrochemical surface area (ECSA) through three main mechanisms: coarsening (Ostwald ripening), coalescence, and dissolution of Pt nanoparticles.²⁹⁻³⁰ Carbon black supports can also undergo electrochemical oxidation to form surface oxides and finally carbon dioxide (CO_2).³⁶ Additionally, during startup and shutdown, O_2 -rich sections of the anode can perform ORR, elevating regions of the cathode to extremely high potentials ($\sim 1.4 \text{ V}$), which further speeds up carbon corrosion. This phenomenon is known as reverse current decay (RCD).⁸⁰⁻⁸² The loss of carbon support will lead to dislocation of Pt nanoparticles from the electrode or a reduction of Pt ECSA through Pt agglomeration.¹¹ Even the partial oxidation of the carbon support changes the surface hydrophobicity, which leads to both water and gas transport difficulties.³⁶ Consequently, new promising catalysts are required to be cheaper, more active, and more durable than the conventional carbon black supported Pt nanoparticles.

Strategies to improve catalyst durability include generating a support-less catalyst, as shown in our previous work⁵², or increasing the durability of the catalyst

support. Nanostructured carbon supports (e.g. multi-walled carbon nanotubes (MWCNT), carbon nanofibers, and graphene)^{11, 36, 49, 83} have reduced surface defects and greater graphitic nature, which enhances their resilience to corrosion when compared with traditional carbon black supports.³⁶ Additionally, these nanostructured supports have the potential to anchor Pt nanoparticles stronger than carbon black supports, decreasing Pt loss over extended periods.⁸³ The high cost of MWCNT (\$20-50 g⁻¹) hinders their commercialization; however, the relatively cheap cost of carbon nanofibers (\$0.01-0.02 g⁻¹), in particular cup-stacked carbon nanofibers (CS-CNF), makes these nanostructured supports an attractive option.⁸³

Another alternative to reduce costs in polymer electrolyte membrane fuel cells is to utilize a hydroxide exchange membrane (HEM) instead of a proton exchange membrane. HEMs transport hydroxide ions instead of protons and generate a basic environment that allows for a wider variety of stable catalytic materials to be used. However, the question of catalyst durability in hydroxide exchange membrane fuel cells (HEMFCS), especially at the high potentials in the cathode, has yet to be sufficiently addressed.⁸⁴⁻⁸⁵ In this paper, we compare the stability of Pt supported on carbon black (Vulcan XC-72) and CS-CNFs in both acid and base electrolytes. Both the Pt-catalyzed and non-catalyzed supports will be investigated. A high potential (1.4 V vs RHE) accelerated durability test (ADT) was conducted to show the differences in stability of the carbon supports through the change in ECSA and ORR performance at 0.9 V vs RHE for the Pt containing catalysts and the specific charge of the non-catalyzed carbon supports.

4.2 Methods

4.2.1 Synthesis of Pt/CNF

The four materials investigated are E-tek 30% Pt/Vulcan XC-72 (Pt/C), Vulcan XC-72 (C), 30% Pt/CS-CNF (Pt/CNF), and CS-CNF (CNF). Pt/CNF catalyst was prepared through a modified ethylene glycol (EG) synthesis. Initially the CNFs were pre-oxidized in a solution of 2.0 M H_2SO_4 and 4.0 M HNO_3 at reflux (110 °C) for 8 h. Next the surface-activated CNFs were suspended in an EG solution and hexachloroplatinic acid in EG was added dropwise under an inert headspace. The pH was adjusted to 12 with sodium hydroxide in EG. After mixing properly, the solution was heated to 135 °C for 3 h and then cooled overnight. The pH was then lowered to 2 with an aqueous solution of hydrochloric acid. The resulting Pt/CNFs were filter collected and dried overnight in a vacuum oven at 180 °C.^{36, 83, 86}

4.2.2 Electrochemical measurements

Catalyst ink solutions were generated from a 1.503 mg mL^{-1} (catalyzed) and 1.052 mg mL^{-1} (non-catalyzed) water dispersion of catalyst particles. A thin film catalyst layer was deposited on a 5 mm glassy carbon working electrode (Pine Instruments) by pipetting 15 μL of catalyst ink. A final catalyst loading of 115 $\mu\text{g cm}^{-2}$ (catalyzed) and 80.5 $\mu\text{g cm}^{-2}$ (non-catalyzed) was achieved. The carbon loading was held constant (80.5 $\mu\text{g cm}^{-2}$) in all films tested to more accurately compare the carbon corrosion on the tested materials. An additional 10 μL drop of 0.05 % Liquion binder solution was dropped onto the catalyst surface to maintain adhesion during the ADT.

Rotating disk electrode (RDE) experiments were conducted in a three-electrode cell equipped with a saturated calomel reference electrode (SCE), Pt wire counter electrode, and the catalyst coated working electrode. The cell was controlled by a multichannel potentiostat (VMP2, Princeton Applied Research) and the working electrode was connected to a modulated speed rotator (Pine Instruments). All acid tests were performed in 0.1 M perchloric acid (HClO_4) (diluted from 70% HClO_4 , EMD Millipore) and all base tests were performed in 0.1 M potassium hydroxide (KOH) (Sigma-Aldrich semiconductor grade, 99.99%).

To probe the stability of the catalysts in the different environments a high potential ADT was utilized. A potential of 1.4 V vs RHE was applied in the presence of Ar for 24 h and the corrosion current was measured. In between every 24 h test, electrode characterization was performed; ECSA and ORR activity were measured for Pt containing catalysts and a cyclic voltammogram (CV) was measured for the non-catalyzed carbon supports. The test was carried out for a total of 7 days.³⁶

To determine ECSA, the CV measurement was taken from 0.05 - 1.1 V vs RHE in acid and 0.05 – 1.0 V vs RHE in base at a scan rate of 50 mV s^{-1} in saturated Ar.⁷¹ A lower upper potential bound is used in base to lessen the effects that the Pt-O has on the H_{UPD} scan window. The ECSA was determined from the double layer corrected average charge of the Pt under-potential deposited hydrogen (H_{UPD}) adsorption and desorption regions between 0.05 V and 0.4 V (the onset of the double layer region), assuming a Pt surface charge density of $210 \mu\text{C cm}_{\text{Pt}}^{-2}$.²¹

On the carbon-only film, a CV was taken from 0.2 - 0.9 V vs RHE at a scan rate of 10 mV s⁻¹ in a saturated Ar solution. The current measured in this voltage window is related to the surface oxidation of the carbon.³⁶ The charge calculated from these curves demonstrates the change in surface oxidation of the carbon films.

ORR measurements were performed from 0.05 - 1.1 V vs RHE at 20 mV s⁻¹ in saturated O₂ at a rotation rate of 1600 rpm. The kinetic current (i_k) was calculated from the Koutecky-Levich equation (Eq. 4.1),

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (4.1)$$

where i_d is the diffusion limiting current and i is the measured current. Mass activity (MA) were determined from normalizing the kinetic current of the anodic scan at 0.9 V vs. RHE.⁷¹⁻⁷² The diffusion limiting current was determined experimentally the current at high ORR overpotentials and verified against the calculated diffusion limited current calculated from Eq. 3.2.

$$i_d = 0.62zFD^{2/3}\omega^{1/2}\nu^{-1/6}c_o \quad (5.2)$$

Where z is the number of electrons involved in the reaction, F is Faraday's constant, D is the diameter of the RDE electrode, ω is the rotation rate, ν is the kinematic viscosity, and c_o is the concentration of the reactant in the bulk of the solution. For the ORR at 1600 RPM the theoretical i_d is 5.8 mA cm⁻².

4.2.3 TGA, XRD, and Microscopy

Thermogravimetric analysis (TGA, Metler Toledo) was performed on the samples to identify Pt loading as well as detect thermal stability of both the catalyzed and non-catalyzed samples. The temperature was scanned from 25 - 1000 °C at a ramp of 10 °C min⁻¹ under an air atmosphere.

X-ray diffraction (XRD) measurements were taken with a monochromatic Cu K α 1 line with a Bruker D8 XRD. Scanning electron microscopy (SEM) images were taken at 9 kV with a JSM-7400F microscope. Transmission electron microscopy (TEM) images were taken at 200 kV with a JEM-2010F microscope. The TEM samples were prepared by adding a drop of the catalyst suspensions on lacey carbon Cu grids (Ted Pella, Inc.).

4.3 Results and Discussion

4.3.1 Physical Characterization and Thermal Degradation

Pt/CNFs were synthesized with a Pt particle size of 2.8 ± 0.5 nm, which is comparable to the commercial Pt/C sample's 2.6 ± 0.4 nm. Both samples had a Pt loading of 30% determined through TGA measurements. The XRD of the samples shows more graphitic carbon in the CNF supported samples. This more stable form of carbon is known to demonstrate an enhanced stability. (Figure 4.1)

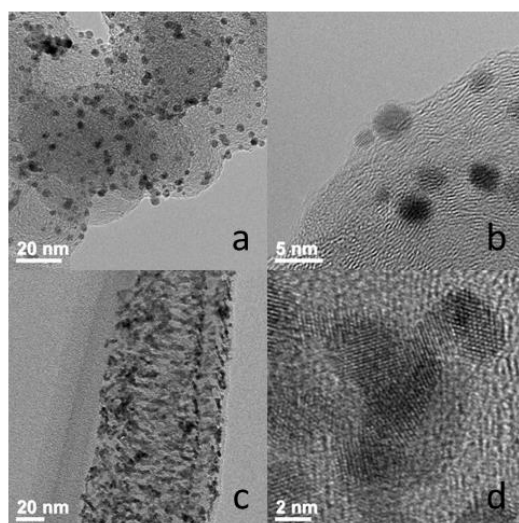
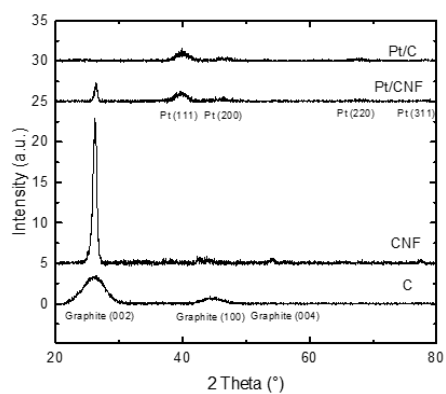


Figure 4.1 XRD (top) of Pt/C, Pt/CNF, CNF, and C samples. TEM (bottom) images of Pt/C (a-b) and Pt/CNF (c-d) taken before durability testing is performed.

