Robust Platinum-Based Electrocatalysts for Fuel Cell Applications

DISSERTATION

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Abstract

Polymer electrolyte fuel cells (PEMFCs) are energy conversion devices that exploit the energetics of the reaction between hydrogen fuel and O$_2$ to generate electricity with water as the only byproduct. PEMFCs have attracted substantial attention due to their high conversion efficiency, high energy density, and low carbon footprint. However, PEMFC performance is hindered by the high activation barrier and slow reaction rates at the cathode where O$_2$ undergoes an overall 4-electron reduction to water.

The most efficient oxygen reduction reaction (ORR) catalyst materials to date are Pt group metals due to their high catalytic activity and stability in a wide range of operating conditions. Before fuel cells can become economically viable, efforts must be taken to decrease Pt content while maintaining a high level of ORR activity. This work describes the design and synthesis of a Pt-Cu electrocatalyst with ORR activity exceeding that of polycrystalline Pt. Production of this novel catalyst is quite simple and begins with synthesis of a porous Cu substrate, formed by etching Al from a Cu-Al alloy. The porous Cu substrate is then coated with a Pt layer via a spontaneous electrochemical process known as galvanic replacement. The Pt layer enhances the ORR activity (as measured by a rotating ring-disk electrode (RRDE)) and acts as a barrier towards corrosion of the Cu understructure. Growth of the Pt layer can be manipulated by time, temperature, concentration of Pt precursor, and convection rate during galvanic replacement. Data from
analytical and electrochemical techniques confirm multiple Pt loadings have been achieved via the galvanic replacement process. The boost in ORR activity for the PtCu catalyst was determined to be a result of its lower affinity towards (site-blocking) OH adsorption. A unique catalyst degradation study explains the mechanism of initial catalyst ORR deactivation for both monometallic and bimetallic Pt-based catalysts. Finally, a rigorous and pioneering examination of how Pt surface passivation affects ORR dynamics is presented.
Dedication

To my parents, my fiancé Kandice, and a great deal of other friends and family who always supported my academic pursuits and dreams. This is for everyone who was with me “shooting in the gym.”
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Chapter 1: Introduction

1.1 Motivation and Introduction to Fuel Cells

Atmospheric CO$_2$ concentration exceeded 400 ppm in 2014, and continues to grow annually. CO$_2$ is the main greenhouse gas emitted from human sources (fossil fuel burning) and has been found to be chiefly responsible for changes in climate and global warming. One of the key steps to building a sustainable future is to mitigate the combustion of fossil fuel. Electric power generation accounts for approximately 35% of U.S. greenhouse gas emissions, while the transportation sector accounts for another 30% (both approximations include greenhouse contributions from NO$_x$ and SO$_x$). Simply developing new power generation/vehicle technologies that do not rely on fossil fuels would (alone) dramatically reduce greenhouse emissions. In the transportation sector, battery technology has made great strides, but battery technology is inherently limited to energy storage—batteries have a finite capacity. Another useful concept is to take a stream of fuel and a stream of oxidant and physically separate them into two half cells (where either oxidation or reduction occurs) and force the transferred electrons to take an external path to create electricity. This is the fundamental premise of fuel cells. A convenient fuel is hydrogen, (H$_2$, because it can be produced from water) and an excellent oxidant is oxygen (O$_2$), which is present in the atmosphere. These are the reactants in a low-temperature proton exchange
membrane fuel cell (PEMFC). As this is an electrochemical device, hydrogen is oxidized to protons at the anode and oxygen is reduced to water at the cathode (see Figure 1.1). To complete this circuit, protons are forced to take a path through the proton exchange membrane to reach the cathode where they combine with electrons (traveling externally, as in Figure 1.1) and oxygen at the cathode surface. PEMFCs offer a variety of benefits over internal combustion engines such as reduction of greenhouse emissions, no requirement for maintenance (no moving parts), and very low noise. Fuel cells also offer quite a few benefits over batteries like long operating times and quick “refueling”. These benefits and other technological advances have led to the realization of the fuel cell vehicle (FCV), with Hyundai and Toyota releasing FCVs this year (2015) in the US. Moreover, fuel cells are currently used to power some buses and small equipment (i.e. forklifts) across the world.

The reaction between hydrogen and oxygen is indeed energetically favorable and it could be utilized in an internal combustion engine, where it would theoretically provide the same -237 kJ/mol of heat, and bypass all of the extra components of a fuel cell. The problem with the combustion process is that to do any useable work, it must proceed through a 2\textsuperscript{nd} conversion, where heat must be converted to work. This heat conversion to work process is limited by the second law of thermodynamics which essentially states that not all of the heat in the heat engine can be used to do work (unless the heat could be dispelled into a reservoir at 0 K)\textsuperscript{3}. The electricity to work actuation process is much more efficient
(theoretical efficiency limited only by $-T\Delta S$), so it is best to utilize the fuel cell concept rather than the internal combustion process.

With this said, PEMFCs are not without some limitations. Hydrogen cannot simply be put into a closed chamber with a high surface area inert electrode and converted to protons. Likewise, oxygen will not spontaneously add with two protons and two electrons to form water (at least not in a time frame that is conducive for an energy conversion device). Catalysts are necessary at both the anode and the cathode. These electrocatalysts speed up the reaction by lowering the energy of the activated complex.

Currently, the best catalysts for oxidation of hydrogen and reduction of Pt are metal-based catalysts. In this category, platinum (Pt) is optimal for both hydrogen oxidation and oxygen reduction. However, the current price for platinum is ca. $1100/oz.\textsuperscript{4}$ For perspective, nickel (which is not considered to be a cheap industrial metal) is currently $0.39/oz.\textsuperscript{5}$ To make matters worse, Pt is a very good catalyst for hydrogen oxidation, but not efficient enough for oxygen reduction. As a result, researchers look for ways to reduce Pt loading without sacrificing oxygen reduction reaction (ORR) performance.

There are several approaches for reducing platinum loading. Among the most obvious of them is to mix Pt with another metal. This can be via forming a true bimetallic alloy\textsuperscript{6-9} or by coating a thin layer of Pt onto another metal substrate (core@shell structure).\textsuperscript{10-14} The other approach for reducing platinum loading is to increase the dispersion or surface area
of the catalyst, so this entails 1) making Pt particles smaller, and/or 2) more efficiently supporting the catalyst particles.

As mentioned earlier, it is important to ensure that the catalyst’s activity is not decreased as the platinum loading is increased. Theorists have discovered that Pt-based catalysts’ activity can be related to its oxygen binding energy.\textsuperscript{15,16} The general principal is that when a catalyst binds oxygen too strongly its activity is inhibited because the catalyst will essentially become oxidized (i.e. iron). On the contrary, if a catalyst binds oxygen too weakly its activity is inhibited because the oxygen is not on the surface long enough to become activated (i.e. gold). The best catalysts have an oxophilicity that hits the “sweet-spot”. Monometallic nanoparticle Pt catalysts bind oxygen too strongly,\textsuperscript{17} due to the relatively low coordination number of the surface Pt atoms. As a result, larger Pt particles (smaller surface area) favor higher ORR turnover. Making Pt particles smaller is then not a good solution because ORR activity will be reduced (activity per unit Pt). However, it has been discovered that by mixing Pt with 3d transition metals (alloying or core-shell) the average oxophilicity of the catalyst decreases to more favorable numbers.\textsuperscript{16} Ni@Pt is currently the highest activity ORR catalyst due to its optimal oxygen binding energy.\textsuperscript{18} However, PtCu is not nearly as widely studied because it does not fit the trend of the oxygen binding energy argument. It is my opinion that PtCu has the optimal binding energy for ORR (as calculated by density functional theory), but early experiments showed PtCu alloys to possess only a modest boost in ORR activity (relative to Pt). As a result, PtCu has never been included on any Sabatier plots (which relate oxygen binding energy to catalyst
activity),\textsuperscript{16,19} and is seldom mentioned in the literature (although Cu is \(\sim\) 3x cheaper than Ni). Therefore, it has been my goal to develop a new PtCu nanostructured catalyst with optimized ORR activity. To accomplish this goal I utilized a facile electroless plating method (galvanic displacement) to coat Pt onto a nanostructured Cu support.

**1.2 Galvanic Displacement as a Method for Producing PtCu Catalysts**

The process begins with a CuAl alloy which is prepared in-house at the OSU foundry. The aluminum can be selectively etched out of the alloy using a solution of hot (85 °C) 6 M NaOH. A mortar and pestle can then be used to powderize this monolithic solid. After powderizing the copper, it can be drop-cast to the surface of a glassy carbon disk electrode and allowed to dry. After drying the copper precursor is ready for deposition of Pt. Pt is deposited via galvanic displacement, which is a redox reaction where a more noble metal (Pt) becomes reduced and a less noble metal (Cu) becomes oxidized spontaneously. The only requirements for this reaction are the copper coated electrode and a solution containing Pt ions. The net reaction can be given as:

\[
\text{PtCl}_4^{2-} + \text{Cu(s)} \rightarrow \text{Pt(s)} + \text{Cu}^{2+} + 4\text{Cl}^{-}
\]

The entire catalyst prep procedure is summarized in Figure 1.2.

**1.3 Scope of this Thesis**

While high activity ORR catalysts are desirable, it is also of equal importance that the catalyst does not physically degrade or deactivate quickly. Another consideration is that the catalyst should be selective to the full four electron reduction of oxygen to water, rather
than the two electron reduction of oxygen to peroxide. Peroxide formation is undesirable as it involves the transfer of only 2 electrons (i.e. lower current density per oxygen molecule), and it is a strong oxidant which will promote degradation of fuel cell materials. The desire to use less platinum and more non-noble metals (Cu, Ni, Fe, etc.) have also necessitated the resurgence of alkaline fuel cells. These fuel cells perform the alkaline analog of the oxygen reduction reaction:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \]

It is therefore important to design experiments that verify that catalysts are also stable in alkaline electrolyte. In addition, alkaline catalysts should remain selective to the full four electron transfer.

The design/synthesis, physical characterization and preliminary electrochemical characterization of the PtCu catalyst are described in chapter 2. Chapter 3 provides a more detailed electrochemical analysis of the catalyst in acid and alkaline electrolyte and justification that the catalyst is selective to the full four electron transfer in both acidic and alkaline media.

Chapter 4 builds on the work from chapters 2 and 3 by providing a fundamental electrochemical explanation of the most critical phase of catalyst degradation for Pt/C and PtCu/C. The aim of this chapter is to outline a blueprint for resilient ORR catalyst design.
Although the design and thorough characterization of a new class of PtCu is the main motivation of this thesis, it is important to take a holistic approach and understand that eventually these catalysts may be utilized in an actual fuel cell, and they will be subject to a sort of utilization that we cannot easily imitate in our fundamental chemistry lab. With this consideration, we should seek to design fundamental experiments that may elucidate future issues that will affect the overall fuel cell efficiency. Advances in Pt-based oxygen reduction reaction fuel cell catalysts will continue to lead to remarkably more efficient fuel cells. However, more efficient cathode catalysts will be required to deliver a higher energy density, which will result in them becoming oxidized over periods of prolonged use (see Figure 1.3). The effects of surface oxidation on the ORR have largely been overlooked because current (and past) commercial fuel cell catalysts have had more modest ORR activities. Chapter 5 provides a comprehensive study which explains how the ORR is affected (pH 1 and pH 13) when an oxide layer is present and as the oxide layer is removed from a Pt catalyst. This investigation will become very valuable as PtCu and other high activity Pt-based ORR catalysts begin to become feasible.

1.4 References

1. CO₂Now. Atmospheric CO₂ from Mauna Loa Observatory. <http://co2now.org/>


4. APMEX. Precious Metal Spot Prices. <www.apmex.com>


Figure 1.1: Proton exchange membrane fuel cell schematic
Figure 1.2: Procedure for synthesis of PtCu catalyst
Figure 1.3: Outline of fuel cell operating potential and concurrent surface phenomena for current fuel cells (with “good catalyst” of Pt/C) and hypothetical future fuel cells (with “great catalyst” of Pt₃Ni, which has >20 fold increase in activity relative to Pt/C).
Chapter 2: Galvanic Displacement of Pt on Nanoporous Copper: An Alternative Synthetic Route for Obtaining Robust and Reliable Oxygen Reduction Activity

2.1 Introduction

Fuel cell technology has played a key role in providing electricity on spacecraft since the 1960s and will continue to play a significant role in next generation alternative energy systems, with terrestrial applications in exhaust-free automobiles, portable devices and electricity-generating power plants. The deployment of proton exchange membrane fuel cells (PEMFCs) is limited by the high cost and low durability of electrocatalysts, where most of the energy loss occurs at the cathode, due to the high energy barrier of the oxygen reduction reaction (ORR) process. Despite vast efforts in the past decades to develop non-Pt based catalysts for low temperature PEMFCs, Pt remains the catalyst of choice for ORR in acidic medium.

Significant progress on the development of cathode catalysts has been made through the efficient utilization of Pt by creating nanoparticles,\(^1\)\(^{-7}\) decoration of Pt nanoparticles on carbon nanotubes,\(^8\) Au and Pd-alloy substrates,\(^9\)\(^{-14}\) core-shell catalysts,\(^2,\)\(^8,\)\(^15\)\(^{-32}\) Pt-based alloys.\(^3,\)\(^5,\)\(^16\)\(^{-27},\)\(^33\) The surface electrochemistry of PtX alloys, typically involving 3d-transition metals (X=Fe, Ni, Co, Cu)\(^3,\)\(^5,\)\(^16\)\(^{-27}\) is of great interest due to their enhanced
surface activity towards the electrochemical reduction of O₂ (ORR) compared to polycrystalline Pt. Nanoparticles and core-shell (core = Ni, Co, Au, Pd, Cu or PtX; shell = Pt) studies suggest that a very thin Pt surface layer introduces lattice strain to the Pt shell which increases the overall ORR activity.¹⁵,²⁷

In recent years, there has been substantial interest in developing new bimetallic catalyst systems utilizing Cu,⁸,¹⁵,¹⁷,²³,²⁹,³³-³⁶ rather than Ni or Co. Copper is more abundant than Ni and Co and has been found to have similar ORR enhancements from lattice strain when it is incorporated in a core-shell structure with Pt or Pd.⁸,¹⁵,²³,³⁶ Typically Cu and Pt containing ORR catalysts achieve this core-shell structure from employing galvanic displacement reactions on Cu nanoparticles⁸,¹⁷ and subsequent dealloying. Dealloying can be achieved either electrochemically,⁸,¹⁷,²³,³³ via acid washing,¹⁷ or via annealing.³⁷

Most Cu-Pt catalyst materials developed in the last several decades involve complex nanoparticle synthesis protocols, which include high temperatures, hazardous chemicals, and multiple washing steps. The catalyst described in this paper is a facile alternative which does not require stabilizing ligands or surfactants and which consolidates many of the nanoparticle synthesis steps, without sacrificing ORR activity, reproducibility, or stability. Instead of a nanostructured catalyst prepared via a typical nanoparticle synthesis, we describe a catalyst prepared in one pot from a monolithic nanoporous copper support. This is made possible by a novel method of performing galvanic displacement on an immersed nanoporous copper support under convection control. During the displacement, a variety
of parameters can be manipulated, many of which will be described in detail in this chapter. This method of performing galvanic displacement allows an unprecedented degree of control over the Pt coating process, is reproducible, and allows the catalyst to be quickly characterized. In the past, researchers have agreed that performing galvanic displacement reactions at elevated temperatures is usually undesirable, but we have found that the final catalyst particle size is highly dependent on the temperature of galvanic displacement—with higher temperature displacements resulting in smaller particle size.

Described herein is a class of PtCu catalysts produced from varying key displacement parameters to improve ORR activity and stability. All of the catalysts have a (quasi)core-shell structure with a PtCu alloy core and a Pt enriched PtCu shell. Specific and mass ORR activities for the PtCu catalysts are over 2x higher than commercially available Pt/C (20% Pt 25-30 m²/g from Johnson Matthey), and the catalysts have < 40% loss in electrochemical surface area (ECSA) over 30,000 cycles. Galvanic displacement of a more noble metal on to a metallic porous monolithic substrates, such as nanoporous Cu, Au, Ag, Ni, can be implemented for industrial scale catalyst production at a low price. It is my hope that this chapter provides a comprehensive look into the galvanic displacement process, and highlights an alternative synthetic strategy of modifying the surface activity of other bimetallic catalyst systems.
2.2 Experimental Methods

2.2.1 Nanoporous (np) Cu synthesis

An AlCu alloy (83 at% Al) was prepared from bulk high purity (99.9%) metals at The Ohio State University Solidification and Metal Casting Laboratories (OSU foundry). The alloy was cut into ‘coins’ (24 mm diameter x 2 mm thick). The nanoporous Cu (npCu) structure was created by etching CuAl alloys in NaOH (1 and 6 M, at 80 °C for 16 hours), followed by continuous rinsing in ultrapure water (> 2 hours) to remove residual solvent and byproducts. The npCu was dried and stored in a desiccator soon after preparation. The absence of Al in the final porous structure was confirmed by EDX and XPS (negligible signals below the detection limit). Prior to its use as an ORR catalyst support, npCu was heated in H₂ atmosphere (2 hrs at 450 °C), to ensure the reduction of any formed Cu oxides (during the etching and storage process) to Cu metal.