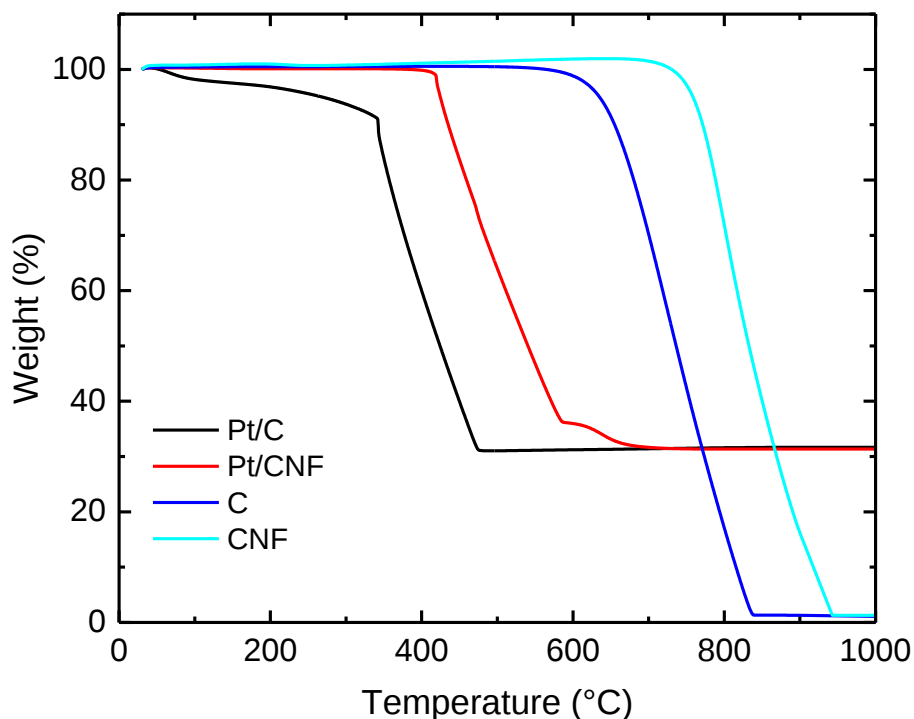


Figure 4.2 TGA analysis of Pt/C, Pt/CNF, C, and CNF samples. Temperature was ramped from 25 – 1000 °C at a ramp of 10 °C min⁻¹ under an air atmosphere.

Thermal stability of all the samples were tested through TGA experiments (Figure 4.2). CNF based materials demonstrated a higher thermal stability than the C based ones. The non-catalyzed CNF's onset of thermal degradation occurred at 800 °C where the C degraded at 650 °C. The catalyzed samples mirror this trend as well. Pt/CNF begins thermal decay at 400 °C, whereas the Pt/C starts at 320 °C. This enhanced thermal stability is due to the higher graphitic content of the CNF support.

4.3.2 Electrochemical ADT

4.3.2.1 Corrosion Current Analysis

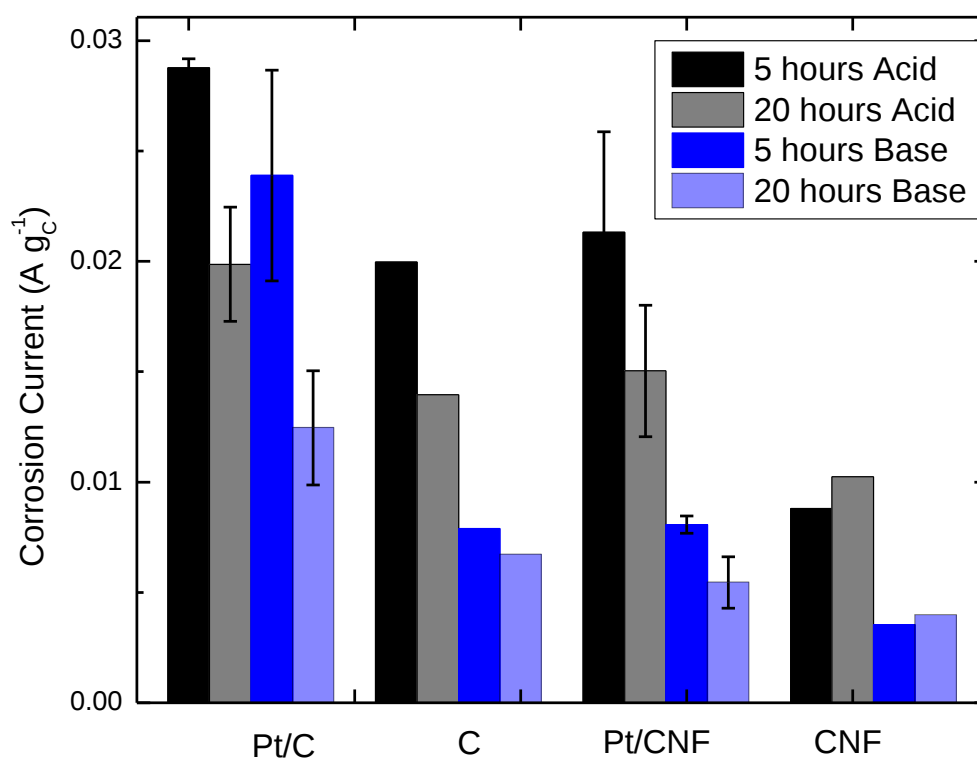


Figure 4.3 Corrosion current measured during the first day of the ADT. Two different segments of the data are displayed, the first during the initial part of the test (5 hours in) and the second is towards the end of the 24-hour test (20 hours). A 20-minute window of times were averaged to get each single data point and three repetitions of the Pt containing catalysts were performed. Error bars represent standard error of three repetitions of Pt catalyzed support samples.

The current measured during the ADT correlates with the corrosion of the catalyst tested. The corrosion current was plotted for each of the materials tested in both acidic and basic environments (Figure 4.3). The addition of Pt to the supporting material

clearly increases the corrosion of the material tested in all media and for all supports. The Pt/C and C catalysts demonstrate higher corrosion current compared to the Pt/CNF and CNF catalysts. The basic environment shows a lower corrosion current than the acid test for all materials tested. These results show that the CNF based catalysts degrade slower while being exposed to the same ADT and that a basic environment will show less corrosion on the catalyst.

4.3.2.2 ECSA and Surface Oxidation Analysis

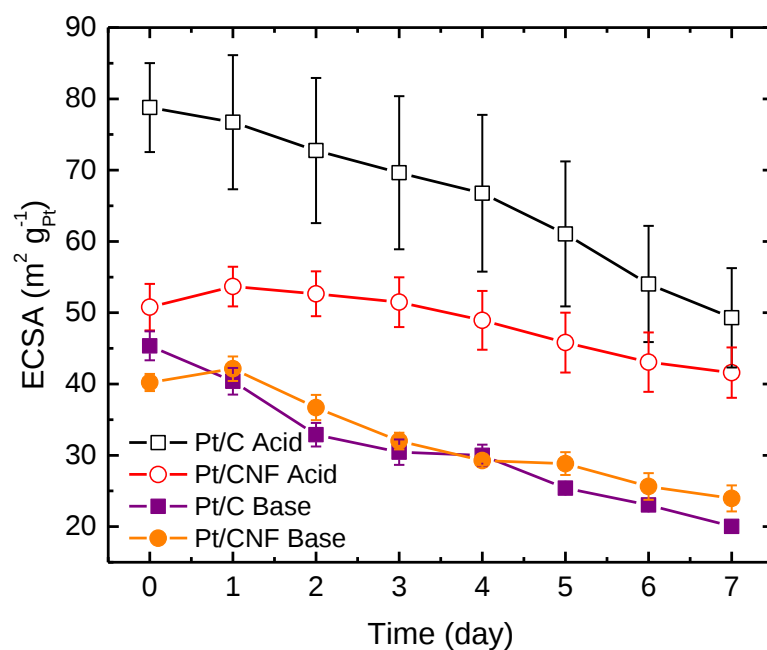


Figure 4.4 ECSA for Pt containing catalysts in acid and base calculated from the double layer corrected H_{UPD} region of the CV. The CV scans for ECSA measurements were taken at 50 mV s^{-1} in Ar saturated 0.1 M HClO_4 or 0.1 M KOH . Error bars represent the standard error of all repetitions.

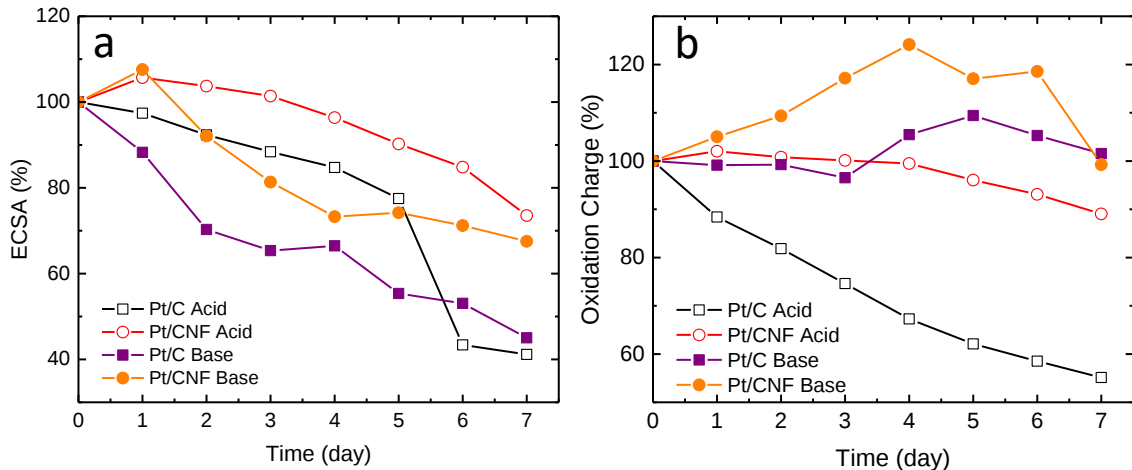


Figure 4.5 (a) ECSA normalized to initial value for Pt containing catalysts in acid and base. (b) Charge associated with the oxidation region of the CV scans for ECSA measurements were taken at 50 mV s^{-1} in Ar saturated 0.1 M HClO_4 or 0.1 M KOH .

ECSAs values were calculated from Pt/C and Pt/CNF CV curves in acid and base solutions at the start of the test and every 24 h during the ADT (Figure 4.4). The ECSA was determined from the double layer corrected H_{UPD} region of the CV scans shown in Figure 4.6. The initial ECSAs for Pt/C and Pt/CNF in acid are 78.8 ± 6.2 and $50.8 \pm 3.3 \text{ m}^2 \text{ g}^{-1}$ and in base are 44.2 ± 2.2 and $41.1 \pm 1.1 \text{ m}^2 \text{ g}^{-1}$. The lower of ECSA values measured in base compared to acid are a result of the up-shift in H_{UPD} and down shift in OH adsorption potentials.^{15, 87-88} This leads to a larger double layer region and a smaller measured ECSA. This effect is more pronounced for the Pt/C samples due to the larger double layer measured for amorphous carbon supported samples.¹⁵ The final ECSA after 7 days of testing for Pt/C and Pt/CNF in acid are: 49.3 ± 6.9 and $41.6 \pm 3.5 \text{ m}^2 \text{ g}^{-1}$ and in base are: 20.0 ± 0.1 and $23.9 \pm 1.8 \text{ m}^2 \text{ g}^{-1}$. The CNF supported Pt catalysts maintain a greater ECSA (73.5 % for acid and 67.5 % for base) at the end of the test

(Figure 4.5a). The C supported samples only show 41.2 % and 45.0 % for the acid and base respectively.

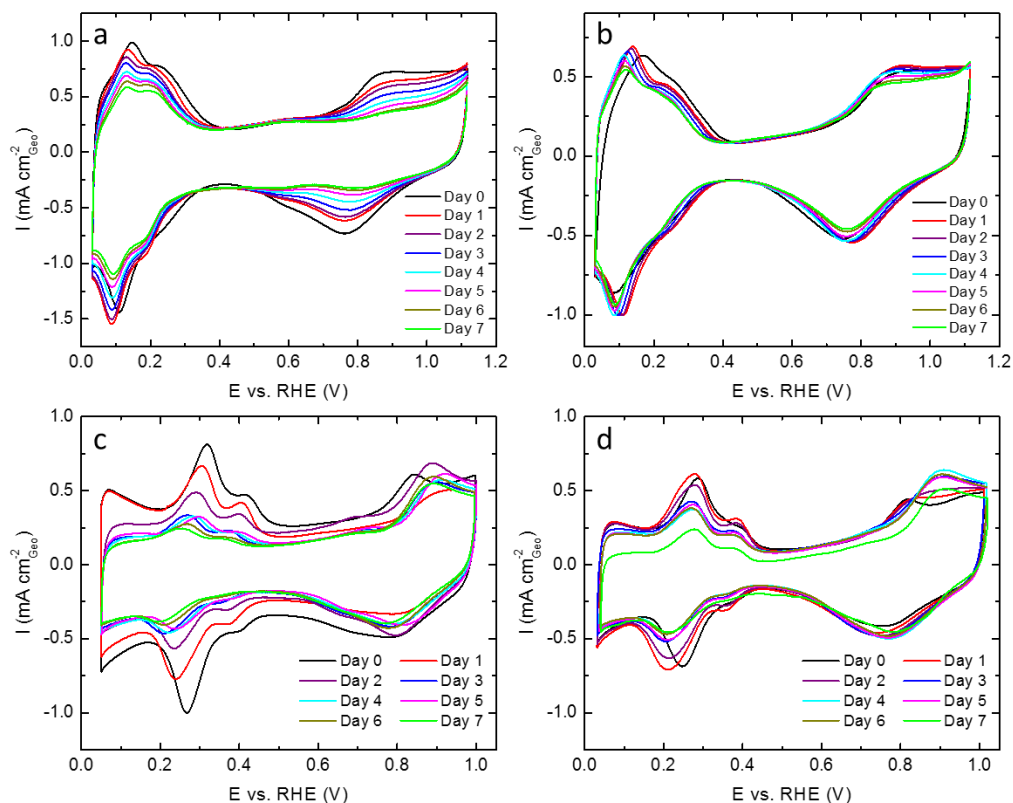


Figure 4.6 CV scans for ECSA measurements taken initially and every day during the ADT for (a) Pt/C in acid, (b) Pt/CNF in acid, (c) Pt/C in base, and (d) Pt/CNF in base. The conditions of the CV scans are 50 mV s^{-1} in either Ar saturated 0.1 M HClO_4 or 0.1 M KOH between $0.05 - 1.1 \text{ V}$ vs RHE in acid and $0.05 - 1.0 \text{ V}$ vs RHE in base.

On initial inspection, it appears that the ECSA is both initially higher and more stable, or at least similarly stable, in acid than base. The higher ECSA observed in acid compared to base is typically observed on similar catalysts.⁸⁷⁻⁸⁸ The two main reasons for the ECSA differences are the greater double layer in basic solutions caused by the increased polarizability of the potassium cation compared to the hydrogen cation and

the earlier onset of Pt oxidation which interferes with H_{UPD} . Interaction of Pt oxidation in base also causes the observed ECSA stability in acid. Over the first few days of the durability test, the Pt-O peaks of the CVs are enhanced then stay relatively constant. In acid, the Pt-O peaks steadily decrease over the course of the test (Figure 4.5b). Also, it is important to note that there is an increase in the Pt oxidation potential in base over the first few days of the test (Figure 4.6). This is indicating a shift from reversible Pt oxidation to a more irreversible form of Pt oxidation.⁸⁹ When the rate of ECSA loss over the whole test is compared to the rate of ECSA loss after this initial transition of Pt oxidation is compared, the stability conclusions change (Figure 4.7). We see that the rate of corrosion slows down for both base samples and while the acid ECSA loss speeds up for both catalysts. This change in corrosion indicates that the initial loss in CV for the base samples is due to an increased Pt-O coverage and that is interfering with the Pt- H_{UPD} adsorption.

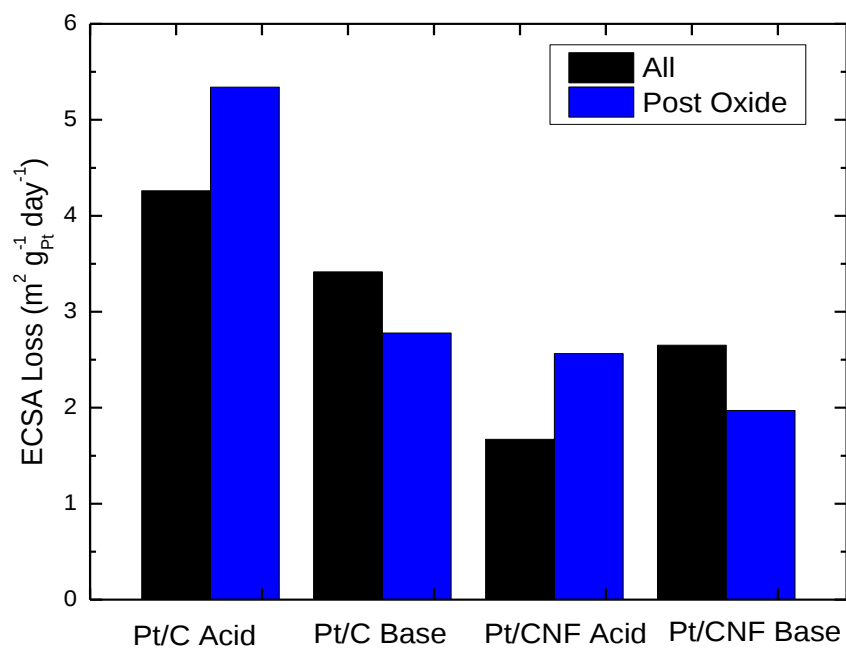


Figure 4.7 ECSA loss and ECSA post oxidation period (72 hours) for Pt containing catalysts in acid and base.

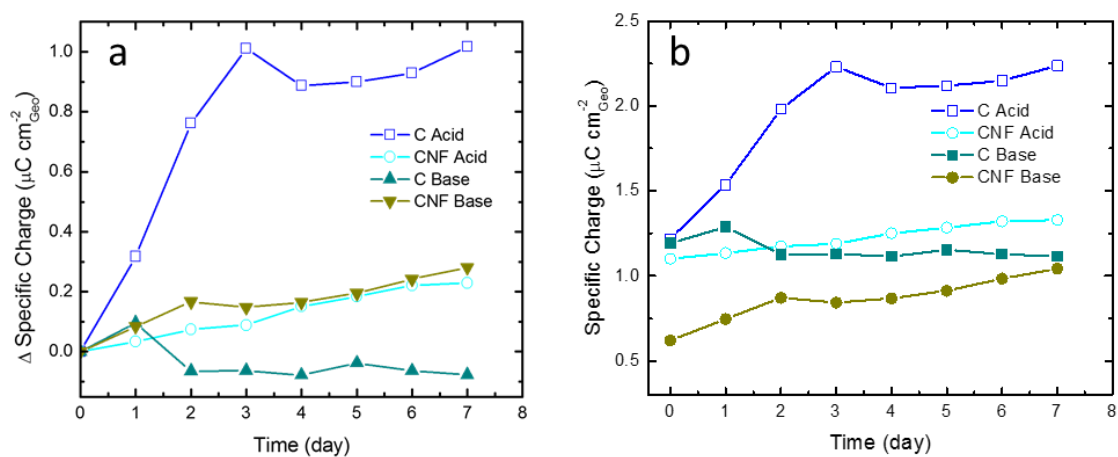


Figure 4.8 (a) Change in charge for the carbon containing catalysts corrected for the initial charge. (b) Absolute specific charge measured initially and after each ADT. CV

scans for specific charge measurements were taken at 10 mV s^{-1} in Ar saturated 0.1 M HClO_4 or 0.1 M KOH .