2.2.2 Thin-layer Pt on np Cu electrode preparation

Following heat treatment of the npCu in H₂, the reduced copper coin was ground into a fine powder using a mortar and pestle. For unsupported catalysts, npCu powder (15 mg) was dispersed ultrasonically in ultrapure H₂O (10 mL) for 10 minutes. A diluted Nafion® solution (5 wt %, Alfa Aesar, 40 μL) was added to the NP Cu dispersion. The resulting solution was sonicated for another 10 min. Immediately following sonication, a suspension (20 μL) was drop-casted onto a mirror polished glassy carbon (GC) disk electrode (PINE,
5 mm diameter). The prepared electrode was dried under vacuum (55 °C for 1.5 hours). After drying, the coated electrode was allowed to cool down to room temperature. For carbon supported catalysts, np Cu powder (7.5 mg) was added to Vulcan XC-72 carbon (7.5 mg) and dispersed ultrasonically in ultrapure H₂O (10 mL) for 10 minutes and drop casted onto GC. The remaining procedure is the same as described. For comparison, Pt/C was prepared by dispersing 20 wt% Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) in ultrapure H₂O (10 mL) for 10 minutes. There were no other variations from the prior procedure. A bulk polycrystalline platinum (BPPt) electrode (PINE, 5 mm diameter) was also used as a reference during electrochemical measurements.

2.2.3 Deposition of Pt

The deposition of Pt onto the np Cu was conducted by depositing K₂PtCl₄ (120 mL of a 1.2 mM or 0.12 mM, (Sigma-Aldrich) solution (ultrapure H₂O from Milli-Q 18.2 MΩ) onto the np Cu substrate in a standard 3-electrode cell equipped with a heating jacket. Depending on the deposition, the cell was thermostatically controlled between 5 and 60 °C. The np Cu coated GC electrode was attached to a Pine electrode rotator and immersed in the K₂PtCl₄ solution (1-60 minutes). To ensure uniform deposition of platinum, the electrode was rotated (500 rpm) during deposition. Immediately after the timed deposition, the electrode was removed from the platinum solution and rinsed in ultrapure water (200 mL for 2 minutes at 500 rpm), twice, to quench the reaction.
2.2.4 Electrochemical study

Electrochemical measurements were performed in a jacketed standard 3-electrode cell using a ring-disk electrode (PINE) equipped with a PINE bi-potentiostat (PINE WaveDriver) capable of concurrent rotation control. A reversible hydrogen electrode (RHE) with a luggin capillary was used as the reference electrode for all electrochemical measurements. The counter electrode was a Pt mesh. The electrolyte used was 0.1 M HClO₄, which was prepared by diluting concentrated trace metal grade acid (Fisher) with 18 Mohm ultrapure de-ionized H₂O (Millipore). All cyclic voltammograms were recorded at 298K with a scan rate of 10-100 mV s⁻¹ and a rotation rate of 0 to 1600 rpm. The prepared electrodes were transferred to the electrochemical cell and immersed in nitrogen-saturated electrolyte, deareated for at least 45 min. The electrodes were ‘primed’ via electrochemical dealloying using a modification of the method first described by Koh et al. The potential was cycled 50 times between 0.5 V and 1.2 V at 1 V/s to dealloy/stabilize the catalyst. CV scans between 0 V and 1.2 V at 100 mV/s were measured until a steady-state voltammogram was attained. The Pt electrochemical surface area (Pt ECSA) was determined from a N₂ saturated voltammogram via the average integrated charge of the underpotentially deposited hydrogen (Hupd) region (0.05 V to 0.40) after double-layer correction. The widely accepted conversion of 210 μC cm⁻²pt for polycrystalline Pt was assumed. ORR CV measurements were performed in an oxygen-saturated electrolyte with the potential cycled between 0.0 V and 1.2 V at 100 mV/s. Polarization curves were obtained by subtracting the N₂ saturated voltammogram from the O₂ saturated voltammogram to remove any contributions from capacitance. Polarization curves
obtained at 100 mV/s are identical to those obtained at lower sweep rates (20 mV/s) using this blank-subtraction protocol. Kinetic ORR activity \( (i_k) \) was calculated for the *anodic sweep* polarization curve via the following relationship:

\[
    i_k = \frac{i_{lim}}{i_{lim} - i_{tot}}
\]

(2.1)

where \( i_{lim} \) is the limiting current, and \( i_{tot} \) is the total current. Pt specific activities \( (i_{Pt}) \) were determined from Pt-ECSA data as follows:

\[
    i_{Pt} = \frac{i_k}{Pt \ ECSA}
\]

(2.2)

Electrochemical impedance spectroscopy (EIS) was used to determine the solution resistance for the electrochemical system to correct for IR loss \( (E_{IR}) \) using a Princeton Applied Research 263A potentiostat in conjunction with a Solartron 1260 Impedance Analyzer. The impedance was measured at OCP and at 0.9 V (amplitude of 5 mV from 10,000 Hz to 0.01 Hz). The correction was applied to raw data as follows:

\[
    E_{real} = E_{measured} - E_{IR}
\]

(2.3)

An accelerated half-cell degradation test was performed by cycling the potential between 0.6 and 1.1 V at 50 mV/s in 0.1 M HClO4 for 30,000 cycles under continuous O2 flow. Cyclic voltammograms (0 V - 1.2 V, 10 and/or 100 mV/s) were obtained intermittently in N2 (every 2500 cycles until 10,000 cycles; after, every 5000 cycles) to measure the Pt ECSA.
2.2.5 Catalyst characterization

Pt and Cu content of the catalyst before and after ORR experiments are quantified using a Perkin-Elmer Sciex Elan 6000 ICP-MS. PtCu/C catalysts coated on GC electrodes were dissolved in aqua regia (3 HCl:1 HNO₃) for 18 hours and diluted with deionized water for ICP-MS measurements. Catalysts loading and mass activity are reported based on mass of the catalysts on the electrode as obtained from ICP-MS measurements.

Specific surface area, S_{BET}, were determined by measuring a volume of nitrogen adsorbed onto a specific mass of each sample as a function of gas pressure on a Quantachrome Autosorb iQ₂ instrument. All samples were degassed before analysis at 100 °C for 6 hrs to remove any physically adsorbed species.

Morphology and size of the catalysts were studied using a scanning electron microscope (SEM; FEI Sirion XL 30 or FEI Helios Nanolab 600 Dual-Beam) and a transmission electron microscope (TEM/STEM; FEI Tecnai F20). The STEM EDX analysis was done at 200 kV using the FEI and EDAX TEAM software with a silicon drift detector (EDAX Inc). The STEM line-scan EDX profiles have about a 1.5 nm resolution. Particle size distributions were determined from SEM images using ImageJ software and accounting for more than 250 non-agglomerated catalyst particles for each distribution.

X-ray photoelectron spectrum (XPS) studies were collected on an Axis 165 (Kratos) under a base pressure of 1x 10⁻⁸ Pa. The photoelectron spectra were excited using an Al Kα
radiation ($h\nu=1486.6$ eV) with a total instrumental resolution of $\sim 1$ eV. Take-off angle of the electron is at $0^\circ$ with respect to the surface normal. Fixed analyzer transmission (FAT) mode was used with the analysis area of 600 $\mu$m. The spectrometer’s work function was calibrated using a linear regression of cleaned metallic Ag, Au and Cu. The C 1s line of the adventitious carbon at 285.0 eV was used as internal standard to calibrate the binding energies (BE). Survey scans (0 – 1400 eV) were collected at pass energy of 80 eV. Cu 2p, O 1s and C 1s XPS spectra were recorded at pass energy of 20 eV. The accuracy of the BE’s measured was $\pm 0.1$ eV. Samples could be cleaned by argon sputtering (5 keV, 50 $\mu$A). The photoelectron spectra were corrected by subtracting a Shirley-type background and were quantified using the peak area and Scofield’s photo-ionization cross sections. CasaXPS software (version 2.3.16) provides a least-square fit of a product of Gaussian and Lorentzian peaks. GL (30), which consists of 30% Lorentzian, is used for all peak quantification.

2.3 Results and Discussion

2.3.1 Preparation and characterization of Pt on nanoporous Cu

Figure 2.1a is an SEM image of a chemically etched nanoporous Cu (np Cu) from a Cu$_{17}$Al$_{83}$ alloy. A 6 M NaOH etchant maintained constantly at 80$^\circ$C over a 24 hour period gave a continuous monolithic np Cu structure with ligament and pore sizes in the range of 40 – 130 nm. The BET surface area of the np Cu support used in this study was $\sim 10$ m$^2$/g. It is important to note that the feature size of the np Cu can be tuned between 8 to 40 m$^2$/g
by different conditions during the initial synthesis (pouring temperature, etching conditions, annealing, etc.).

Galvanic displacement reactions of Pt onto the np Cu support at room temperature gave agglomerated PtCu dispersed across the electrode (Figure 2.1b). Displacement reactions conducted at higher temperatures of 50 and 60 °C gave predominantly spherical shaped PtCu particles approx. 80 – 120 nm in diameter, though larger agglomerates were still found sparsely distributed across the electrode (Figure 2.1c). The addition of a Vulcan XC-72 carbon support (ca. 50-80 wt%) and Pt displacement at 50 °C, further improved the dispersion of the PtCu catalysts as shown in Figure 2.1d, with relatively narrow size distribution and no large agglomerates. Notably, the Pt:Cu atomic ratio from EDX analysis of both the monodispersed PtCu and PtCu agglomerates were statistically similar at ~2:1. By design, some of the Pt$_{1-x}$Cu$_x$ available directly after galvanic displacement still contains some regions of exposed copper, the amount of which is dependent on the parameters used during galvanic displacement. These accessible copper regions on the catalyst can be removed by electrochemically cycling from 0 to 1.2 V until a steady-state CV is obtained which resembles a clean polycrystalline Pt surface—usually within 50 cycles (Figure 2.2). This procedure is analogous to the widely-accepted “dealloying” technique first employed by Koh et al.$^{38}$ The broad oxidative peaks in the CVs shown in Figure 2.2 illustrate how the magnitude of Cu dissolution, and hence, the accessible Cu is dependent on the length of time of galvanic displacement. As the deposition time is increased (while temperature is held constant at 50 °C), there are fewer accessible areas of exposed Cu, and after a 30 min
galvanic displacement, the initial CV scan closely resembles the steady-state CV. This indicates there are very few regions of exposed Cu remaining, and dealloying is not significantly altering the surface composition.

Despite CVs showing Cu removal and eventually achieving a steady-state Pt signature, EDX line-scan data from TEM analysis, shown in Figure 2.3, suggests that the composition of the most active ORR catalyst (50 °C, 2.5 min), after electrochemical cycling, is only mildly “core-shell” (5-7% Pt enrichment at shell) and is very similar to the as-prepared catalyst, except with an overall composition about 6% more Pt-rich. This is contrary to the well-accepted view that electrochemical dealloying produces a monometallic/bimetallic core and a largely monometallic shell structure. However, Oezaslan et al. discovered that Pt-rich alloys do not always demonstrate significant surface segregation upon voltammetric dealloying, rather they only attain a Pt-shell structure after annealing. The TEM data also suggests that the exposed Cu in Figure 2.2 is not primarily surface Cu. In fact, the bulk Pt:Cu ratio is consistently higher after potential cycling, suggesting the removal of Cu is extended into the bulk, as long as the Cu is accessible to the corrosive acid during the priming procedure, possibly through microchannels within the particles. In any case, all PtCu in this study was primed to reach steady state prior to ORR measurements.
2.3.2 Surface analysis via XPS

XPS data for the most active PtCu catalyst (2.5 min, 50 °C) indicate metallic Pt (binding energy 71.5 and 74.8 eV for Pt 4f7/2 and Pt 4f5/2, respectively) is present at the surface of both as-prepared and dealloyed catalysts (Figure 2.4). XPS peaks also confirm the presence of metallic Cu (932.5 and 952.2 eV for 2p3/2 and 2p1/2, respectively), and CuO (935 eV and satellite bands between 938-945 eV and 960-967 eV), on the surface of as-prepared PtCu (Figure 2.4a). A predominant CuLMM Auger peak at a kinetic energy of 918.8 eV also confirms the presence of metallic Cu on the surface of the as-prepared catalyst (Figure 2.4b). XPS measurements on the PtCu catalysts after dealloying (Figure 2.4a,b) show that Cu metal is still present at the surface of the dealloyed catalyst, with no detectable copper oxide. These qualitative measurements endorse the idea that the PtCu catalysts do not have a monometallic Pt-shell structure, rather more of a platinum enriched Pt-Cu alloy shell.

2.3.3 Tuning particle size through galvanic displacement conditions

The amount of Pt displaced onto the np Cu substrate is highly dependent on the deposition time, deposition temperature, and concentration of Pt precursor (K2PtCl4). The fundamental effects of each parameter can be isolated by manipulating a single variable while holding the other two constant (Figure 2.5). To assess the effects of each parameter, Pt area, Pt weight, and Pt:Cu atomic ratio are monitored (post-dealloying) on unsupported PtCu catalysts. Pt electrochemical surface area is measured from the H_UPD region of a steady-state CV after double-layer correction, assuming 210 µC/cm². Pt weight and Pt:Cu
are measured with ICP-MS after the electrodes have been dissolved for 18 hours in concentrated aqua regia. Figure 2.5a summarizes the resulting Pt surface area as a function of galvanic deposition time, while keeping all other variables constant. Figure 2.5a shows an initial increase in the Pt area to 2.5 min of deposition, followed by continuous decrease in Pt area with longer deposition time. This indicates that the amount of accessible Pt is not proportional to the amount of deposition time, as one might expect. We postulate that longer deposition times, past the 2.5 min threshold, may begin to clog pores and/or increase particle size. This conclusion is corroborated by Figures 2.5b-c which show that the mass of Pt deposited as well as the Pt:Cu ratio is proportional to time of deposition. Hence, the galvanic replacement is not stopping after the time required to reach a peak Pt area, but Pt sites are becoming inaccessible. Interestingly, Pt growth does not progress in the same manner when the temperature during galvanic displacement is increased and all other factors are held constant. In the case of increasing temperature and hence, rate of galvanic displacement (Figures 2.5d-f), all three metrics (i.e. Pt area, Pt:Cu atomic ratio and Pt mass) increased proportionally. This phenomena has several interesting implications. First, it shows that there isn’t pore-clogging or significant particle growth at higher temperatures (Figures 2.5d,f). Next, the Pt:Cu atomic ratio (Figure 2.5e) in the material indicates that Cu is continually displaced. This can only be indicative of the partially displaced PtCu particles fragmenting into smaller particles, exposing more copper surface for galvanic displacement to occur with which simultaneously increases electrochemically active area. Moreover, it is important to note that all tests were measured after catalysts reached their steady-state CVs. One would expect to see very similar Pt:Cu ratios because all accessible
Cu in lower Pt-content catalysts should have dissolved during the dealloying process, rendering a very similar active catalyst. However, the presence of an increasing Pt:Cu ratio indicates that each of the PtCu materials produced from each of the temperatures consists of an active catalyst with its own unique composition. We conclude that as long as the temperature of galvanic displacement is increased, the particle size of the catalyst material will decrease. The particle size histograms and SEM images in Figure 2.6 confirm this assumption and show that there is a 41% decrease in particle diameter as a result of increasing the galvanic displacement temperature from 50 °C (Figure 2.6A) to 75 °C (Figure 2.6C). Figure 2.6B also shows an expected slight decrease in size distribution and average particle size (~ 10%) when the catalyst is supported with Vulcan carbon. Finally, if the concentration of K₂PtCl₄ is decreased by a factor of ten (50 °C displacement, 2.5 minutes), there is a proportional decrease in all three metrics (Figure 2.5g-i). This indicates that the galvanic displacement is proceeding at a slower rate, which is expected. We also expect a larger particle size for smaller K₂PtCl₄ concentrations, despite both experiments occurring at the same temperature, because of the slower rate of reaction from low K₂PtCl₄ concentration. Collectively, it can be concluded that the particle size of our PtCu catalyst is inversely proportional to the initial rate of the galvanic displacement reaction for a given set of parameters. If these observations can be extended to other systems, temperature regulation during galvanic displacement could become another effective method for particle size control in the synthesis of new bimetallic materials.
2.3.4 Electrochemical activity towards ORR

The electrocatalytic activity of a PtCu/C catalysts and a commercially available 20 wt% Pt/C (Johnson-Matthey Pt on Vulcan XC-72) towards the ORR is demonstrated by the (blank-subtracted) anodic sweep (0-1.2 V_RHE, 100 mV/s) in O_2 saturated 0.1 M HClO_4 electrolyte using a rotating disc electrode (RDE). Figure 2.7a shows typical polarization curves obtained with a PtCu/C catalyst and a Pt/C catalyst. The two catalysts used to generate the curves depicted in Figure 2.7a have comparable Pt ECSAs. The enhancement in the ORR activity from the PtCu/C catalyst (2.5 min, 50 °C) is indicated by a positive shift in half-wave potential of about 40 mV (E_{1/2} measured at j = -3 mA cm^{-2}). However, both catalysts do not have the same diffusion limited current, which is due to unavoidable differences in electrode coverage. Therefore, a more useful metric for comparing ORR activity is the mass transport-corrected activity per area of Pt. These Pt area-based ORR activities at 0.9 V_RHE are given for many of the PtCu/C catalysts in Figure 2.7b. All PtCu/C catalysts screened have at least a twofold improvement in ORR activity when compared to the commercially available Pt/C catalyst. The best performing catalyst was prepared with a 2.5 min 50 °C galvanic displacement and shows a fourfold improvement in ORR activity per Pt area.