The capacitance of the non-catalyzed supports was measured from the CV scans and the change in capacitance over the 7-day test period was plotted (Figure 4.8a). The capacitance represents the surface oxidation of the carbon.^{34, 36} C in acid shows the highest propensity for surface oxidation. During the first three days there is an increase in the surface oxidation of C followed by period of constant surface oxidation. This period of constant surface oxidation hints at an equilibrium with bulk carbon corrosion and surface oxidation.³⁶ The trend in the difference of specific charge also shows that the CNF without Pt is relatively resistant to oxidation in both pH environments. This is due to the defect free surface of the graphitic CNFs.⁸³ The C surface oxidation is also dramatically reduced in the basic environment. This infers that the amorphous carbon structure is more stable in the basic environment. The absolute capacitance (Figure 4.8b) shows the CNF with a lower overall capacitance compared to the other samples and that the initial surface oxidation in both acid and base for the C samples are about the same. The difference in initial capacitance between the acid and base CNF tests demonstrates that the HClO_4 solution is able to rapidly oxidize the surface of the CNF to some degree, but after the initial oxidation relatively little electrochemical oxidation takes place.^{83, 90}

4.3.2.3 ORR Performance

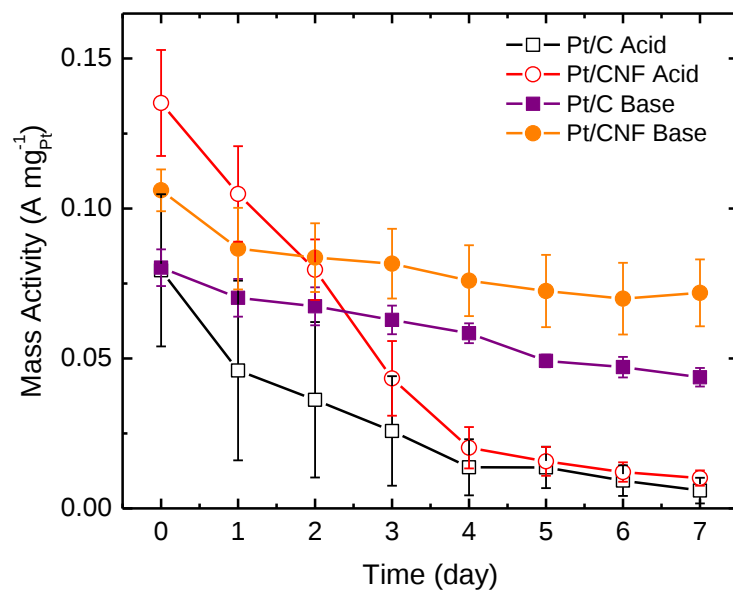


Figure 4.9 MA for Pt containing catalysts measured initially and every day during the ADT. ORR scans were taken at 20 mV s^{-1} and 1600 rpm in O_2 saturated 0.1 M HClO_4 or 0.1 M KOH . Activity was determined from the kinetic current at 0.9 V vs RHE.

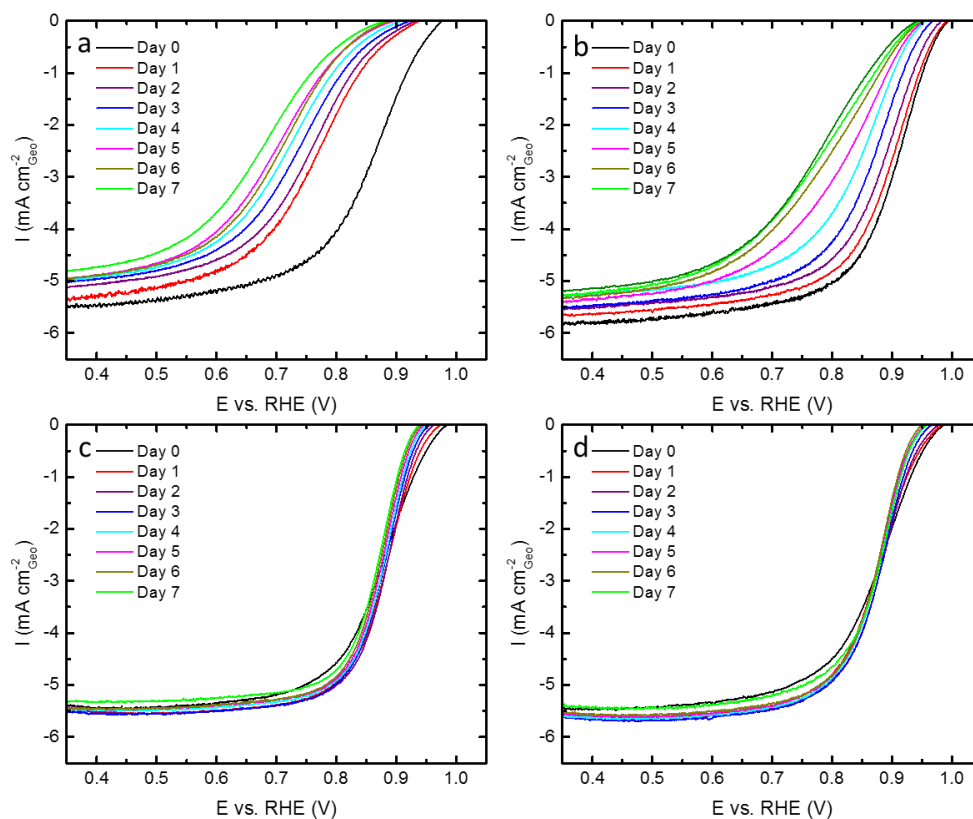


Figure 4.10 Anodic polarization curves taken initially and every day during the ADT for (a) Pt/C in acid, (b) Pt/CNF in acid, (c) Pt/C in base, and (d) Pt/CNF in base. The conditions of the polarization scans are 20 mV s^{-1} at 1600 rpm in either O_2 saturated 0.1 M HClO_4 or 0.1 M KOH between $0.05 - 1.1 \text{ V}$ vs RHE.

ORR MA was presented for C and CNF supported Pt in acid and base environments over the seven day ADT (Figure 4.9). The ORR MA was determined from the anodic polarization curves shown in Figure 4.10. The initial ORR performance for C and CNT in acid and base environments are as follows: $0.0794 \pm .025$, 0.135 ± 0.017 , 0.0739 ± 0.0039 , and $0.105 \pm 0.0084 \text{ A mg}^{-1}$. The final ORR performance for C and CNF in acid and base environments are as follows: $2.95\text{E-}4 \pm 1.1\text{E-}4$, 0.0123 ± 0.011 , 0.0400 ± 0.0043 , and $0.0697 \pm 0.010 \text{ A mg}^{-1}$. The CNF supported catalysts demonstrate

a higher activity when compared to the C supported ones and the ORR performance in base is much more stable on both supports when compared to their acid counterparts (Figure 4.11).

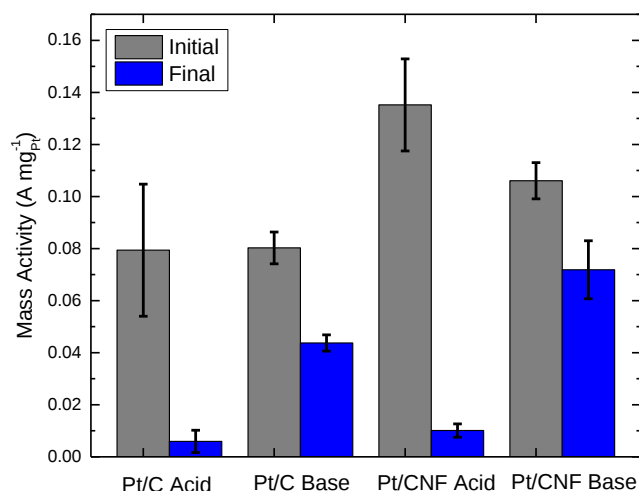


Figure 4.11 Initial and final ORR measurements plotted for Pt containing catalysts. ORR scans were taken at 20 mV s^{-1} and 1600 rpm in O_2 saturated 0.1 M HClO_4 or 0.1 M KOH . Activity was determined from the kinetic current at 0.9 V vs RHE.

In the basic environment, both C and CNF catalysts show relatively similar stability (30-40 %) where the acid catalysts lose nearly all ORR activity. The stability trend indicates that in the acid solution there is still Pt available for H_{upd} adsorption, but the Pt surfaces is deactivated almost entirely for ORR. In the basic environment, the enhanced Pt-O that is observed in the CV scans seems to protect the Pt surface allowing it to maintain a higher ORR performance. The more stable CNT support also seems to provide a better platform for enhanced catalyst stability, but the enhancement is much less significant in the base environment.

4.4 Conclusions

Using a high-potential ADT in both acidic and basic environments, an enhanced stability of Pt supported on carbon catalysts and carbon supports in base is demonstrated. In base, a lower corrosion current is observed for all materials, a more stable ECSA is attained (after the initial Pt oxidation period), a more stable carbon capacitance (surface oxidation), and a relatively constant ORR performance is observed over the course of the ADT. It is also demonstrated that CNF supported catalysts possess a higher stability and performance over their C supported counterparts. Aside from Pt/C's higher initial ECSA, the CNF catalysts outperform the C samples in every way; although, this difference in performance is much greater in acid than in base.

In summary, the stability of supported Pt catalysts for ORR is not as serious of an issue for HEMFCs as it is for PEMFCs. More durable carbon supports can still help facilitate higher performance over the HEMFC's life, but unlike the acid environment in the PEMFC where carbon black will not survive the harsh environment, a more cost-effective carbon support should be utilized.