Figure 2.7c shows the mass transport-corrected Pt area-based Tafel plot for the best performing PtCu/C catalyst and the commercial Pt/C catalyst. The Tafel plot indicates that the PtCu/C catalyst maintains higher ORR performance across a wide range of potentials. In addition, the slope of the lines on the Tafel plot give mechanistic information about the
rate determining step (RDS) of the ORR pathway. Typically, Tafel slopes of ~60 mV/dec are reported for polycrystalline Pt nanoparticles in the low overpotential regime (E > 0.85 V_{RHE}).\textsuperscript{23, 45, 46} The Tafel slope for the PtCu/C and Pt/C catalysts are in good agreement with each other and the previously reported 60 mV/dec. This indicates that the ORR for the PtCu/C catalyst follows the same reaction pathway as Pt/C and is being catalyzed on active sites very similar to the active sites on a monometallic polycrystalline Pt nanoparticle catalyst.

The enhancement in ORR specific activity can be credited to several factors. Most researchers attribute core-shell catalyst activity enhancement to a lattice contraction in the Pt overlayer caused by subsurface alloying.\textsuperscript{17, 23, 27, 32, 47} The compression of the Pt lattice has been found to shift the Pt d-band center away from the Fermi level which weakens oxygen binding, increasing overall ORR activity.\textsuperscript{48} We believe lattice strain may have contributed to the high specific activity the PtCu/C catalyst, but there is no experimental evidence of a significant monometallic Pt shell structure except that the CV of the PtCu/C catalyst (in N\textsubscript{2} saturated HClO\textsubscript{4}) exhibits the signature of a clean polycrystalline Pt surface. However, there is a 6\% enhancement in Pt at the shell of the catalysts (TEM/EDX Figure 2.3) which cannot be ignored, and is significant enough for the surface lattice parameter of the catalyst to be significantly different from the bulk, such that a shift in d-band from slight surface lattice modification is extremely likely. With that said, PtCu/C alloy catalysts without any core-shell structure have been shown to exhibit an upward d-band shift.\textsuperscript{49}
Therefore, the overall concentration of copper in our PtCu catalysts is enough to cause a d-band shift which should improve ORR activity.

The improvement in ORR specific activity may also be potentially related to the average coordination number of surface Pt atoms in the catalyst. It has been shown that Pt tends to bind oxygen reduction intermediates (O$_{ads}$ and OH$_{ads}$) too strongly, which can block active sites from adsorbing O$_2$ and/or breaking the O-O bond.$^{50}$ Therefore, if the affinity for these intermediates can be lowered, Pt will have a higher per-site activity. The affinity of Pt for these oxygen containing intermediates is linked to the coordination of the Pt atoms. Pt atoms having few neighbours, like those found at edge and corner sites form a strong bond with adsorbed oxygenated species which inhibits the rate of ORR. More coordinated Pt atoms do not form such a strong bond with oxygen and are more desired. Literature has shown that there is a significant particle size effect for Pt nanoparticle catalysts with specific activity increasing as particle size increases,$^{50-53}$ mainly because there is a smaller percentage of undercoordinated Pt atoms on larger Pt nanoparticles.$^{53}$ The effect can be confirmed for the PtCu catalyst reported here with careful inspection of CVs (0-1. V$_{RHE}$ 100 mV/s) measured in an N$_2$-purged 0.1 M HClO$_4$ solution (Figure 2.8). During the forward scan of the CV, OH adsorption begins to occur after 0.6 V$_{RHE}$, and when the scan is reversed, adsorbed OH is desorbed between 1.2 and 0.5 V$_{RHE}$, forming a peak. If a catalyst has a lower affinity for oxygenated species, the peak corresponding to OH desorption should shift to more positive potentials, indicating it is thermodynamically less favorable to bind oxygenated species. In Figure 2.8, an OH desorption peak shift of about +30 mV is
observed for the PtCu/C 50 °C catalyst relative to Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72; particle size ~4 nm). Kibsgaard et al. and Mayrhofer et al. have shown that the magnitude of the positive shift can be correlated to average particle size, with greater positive shifts corresponding to larger particles, which have an increased average Pt coordination number.\(^{50,51}\) This shift is also observed within our own PtCu catalysts and is illustrated by the inset of Figure 2.8 which shows a negative shift (relative to PtCu/C 50 °C) in the OH desorption peak as the catalyst particle size is decreased by performing galvanic displacement at 75 °C. Hence, we believe that part of our enhancement in ORR activity is due to the decrease in average Pt oxophilicity caused by the relatively large size of our particles and features.

Some variations in specific ORR activity (Figure 2.7b) for the PtCu catalysts can be logically explained with analysis of the galvanic displacement process. However, the extent of enhancement due to lattice strain and the extent of enhancement due to particle size effects cannot be deconvoluted in all cases without experiments specifically designed to isolate these effects. Generally, if the time of galvanic displacement exceeds the “threshold time” (time after which, further galvanic displacement results in lower Pt area), there is a decrease in porosity and a less pronounced core-shell structure. These catalysts exhibit enhanced activity relative to Pt/C due to particle size and lattice strain, but see a decrease in magnitude of specific activity because enhancements from lattice strain are reduced. This can be observed in the decrease in activity from the 2.5 min PtCu/C (50 °C) to the 3 min PtCu/C (50 °C). After the threshold time, the ORR activity is expected to
approach that of bulk polycrystalline Pt (BPPt; specific activity of 1.5 mA/cm$^2$). It is important to note that a PtCu catalyst with only an enhancement from particle size would never exceed the activity of BPPt—this is the ceiling, indicating a catalyst with essentially the same surface/electronic structure as BPPt. Although BPPt has a relatively high ORR area-based activity, a galvanically displaced PtCu catalyst with BPPt properties would be extremely undesirable as an ORR catalyst due to low mass activity and low surface area.

Mass-specific ORR activity and electrochemically active surface area per gram Pt (ECSA/gPt) for the 2.5 min PtCu/C (50 °C) and 3 min PtCu/C (50 °C) are compared to Pt/C in Table 2.1. The decrease in mass activity between 2.5 and 3 min can be attributed to the decreasing porosity which occurs when galvanic displacement exceeds the threshold time. Decreasing mass activity as the duration of galvanic displacement is extended is a trend that is representative of all the galvanic displacement temperatures. As a result, we elected to report only the most competitive catalysts for this class of PtCu catalysts against the commercially available Pt/C catalyst. Both the 2.5 and 3 min PtCu catalysts exhibit at least 40% higher ORR mass activities (at 0.28 and 0.25 A/gPt, respectively) than Pt/C (0.18 A/gPt). However, this increase is modest in comparison to the target mass activity of 0.44 A/mgPt for a commercially viable transportation application. Nonetheless, the relatively low ECSA/gPt of the PtCu catalysts compared to Pt/C suggests that higher mass activity could be obtained for these catalysts simply by increasing the Pt area. Galvanic displacement statistics explained earlier in this manuscript indicate that increasing Pt area while decreasing Pt mass may be somewhat straightforward for this class of PtCu catalysts.
if the correct combination of parameters is used during galvanic displacement (e.g. higher temperatures and lower concentrations of K₂PtCl₄).

2.3.5 Catalyst stability

PEM fuel cell catalysts with high durability are very important, and numerous Pt-based catalysts with extremely high activities are somewhat deceiving because many are highly dependent on a specific crystal facet which may not be mechanically stable upon cycling. Other highly active catalysts show a great deal of particle aggregation over time. These properties are unfavorable and can be screened experimentally before the catalyst is used in a membrane electrode assembly (MEA). To measure the degradation of our catalyst, we used an accelerated stability test similar to that used by Kibsgaard et al., Kou et al. and others. The test was performed by cycling the potential between 0.6 and 1.1 V<sub>RHE</sub> in O₂ saturated 0.1 M HClO₄ for 30,000 cycles (50 mV/s, RT). This test is especially rigorous because of the successive oxidation/reduction of the Pt surface. The electrochemically accessible Pt area was measured every 2500 cycles. The 2.5 min PtCu/C (50 °C) experienced a 35% loss in Pt area during the 30,000 cycles (Figure 2.9). It is important to note that the major loss in area occurred during the first 2500 cycles (25% loss). After the first 2500 cycles, there was only a marginal decrease in Pt area every 2500 cycles. The Pt:Cu ratio of the catalyst was maintained during the stability test as confirmed by EDX analysis before and after. Both Kibsgaard et al. and Kou et al. found Pt/C (20 wt% ETEK) to lose ~ 60% of its area within 5,000-10,000 cycles. This degradation occurs at least 2 times faster than our PtCu catalyst, and our test duration is 3 times longer. While the
PtCu catalyst meets the DOE protocol of < 40% loss in area over 30,000 cycles,\textsuperscript{54} we believe it can be further improved by optimizing the catalyst loading to find the best catalyst dispersion. However, it is also known that conditions during fuel cell start-up and shut-down are particularly hazardous for supported catalysts, usually leading to corrosion of the C support. To date, we have also performed preliminary stability testing on our unsupported PtCu catalyst and found our 2.5 min 50 °C catalyst to be highly stable, exhibiting only a 20% loss in Pt area over 10,000 cycles with the same testing protocol.

2.4 Conclusions

This study demonstrates a feasible, robust preparation methodology for depositing Pt-enriched shells onto a tunable base-metal nanoporous support which results in sustained catalyst durability over 30,000 cycles. We attribute our increase in activity to a combination of particle size and lattice strain effects. The synthesis of these catalysts involved a novel method of performing galvanic displacement via rotating a copper coated GC disk electrode, where no successive washing of nanoparticles was necessary, and catalysts could be immediately characterized after displacement. This innovative method of coating catalysts also makes it possible to make other in situ galvanic displacement measurements, such as measuring the OCP during galvanic displacement, which could provide useful thermodynamic/kinetic information. In addition, previous literature accounts have found it impractical to perform galvanic displacement on porous structures at higher temperatures, as it destroys the nanoporous network,\textsuperscript{29} but we have shown that it cannot be discounted as
a synthetic approach for producing monodisperse nanoparticles. In the future we will continue exploring modifications of galvanic displacement and the manifestations of catalysts they produce. The results found here suggest that galvanic displacement may be a useful general synthetic strategy for altering the surface catalytic activity of other noble metal catalysts (ie. Pt+ galvanically displaced Co or Pt+galvanically displaced Ni).

2.5 Acknowledgements

This work was supported by the Department of Chemistry and Biochemistry and also in part by The Ohio State University Graduate Enrichment Fellowship. We would also like to thank Dr. Sarum Boonmee for his generous help with operation of the furnace at the OSU foundry, and his preparing of the CuAl alloys. Ann Lii is acknowledged for conducting XPS analysis on the samples, Muntasir Chowdhury for the electrochemical characterization of some catalysts, Anthony Lutton for measuring the ICP-MS and Hendrik Colijn for the TEM measurements.

2.6 References


Figure 2.1: SEM images of np Cu a) as-prepared before galvanic displacement, b) after 2 min galvanic displacement at room temperature, c) after 2 min galvanic displacement at 50 °C, and d) carbon supported 2 min galvanic displacement at 50 °C, in 1.2 mM K$_2$PtCl$_4$ in H$_2$O.
Figure 2.2: Cyclic voltammogram (CV) for the initial three cycles and the steady-state signature of PtCu/C as a function of duration of galvanic displacement. Steady-state CV recorded after 50 dealloying cycles between 0.6-1.2 V\textsubscript{RHE} at 1 V/s. Galvanic displacement solution is 1.2 mM K\textsubscript{2}PtCl\textsubscript{4} @ 50 °C. CVs shown are measured at 100 mV/s in N\textsubscript{2} purged 0.1 M HClO\textsubscript{4} at 25 °C.
Figure 2.3: TEM images and corresponding EDX line-scans showing Pt:Cu composition before and after dealloying/potential cycling. PtCu catalysts displaced for 2.5 min at 50 °C in 1.2 mM K₂PtCl₄ in H₂O.
Figure 2.4: XPS profile for 2.5 min PtCu (50 °C) as-prepared and after voltammetric dealloying  A) Cu 2p region B) Cu LMM auger region and C) Pt 4f region.
Figure 2.5: Pt ECSA, Pt mass, and Pt:Cu as a function of changing galvanic displacement parameters for unsupported PtCu catalysts. All measurements taken after catalysts are dealloyed via potential cycling. A-C show effects from manipulating time of galvanic displacement (1.2 mM K$_2$PtCl$_4$; temp 50 °C; rotation rate 500 rpm), D-F show effects from manipulating temperature of galvanic displacement (1.2 mM K$_2$PtCl$_4$; time 2.5 min; rotation rate 500 rpm), and G-I show effects from manipulating concentration of K$_2$PtCl$_4$ (temp 50 °C; time 2.5 min; rotation rate 500 rpm).
Figure 2.6: Particle size distribution histograms with corresponding SEM images for PtCu catalysts galvanically displaced at A) 50 °C (unsupported), B) 50 °C (w/Vulcan carbon support), and C) 75 °C (unsupported).
Figure 2.7: Comparison of the ORR catalytic properties of PtCu/C catalysts and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72). A) ORR polarization curves for 2.5 min PtCu/C (50 °C) and Pt/C. B) ORR activity @ 0.9 V RHE normalized to Pt area for PtCu/C and Pt/C catalysts. C) Tafel plot of kinetic current density during ORR for 2.5 min PtCu/C (50 °C) and Pt/C catalysts. Conditions for all figures: O2 saturated 0.1 M HClO4, room temperature, 100 mV/s sweeprate (blank subtracted). † indicates catalyst displaced with 0.12 mM K2PtCl4 which is 1/10th the normal concentration.
Figure 2.8: Steady-state cyclic voltammogram (CV) of PtCu/C (50 °C), PtCu/C (75 °C) and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) measured in N₂-purged 0.1 M HClO₄ at room temperature, 100 mV/s. Inset shows zoom-in of OH desorption peak region and potential of OH desorption peak for each catalyst.
Figure 2.9: Relative Pt area as a function of duration of cycling during accelerated stability testing. Accelerated stability test performed by cycling potential between 0.6-1.1 $V_{\text{RHE}}$ in O$_2$ saturated 0.1 M HClO$_4$. 