Chapter 5

PERFORMANCE AND DURABILITY FOR NON-PRECIOUS METAL CATALYSTS FOR THE OXYGEN REDUCTION REACTION IN HYDROXIDE EXCHANGE MEMBRANE FUEL CELLS

The cost associated with the Pt catalyst required to withstand the acidic environment of traditional proton exchange membrane fuel cell (PEMFC) is a major barrier for the commercialization of this clean energy alternative. An alternate configuration utilizing the transport of basic hydroxide ions is known as a hydroxide exchange membrane fuel cell (HEMFC). The HEMFC has the potential for incorporating a wide variety of non-precious metal catalysts and hopes to dramatically lower the material cost associated with fuel cell manufacturing. One particular non-precious metal catalyst that is commercially available is Acta 4020. This carbon-based catalyst containing 3.5 wt. % transition metals demonstrates oxygen reduction reaction (ORR) performance comparable to Pt supported on carbon (Pt/C) catalysts. In this paper, we demonstrate comparable performance and superior durability while exposed to a potential cycling (0.6 – 1.1 V vs RHE) accelerated durability test (ADT). Fuel cell data is also shown demonstrating the feasibility of the incorporation of this non-precious metal catalyst into the cathode electrode of a membrane electrode assembly (MEA).

5.1 Introduction

Proton exchange membrane fuel cell (PEMFC) technologies for automotive applications is a clean and efficient alternative to conventional combustion engines. A

fuel cell is a power generating device that electrochemically combines hydrogen and oxygen through two half reactions: the hydrogen oxidation reaction (HOR) at the anode and the oxygen reduction reaction (ORR) at the cathode. PEMFCs can reach high peak power densities of 2 W cm^{-2} or higher.⁷⁸⁻⁷⁹ In order to achieve these high power densities and survive the harsh acidic conditions of the PEMFC, platinum catalysts supported on carbon black are used.⁵³⁻⁵⁴ High material costs create a significant commercialization barrier for these electrochemical devices.¹¹ In order to drive commercialization of fuel cell technologies, the US Department of Energy (DOE) has established several benchmarks for fuel cell performance, durability, and cost.⁹¹ State of the art fuel cells are able to surpass all performance and durability benchmarks, but the long term fuel cell cost target of US $\$30 \text{ kW}^{-1}$ or approximately US $\$2,400$ per vehicle is still out of reach.¹⁶⁻¹⁷ Over the past 15 years the mass-produced cost estimate for an automotive fuel cell has dropped from US $\$248 \text{ kW}^{-1}$ to US $\$52 \text{ kW}^{-1}$.¹⁸⁻¹⁹ The main driver for this cost reduction is an increased power density and stability of the catalyst and membrane materials along with the reduced platinum (Pt) catalyst loading in the fuel cell electrodes. But, even with the current state of the art technology, the automotive fuel cell is too expensive for commercialized. The cost associated with a fuel cell with reduced Pt loadings ($0.22 \text{ g kW}_{\text{net}}^{-1}$) only accounts for 20 % of the total cost of the device (US $\$10.57 \text{ kW}^{-1}$).¹⁶ Further cost reduction could be achieved with increasing catalyst utilization, but even if the Pt cost were completely removed the overall PEMFC cost is still greater than the DOE's cost benchmark. Therefore, hydroxide exchange membrane fuel cells (HEMFC) have been investigated.¹³

HEMFC's alkaline environment allows cheap earth-abundant non-precious metal catalysts in the anode and cathode electrodes nearly eliminating the HEMFC's catalyst cost. As stated before, this cost reduction alone is not enough. The enhanced stability of the HEMFC's alkaline environment allows for less expensive metals and coatings to be used in the fuel cells bipolar plates. Additionally, a hydrocarbon-based membrane and ionomer is used for hydroxide transport instead of PEMFC's costly perfluorinated counterpart.^{24, 92-93} Finally, in order to achieve high power with reduced Pt loading the PEMFC requires system operational parameters that lead to high cost in components such as the air loop.¹⁶ For the HEMFC these operational parameters can be re-optimized to reduce cost of these expensive components.¹⁸ With all of the potential cost savings associated with the HEMFC it is realistic to assume this technology can bring the total fuel cell cost closer to the US\$30 KW⁻¹ target.

As stated previously, HEMFS's alkaline environment allows for more options in choosing high performance and cost effective anode and cathode catalysts.²¹ The HEMFC undergoes the same half-reactions as the PEMFC, but due to the alkaline environment the absolute potential window is shifted. A PEMFC operates between 0 V vs SHE (HOR/HER) and 1.23 V vs SHE (ORR/OER); whereas a HEMFC operates between -0.83 V vs SHE (HOR/HER) and 0.4 V vs SHE (ORR/OER).⁵⁰ This shift allows for the use of more earth abundant materials such as nickel (Ni, $E^0 = -0.26$ V vs SHE), cobalt (Co, $E^0 = -0.28$ V vs SHE), copper (Cu, $E^0 = 0.34$ V vs SHE), and even carbon (C, 0.21 V vs SHE). For the PEMFC only noble metals such as ruthenium (Ru,

$E^{\circ} = 0.46 \text{ V vs SHE}$), palladium (Pd, $E^{\circ} = 0.95 \text{ V vs SHE}$), iridium (Ir, $E^{\circ} = 1.16 \text{ V vs SHE}$), and platinum (Pt, $E^{\circ} = 1.18 \text{ V vs SHE}$).⁹⁴

However, the question of catalyst durability in hydroxide exchange membrane fuel cells (HEMFCs), especially at the high potentials in the cathode, has yet to be sufficiently addressed.⁸⁴⁻⁸⁵ In this paper, we compare the performance and durability of Pt supported on carbon black (Pt/C Tanaka Kikinzoku Kogyo, 46 % Pt) and the carbon based ORR catalyst Acta 4020 (ACTA S.P.A). An accelerated durability test (ADT) based off the DOE's PEMFC potential cycling (0.6 - 1.1 V vs RHE) ADT was conducted to show the differences in stability between the carbon based Acta catalyst and traditional Pt/C based catalysts.^{52, 57, 95} Electrochemical surface area (ECSA) for Pt/C catalyst, change in specific charge for the Acta catalyst, and ORR performance at 0.9 V vs RHE for both catalysts were used as criteria for the stability comparison.⁹⁶ The non-precious metal catalyst, Acta 4020, was also demonstrated in the cathode of a HEMFC to show the feasibility for incorporation into the fuel cell as well as illuminate potential issues of a new catalyst system.

5.2 Method

5.2.1 Electrochemical measurements

Catalyst ink solutions for Acta (ACTA S.P.A, Acta 4020 cathode catalyst, 3.5 wt. % transition metal) and Pt/C (Tanaka Kikinzoku Kogyo, or TKK, 46% Pt on high-surface-area C) were generated from a 1.31 mg mL^{-1} water dispersion of catalyst particles. A thin film catalyst layer was deposited on a 5 mm glassy carbon working

electrode (Pine Instruments) by pipetting 15 μL of catalyst ink to achieve a final catalyst loading of $100 \mu\text{g cm}^{-2}$. This relates to a Pt-equivalent loading for the Pt/C catalyst of $46 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. An additional 10 μL drop of 0.05 % Liquion binder solution was dropped onto the catalyst surface to maintain adhesion during the ADT.

Rotating disk electrode (RDE) experiments were conducted in a three-electrode cell equipped with a saturated calomel reference electrode (SCE), Pt wire counter electrode, and the catalyst coated working electrode. The cell was controlled by a multichannel potentiostat (VMP2, Princeton Applied Research) and the working electrode was connected to a modulated speed rotator (Pine Instruments). All tests were performed in 0.1 M potassium hydroxide (KOH) (Sigma-Aldrich semiconductor grade, 99.99%)

To determine electrochemical surface area (ECSA) for the Pt/C catalyst, a cyclic voltammogram (CV) measurement was taken from 0.05 – 1.0 V vs RHE in base at a scan rate of 50 mV s^{-1} in saturated Ar.⁷¹ A lower upper potential bound compared to the ADT is used to lessen the effects that the Pt-O has on the H_{UPD} scan window. The ECSA was determined from the double layer corrected average charge of the Pt under-potential deposited hydrogen (H_{UPD}) adsorption and desorption regions between 0.05 V and 0.4 V (the onset of the double layer region), assuming a Pt surface charge density of $210 \mu\text{C cm}_{\text{Pt}}^{-2}$.¹⁵

On the Acta catalyst film, specific charge found from CV measurements taken from 0.05 - 1.0 V vs RHE at a scan rate of 10 mV s^{-1} in a saturated argon (Ar) solution. The current measured in this voltage window is related to the surface oxidation of the

carbon.³⁶ The charge calculated from these curves demonstrates the change in surface oxidation of the carbon films.

ORR measurements were performed from 0.05 - 1.1 V vs RHE at 20 mV s⁻¹ in saturated O₂ at a rotation rate of 1600 rpm. The kinetic current (i_k) was calculated by extracting the diffusion limiting current (i_d) component from the measured current (i) with the Koutecky-Levich equation (Eq. 5.1):

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d} \quad (5.1)$$

The diffusion limiting current can be determined experimentally from the measured current at high overpotentials where the current value levels off or can be calculated for a rotating disk from Eq. 5.2.

$$i_d = 0.62zFD^{2/3}\omega^{1/2}\nu^{-1/6}c_o \quad (5.2)$$

Where z is the number of electrons involved in the reaction, F is Faradays constant, D is the diameter of the RDE electrode, ω is the rotation rate, ν is the kinematic viscosity, and c_o is the concentration of the reactant in the bulk of the solution. For the ORR reaction at 1600 RPM the theoretical i_d is 5.8 mA cm⁻². Lower measured diffusion limiting current indicates inconsistencies in the catalyst film or electrochemically isolated catalyst on the electrode surface. ORR activity was determined from the kinetic current at 0.9 V vs. RHE from the anodic scan for Pt/C and the cathodic scan for the Acta catalyst.^{71-72, 97}

5.2.2 Accelerated durability test

To compare the durability of the catalysts an ADT was conducted via potential cycling at 50 mV s^{-1} between 0.6 and 1.1 V vs RHE in an Ar saturated solution. Electrode characterization and ORR performance was measured at 1,000; 5,000; 10,000; 15,000; 20,000; and 30,000 cycles. For Pt/C electrode characterization consisted of Ar CV to measure ECSA and for the Acta catalyst electrode characterization consisted of Ar CVs to measure specific charge.