49
Table 2.1: Mass activity, specific activity, and electrochemically active surface area per gram Pt (ECSA/gPt) for top performing PtCu catalysts and Pt/C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mass activity(^{[a]}) (A mg(^{-1})Pt)</th>
<th>Specific activity (mA cm(^{-2})Pt)</th>
<th>ECSA/gPt (m(^2)Pt g(^{-1})Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5 min PtCu/C (50 °C galv. disp.)</td>
<td>0.280 ± 0.02</td>
<td>2.124 ± 0.2</td>
<td>13.18 ± 0.1</td>
</tr>
<tr>
<td>3 min PtCu/C (50 °C galv. disp.)</td>
<td>0.253 ± 0.02</td>
<td>1.696 ± 0.2</td>
<td>14.91 ± 0.1</td>
</tr>
<tr>
<td>Pt/C</td>
<td>0.178 ± 0.004</td>
<td>0.498 ± 0.032</td>
<td>34.13 ± 0.01</td>
</tr>
</tbody>
</table>

\(^{[a]}\) mass quantified by ICP-MS
Chapter 3: Electrochemical Insights into the Oxygen Reduction Reaction Activity of Pt/C and PtCu/C Catalysts

3.1 Introduction

The oxygen reduction reaction (ORR) is one of the key reactions in fuel cells and metal air batteries. Despite vast efforts in the past decades to develop non-Pt based catalysts, Pt remains the catalyst of choice for ORR in aqueous medium. Recently, alkaline electrolytes have been gaining interest due to the general enhanced stability of catalysts in basic conditions, the absence of specific adsorption of spectator ions present in acidic medium, and the possibility of using non noble metal catalysts.

Significant progress towards the development of cathode catalysts has been made through the efficient utilization of Pt by creating nanoparticles, decorating Pt nanoparticles on carbon nanotubes, Au and Pd-alloy substrates, core-shell catalysts, Pt-based alloys, and Pt-based alloys. The surface electrochemistry of PtX alloys, typically involving 3d-transition metals (X=Fe, Ni, Co, Cu) is of great interest due to their enhanced surface activity towards the electrochemical reduction of O2 (ORR) compared to polycrystalline Pt. Nanoparticles and core-shell (core = Ni, Co, Au, Pd, Cu or PtX; shell = Pt) studies suggest that a very thin Pt surface layer introduces lattice strain to the Pt shell
which increases the overall ORR activity according to both experiment and theory\textsuperscript{20}. Pt-Cu core-shell nanoparticles with improved ORR activity over commercial Pt catalysts has been reported by our group as well as others\textsuperscript{6, 7, 33}. PtCu has also been used in heterogeneous catalysis for CO oxidation\textsuperscript{35}, in the dehydrogenation of parafins\textsuperscript{36}, in the synthesis of methyl isobutyl ketone\textsuperscript{37}, and as a material for sensors\textsuperscript{38}.

In the present study, we investigated the ORR activity of a carbon supported PtCu core-shell structure prepared by galvanically displacing Pt on a tunable nanoporous Cu support made by dealloying Cu alloys. We have previously reported ORR activities of these PtCu catalysts in acidic solution with over four-fold activity enhancement compared to commercially available Pt black (Johnson Matthey) catalysts\textsuperscript{39}. This chapter examines the surface electrochemical processes, for example, the effect of O/OH coverage, which leads to the enhanced activity of this new class of material compared to Pt/C. In this chapter we will focus on the activity of carbon supported PtCu in alkaline solution (0.1 M KOH) and the comparison of its activity to acidic medium (0.1 M HClO\textsubscript{4}). We present detailed analysis of the electrochemical evolution of the catalyst’s surface, kinetic parameters for the ORR, the effects of reversible and irreversible surface oxygenation, and the observed pH independence of the rate limiting step for the ORR.
3.2 Experimental Methods

3.2.1 Nanoporous copper synthesis
Nanoporous copper synthesis was described in Chapter 2 (section 2.2.1)

3.2.2 Thin-layer Pt-npCu electrode preparation
Following heat treatment of the npCu in H₂, the reduced copper coin was ground into a fine powder using a mortar and pestle. 7.5 mg of npCu powder was added to 7.5 mg of Vulcan XC-72 carbon, and dispersed ultrasonically in 10 mL of ultrapure H₂O for 10 minutes. A diluted Nafion® solution (5 wt %, Alfa Aesar, 40 μL) was added to the npCu dispersion. The resulting solution was sonicated for another 10 min. Immediately following sonication, 20 μL of the suspension was drop-casted onto a mirror polished glassy carbon (GC) disk electrode (PINE, 5 mm diameter). The prepared electrode was dried under vacuum (55 °C for 1.5 hours). After drying, the coated electrode was allowed to cool down to room temperature. For comparison, Pt/C was prepared by dispersing 15 mg of 20 wt% Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) in 10 mL of ultrapure H₂O for 10 minutes. There were no other variations from the prior procedure.

3.2.3 Deposition of Pt
120 mL of a 1.2 mM K₂PtCl₄ (Sigma-Aldrich) solution (ultrapure H₂O from Milli-Q 18.2 MΩ) was added to a standard 3-electrode cell with heating jacket. The cell was thermostatically controlled at 50 °C. The nanoporous copper coated GC electrode was
attached to a Pine electrode rotator and immersed in the K₂PtCl₄ solution for 2.5 minutes. To ensure uniform deposition of platinum, the electrode was rotated at 500 rpm during deposition. Immediately after the timed deposition, the electrode was removed from the platinum solution and rinsed in 200 mL of ultrapure water for 2 minutes at 500 rpm, twice, to quench the reaction.

3.2.4 Electrochemical study

Electrochemical measurements were performed in a jacketed standard 3-electrode cell using a ring-disk electrode rotator (Pine) equipped with a CH Instruments bi-potentiostat (CH 760D) capable of concurrent rotation control. A reversible hydrogen electrode (RHE) with a Luggin capillary was used as the reference electrode for all electrochemical measurements. The counter electrode was a Pt mesh. The electrolyte used was 0.1 M HClO₄ or 0.1 M KOH. A 0.1 M HClO₄ solution was prepared by diluting concentrated trace metal grade acid (Fisher) with ultrapure deionized H₂O. A 0.1 M KOH solution was prepared by dissolving KOH pellets (Sigma-Aldrich, ACS grade) in ultrapure deionized H₂O. All cyclic voltammograms were recorded at 298 K with a scan rate of 10-100 mV/s and a rotation rate of 0 to 1600 rpm. The prepared electrodes were transferred to the electrochemical cell and immersed in nitrogen-saturated electrolyte, deareated for at least 45 min. The electrodes were ‘acid washed’ via electrochemical dealloying using a modification of the method first described by Koh and Strasser⁴⁰. The potential was cycled 50 times between 0.5 V and 1.2 V at 1 V/s in 0.1 M HClO₄ solution to dealloy and stabilize the catalyst. Then CV scans between 0.03 V- 1.2 V at 20 and 100 mV/s were measured.
until a steady-state voltammogram was attained. The Pt electrochemical surface area (Pt ECSA) was determined from a N₂ saturated voltammogram via the average integrated charge of the underpotentially deposited hydrogen (H_{upd}) region (0.05 < E < 0.45 V for acid and 0.05 < E < 0.45 V for base) after double-layer correction. The widely accepted conversion of 210 μC cm⁻²Pt for polycrystalline Pt was assumed. ORR CV measurements were performed in an oxygen-saturated electrolyte (0.1 M HClO₄ or 0.1 M KOH) with the potential cycled between 0.03 V and 1.2 V at 20 mV/s. Polarization curves were obtained by subtracting the N₂-saturated voltammogram from the O₂-saturated voltammogram to remove background contributions. Kinetic ORR activity (i_k) was calculated for the anodic sweep polarization curve via the following relationship:

\[
\frac{i_d - i_{tot}}{i_d} = \frac{i_k}{i_{tot}}
\]

where \(i_d\) is the diffusion limited current, and \(i_{tot}\) is the total current. Pt specific activities were determined from Pt-ECSA data as follows:

\[
\text{Specific activity} = \frac{i_k}{\text{Pt ECSA}}
\]

Hydrogen peroxide production during ORR was measured via a rotating ring disk electrode (RRDE, Pine) with a Pt ring electrode held at 1.2 V vs. RHE during the measurement of the ORR on the disk. The RRDE experiments were conducted in O₂ saturated 0.1 M HClO₄ or 0.1 M KOH at room temperature. Before the ORR RRDE scan, a potential hold was measured at the ring in the absence of an applied potential at the disk to establish a background current. The ring background current was subtracted from the peroxide
oxidation ring current. The collection efficiency, $N$, for the RRDE was 0.28. All electrochemistry experiments were repeated at least 4 times to ensure reproducibility.

Hydrogen peroxide reduction was measured independently with the PtCu/C catalyst on the disk electrode by diluting a 30% hydrogen peroxide (Fisher, ACS grade) solution to $5 \times 10^{-4}$ M in 0.1 M KOH electrolyte. CV scans were obtained between 0.03 V- 1.2 V at 20 mV/s and rotation rates varying between 500 -1600 RPM.

Electrochemical impedance spectroscopy (EIS) was measured to determine the solution resistance for the electrochemical system to correct for IR loss, using a Princeton Applied Research 263A potentiostat in conjunction with a Solartron 1260 Impedance Analyzer. The impedance was measured at OCP and at 0.9 V (amplitude of 5 mV from 10,000 Hz to 0.01 Hz). The correction was applied to raw data as follows:

$$E_{\text{real}} = E_{\text{measured}} - E_{\text{IR}} \quad (3.3)$$

3.3 Results and Discussion

3.3.1 Electrochemical behavior of Pt-npCu/C in 0.1 M KOH

As previously reported by our group$^{39}$, fresh galvanically displaced Pt-npCu/C occasionally results in residual Cu on the surface of Pt, the amount of which depends on the displacement conditions. Figure 3.1a shows the electrochemical features of a freshly deposited Pt-npCu reaching a steady state within 16 potential cycles in N₂ deaerated 0.1
M KOH. A comparison of the voltammograms between a freshly displaced Pt-npCu/C and Pt-npCu/C after acid washing is given in Figure 3.1b. A freshly deposited Pt-npCu/C (Figure 3.1a) typically shows a slightly distorted H$_{upd}$ feature in the region between $0.4 < E < 0.05$ V. Oxidative and reductive peaks in the region between 0.50 and 0.9 V, could be from a combination of Cu oxidation/reduction between Cu, Cu$_2$O and Cu(OH)$_2$ and Pt oxidation/reduction between Pt$^0$ and platinum oxide/hydroxides. The literature has reported possible dissolution of Cu$_2$O to HCuO$_2$ at pH 13 during the anodic sweep, which can be re-deposited back to the electrode upon the cathodic sweep$^7$.

On the other hand, residual Cu species on the surface dissolve readily in acid. After being subjected to acid washing, Pt-npCu/C catalysts measured in both 0.1 M HClO$_4$ and 0.1 M KOH show classical Pt features and Pt oxidation and reduction peaks at ca. 0.8 V, indicative of exposed Pt at the surface layer. Unless specifically stated otherwise, ORR studies in both acid and alkaline electrolytes reported in this paper were measured after residual Cu is removed upon cycling in acid (ca. 50 cycles at 1 V/s between 0.6 and 1.2 V) until a steady state voltammogram and ECSA is obtained. The acid washed catalysts from hereon will be referred to as PtCu/C.

### 3.3.2 ORR activity and $H_2O_2/HO_2^-$ detection on PtCu/C

In both 0.1 M HClO$_4$ and 0.1 M KOH solutions, the oxygen reduction reaction is generally described as having 3 regions: the kinetic controlled region, ($> 0.85$ V), combined kinetic-diffusion control ($0.6 < E < 0.85$ V), followed by a well-defined diffusion limiting current
indicating the ORR is purely transport controlled at < 0.6 V. The kinetics of the reduction of O₂ are known to be different under different sweep directions for Pt-based catalysts\textsuperscript{41}. The voltammetric curves recorded in the anodic (positive) sweep represent O₂ reduction on essentially oxide-free surface, while during the cathodic (negative) sweep the reaction occurs on partially oxidized surfaces. The most recent convention is to compare ORR activity of Pt-based catalysts via the anodic sweep, assuming an oxide-free surface. Unless otherwise stated, oxygen reduction and hydrogen peroxide reduction/oxidation polarization curves presented in this paper were anodic sweeps only. The ORR polarization curves were obtained by subtracting the background current caused by capacitance and surface processes on the electrode (measured in N₂) from the O₂ saturated voltammogram. ORR polarization curves (before subtraction), along with their associated background currents are shown in Figure 3.2 for the PtCu/C catalyst in 0.1 M HClO\textsubscript{4} and in 0.1 M KOH.

Hydrogen peroxide produced during the course of the ORR was detected in the corresponding ring current where the ring potential was held constant at 1.2 V, such that peroxide oxidation occurred under diffusion control. The % peroxide production can be calculated from the ring-disk measurement according to the following equation, where the collection efficiency, \( N = 0.28 \).

\[
x \times H_2O_2 \ (\%) = \frac{I_{\text{ring}}}{I_{\text{disk}} N} \times 100 \quad (3.4)
\]

Figures 3.3 and 3.4 show that ORR on PtCu/C in both 0.1 M HClO\textsubscript{4} and 0.1 M KOH proceeds entirely through a four electron pathway. The amount of peroxide produced on
the PtCu/C catalyst (Figure 3.3) is essentially negligible throughout the potential region between 0.9 to 0.2 V in base and between 0.9 to 0.4 V in acid. Detectable H₂O₂ production in the region of H₂ desorption, below ~0.4 V in acid, indicates that a surface covered with hydrogen adatoms may facilitate the formation of peroxide. Interestingly, the as-prepared Pt-npCu/C which contains residual surface Cu, did not produce any detectable peroxide during the ORR, whereas on a monometallic polycrystalline Cu surface, the ORR clearly goes through a 2e⁻ reduction process, producing predominantly H₂O₂ between 0.8 and 0.3 V.

The four electron ORR pathway for PtCu/C in alkaline solution can also be confirmed via analysis of Levich plots of the anodic sweeps from 0 to 1.2 V,

\[
\frac{1}{i_{tot}} = \left( \frac{1}{i_k} + \frac{1}{i_d} \right) = \left( \frac{1}{i_k} + \frac{1}{B \omega^{-1/2}} \right) \tag{3.5}
\]

\[
i_d = 0.62 nFD^{2/3} \nu^{-1/6} C \omega^{1/2} = B \omega^{1/2} \tag{3.6}
\]

where n, F, D, ν, C and ω are the total number of electrons, Faraday constant, diffusion coefficient (cm²/s), kinematic viscosity (cm²/s), concentration (mol/cm³) and rotation rate (rad/s), respectively. Figure 3.4b shows the Levich plot (i⁻¹ vs. ω⁻1/2) for ORR in alkaline solution at various potentials ranging from 0.8 to 0.2 V. The B-factor obtained from the slope of a Levich plot was 9.1 (±2) × 10⁻² mA rpm⁻¹/² which agrees with a theoretical four-electron reduction process (3.99 × 10⁻² mA rpm⁻¹/²) from 0.8 to 0.2 V, calculated with literature data for O₂ concentration of 1.21 × 10⁻⁶ mol/cm³, kinematic viscosity, ν, of 1.008
× 10⁻² cm²/s, and O₂ diffusivity of 1.86 × 10⁻⁵ cm²/s in 0.1 M KOH at 293 K⁴¹. The intercepts of the Levich plot corresponds to the kinetic currents, and it is also noteworthy that at potentials < 0.6 V the plot intercepts i¹ at the origin, proving that the current at potentials < 0.6 V are diffusion limited. Consistent with our ring data, Pt-npCu/C (which may contain surface Cu residue) also suggests a four electron reduction pathway in alkaline solution, as shown in the Levich plot in Figure 3.4b.

3.3.4 H₂O₂ reduction reaction on PtCu/C

Hydrogen peroxide reduction was conducted on the PtCu/C catalyst in a solution free of oxygen to simulate the chemical environment when H₂O₂ is produced as an intermediate or final product during the O₂ reduction process. In basic conditions, H₂O₂ dissociates to HO₂⁻ and H⁺ (pKa 11.6). Figure 3.5a shows a family of polarization curves for HO₂⁻ reduction obtained on the PtCu/C catalysts in 0.1 M KOH at varying rotation rates and the corresponding Levich plot. Unlike oxygen reduction/oxidation, the reduction/oxidation process of hydrogen peroxide is highly reversible on PtCu/C as indicated by the oxidation and reduction currents in Figure 3.5a and a wide region of well-defined mass transport controlled oxidation and reduction.

The Levich plot in Figure 3.5b confirms a 2 electron reduction and oxidation of H₂O₂ to H₂O and O₂, respectively, assuming kinematic viscosity of 1.008 × 10⁻² cm²/s, HO₂⁻ diffusivity of 8.75 × 10⁻⁶ cm²/s in 0.1 M KOH at 293 K, and a peroxide concentration of 5 × 10⁻⁴ M. Except for 0.9 < E < 0.95 V, the Levich plot between 0.2 and 1.2 V intercepts
the origin, indicating a pure mass transfer control of the peroxide reaction over a wide range of potentials.

A comparison of the ORR polarization curve to the hydrogen peroxide polarization curve is shown in Figure 3.6. The overpotential for hydrogen peroxide reduction on PtCu/C is smaller than of the oxygen reduction on PtCu/C, indicating that if peroxide is formed as an adsorbed intermediate of the ORR, it could be electrochemically reduced immediately to \( \text{H}_2\text{O} \). This finding is consistent with the observed overall 4\( \text{e}^- \) reduction of O\(_2\) on PtCu/C, and it suggests that ORR on PtCu/C in 0.1 M KOH could occur through a 4\( \text{e}^- \) series pathway, or a one-step direct pathway (from O\(_2\) to H\(_2\)O).

\[
\begin{align*}
\text{O}_2 & \rightarrow \text{H}_2\text{O}_2 \xrightarrow{2\text{e}^-} \text{H}_2\text{O} \\
\text{4e}^- & \\
\end{align*}
\]

(3.7)

### 3.3.5 Tafel analysis and effect of OH\(_{ads}\)

To provide further insight into the mechanistic pathway of the ORR, Tafel plots showing mass transport corrected ORR current densities (anodic sweep) for PtCu/C after acid washing are presented in Figure 3.7. For PtCu/C, one may extrapolate a line at low current densities (\( \text{lcd} \)) (defined as spanning the range of potentials where kinetic current is between 0.25 % of the limiting current and where the Tafel line begins to deviate from linearity), giving Tafel slopes of \(~50\) mV/dec in acid and base. A line can also be extrapolated for higher current densities (\( \text{hcd} \)) (defined as the linear Tafel range between the \( \text{lcd} \) Tafel...
region and the diffusion limited current region), giving a Tafel slopes of ~90 mV/dec of i in base and ~80 mV/dec of i in acid. The similarity of the \textit{lcd} and \textit{hcd} Tafel slopes at the two extreme pHs suggests that the rate limiting step (RLS) of the ORR on PtCu/C is the same, regardless of pH. Moreover, the Tafel slopes over the entire current range for PtCu/C are very similar to the associated Tafel slopes for Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72), indicating that the mechanistic pathway for ORR on PtCu/C is very similar to the pathway on commercially available Pt/C.

There is a general consensus that the ORR rate limiting step for Pt catalysts, regardless of current density, involves the first electron transfer to \( \text{O}_2 \)\textsubscript{ad}\( ^{41,42} \). The change in Tafel slope from \( \sim50 \) to \( >85 \) mV/dec is not linked to a change in the RLS, but attributed to differences in adsorption of oxygen-containing species. These adsorbates are generally believed to be attributed to 1) ORR reaction intermediates\( ^{43} \) or 2) chemisorbed hydroxyl groups (OH\textsubscript{ads}) from the electrolyte\( ^{41,44} \). Both theories hold that the change in Tafel behavior is primarily related to a marked change in electrode adsorbate coverage. However, it has been very difficult for any research group to provide conclusive findings that completely deconvolutes the entire ORR mechanistic pathway, particularly on a polycrystalline Pt-based catalyst material.

Regardless, most reports of ORR on Pt surfaces in acidic and alkaline conditions imply that OH\textsubscript{ads} blocks active sites for electron transfer to \( \text{O}_2 \)\textsubscript{ad}\( ^{44} \). Moreover, studies by Markovic et al. show that activity of Pt is essentially dependent on structure sensitive adsorption of
OH on the various Pt(hkl) facets\textsuperscript{45}, with the lowest OH\textsubscript{ads} coverage on Pt(111) correlating to the highest activity (in alkaline solution)\textsuperscript{40,44}.

To present a more concrete depiction of the effect of OH\textsubscript{ads} coverage on the catalyst surface, we will endeavor to quantify OH\textsubscript{ads} coverage on PtCu/C relative to Pt/C. We will proceed by accepting the hypothesis that for hydrogen adsorption/desorption on a polycrystalline Pt surface, \( \approx 210 \mu \text{C/cm}^2_{\text{Pt}} \) corresponds to a full monolayer coverage (1 e- per Pt atom)\textsuperscript{46}. Next, we assume that pseudocapacitance from hydrogen adsorption/desorption occurs only at potentials between \( 0.05 < E < 0.4 \text{ V in 0.1 M HClO}_4, \) and \( 0.05 < E < 0.45 \text{ V in 0.1 M KOH} \). Based on the overlap in the blank and ORR CVs for \( E > 0.95 \text{ V} \) shown in Figure 3.2, we will also assume that OH\textsubscript{ads} coverage at all potentials is unchanged by the presence of O\(_2\). Finally, we assume that the double layer capacitance from the carbon support is constant over the potential range \( 0 < E < 1.2 \text{ V} \). Thus, at potentials more positive than 0.4 V (acid) or 0.45 V (base), any pseudocapacitive feature must be the result of adsorption/desorption of OH\textsuperscript{41,47}, on the basis that our experiments are performed in N\(_2\) (or O\(_2\))-purged electrolyte that is not known to adsorb any other spectator anions on the Pt surface\textsuperscript{44}. Under these assumptions, we can use the N\(_2\)-purged “blank” voltammogram to calculate the effective surface area of the Pt catalyst, using the average charge from adsorption/desorption of the hydrogen monolayer after double layer correction. Using the anodic sweep of the blank voltammogram, the charge associated with OH\textsubscript{ads} at potentials > 0.4 V in HClO\(_4\) and > 0.45 V in KOH can then be expressed as

\[
Q_{OH_{ads}} = \int \frac{i_E \, dE}{v} - Q_{DL} \quad (3.8)
\]

63
where \( i \) is the observed current, \( v \) is the sweep rate (0.02 V/s), and \( Q_{DL} \) is the total charge associated with the double layer capacitance. It follows that the coverage of OH ads should then be

\[
\theta_{OH_{ads}} = \frac{Q_{OH_{ads}}}{210 \, \mu C/cm^2} = \frac{Q_{OH_{ads}}}{Q_{H_{ads}}} \tag{3.9}
\]

It should be noted that 210 \( \mu C/cm^2_{Pt} \) is assumed, which may be the most extreme assumption of this method, but we believe that as long as the same constant is utilized for both H_{upd} and OH_{ads} this assumption can be justified, at least from a qualitative standpoint. Figure 3.8 shows the blank voltammetry from which \( \theta_{OH_{ads}} \) was calculated. Close inspection of this figure will show that both PtCu/C and Pt/C catalysts exhibit similar electrochemical behavior. \( \theta_{OH_{ads}} \) as a function of electrode potential is shown in Figure 3.9. In 0.1 M HClO₄, OH_{ads} coverage on PtCu/C is at least 1.5 times less than OH_{ads} coverage on Pt/C at all potentials shown. Similarly, in 0.1 M KOH, OH_{ads} coverage on PtCu/C is at least 2 times less than OH_{ads} coverage on Pt/C. These observations provide some quantitative rationale for the increase in ORR specific activity (\( @0.9 \) V) for PtCu/C catalysts relative to Pt/C, i.e.,

\[
\frac{i_{kPtCu/C}}{i_{kPt/C}} \approx \frac{\theta_{OH_{ads Pf/C @0.65V}}}{\theta_{OH_{ads PfCu/C @0.65V}}} \tag{3.10}
\]

where \( i_{kPtCu/C} \) and \( i_{kPt/C} \) are the Pt area-based kinetic activities for PtCu/C and Pt/C, respectively. This linear approximation is more accurate for catalysts that were tested in alkaline conditions; in acid, the activity enhancement is underestimated, but there is still a very strong negative correlation between activity and coverage (Table 3.1). We believe other related (carbon-supported) bimetallic Pt-based catalysts can be analyzed similarly.
and their activity (in a given electrolyte/pH) will also scale inversely with the reversible OH\textsubscript{ads} coverage. Our conclusions here are in agreement with the theory that OH\textsubscript{ads} is blocking electron access to O\textsubscript{2} and that OH\textsubscript{ads} determines the activity and mechanistic pathway of the ORR\textsuperscript{34,41,44,45}.

Potentials above 0.75 V are omitted in Figure 3.9 because it is widely believed that the adsorption of OH is no longer reversible at potentials greater than 0.75 V\textsuperscript{41,47}. This is illustrated in Figure 3.8 as the non-symmetry between anodic and cathodic currents at potentials greater than 0.75 V. However, we believe that the reversible OH\textsubscript{ads} (0.5 < E < 0.75 V) coverage and the rate of increase of the reversible coverage (d\theta/dE), henceforth called differential coverage, is an intrinsic property of the catalyst material. This hypothesis is illustrated in Figure 3.10, which shows the differential coverage (d\theta/dE) as a function of potential. In both alkaline and acidic electrolyte, there are two plateaus (per catalyst) which correspond to potential regions where the change in \theta_{OH\textsubscript{ads}} is constant. The lower of the two plateaus at \textit{ca.} 0.66 < E < 0.74 V (0.1 M HClO\textsubscript{4}) and 0.63 < E < 0.70 (0.1 M KOH) clearly shows that the rate of change of OH\textsubscript{ads} coverage is higher for Pt/C than PtCu/C in both electrolytes. Conversely, the higher of the two plateaus at \textit{ca.} 0.90 < E < 0.95 V (0.1 M HClO\textsubscript{4}) and 0.83 < E < 0.90 V (0.1 M KOH) shows that the two different catalyst surfaces reach the same rate of change of OH\textsubscript{ads} coverage, \textit{d}\theta/\textit{d}E \approx 4 in acid, and \textit{d}\theta/\textit{d}E \approx 3.75 in base. If the coverage is changing by a constant rate of 4 monolayers per volt, then the catalyst is almost certainly accruing an irreversible layer of oxide, which should be measurable on any platinum surface as a very similar differential coverage.
However, the lower plateau on the plot of differential coverage provides the rate at which
the reversible OH$_{ads}$ species is adsorbing to a surface, and this quantity is unique for
different catalysts. Therefore, at a given pH, the higher of the two plateaus on the plot of
differential coverage corresponds to the \textit{universal} rate of growth of an irreversible oxide
layer on a Pt-containing surface, whereas the lower plateau is the \textit{intrinsic} rate of growth
of the reversible OH$_{ads}$ on the surface of a Pt-containing catalyst.

It should be stressed that Pt catalysts are not directly comparable unless the electrochemical
measurements are performed at the same pH and electrolyte conditions. As of yet, we have
been unable to relate the quantified coverage of OH$_{ads}$ across different electrolytes. A
manifestation of this can be deduced from Figure 3.9, where lower OH$_{ads}$ coverage for
PtCu/C in base should in principle have better performance in base than in acid, which is
not observed. This observation suggests that the oxygen reduction reaction is primarily
ddictated by its inherent rate, which depends on the electrolyte conditions (i.e. pH in this
case), whereas the OH coverage can be used as a descriptor for comparing across materials
tested in the same conditions. Further, this method of analysis will only hold for catalysts
that are 1) Pt-based, or 2) have an X@Pt core-shell structure (X=transition metal).

\subsection*{3.3.6 ORR specific activity analysis}

While the mechanism of the ORR may be very similar in acidic and alkaline conditions,
the catalytic activity in acid and base are clearly distinct. PtCu/C is most active in acidic
conditions, with an onset potential of ca. 1.0 V, compared to ca. 0.95 V in alkaline
conditions. In the presence of residual Cu on the surface, the onset of ORR occurs at a higher overpotential of $\sim 0.85$ V. Specific activity of each catalyst was obtained from the background/mass transport-corrected anodic sweep (0 to $1.2 \, V_{RHE}$, 20 mV/s) in O$_2$ saturated 0.1 M HClO$_4$ and 0.1 M KOH solutions. Figure 3.11 displays the specific activity at 0.9 and 0.85 V for PtCu/C and Pt/C catalysts 1) before acid cleaning in 0.1 M KOH, 2) in 0.1 M HClO$_4$, and 3) after acid cleaning in 0.1 M KOH. The PtCu/C catalyst, even with regions of exposed Cu, experiences higher activity than Pt/C. The activity enhancement for PtCu/C compared to Pt/C is about threefold in acid, and twofold in base. It is worth mentioning that the specific activity of the catalyst in KOH is virtually the same before and after acid cleaning. The surface area of the Pt-npCu/C catalyst is much smaller before cleaning, so we believe that the active catalytic site on both pre- and post-acid washed surfaces is the same, but there is a higher density of available active sites on the acid washed catalyst, resulting in a similar specific activity. This observation is in agreement with the ring data for np-PtCu/C in Figure 3.3, and the Levich plot for PtCu/C in Figure 3.4.

The high activity of the PtCu/C catalysts is likely the result of two key factors: 1) lattice strain from alloying Pt with Cu, and 2) reduced surface affinity towards OH$_{ads}$. Lattice strain on Pt is generally accepted for providing enhancement of ORR activity on Pt-based bimetallic catalysts$^{6,7,30}$, particularly for core-shell catalysts with a shell thickness of $< 1$ nm. The enhanced activity observed for the PtCu catalysts reported here is due to some contribution from lattice strain$^{39}$ on Pt. A measure of catalyst’s oxophilicity is exemplified in its affinity towards OH$_{ads}$ and the ease of oxide/OH$_{ads}$ removal. The change in reversible
OH\textsubscript{ads} coverage per unit change of voltage (Figure 3.10) is consistently higher for Pt/C than PtCu/C in both alkaline and acidic conditions, indicating a stronger affinity towards OH\textsubscript{ads} for Pt/C than PtCu/C. The oxide removal peak on the reverse sweep also reveals analogous behavior where the reduction of the Pt oxide film on PtCu/C has a 30 mV lower overpotential than Pt/C\textsuperscript{39}. The altered oxophilicity of the catalyst may be due to the electronic contributions of the alloying metal, surface structure of the catalyst, and the size of the catalyst particles. Our earlier manuscript reports the effect that PtCu/C particle size\textsuperscript{39} has on the oxophilicity of the surface and its influence on the ORR activity. In this paper, we have observed an inverse correlation between ORR activity and the surface OH\textsubscript{ads} coverage/affinity. Based on our work, it is observed that Pt-based catalysts exhibiting a weaker Pt-O or Pt-OH bond benefit from an ORR activity enhancement.

3.4 Conclusions

Herein, the kinetics of the oxygen reduction reaction was studied on the highly active PtCu/C catalyst at extreme pHs. The initial catalyst structure with exposed copper was introduced, as well as the voltammetric evolution towards the final active form of the catalyst. The catalyst was shown to facilitate either a 4e\textsuperscript{-} direct or series path to water, with almost no measurable peroxide formation at useful potentials. Tafel slopes for the catalyst indicate the rate determining step is likely the transfer of the first electron. A detailed look at OH\textsubscript{ads} provides further verification that OH\textsubscript{ads} blocks electron access to O\textsubscript{2} and shows that the PtCu/C catalyst has a reduced surface affinity towards OH\textsubscript{ads} as compared to Pt/C.
Based on the OH$_{ads}$ study, it was observed that 1) Pt-based catalyst materials have a unique initial rate of change of OH$_{ads}$ coverage which is directly correlated with their ORR activity, and 2) there is a universal rate of change of OH$_{ads}$ coverage (~3.75 - 4 monolayers per volt) that describes the formation of an irreversible oxide film on any Pt-based catalyst. The electrochemical methods and results described in this work can provide insight into the nature of the ORR activity for Pt-based catalyst materials.