5.2.3 Membrane-electrode assembly construction

Membrane-electrode assemblies (MEAs) for fuel cell testing were constructed using a robotic sprayer (Sono-Tech ExactaCoat) to depositing 5 cm^2 catalyst traces onto both sides of hydroxide exchange membrane (Tokuyama Corp. A201). This MEA processing technique is known as catalyst coated membrane (CCM). A Pt/C catalyst was used for the anode and either Pt/C or the Acta catalyst was used for the cathode. The Pt/C ink was prepared adding 254 mg of catalyst and 1.27 g of ionomer (Tokuyama Corp. AS-4) to 22 g of a solvent containing equal parts water and isopropanol, followed by 1 hour of sonicating in an ice water bath. The target Pt/C catalyst loading was $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ with a 20 wt. % ionomer content. The Acta catalyst ink was prepared adding 254 mg of catalyst and the desired amount of ionomer (Tokuyama Corp. AS-4) to 22 g of a solvent containing equal parts water and isopropanol, followed by 1 hour of sonicating in an ice water bath. Ink parameters are outlined in Table 5.1. The target Acta catalyst loading was 0.80 mg cm^{-2} with a varying ionomer content and was chosen to

give the same total catalyst loading as the Pt/C electrode. A gas diffusion layer (GDL) (Toray unwetproofed TGP-H-060 carbon paper) is added to each electrode to facilitate uniform gas flow and help with water management during fuel cell operation. Prior to testing the MEA was installed into the fuel cell test assembly which consists of a uniform sandwich of gold-plated current collectors, graphite flow channelled plates, and 5 μm silicone gaskets. The test cell is assembled at 30 in-lbs. of torque.⁹⁸⁻⁹⁹

Table 5.1: Fuel cell ink parameters.

	Pt/C Ink Recipe	Acta 4020 20 % Ionomer Ink Recipe	Acta 4020 30 % Ionomer Ink Recipe	Acta 4020 40 % Ionomer Ink Recipe	Acta 4020 50 % Ionomer Ink Recipe
Target loading [$\text{mg}_{\text{Pt}} \text{cm}^{-2}$]	0.4	0.80	0.80	0.80	0.8
Ionomer content [wt. %]	20	20	30	40	50
Water [g]	11	11	11	11	11
IPA [g]	9.7	9.7	8.8	7.6	5.9
Total Catalyst [mg]	254	254	254	254	254
Ionomer [mg]	1270	1270	2177	3386	5080

5.2.4 MEA testing

Fuel cell testing were performed with a Scribner 850e fuel cell test station. Testing was performed at 50 °C at 100 % relative humidity with a back pressure of 250 kPa_g and an anode (H₂) and cathode (O₂) gas flow rate of 0.4 L min⁻¹. The MEA was broken in through a combined rapid current scanning (open current voltage (OCV) to 0.3 V) and low voltage (0.1 V) fixed voltage operation. After activation, performance was tested by scanning the current at a rate proportional to the overall performance of the fuel cell. Internal resistance (IR) was monitored through a current interrupt technique built in to the fuel cell test station.

5.2.5 Microscopy

Scanning electron microscopy (SEM) was performed with a JSM-7400F microscope equipped with an ultra-thin-window energy-dispersive X-ray spectrometer (EDS). Micrographs were obtained at accelerating voltages of 7 – 10 kV.

5.3 Results and Discussion

5.3.1 Electrochemical ADT

Catalyst ORR performance and durability for Pt/C and Acta were characterized through the ADT. The major metrics for performance during the ADT were the ECSA for the Pt/C catalyst, specific charge for the Acta catalyst, and ORR performance at 0.9 V vs RHE for both catalysts. The results were reported initially and at 1000, 5000, 10,000, 20,000, and 30,000 cycles during the ADT (Figure 5.1). This durability test mimics the DOE standard for fuel cell operation for PEMFCs. It can be observed in Figure 5.1a that the ECSA measured for the Pt/C catalyst drops dramatically from its initial $43 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ to only $4 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$ remaining at the end. The reduced stability of the Pt/C catalyst seem to contradict with the enhanced support stability shown in Chapter 4 (Figure 4.4, Figure 4.9), but it is important to note that the target of the ADT used was different. Chapter 4's ADT targeted the catalyst support with a fixed high potential test, whereas in this test the potential cycling ADT targets the durability of the Pt catalyst.¹⁰⁰ On the other hand, the specific charge, or shape of the Acta CV curve (Figure 5.1c), does not change after a slight reduction of peaks in the carbon oxidation region above

0.5 V vs RHE. This indicates carbon and transition metal complexes in the Acta catalyst are stable in the alkaline environments and under high potential cycling.

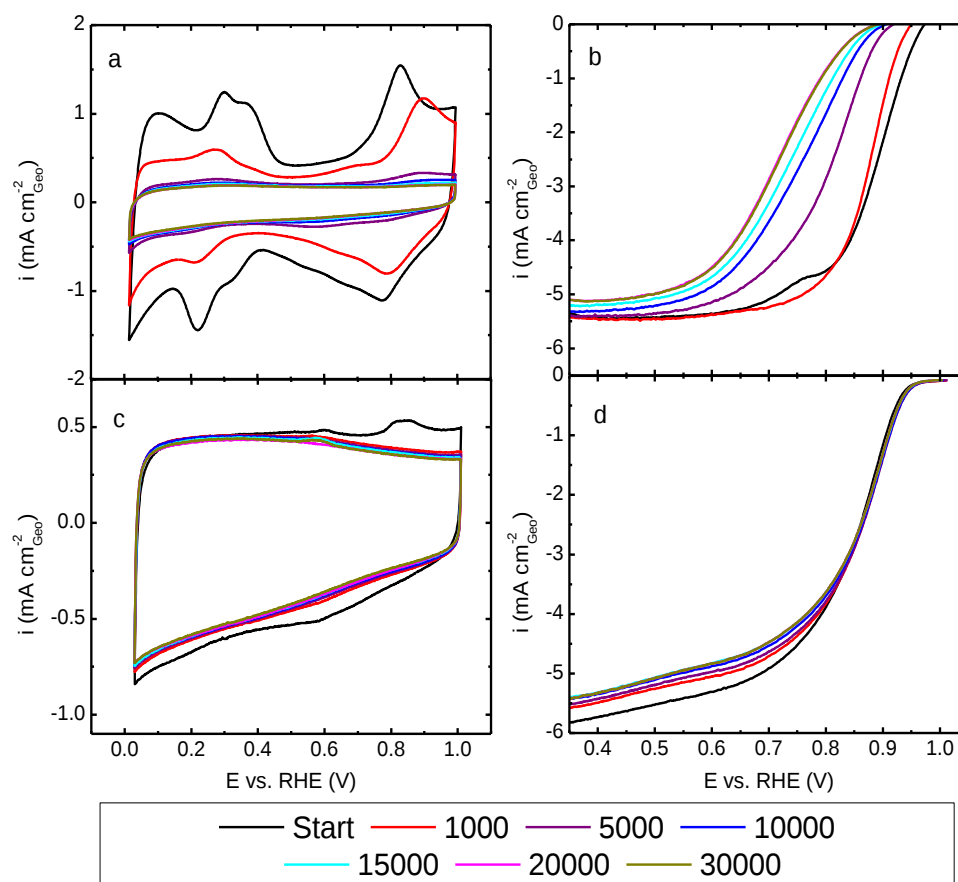


Figure 5.1: CV and ORR measurements for Pt/C (a,b) and Acta (c,d) catalysts taken throughout the ADT. CV scans ran from 0.05 to 1.1 V vs RHE at 50 mV s^{-1} in Ar purged 0.1 M KOH environment. ORR Scans ran from 0.05 to 1.1 V vs RHE at 20 mV s^{-1} in O_2 purged 0.1 M KOH environment at 1600 rpm. Anodic scans were used for Pt/C and cathodic scan were used for Acta.

The ORR activity expresses similar results to the CV data. The Pt/C ORR scans show initially high activity at 0.9 V vs RHE, but very rapidly decline after 1000 cycles (Figure 5.1b). The Acta curves show no change in shape and only a slight increase in diffusion limiting current (Figure 5.1d). This increase is due to small amounts of catalyst becoming dislodged or electrically insulated from the rest of the electrode during the ADT. The cathodic scan was used to represent the ORR curves for the Acta catalyst because of the slightly higher performance. For Pt/C the anodic scan gives slightly higher performance due to the reduction of Pt-O species formed at high potential during the ORR scans generating a more pristine surface for ORR to take place.^{7, 71} The Acta catalyst does not benefit from these reducing potential effects, and therefore, cathodic scans deliver slightly higher performance. The ORR activity normalized to the geometric area of electrode was summarized in Figure 5.2a with a comparison of beginning of life (BOL) and end of life (EOL) ORR curves shown in Figure 5.2b. In this comparison it is clear that the Acta catalyst holds constant performance throughout the entire test while the Pt/C's initially higher activity quickly drops off to the point where no performance can be measured at 0.9 V vs RHE.

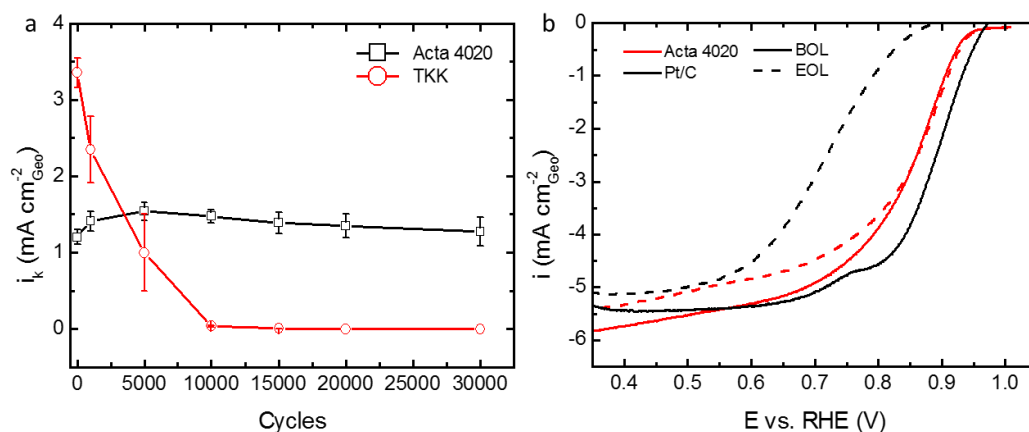


Figure 5.2: (a) ORR performance measured at 0.9 V vs RHE plotted over the course of the ADT for Acta and Pt/C catalysts. Error bars represent the standard error of the triplicate experiments ran. (b) Beginning of Life (BOL) and end of life (EOL) ORR scans taken during the ADT for Acta and Pt/C catalyst. ORR measurements were performed from 0.05 to 1.1 V vs RHE at 20 mV s⁻¹ in O₂ purged 0.1 M KOH environment at 1600 rpm. Anodic scans were used for Pt/C and cathodic scan were used for Acta.