### 3.5 References


Figure 3.1: Cyclic voltammogram (CV) of a freshly displaced Pt-npCu/C catalyst: (a) the initial 16 cycles in N₂ deaerated 0.1 M KOH and (b) steady state CVs recorded 1) in base, 2) after 50 cycles 0.6-1.2 V (1 V/s) in acid, and 3) again in base.
Figure 3.2: CV of acid washed PtCu/C in N₂ deaerated electrolyte along with anodic scan of PtCu/C in O₂ saturated electrolyte. Electrolytes are (a) 0.1 M HClO₄ and (b) 0.1 M KOH. Corresponding CVs of Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) are shown in (c) and (d) for acid and base electrolytes, respectively. All electrochemical measurements performed at 20 mV/s, 1600 RPM, and 298 K.
Figure 3.3: H₂O₂ (in base HO₂⁻) formation measured from Pt ring held at 1.2 V during ORR anodic sweep for PtCu/C and polycrystalline Cu catalysts in 0.1 KOH and 0.1 M HClO₄. Disk electrode swept from 0.03 V to 1.2 V at rotation rate of 1600 rpm; 25 °C.
Figure 3.4: ORR on PtCu/C in 0.1 M KOH. (a) Background-subtracted polarization curves (anodic sweep) obtained from CV scans in O₂ saturated electrolyte at rotation rates varying from 0 to 1600 rpm. (b) corresponding Koutecky-Levich plots, and (c) number of electrons exchanged for ORR as a function of applied potential, calculated from Koutecky-Levich plots. †indicates data obtained from Pt-npCu/C catalyst in KOH before acid washing (contains regions of exposed copper).
Figure 3.5: Hydrogen peroxide reduction on PtCu/C in 0.1 M KOH. (a) Background-subtracted polarization curves (anodic sweep) obtained from CV scans at rotation rates varying from 0 to 1600 rpm. (b) corresponding Koutecky-Levich plots, and (c) number of electrons exchanged for hydrogen peroxide reduction as a function of applied potential, calculated from Koutecky-Levich plots.
Figure 3.6: Polarization curves of ORR and peroxide reduction for PtCu/C in 0.1 M KOH. Anodic scans only.
Figure 3.7: Tafel plot of specific kinetic current density during ORR for PtCu/C and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) catalysts in (a) 0.1 M HClO₄ and (b) 0.1 M KOH after acid washing. Conditions: O₂ saturated; anodic sweeps only; mass transport and IR corrected.
Figure 3.8: Comparison of background CVs for PtCu/C and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) in N\textsubscript{2} dearated (a) 0.1 M HClO\textsubscript{4} and (b) 0.1 M KOH.
Figure 3.9: Comparison of reversible OH_ads coverage as function of potential for PtCu/C and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) catalysts in (a) 0.1 M HClO4 and (b) 0.1 M KOH. Derived from anodic sweep of N2 deaerated CV.
Figure 3.10. Rate of change of reversible OH$_{\text{ads}}$ coverage as function of potential for PtCu/C and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) catalysts in (a) 0.1 M HClO$_4$ and (b) 0.1 M KOH. Derived from anodic sweep of N$_2$ deaerated CV.
Figure 3.11: (a) Comparison of ORR specific activity at 0.9 V and 0.85 V for PtCu/C and Pt/C (Johnson Matthey 20 wt% on Vulcan XC-72) catalysts. Derived from anodic sweeps; 20 mV/s; 298 K; mass transport and IR corrected. (b) particle size distribution of PtCu/C.
Table 3.1: Comparison of reversible OH$_{ads}$ coverage to enhancement in ORR specific activity

<table>
<thead>
<tr>
<th>System</th>
<th>$\theta_{OHads@0.55,V,Pt/C}$</th>
<th>$\theta_{OHads@0.85,V,Pt/C}$</th>
<th>$\theta_{OHads@0.9,V,Pt/C}$</th>
<th>$i_{k@0.85,V,Pt/C}$</th>
<th>$i_{k@0.9,V,Pt/C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M HClO$_4$</td>
<td>2.06</td>
<td>1.21</td>
<td>1.12</td>
<td>2.86</td>
<td>2.82</td>
</tr>
<tr>
<td>0.1 M KOH</td>
<td>2.09</td>
<td>1.50</td>
<td>1.33</td>
<td>1.99</td>
<td>2.30</td>
</tr>
</tbody>
</table>
Chapter 4: Quantifying Relative Abundance of Pt Crystal Facets for Understanding Degradation of Oxygen Reduction Catalysts

4.1 Introduction

Fuel cell technology will continue to be a viable contender in the field of energy conversion. Fuel cell vehicles offer the unique advantages of battery powered electric vehicles (near-zero emissions, long range), and internal combustion vehicles (quick refueling, and low noise). However, fuel cell technology is not yet economically viable because of the slow kinetics that plague the cathode, where the oxygen reduction reaction (ORR) occurs: $4\text{H}^+ + 4e^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$.

Commercially available ORR catalysts utilize Pt nanoparticles supported on a carbon support, but even with this expensive catalyst material, the ORR is still kinetically limiting. Recently there has been a great deal of research on new Pt-based catalysts which offer reduced Pt-loadings and enhanced kinetics.\textsuperscript{1,2} These catalysts usually involve synthesis of Pt-alloys or core-shell materials containing a Pt enriched shell and a 3d transition metal core (usually Ni, Fe, Co, Cu).\textsuperscript{1,3-21} These newer bimetallic catalyst materials have been shown to increase the ORR activity up to 90-fold.\textsuperscript{6}
Despite the high activity of this new class of ORR catalysts, steps must be taken simultaneously to ensure that these high activity catalysts maintain their ORR activity and physical integrity over long periods of time. Due to recent DOE technical targets, researchers have sought to prove that their ORR catalyst maintains its activity and electrochemically accessible surface area over tens of thousands of cycles (cycling is used as an accelerated durability test). In many cases, the catalyst meets the DOE technical targets, but a close inspection of the data shows that the catalyst experiences the greatest percentage of its ORR deactivation and physical deterioration during the first 2500 cycles.2, 12, 13, 22, 23

Researchers have typically associated carbon-supported catalyst deterioration with losses in Pt electrochemically accessible surface area (Pt-ECSA), which are the result of 1) Pt agglomeration 2) carbon corrosion, and 3) dissolution of Pt.2, 24 These three phenomena will result in physical deterioration/Pt-ECSA, but the literature is not very clear on what causes the concurrent loss in area-normalized ORR activity (deactivation) of the catalyst material. Typically, catalyst deactivation is loosely related to losses in Pt ECSA.2, 23 However, loss of Pt ECSA should not necessarily result in a loss of ORR activity. In this work, we seek to truly understand the mechanism of deactivation of commercially available Pt/C and compare it to the mechanism of deactivation of a more active bimetallic Pt-based catalyst (PtCu/C). To accomplish this goal, we performed a detailed analysis of the first 500 cycles of catalyst degradation in 100 cycle intervals. We chose to use an alkaline electrolyte in this work because alkaline electrolyte should slow down catalyst
deterioration, making it easier to probe subtle changes that occur within the first 500 cycles. Our studies indicate that as the commercially available Pt/C catalyst physically degrades, it also loses its Pt(111) surface sites, which are the most active sites for ORR.\textsuperscript{25} The bimetallic catalyst has an entirely different mode of deactivation which is based on dissolution of the alloying metal, in our case copper. The objective of this study is to provide insight into how ORR catalysts must be designed to mitigate catalyst degradation and deactivation.

4.2 Experimental Methods

4.2.1 Thin-layer electrode preparation

This procedure for preparing nanoporous copper (npCu) is described in Chapter 2.\textsuperscript{26} 7.5 mg of npCu was added to 7.5 mg of Vulcan XC-72 carbon, and the resulting mixture was dispersed ultrasonically in 10 mL of ultrapure H\textsubscript{2}O (Milli-Q 18.2 MΩ) for 10 minutes. A diluted Nafion\textregistered{} solution (5 wt %, Alfa Aesar, 40 μL) was added to the npCu/C dispersion. The resulting solution was sonicated for another 10 min. Immediately following sonication, 20 μL of the suspension was drop-casted onto a mirror polished glassy carbon (GC) disk electrode (Pine, 5 mm diameter). The prepared electrode was dried in the oven (55 °C for 1.5 hours). After drying, the coated electrode was allowed to cool down to room temperature. Pt/C was prepared analogously, except with 15 mg of Pt/C (20 wt % on Vulcan XC-72; Johnson Matthey).
Deposition of Pt was performed on npCu electrodes using a procedure described in an earlier publication. A 120 mL portion of a 1.2 mM K$_2$PtCl$_4$ (Sigma-Aldrich) solution was added to a standard three-electrode cell with heating jacket. The cell was thermostatically controlled at 50 °C. The nanoporous copper-coated GC electrode was attached to a Pine electrode rotator and immersed in the K$_2$PtCl$_4$ solution for 2.5 min. To ensure uniform deposition of platinum, the electrode was rotated at 500 rpm during deposition. Immediately after the timed deposition, the electrode was removed from the platinum solution and rinsed in 200 mL of ultrapure water for 2 min at 500 rpm, twice, to quench the reaction.

### 4.2.2 Basic electrochemical study

Electrochemical measurements were performed in a jacketed standard 3-electrode cell using a ring-disk electrode rotator (Pine) equipped with a CH Instruments bi-potentiostat (CH 760D) capable of concurrent rotation control. A reversible hydrogen electrode (RHE) with a Luggin capillary was used as the reference electrode for all electrochemical measurements. The counter electrode was a Pt mesh. The electrolyte used was 0.1 M HClO$_4$ or 0.1 M KOH. 0.1 M HClO$_4$ was prepared by diluting concentrated trace metal grade acid (Fisher) with ultrapure deionized H$_2$O. 0.1 M KOH was prepared by dissolving KOH pellets (Sigma-Aldrich, ACS grade) in ultrapure deionized H$_2$O. All cyclic voltammograms were recorded at 298 K with a scan rate of 20 mV/s and a rotation rate of 1600 rpm. The prepared electrodes were transferred to the electrochemical cell and immersed in argon-saturated electrolyte. To stabilize Pt/C, the electrodes were ‘primed’
by cycling the potential 50 times between 0.5 V and 1.2 V at 1 V/s in 0.1 M KOH solution. To stabilize PtCu/C, the electrodes were primed/dealloyed by cycling the potential 50 times between 0.5 and 1.2 V at 1 V/s in 0.1 M HClO₄. Then CV scans between 0.03 V - 1.2 V at 20 and 100 mV/s were measured in 0.1 M KOH until a steady-state voltammogram was attained. The Pt electrochemical surface area (Pt ECSA) was determined from an Ar saturated voltammogram via the average integrated charge of the underpotentially deposited hydrogen (H_{upd}) region (0.05 < E < 0.45 V for base) after double-layer correction. The widely accepted conversion of 210 μC cm⁻²Pt for polycrystalline Pt was assumed. All ORR CV measurements were performed in O₂-saturated 0.1 M KOH with the potential cycled between 0.03 and 1.2 V at 20 mV/s. ORR polarizations curves were obtained by subtracting the N₂ saturated voltammogram from the corresponding O₂-saturated voltammogram to remove background contributions. Kinetic ORR activity (i_k) was calculated for the anodic sweep polarization curve after mass transport correction.²⁶

4.3 Results and Discussion

4.3.1 Changes in Pt steady-state CV signature during stability test

The accelerated stability test was performed by cycling the potential between 0.6 and 1.1 V in O₂-saturated 0.1 M HClO₄ for 500 cycles (50 mV/s, RT, 0 RPM). This process repeatedly oxidizes and reduces the surface of the catalyst while oxygen reduction is occurring. The stability of the catalyst was probed by measuring the accessible Pt area every 100 cycles in the same (Ar-saturated) electrolyte.
Figure 4.1 shows the Ar-saturated CV signature recorded before the stability test and after each 100 cycles for Pt/C and PtCu/C catalysts. Before stability test (marked in Figure 4.1 as “Pre”), both Pt/C and PtCu/C exhibit characteristic features associated with the Pt CV in base.27 As expected, the absolute magnitude of the current decreases as the stability test is performed. For both Pt/C and PtCu/C catalysts, there appears to be subtle shifting of the H_{UPD} features between the pre-stability and post-stability catalysts. For Pt/C, the anodic H_{UPD} peak feature at ~0.285 V (pre-cycling) shifts to ~0.276 V (after cycling), while for PtCu/C the analogous feature shifts from 0.279 V to 0.265 V before and after stability cycling, respectively. The potential values of the H_{UPD} features before the stability test can be used as a relative measure of hydrogen bonding strength for the catalyst material under consideration. The general idea is that surfaces with stronger adsorption of hydrogen adatoms will have higher potentials for all H_{UPD} features (adsorption and desorption) than surfaces that have a weaker affinity for hydrogen. Based on these assumptions, Pt/C likely has a stronger affinity towards hydrogen than PtCu/C. Decreased onset potentials of H_{UPD} features for bimetallic catalysts relative to Pt/C have previously been observed (acidic conditions) in the literature and have been explained similarly.28 The negative shift in H_{UPD} features observed after starting the stability test indicates that a freshly prepared catalyst has a substantially stronger hydrogen binding strength than a catalyst that has undergone potential cycling. This observation may have implications for using PtCu/C for H₂ oxidation/evolution reactions.
The potentials associated with onset of Pt oxidation and the reduction of Pt oxide also change throughout the duration of the stability test. These features have been utilized as measures of oxygen binding strength (higher binding strength results in more negative onset/reduction potentials)\(^2,\, 26\) and appear to shift towards lower oxygen binding strength after the stability test begins. Prior to the stability test, the positive-shifted oxide formation/reduction potentials suggest that Pt/C has a stronger inherent oxophilicity than PtCu/C.\(^{12}\)

### 4.3.2 Changes in ORR activity and Pt ECSA during stability test

The ORR activity of the catalyst during the stability test was determined by performing electrochemical experiments in oxygenated 0.1 M KOH after each 100 cycles. Specific activity at 0.9 V is an inherent value that defines how well the catalyst performs the ORR, and is normalized to the catalysts electrochemically accessible Pt area. Figure 4.2 gives the ORR specific activity at 0.9 V for Pt/C and PtCu/C as a function of stability test cycling. PtCu/C is clearly the optimal ORR catalyst, but it deactivates at a much higher rate than Pt/C. The initial deactivation of PtCu/C and Pt/C follows an exponential decay, of which an exponential fit-line can be extracted and a “half-life” (number of cycles at which catalyst loses half of its initial specific activity) determined. The half-life of the PtCu/C catalyst is calculated to be 858 cycles compared to a half-life of 1135 cycles for Pt/C.

Despite the faster rate of deactivation, PtCu/C appears to maintain its structural integrity longer than Pt/C. Figure 4.3 shows the accessible Pt area as a function of stability test
cycling. Again, there is an exponential trend and the Pt ECSA half-life of PtCu can be calculated to be 1424 cycles vs. 859 cycles for Pt/C. An interesting phenomena occurs here that is rarely ever commented on in the ORR literature. It is intuitive that Pt ECSA should decrease as the catalyst degrades, but if the catalyst was only physically shearing, we would not expect to see decreases in specific activity (it would remain the same). The decrease in specific activity for Pt/C is particularly difficult to rationalize. If the catalyst’s particle size were increasing as the catalyst degrades (Johnson Matthey Pt/C average particle size is 2-4 nm), we would expect an \textit{increase} in specific activity, due to the decreased oxophilicity of larger particles because of fewer under-coordinated Pt atoms (particle size effects). On the other hand, the decrease in activity for PtCu/C may be the result of a loss of catalytic enhancement due to Cu leaching from the catalyst during the harsh conditions of the stability test. PtCu/C is not likely to experience particle growth, as its average particle size is \(~100\) nm.

In an effort to better rationalize why the specific activity of the catalyst is decreasing over the course of the stability test, we will attempt to present an analysis of ORR structural sensitivity that is not common in the literature, but similar to that of Solla-Gullon et al. It is well known that the Pt (FCC) surface is composed of three primary crystal facets: (100), (110), and (111). There is a general consensus in the literature that the (111) facet is the best for ORR in alkaline media, while the (100) is the weakest, in a weakly adsorbing electrolyte, e.g. HClO₄, Pt(110) is the most active, followed by Pt(111), then Pt(100). A detailed study by Markovic et al. shows the background CVs (oxygen-free)
of single crystal Pt electrodes in 0.1 M KOH. Their data illustrates H\textsubscript{UPD} features that are unique to each of the three primary crystal facets (in good agreement with other researchers). We propose that for a given polycrystalline Pt surface, each of the three predominant crystal facets should be expressed to some degree. Since current is additive, it follows that the polycrystalline Pt CV could resemble some linear combination of each of the three Pt single crystal CVs. Figure 4.4 shows the anodic sweep of the CV obtained for Pt/C (before stability test) and the anodic sweep of polycrystalline Pt CV calculated from a linear combination of the Markovic et al. data. In making Figure 4.4, we assumed that each of the crystal facets are expressed equally, i.e. 1:1:1. Figure 4.4 clearly suggests that the H\textsubscript{UPD} region of the calculated Pt CV closely resembles the experimental Pt/C CV (which we measured), with only small variations in the double layer region between 0.45 and 0.65 V. We can assign three distinct H\textsubscript{UPD} regions in the Pt/C system. The first region (UPD 1) spans potentials from 0.05 to 0.185 V, the second region (UPD 2) spans potentials from 0.185 to 0.35 V (encompasses peak at ~0.27 V), and the final region (UPD 3) spans potentials from 0.35 to 0.45 V (encompasses shoulder peak at ~0.38 V). Assuming a 1:1:1 ratio of facet expression (because Markovic et al. single crystals had the same area), we can use the calculated data to obtain the total area under the curve in each H\textsubscript{UPD} region (corrected for double layer). We can then use the digitized Markovic et al. data (from each facet) to calculate how much each facet contributes to each of the three UPD regions, assuming roughness factor of single crystals is 1, and each of the Markovic single crystal electrodes have similar terrace sizes (both assumptions made by Markovic et al. in original work). Under these assumptions, Table 4.1 gives the makeup of each of the H\textsubscript{UPD} regions.
With Table 4.1, we can conclude that UPD 1 is primarily composed of Pt(111), while UPD 3 is primarily composed of Pt(100). UPD 2 is a mixed region with slightly more contribution from Pt(110) than the other two facets. If each facet is not quite expressed at a ratio of 1:1:1, we can still safely propose that UPD 1 and UPD 3 are representative of Pt(111) and Pt(100), respectively. Solla-Gullon et al. performed a similar analysis in acidic conditions, and they found that strong correlations existed between (110)-type sites (0.125 V) and (100)-type sites (0.26 V)33.