5.3.2 Fuel Cell Incorporation

The Acta catalyst demonstrates sufficient ORR performance and excellent stability over the duration of the ADT, but incorporation into the fuel cell cathode presented many challenges. The main issues were reactant and product mass transport and membrane/catalyst connectivity. Figure 5.3 summarized the fuel cell polarization and power density curves for Acta based MEA's (Figure 5.3a) and the Pt/C MEA (Figure 5.3b). Figure 5.3a demonstrates the increased performance caused by increasing the ionomer percent in the catalyst layer. For the Acta cathode with 20 wt. % ionomer the peak power density was 50 mW cm⁻² and the internal resistance was 407 mΩ cm². Doubling the ionomer content to 40 wt. % increased the peak power density to 106 mW cm⁻² and the internal resistance decreased to 142 mΩ cm². The increased ionomer

content allows for enhanced triple phase and water management throughout the catalyst layer.⁸⁵ Further increasing the ionomer content to 50 wt. % resulted in a reduction of performance to 65 mW cm^{-2} . This drop in performance is caused by the overabundance of ionomer in the cathode, which covers the catalyst area and reduces the total active sites for the ORR to take place.¹⁰¹

The low triple phase and poor water management can be directly observed in the shape of the polarization curves and power density curves shown in Figure 5.3a. As the ionomer content is increased the early onset of the mass transport region is pushed to higher current and the asymmetry (left skew) of the power density curve is reduced. This indicates a more established triple phase interface and better reactant/product management. Even with the ionomer content increased to 40 wt. % this issue is not solved. The mass transport losses still occur too early preventing the full potential of the catalyst to be realized. The Acta catalyst's hydrophobic character leads to excess drying in the catalyst layer. This drying reduces the performance of the ionomer causing transport issues. Higher ionomer content is not the solution to this problem, but a different ionomer that is either more hydrophilic or one that could operate in the Acta cathode's dry conditions.^{98, 102}

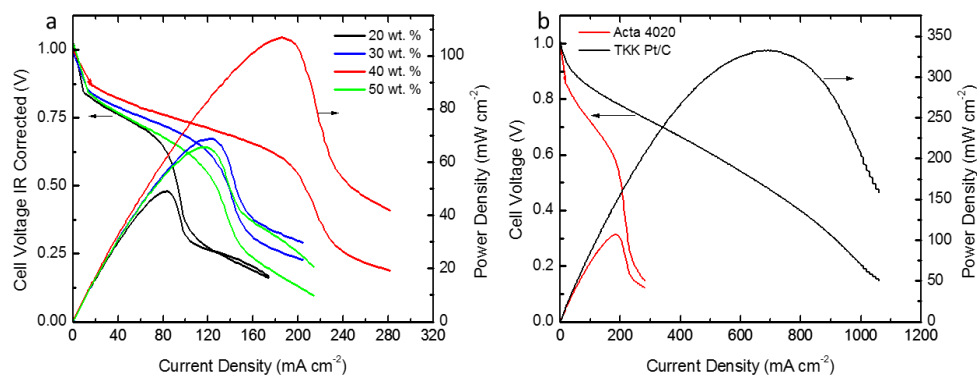


Figure 5.3: Fuel cell polarization and power density curves for (a) Acta based MEA's with different cathode ionomer loadings. MEA materials: Tokuyama A201 membrane, Tokuyama AS-4 ionomer, anode Pt/C catalyst loading of $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ with 20 wt. % ionomer, cathode Acta catalyst loadings of 0.8 mg cm^{-2} with reported ionomer loadings, and Toray TGP-H-060 carbon GDL. (b) Fuel cell performance comparison between the highest performing 40 wt. % ionomer Acta MEA and Pt/C MEA. Pt/C MEA used a Pt/C catalyst for the cathode with a loading of $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ with 20 wt. % ionomer. All other parameters were held constant. Fuel cell operation parameters: at 50°C at 100 % relative humidity with a back pressure of 250 kPa_g and an anode (H_2) and cathode (O_2) gas flow rate of 0.4 L min^{-1} .

The other major issues the Acta MEA deals with is a poor connectivity between the Acta catalyst layer and the membrane seen in Figure 5.4. In Figure 5.4 a,b the low ionomer content leads to dislocation and delamination between the membrane and catalyst layer severely reducing the catalyst utilization. This delamination could be addressed by hot pressing during the MEA construction, but the current ionomer and membrane are not thermally stable at the necessary temperatures.¹⁰³⁻¹⁰⁴ The higher ionomer content (Figure 5.4 c,d) shows no delamination between the two layers. This enhanced cohesiveness allows for the MEA to reach higher current densities without

layer delamination. Again, a more compatible membrane and ionomer would help increase the overall performance of the Acta cathode.^{21, 105-106}

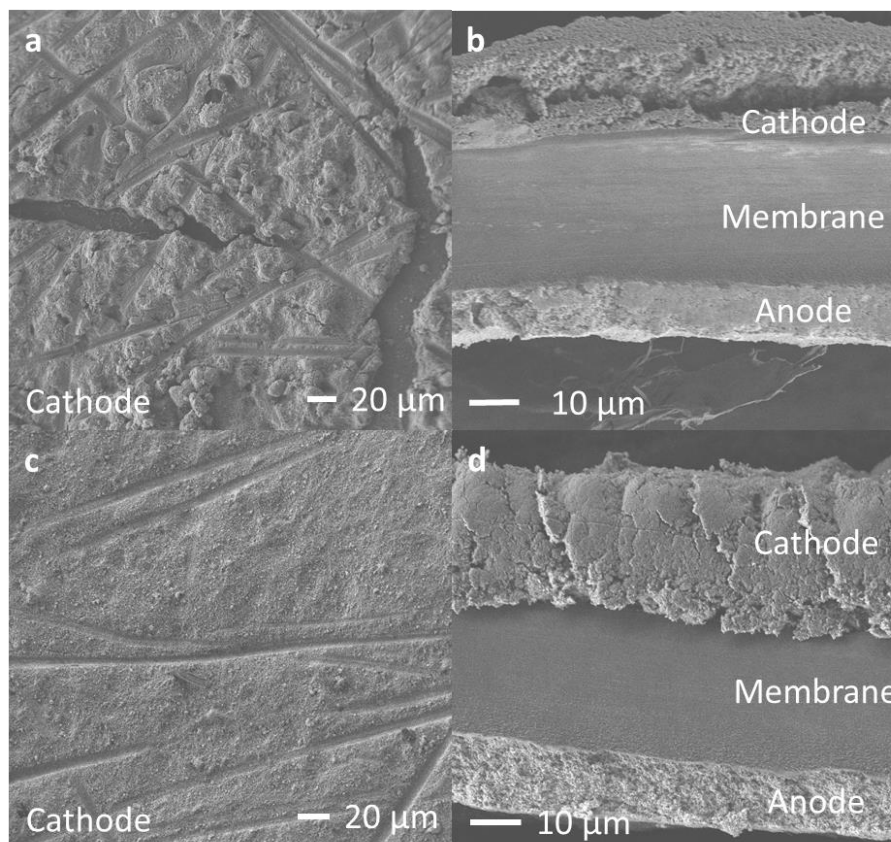


Figure 5.4: Cathode top down and cross sectional SEM micrographs of Acta based MEAs post testing with low (20 wt. % ionomer) (a,b) and high (40 wt. % ionomer) (c,d) ionomer loading. MEA materials: Tokuyama A201 membrane, Tokuyama AS-4 ionomer, anode Pt/C catalyst loading of $0.4 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ with 20 wt. % ionomer, cathode Acta catalyst loadings of 0.8 mg cm^{-2} with reported ionomer loadings.

The Pt/C based MEA operating under the same conditions achieves a peak power density of 330 mW cm^{-2} with an internal resistance of $155 \text{ m}\Omega \text{ cm}^2$ (Figure 5.3b). In comparing the Acta based cathode to a standard Pt/C based cathode the performance

is still much lower, but this is less to do with the Acta catalyst's performance and more because of the un-optimized catalyst ionomer/membrane interaction.

5.4 Conclusions

A high potential cycling ADT similar to the DOE's catalyst ADT for PEMFC demonstrated that a carbon based non-precious metal is a potential replacement for Pt/C in HEMFCs. The Acta catalyst showed an initially lower ORR performance than Pt/C, but after 5,000 cycles the Acta catalyst superseded the Pt counterpart. The Acta catalyst maintained the same ORR activity throughout the rest of the 30,000 cycles. As for fuel cell MEA incorporation, the Acta cathode layer needed a higher ionomer content than Pt/C based electrodes to achieve high performance. This performance is still lower than a fully Pt MEA, but with proper ionomer and membrane design the Acta based fuel cell could achieve comparable performance at a fraction of the catalyst cost.

Ultimately, the performance and the durability of Acta's non-precious metal catalyst demonstrates the feasibility of using alternate catalyst materials in HEMFCs, but it is also necessary to optimize catalyst and membrane/ionomer interactions. This will allow both the catalyst and membrane/ionomer to operate at their fullest potentials.

Chapter 6

CONCLUSIONS AND FUTURE WORK

Low temperature polymer electrolyte membrane fuel cells are cost-effective and green power generating devices with the potential to replace conventional ICEs in transportation. PEMFCs are the more mature fuel cell technology, but the cost and durability of these fuel cells makes them difficult to commercialize. HEMFCs provide an opportunity to greatly reduce the fuel cell cost by allowing for the use of cheaper catalysts, membranes, and peripheral components. Both PEMFC and HEMFC's ORR demonstrates poor performance and durability which hinder the eventual commercialization of fuel cell technologies.