Using the aforementioned findings, we can reasonably correlate changes in $H_{UPD}$ composition during catalyst degradation to changes in expressed surface facets. This will provide another degree of knowledge when specifically determining why the catalyst is deactivating over the course of the stability test. To use this analysis, we 1) measured the total anodic Pt-ECSA during the stability test intervals (from 0.05 to 0.45 V) and 2) calculated what fraction of the total UPD was made up by each of the three UPD regions. This method allows for careful analysis of each UPD region and is not biased by changes that could simply attenuate total currents. Interestingly, Pt/C has a lower UPD 1 composition than PtCu/C (see Fig. 4.5). This suggests that before any cycling has occurred, PtCu has more Pt(111) character, which could explain (at least in part) its higher ORR activity.12 Moreover, the least active facet, Pt(100), is expressed in lower quantities in PtCu/C, which provides more qualitative evidence for the increased ORR activity of PtCu/C relative to Pt/C. The convolution of crystal facets in UPD 2 makes it more difficult to draw any definitive conclusions about catalyst surface structure from the UPD 2 region.
Particle size differences may result in differences in ORR activity between Pt/C and PtCu/C, but this should complement, rather than interfere with the HUPD analysis.

As the Pt/C catalyst is degrading, Fig. 4.5 and Fig. 4.6 show that the only real correlation between ORR activity and UPD region(s) for Pt/C is UPD 1. UPD 1 decreases proportionally during the entirety of the stability test as the catalyst deactivates (see Fig. 4.6). A marked attenuation in the characteristic Pt(111) feature at ~0.8 V also occurs after the first 100 cycles (see Fig. 4.1a). These findings provide quantitative evidence that Pt/C is losing its most active crystal facet, Pt(111), over the course of the stability test, which rationalizes its decreasing specific activity.

For PtCu/C, the explanation is not quite as straightforward. Fig. 4.5 and 4.6 show the evolution of UPD regions during the stability test for PtCu/C. However, there is no real correlation between any of the UPD regions and the decreasing ORR activity (see Fig. 4.6). This suggests that ORR on the PtCu/C catalyst is not as structure sensitive as ORR on the Pt/C catalyst. The rapid deactivation of PtCu/C is most likely linked to the dissolution of copper.³² The presence of copper in the catalyst is crucial to maintaining the Pt lattice contraction which weakens oxygen binding, resulting in increased ORR activity.³⁷

Our HUPD/surface facet correlation analysis is in no way exhaustive (we do not consider smaller current contributions from step/kink sites), but rather a rational approximation to provide a platform to analyze real changes that could not otherwise be explained. The
purpose of this analysis is not to deconvolute a polycrystalline UPD region into individual facet contributions as Solla-Gullon et al. did, but to provide a degree of confidence that a given range of UPD potentials contains contributions primarily from a given facet. This line of thinking only corroborates findings of previous authors.\textsuperscript{25,33,36}

An optimal monometallic Pt catalyst should be constructed to have a very high density of active Pt(111) sites, which are resistant to degradation.\textsuperscript{2} This sort of catalyst construction would not be trivial, particularly when mass activity is considered. The most logical solution will continue to be bimetallic Pt-based catalyst systems. The bimetallic catalyst that would be resistant to deactivation should somehow seek to “trap” the less noble metal beneath the surface. A problem with this theory is if the catalyst were exposed to potential extremes, which is very possible during fuel cell start-up and shut-down, the Pt surface will become oxidized, which is thought to lead to a phenomena known as “place-exchange” where Pt atoms shift, which may result in exposure of “trapped” less noble metal atoms, leading to dissolution of the exposed less noble atoms.\textsuperscript{38-42} However, this may become more of a systems engineering problem than a fundamental design issue.

4.3.4 Oxide binding shifts during catalyst degradation/deactivation

In the past, researchers have used the oxide reduction peak (cathodic scan) shift to characterize how strongly their catalyst binded oxygen. Originally, the theory stemmed from Pt nanoparticles of different sizes having different oxophilicity due to increasing under-coordination of Pt atoms as the particle size decreased.\textsuperscript{31} The theory has been utilized
more recently to screen ORR catalyst materials.\textsuperscript{2,12} Typically, Pt-based materials that bind oxide (or adsorb OH) too strongly are poor ORR catalysts, while Pt-based materials that have a weaker affinity towards oxide (OH\textsubscript{ads}) are better ORR catalysts.\textsuperscript{2,6} Throughout the stability study, we observe that the relative ORR activity of Pt/C compared to PtCu/C can be determined solely based on the oxide reduction peak potential. Pt/C has a less positive oxide reduction peak potential which indicates it is a stronger binder of oxygen, and its activity shows clearly that it is a worse ORR catalyst (Table 4.2). However, our data shows that this method of analysis may not be suitable for Pt-based catalysts as they undergo the initial stages of degradation/deactivation. As Pt/C deteriorates, its initial oxide reduction peak potential is 0.734 V (Table 4.2). After the first 100 cycles, the peak potential shifts negatively to 0.728 V—as expected, because the catalyst’s ORR activity decreases. However, after 200 cycles (and thereafter), the peak shifts in the positive direction—but we clearly see that the ORR activity is decreasing. Contrastingly, for PtCu/C, the initial oxide reduction peak potential is 0.768 V, but shifts positively to 0.789 V after 100 cycles. After 200 cycles, the peak potential shifts positively again to 0.792 V, but thereafter the peak potential decreases. The unusual behavior of the oxide reduction peak potential makes it very difficult to correlate catalyst deactivation with increasing oxophilicity. The changes in peak potential and ORR activity are real and reproducible, but could indicate that catalyst degradation and deactivation (at least initial phases) is more complex than the simple oxophilicity argument accounts for.
4.4 Conclusions

The work presented here clearly demonstrates a concise theory and analysis of the most critical stages of ORR catalyst degradation and deactivation in alkaline media. Commercially available Pt/C is used as a baseline and compared to a newer and more active bimetallic Pt-based catalyst (PtCu/C). PtCu/C is found to have a faster ORR deactivation rate than Pt/C, but PtCu/C has a much slower physical degradation rate (as measured from Pt ECSA). A unique method utilizing experimental results from single crystal studies (Markovic et al.)\textsuperscript{25} enables an estimation of the relative abundance of the three dominant Pt crystal facets ((100), (110) and (111)) in polycrystalline Pt-based catalysts. PtCu/C has a higher initial ORR activity than Pt/C because it has more Pt(111) character and less Pt(100) character (most and least active facets for ORR, respectively). The decline in specific activity as Pt/C catalysts degrade is due to a reduction in the quantity of Pt(111), while the decline in specific activity for PtCu/C is likely due to leaching of the copper (and hence loss of the catalytic enhancement). This work also dictates that the well-known correlation between oxygen binding energy and ORR activity become less straightforward as catalysts degrade. These findings offer a greater understanding of the mechanisms of ORR catalyst degradation and deactivation, and provide some insight into how the next generation of ORR catalysts should be designed to mitigate these issues.
4.5 References


28. Wakisaka, M., Morishima, S., Hyuga, Y., Uchida, H. & Watanabe, M. Electrochemical behavior of Pt−Co(111), (100) and (110) alloy single-crystal electrodes in 0.1 M HClO4 and 0.05 M H2SO4 solution as a function of Co content. *Electrochem. Commun.* 18, 55-57 (2012).


4.6 Figures & Tables

Figure 4.1: Evolution of background electrochemical characteristics throughout stability test for (a) Pt/C (Johnson Matthey 20 wt. %) and (b) PtCu/C. All electrochemical measurements performed with 0.1 M KOH at 298 K, 20 mV/s, and 1600 rpm.
Figure 4.2: Absolute and relative ORR specific activity at 0.9 V after each 100 cycles of stability test for PtCu/C and Pt/C. All electrochemical measurements performed with 0.1 M KOH at 298 K, 20 mV/s, and 1600 rpm.
Figure 4.3: Absolute and relative Pt electrochemically accessible surface area (Pt ECSA) as measured from H\textsubscript{UPD} after each 100 cycles of stability test for PtCu/C and Pt/C. All electrochemical measurements performed with 0.1 M KOH at 298 K, 20 mV/s, and 1600 rpm.
Figure 4.4: Anodic sweep of background polycrystalline Pt CV from (dotted line) linear combination of Pt(100) Pt(110) and Pt(111) single crystal studies measured by Markovic et al.\textsuperscript{25} and (solid line) experimental Pt/C results obtained in this work. Extrapolated data shows very close agreement with experimental data. Y-axis units are arbitrary, data offset by design. All experimental data measured with 0.1 M KOH at 298 K, 20 mV/s, and 1600 rpm. Markovic data measured with same conditions, except at 50 mV/s.
Figure 4.5: Percentage of total anodic $H_{\text{UPD}}$ occupied by respective UPD regions after each 100 cycles of stability test.

UPD 1 ranges from 0.05-0.185 V, UPD 2 ranges from 0.185-0.35 V, and UPD 3 ranges from 0.35-0.45 V. Derived from electrochemical measurements performed with 0.1 M KOH at 298 K, 20 mV/s, and 1600 rpm.
Figure 4.6: Correlation between UPD regions and ORR specific activity for Pt/C and PtCu/C catalysts during stability test. UPD 1 ranges from 0.05-0.185 V, UPD 2 ranges from 0.185-0.35 V, and UPD 3 ranges from 0.35-0.45 V. Derived from electrochemical measurements performed with 0.1 M KOH at 298 K, 20 mV/s, and 1600 rpm.
Table 4.1: Estimated composition of anodic UPD regions as calculated from Markovic et al. results\textsuperscript{25}

<table>
<thead>
<tr>
<th></th>
<th>Pt\textsuperscript{(100)}</th>
<th>Pt\textsuperscript{(110)}</th>
<th>Pt\textsuperscript{(111)}</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>UPD 1:: 0.05 to 0.185 V</strong></td>
<td>3%</td>
<td>2%</td>
<td>95%</td>
<td>100%</td>
</tr>
<tr>
<td><strong>UPD 2:: 0.185 to 0.35 V</strong></td>
<td>33%</td>
<td>45%</td>
<td>22%</td>
<td>100%</td>
</tr>
<tr>
<td><strong>UPD 3:: 0.35 to 0.45 V</strong></td>
<td>96%</td>
<td>3%</td>
<td>1%</td>
<td>100%</td>
</tr>
</tbody>
</table>
Table 4.2: Breakdown of changes in oxide reduction peak potential during stability test

<table>
<thead>
<tr>
<th>Pt/C Catalyst</th>
<th>Oxide Reduction Peak Potential (V)</th>
<th>PtCu/C Catalyst</th>
<th>Oxide Reduction Peak Potential (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre</td>
<td>0.734</td>
<td>Pre</td>
<td>0.768</td>
</tr>
<tr>
<td>100</td>
<td>0.728</td>
<td>100</td>
<td>0.789</td>
</tr>
<tr>
<td>200</td>
<td>0.733</td>
<td>200</td>
<td>0.792</td>
</tr>
<tr>
<td>300</td>
<td>0.737</td>
<td>300</td>
<td>0.788</td>
</tr>
<tr>
<td>400</td>
<td>0.741</td>
<td>400</td>
<td>0.786</td>
</tr>
<tr>
<td>500</td>
<td>0.744</td>
<td>500</td>
<td>0.784</td>
</tr>
</tbody>
</table>
5.1 Introduction

Fuel cell technology will play a significant role in the next generation of sustainability. By the end of the year (2015), Hyundai and Toyota will commercially release fuel cell vehicles to compete with the rising stable of battery-powered electric vehicles that are on the market.\(^1\)\(^,\)\(^2\) However, there are some fundamental challenges that must be addressed before fuel cell vehicles will truly become the top contender for sustainability. The biggest of these challenges is the slow kinetics of the oxygen reduction reaction (ORR). These sluggish kinetics result in diminished power density as well as the required use of Pt in the catalyst. After factors such as catalyst degradation are factored in, the oxygen reduction reaction provides quite the monetary barrier towards the large-scale deployment of fuel cell vehicles.

Despite these flaws, a great deal of progress has been made on novel catalyst systems for the ORR. Currently, Pt and its alloys are still the most effective catalysts for the ORR, but the more efficient utilization of Pt has led to up to ~90-fold increases in
catalyst activity. Typically these increases in catalyst activity are the result of synthesis of bimetallic Pt based alloys (usually Ni, Fe, Co, Cu). 

As Pt-based fuel cell catalysts become more and more efficient, the power density begins to inch up, such that fuel cells can operate closer to their theoretical thermodynamic voltage of 1.2 V. However, an additional unwanted element comes into play—degradation of the catalyst material. A standard Pourbaix diagram will illustrate that the Pt surface becomes passivated at potentials > 0.8 V (vs. RHE). At these higher fuel cell operating potentials, the efficiency of ORR turnover is affected by the ORR occurring on a surface with an actively growing oxide layer.

In addition to decades of fundamental studies on oxide growth, there have been a wealth of studies of the ORR on Pt surfaces. However these studies, (with the exception of a few) are almost always focused on the forward (anodic) sweep of a Pt electrocatalyst, where the ORR occurs on a relatively oxide-free surface. Therefore, we have conducted this comprehensive study to discover how the ORR is affected when an oxide layer is present and as the oxide layer is removed from the catalyst. To orchestrate this study, we focused on forming Pt oxide films of different thicknesses by performing potential holds at oxidizing potentials for different times and then measuring the ORR activity from the reverse sweep where the ORR is occurring on this oxidized Pt surface. We conduct our experiments in both acidic (pH 1) and alkaline (pH 13) media to examine how ORR
activity and pathway are affected by the oxide formed under these vastly different conditions. The focus in this fundamental study is commercially available Pt/C catalysts, with the intention that this investigation may provide a platform from which future studies can be derived for other highly active Pt-based catalyst materials.

5.2 Experimental Methods

5.2.1 Thin-layer Pt/C electrode preparation

5 mg of high surface area Pt black powder (Johnson Matthey) was added to 10 mg of Vulcan XC-72 carbon, and dispersed ultrasonically in 10 mL of ultrapure H2O for 10 minutes. A diluted Nafion® solution (5 wt %, Alfa Aesar, 40 μL) was added to the Pt/C dispersion. The resulting solution was sonicated for another 10 min. Immediately following sonication, 20 μL of the suspension was drop-casted onto a mirror polished glassy carbon (GC) disk electrode (Pine, 5 mm diameter). The prepared electrode was dried in the oven (55 °C for 1.5 hours). After drying, the coated electrode was allowed to cool down to room temperature.

5.2.2 Basic electrochemical study

Electrochemical measurements were performed in a jacketed standard 3-electrode cell using a ring-disk electrode rotator (Pine) equipped with a CH Instruments bi-potentiostat (CH 760D) capable of concurrent rotation control. A reversible
hydrogen electrode (RHE) with a Luggin capillary was used as the reference electrode for all electrochemical measurements. The counter electrode was a Pt mesh. The electrolyte used was 0.1 M HClO₄ or 0.1 M KOH. 0.1 M HClO₄ was prepared by diluting concentrated trace metal grade acid (Fisher) with ultrapure deionized H₂O. 0.1 M KOH was prepared by dissolving KOH pellets (Sigma-Aldrich, ACS grade) in ultrapure deionized H₂O. All cyclic voltammograms were recorded at 298 K with a scan rate of 20 mV s⁻¹ and a rotation rate of 1600 rpm. The prepared electrodes were transferred to the electrochemical cell and immersed in argon-saturated electrolyte. To stabilize the Pt, the electrodes were ‘primed’ by cycling the potential 50 times between 0.5 V and 1.2 V at 1 V/s in 0.1 M HClO₄ solution. Then CV scans between 0.03 V - 1.2 V at 20 and 100 mV/s were measured until a steady-state voltammogram was attained. The Pt electrochemical surface area (Pt ECSA) was determined from an Ar saturated voltammogram via the average integrated charge of the underpotentially deposited hydrogen (Hupd) region (0.05 < E < 0.40 V for acid and 0.05 < E < 0.45 V for base) after double-layer correction. The widely accepted conversion of 210 μC cm⁻²Pt for polycrystalline Pt was assumed.