A solid understanding of the ORR is essential for understanding how to make better performing and durable cathode catalysts for PEMFCs and HEMFCs. The ORR continues to be a major issue for low temperature polymer electrolyte membrane fuel cells. The major attempts into ORR catalyst improvement have been in developing high-performance durable PtM alloyed catalyst, durable support alternatives, and cost-effective non-precious metal catalysts. Additionally, in conducting ADTs for ORR catalyst, it is important to consider the goal of the test. A poor understanding of what the ADT is aimed at testing can lead to poor conclusions and comparisons.

6.1 High Performance Extended Structure ORR Catalyst

6.1.1 Conclusions

Investigating high-performance and durable ORR catalysts, extended structure Pt catalysts stood out as an attractive solution. Extended structure Pt catalysts demonstrate the high SA compared to other Pt morphology. Depositing an extended Pt structure onto the skin of a sacrificial metal support led to the creation of high performance and cost-effective Pt/CuNW. By incorporating post-synthesis processing (annealing and dealloying) to Pt/CuNWs, a high-performance ORR catalyst with lattice compressive tuning was obtained, the PtCu/CuNW. Our results show that tuning compressive strain in a Pt catalyst correlates with a shift in the Pt-O binding energy which alters the ORR performance of the catalyst. Extended structure Pt alloyed catalysts also demonstrated enhanced durability. The morphology of these catalysts eliminates the support corrosion and greatly reduces the effects from coarsening and coalescence. Pt dissolution is also reduced because of the lower surface energy of an extended structure catalyst compared to Pt nanoparticles.

PtCu/CuNWs have the potential for large scale commercial use in PEMFCs. Its generation through a simple, solution-based CuNW synthesis, coupled with the rapid Pt partial galvanic displacement, and facile post-synthesis processing allow it to be cost-effectively produced at scale. However, applications of these extended structured alloyed catalysts are not limited to PEMFCs and may prove useful in other reactions, including the methanol oxidation reaction (MOR) and HOR in both acidic and basic

environments as well as gas sensors and transparent conductors for solar cell applications. Furthermore, the concept of controlling compressive strain to tune the binding energy is quite general, and may prove insightful for future bimetallic catalyst systems.

6.1.2 Future Work

The PtCu/CuNW extended structure alloyed catalyst has demonstrated high ORR performance and durability in RDE experiments. The next step is to incorporate this catalyst into the cathode of a MEA. The extended structure delivered by the wire morphology can allow for high fuel cell performance even at low loadings. Similar studies using an extended structure catalyst support, carbon nanotubes, have demonstrated high performance with ultra-low loadings.¹⁰⁷ With low loadings the PtCu/CuNW catalyst could also operate with zero or low ionomer content similar to 3M's NSTF catalyst.¹⁰⁸

Alternatively, other catalytic materials could be used in the galvanic replacement step instead of Pt or to further alloy with Pt. Palladium and ruthenium among other metals have been used in the galvanic replacement reaction with CuNW.^{56, 109} By changing the galvanically replaced metal, the CuNW foundation can be made into an appropriate catalyst for many other catalytic applications.

Finally, the CuNW starting material could be changed. Nickel and cobalt nanowires grown through templating methods have been demonstrated as alternative starting materials for the galvanic replacement reaction.¹¹⁰⁻¹¹¹ Other extended metal

structures low on the galvanic series of metals could be well suited for replacing copper as a source material.

6.2 ORR Catalyst Support Durability in Acidic and Basic Environments

6.2.1 Conclusions

Catalyst support materials play an important role in an ORR catalyst's performance and durability. Therefore, it is necessary to understand the durability of different catalyst supports when exposed to ADTs in acidic and basic environments. A high-potential ADT in acidic and basic environments demonstrated that CNF supported catalysts possess a higher stability and performance over their C supported counterparts in both environments. Aside from Pt/C's higher initial ECSA, the CNF supported catalysts outperformed the C supported samples in every way. The degree of the performance increase was much greater in acidic environments over basic ones. We also illustrated the enhanced stability of Pt supported on carbon catalysts and carbon supports in basic environments compared to acidic ones. In base, a lower corrosion current, a more stable ECSA (after the initial Pt oxidation period), a more stable carbon capacitance (surface oxidation), and a relatively constant ORR performance was observed over the course of the ADT.

The stability of an ORR catalyst's support is just as important as the catalytic material's performance and durability. More durable carbon supports can facilitate higher performance over a fuel cell's life. Support durability in HEMFC's basic environment is enhanced compared to the acidic environment of a PEMFC. Therefore,

a more cost-effective carbon support could be utilized for HEMFCs. This could help reduce the overall cost of HEMFC commercialization.

6.2.2 Future Work

The enhanced stability of catalyst supports in the alkaline environment was demonstrated through a high potential ADT in RDE experiments. The next step is to confirm the enhanced durability of the Pt/CNF in the MEA of a fuel cell. Pt/CNF have previously been tested in the MEA of a PEMFC and demonstrated good performance and better Pt utilization compared to Pt/C MEAs, but no long-term durability test was conducted.⁸³ The enhanced durability of the Pt/CNF catalyst can be probed using techniques developed to investigate catalyst degradation under reverse current decay conditions.^{50, 112} Reverse current decay occurs during fuel cell start up and fuel starvation conditions and can lead to local cell voltage as high as 1.4 V. This durability test can be used to compare the Pt/CNF's support durability in PEMFCs and HEMFCs. The insights gained by these experiments will help catalyst support design for both PEMFCs and HEMFCs.

6.3 Non-precious Metal ORR Catalyst in a Basic Environment

6.3.1 Conclusions

In order to probe the performance and durability of alternative catalyst materials for HEMFC cathodes, a potential cycling ADT was used to demonstrate that the carbon based non-precious metal catalyst (Acta 4020) is a potential replacement for Pt/C. The

Acta catalyst showed an initially lower ORR performance than Pt/C at comparable catalyst loadings, but after 5,000 cycles the Acta catalyst surpassed the Pt counterpart. The Acta catalyst maintained the same ORR activity throughout the 30,000 cycles of the ADT. As for fuel cell MEA incorporation, the Acta cathode layer needed a higher ionomer content than Pt/C based electrodes to achieve high performance. The performance demonstrated was still lower than a Pt-based MEA, but with proper ionomer and membrane design and implementation the Acta based fuel cell could achieve comparable performance at a fraction of the fuel cell catalyst cost. Ultimately the performance and the durability of Acta's non-precious metal catalyst demonstrates the feasibility of using alternate catalyst materials in HEMFCs, but it also elucidates the need to optimize catalyst and membrane/ionomer systems. This will allow both the catalyst and membrane/ionomer to operate at their fullest potentials.

6.3.2 Future Work

The non-precious metal ORR catalyst, Acta 4020, demonstrated superior stability compared to Pt/C catalyst when exposed to a potential cycling ADT. This performance, however, did not translate into HEMFC performance. The primary factor reducing the performance of the Acta catalyst in the cathode of a MEA was the poor interaction between the Acta catalyst and the membrane/ionomer materials used. Therefore, the next steps should be to investigate alternative methods for incorporating the Acta catalyst into the Tokuyama membrane and ionomer system.

The Acta catalyst's hydrophobic nature leads to poor interactions with aqueous solutions and hydrophilic materials like the HEMFC's membrane and ionomer. This poor interaction leads to delamination of the Acta cathode in the fuel cell's MEA. The interaction between the Acta catalyst and the ionomer can be enhanced by altering the ink recipe used to fabricate the cathode layer. The ink solvent can be changed from an aqueous water/alcohol mixture to an organic solvent (THF, DMSO, etc.). The appropriate organic solvent can help with the initial binding between the Acta catalyst and the membrane and ionomer. This could lead to a more robust catalyst layer.

If changing the solvent is not enough to achieve a better interaction between the Acta catalyst and membrane/ionomer materials, the Acta catalyst could be altered with post-processing. Previous studies have used heat treatments, acid treatments, and other more unique processes like UV-ozone treatments to encourage adhesion with hydrophobic carbon materials.^{86, 113-114} Exposing the Acta catalyst to one of these processing techniques could help promote the interaction of the Acta catalyst with the membrane and ionomer of the HEMFC.

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Appendix A

ABBREVIATIONS AND IMPORTANT VARIABLES

ICE	Internal combustion engine
AFC	Alkaline fuel cell
PAFC	Phosphoric acid fuel cell
MCFC	Molten carbonate fuel cell
SOFC	Solid oxide fuel cell
PEMFC	Proton exchange membrane fuel cell
HEMFC	Hydroxide exchange membrane fuel cell
PEM	Proton exchange membrane
HEM	Hydroxide exchange membrane
HOR	Hydrogen oxidation reaction
ORR	Oxygen reduction reaction
OCV	Open-current cell voltage
DOE	Department of Energy
RHE	Reference hydrogen electrode
RDS	Rate determining step
i_k	Kinetic current density
i_o	Exchange current density

α	Charge transfer coefficient
η	Overpotential
z	Number of electrons transferred in the RDS
F	Faraday's constant
R	Ideal gas constant
T	Temperature
SHE	Standard hydrogen electrode
ECSA	Electrochemical surface area
ADT	Accelerated durability test
SA	Specific activity
MA	Mass activity
DFT	Density functional theory
RDE	Rotating disk electrode
SCE	Saturated calomel reference electrode
CV	Cyclic voltammetry
i_d	Diffusion limiting current
i	Measured current
SEM	Scanning electron microscopy
EDS	Energy-dispersive X-ray spectroscopy
TEM	Transmission electron microscopy
ICP	Inductively coupled plasma spectrometry
H_{UPD}	Under-potential deposited hydrogen

TGA	Thermogravimetric analysis
XRD	X-ray diffraction
D	Diameter of the RDE electrode
ω	Disk rotation rate
ν	Kinematic viscosity
c_0	Concentration of the bulk reactants
IR	Internal resistance
BOL	Beginning of life
EOL	End of life

Appendix B

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