5.2.3 Pt oxide electrochemical study
Pt oxide was formed on Pt/C electrodes at 1.1 V, 1.2 V, 1.3 V, and 1.4 V for 10 s, 20 s, 40 s, or 60 s. To grow the oxide layer on the Pt surface, (1) the surface was cleaned via 3 CV cycles between 0.03 - 1.2 V (20 mV/s), followed by (2) a 90 s
potential hold in the ‘clean Pt’ region of the Pt CV (0.44 V for HClO₄ and 0.47 V for KOH). (3) Immediately (no dead time) after this ‘cleaning’ potential hold, the potential was stepped to the oxide forming potential, \( E_{ox} \) (1.1 V, 1.2 V, 1.3 V or 1.4 V) for the prescribed time period, \( t_{ox} \) (10 s, 20 s, 40 s, or 60 s). (4) Immediately (no dead time) after the oxide forming potential hold, the oxide layer was stripped off of the electrode by performing 3 CV cycles where the potential was scanned from 1.2 to 0.03 V (20 mV/s; negative initial sweep direction). The 1\(^{st}\) cycle of the CV is representative of the oxide stripping, while the 2\(^{nd}\) and 3\(^{rd}\) are representative of what we refer to as the “steady-state” CV. The entire procedure (step 1 through 4) was repeated until the oxide had been formed at each potential for each period of time (16 total iterations). These experiments were performed in Ar saturated (deaerated) and O\(_2\) saturated electrolyte for both HClO₄ and KOH.

5.2.4 ORR measurements

ORR CV measurements were derived from stripping CVs measured in oxygen-saturated electrolyte (0.1 M HClO₄ or 0.1 M KOH) where the potential was cycled between 1.2 V and 0.03 V at 20 mV/s. Polarization curves were obtained by subtracting the N\(_2\)-saturated stripping voltammogram from the O\(_2\)-saturated stripping voltammogram to remove background contributions. Kinetic ORR activity \( (i\kappa) \) was calculated for the cathodic sweep polarization curve (either steady-state or oxide stripping) via the following relationship:
\[ i_k = \frac{i_d \ i_{tot}}{i_d - i_{tot}} \]

where \( i_d \) is the diffusion limited current, and \( i_{tot} \) is the total current. Pt specific activities were determined from Pt-ECSA data as follows:

\[
\text{Specific activity} = \frac{i_k}{Pt \ ECSA}
\]

5.2.5 Peroxide detection

Hydrogen peroxide production during experiments performed in O\(_2\)-saturated electrolyte was measured via a rotating ring disk electrode (RRDE, Pine) with a Pt ring electrode held at 1.2 V vs. RHE during the measurement on the disk. The RRDE experiments were conducted in O\(_2\) saturated 0.1 M HClO\(_4\) or 0.1 M KOH at room temperature. The collection efficiency, \( N \), for the RRDE was 0.28. All electrochemistry experiments were repeated to ensure reproducibility.

5.3 Results and Discussion

5.3.1 Electrochemical baseline measurements

We begin by showing the steady-state Pt/C CVs in acidic and alkaline electrolyte. A clean Pt surface has a CV with well-defined features. It is important to note that each figure presented in this manuscript has been measured using the same electrode/catalyst system. We do this to ensure self-consistency within the data, but we are aware that the Pt/C catalyst system has a finite shelf-life, especially when
exposed to extreme potential cycling. As a result, we have shown in Figure 5.1 the catalyst’s electrochemical signature before and after the oxide stripping experiments. Given the similarity of the CVs, it is reasonable to suggest that the catalyst’s degradation is relatively negligible during the course of the experiment. From a quantitative standpoint, the ECSA of the catalyst decreases \( \sim 2.7\% \) during the course of the experiment, which again, can be considered negligible. We performed all of the experiments with another identical electrode/catalyst system to confirm that all of the trends we report are consistent and reproducible.

5.3.2 Effect of oxide formation potential and duration

The oxide film on Pt is generally interpreted as a hydrated PtO or PtO\(_2\). For simplicity, we use the term “oxide” and the formula of PtO\(_x\) for Pt surface oxidation\(^40\). The nature of the surface oxide formed on Pt is highly dependent on 1) the Pt oxide formation potential and 2) the duration of time that Pt oxide grows. We performed a series of experiments where the potential of the electrode was held at an oxidizing potential \( (E_{ox}) \) (1.1, 1.2, 1.3, or 1.4 V) for 10, 20, 40, and 60 s \( \left( t_{ox} \right) \) (see Figure 5.2 and 5.3). We immediately stripped off the oxide layer that was formed during the hold via a CV scan from 1.2 V to 0.03 V (negative initial direction). The quantity of oxide \( (q_{oxide}) \) formed is measured from the charge required to completely reduce the oxide back to Pt metal (corrected for double layer and H\(_{ads}\)). To ensure consistency, the stripping CV contained 3 cycles, where the first cathodic wave consisted of stripping the oxide formed from manipulating \( E_{ox} \) and \( t_{ox} \); the second and third cathodic waves consisted
of ‘steady-state’ oxide removal between 1.2 and 0.3 V. Each cathodic wave consists of a peak which is referred to as the oxide removal peak, (referred to in the literature as OC1\textsuperscript{25}). The oxide reduction peak potential ($E_p$) is an interesting metric for any Pt-based catalyst system. In the past, it has been utilized for ORR catalyst screening, with the general theory that a more positive $E_p$ is indicative of weaker oxygen binding, and thus better ORR activity (Pt nanoparticles are generally believed to bind oxygenated species too strongly).\textsuperscript{41-43} For our analysis, we will assume (more appropriately) that the average oxide binding energy is directly correlated with $E_p$; i.e., higher peak potential indicating weaker binding, and lower peak potential indicating stronger binding. The results of manipulating $t_{ox}$ while holding at 1.2 V (arbitrarily chosen; trend is the same regardless of potential) are shown in the stripping CV overlay in Figure 5.2, while the effects of $E_{ox}$ are shown for 40s holds in Figure 5.3. One can observe that manipulation of both $t_{ox}$ and $E_{ox}$ have a considerably different effect on the CV and ORR characteristics. As $t_{ox}$ is increased for a given potential, there will be more oxide formed, as evidenced by increased peak area, but the potential at which it is stripped shifts negative by only about 10 mV in HClO\textsubscript{4} and KOH (Table 5.1). This suggests that the amount of oxide formed and the average strength of the oxide bond to Pt is only weakly dependent on the amount of time the oxide is formed. This is in good agreement with prior findings that oxide growth is directly logarithmic with $t_{ox}$:\textsuperscript{22,25} If we assume that the oxide is blocking active Pt ORR sites, such that

$$i \propto (1 - \theta_{ox})^n$$

(5.1)
where \( i \) is the measured ORR current (or activity), \( \theta_{ox} \) is oxide “coverage” on Pt sites, and \( n \) is reaction order, then for a first order reaction we expect the activity to scale linearly with available Pt sites.\(^3\) We cannot directly measure the availability of Pt sites, but we can use data from the CVs to make a rational approximation. First, the ratio between oxide charge (\( q_{oxide} \)) passed at time \( t_1 \) \((t_1 = 10, 20, 40)\) and oxide charge passed at \( t_2 \) \((t_2 > t_1)\) can be used as a relative measure of Pt site availability. Next, we can compare that ratio with the ratio between ORR specific activity (activity per Pt ECSA) at \( t_1 \) and \( t_2 \). Then, for a reaction that is first order with respect to Pt sites, the following condition should be fulfilled

\[
\frac{q_{oxide}(t_1)}{q_{oxide}(t_2)} \approx \frac{i(t_2)}{i(t_1)} \quad (5.2)
\]

As indicated by the last column in Table 5.1, it can be shown that this condition is satisfied in both HClO\(_4\) and KOH (ratio \(~1\) in last column), providing justification that increasing \( t_{ox} \) to 60 s solely acts to remove active Pt sites by increasing the amount of oxide that is chemisorbed on the surface.

In contrast, the results of manipulating the \( E_{ox} \) tell quite a different story (Figure 5.3). As \( E_{ox} \) is increased (all other parameters constant), there is substantially more oxide formed. Rather than the subtle \( E_p \) shift experienced as \( t_{ox} \) increased, \( E_p \) experiences a negative shift of \(~50\) mV (in HClO\(_4\) and KOH) as the oxide-formation potential is increased. Our findings suggest that there is a strong correlation between amount of oxide, average strength of the oxide bond to Pt, and \( E_{ox} \). This is consistent
with others who have performed similar experiments to elucidate the nature of oxide growth on Pt.\textsuperscript{24-26} Using the same assumptions as mentioned earlier, we can attempt to find the relationship between active ORR sites and measured ORR activity. One will quickly observe that the previous 1\textsuperscript{st} order approximation does not hold for the oxide-formation potential experiments (Table 5.1). In fact, the calculated ratios for acid electrolyte in the last column of Table 5.1 indicate an exponential dependence between ORR activity and availability of active ORR sites (as $E_{ox}$ is increased). Based on these findings, we believe that $E_{ox}$ vastly affects the rate of oxide growth, but the amount of surface oxide coverage may play a more complex inhibiting role during the ORR.

It is worth mentioning that while the oxide growth increases at different rates for manipulations of $t_{ox}$ and $E_{ox}$, an identical oxide can be grown by 1) a very short potential hold at a very anodic potential, or 2) a very long potential hold at a less anodic potential. Figure 5.4a shows the relationship between $q_{oxide}$ and ORR at 0.9 V and Figure 5.4b shows the relationship between $q_{oxide}$ and $E_p$. Figure 5.4 was constructed with all 32 of the different $E_{ox}/t_{ox}$ combinations, and the linearity of the data strongly suggests that amount of oxide has the dominant effect on the ORR, rather than $t_{ox}$ or $E_{ox}$. $t_{ox}$ and $E_{ox}$ are simply parameters that effect the rate of oxide growth.\textsuperscript{19} Figure 5.4a raises a very important conclusion: the ORR activity must also scale exponentially with $q_{oxide}$ as $t_{ox}$ is increased. This does not invalidate the first-
order active site dependency we mentioned earlier, rather it clarifies that the approximation will only hold in the short time scale, i.e. \( t_{ox} \leq 60 \) s.

The most logical conclusion is that the oxide is growing thicker as \( E_{ox} \) is increased.\(^{25}\) Conversely, oxide growth is propagating (spreading) across the surface as \( t_{ox} \) is increased, at least for \( t_{ox} \leq 60 \) s. Of course at reasonably long \( t_{ox} \), the oxide layer becomes thicker, as can be deduced from Figure 5.4. The basis for this explanation is the strict adherence to Eq. 5.2 for all increases in \( t_{ox} \), regardless of \( E_{ox} \).

### 5.3.3 Oxide binding strength

An additional inference that can be drawn from Table 5.1 and Figure 5.4 is that there is substantially more oxide formed in HClO\(_4\) than in KOH. This is a safe conclusion given the method of experimentation and the fact that the same electrode was used in both electrolytes. What is more interesting is the relative bonding strength that we can deduce from \( E_p \). Figure 5.4b shows the overpotential that stripping occurs at as a function of the amount of oxide adsorbed. To describe oxide reduction peak potential, we chose to use overpotential (1.2 V – \( E_p \)) rather than \( E_p \) because we are performing a reduction of the formed oxide layer (and scanning in the reverse direction). It is worth mentioning that the absolute value of potential itself is arbitrary, and our decision to base overpotentials from 1.2 V does not change the observed trend. In Figure 5.4b, one can observe a slope 1.75 times higher for KOH than the HClO\(_4\), indicating that more energy is required to strip off PtO\(_x\) formed in
base than PtO$_x$ formed in acid. This is unambiguously confirmed in the segment of data where there is overlap in \( q_{oxide} \) for KOH and HClO$_4$, indicating that even when the same amount of oxide is on the electrode, PtO$_x$ is more strongly bound in KOH. This observation shows that the nature of the oxide formed in KOH and the oxide formed in HClO$_4$ must be significantly different.

### 5.3.4 ORR product selectivity

We investigated the product selectivity with the ring electrode (1.2 V) to better elucidate mechanistic differences between the ORR in acidic and alkaline media. Figure 5.5a,b shows the ring current during ORR (reverse sweep) as a function of \( E_{ox} \) for both 0.1 M KOH and 0.1 M HClO$_4$. We included the steady-state sweep ring currents to better discern \( E_{ox} \) induced changes. In acidic media, there is a very slight increase in peroxide oxidation for \( E > 0.6 \) V as \( E_{ox} \) is increased. There is a huge increase in peroxide oxidation for \( E > 0.6 \) V as \( E_{ox} \) is increased in alkaline media. This suggests that peroxide formation in acidic and alkaline media is proportional to oxide thickness. An interesting aspect of Fig. 5.5 is that the peroxide formation peak potential does not shift as more oxide is added to the Pt surface. This is contrary to the oxide stripping peak potential which shifts as a function of oxide thickness (see Figure 5.3). From these observations, we can conclude that peroxide formation (\( E > 0.6 \) V) is another factor which is linked solely to the quantity of oxide on the Pt surface. To further probe the effect oxide thickness has on peroxide formation in alkaline media, we normalized the peroxide oxidation ring current to \( q_{oxide} \) (Figure
5.6a). If \( q_{\text{oxide}} \) had a uniform contribution to peroxide formation, one would expect the see the same magnitude of peak currents for all of the \( E_{\text{ox}} \) shown in Figure 5.6a. Instead, the opposite is observed; it appears that when less oxide (lower \( E_{\text{ox}} \)) is on the Pt surface, the normalized ring current is higher (\( i_{\text{ring}}/q_{\text{oxide}} \) @ 1.1 > 1.2 > 1.3 and 1.4 V). The normalized peak current approaches a constant value only for higher \( E_{\text{ox}} \), and hence, thicker oxides. This is interesting, as it suggests that thinner, and perhaps more hydrous oxide films in alkaline media facilitate the 2\( e^- \) reduction process to peroxide better than thicker, more compact oxide layers. The idea can be further illustrated in Figure 5.6b where the ring current is normalized to the amount of remaining oxide at each potential. Again, for oxide formed at 1.3 and 1.4 V, the normalized current is substantially lower than that for oxide formed at 1.1 and 1.2 V. The unique plateau feature observed for 0.6 ≤ \( E \) ≤ 0.75 V in Figure 5.6b is further evidence that peroxide formation is solely related to the amount of oxide remaining on the surface at the corresponding potential rather than potential at which it is stripped. It is worth mentioning that when ring current is normalized to \( q_{\text{oxide}} \) in acidic media, all of the curves show the same magnitude of current. Therefore, any increase in oxide coverage in acidic media will proportionally increase peroxide formation, with no facilitating effect from thinner oxides.

5.3.5 Origin of variance in ORR activity

The ORR appears to be inherently worse in base than acid, even for an electrode covered in an equal faradaic contribution of oxide (Figure 5.4a).
expected and has commonly been reported in literature accounts of the forward ORR sweep (on Pt-OH_ads surface rather than PtO_x). It is currently believed that in alkaline media, specific adsorption of OH results in a mechanistic shift that favours an outer-sphere electron transfer rather than the inner-sphere transfer that is believed to occur in acidic electrolyte.\textsuperscript{36, 37} Our findings seem to corroborate this theory, especially with the observed higher rate of peroxide formation as q_{oxide} is increased, as the outer-sphere model promotes a 2e^{-} reduction pathway to peroxides. Our findings suggest that Pt-OH_ads in the current outer-sphere theory can be substituted with Pt-O_x without altering the mechanism.\textsuperscript{36, 37} The observed lower rate of ORR activity in alkaline media could be stemming from 1) the inherently slower rate associated with performing a kinetically limited electron transfer reaction via an outer-sphere reaction (electron transfer via tunnelling) vs. an inner-sphere reaction (direct electron transfer), and 2) the higher oxophilicity (oxide binding strength) exhibited by the catalyst in alkaline conditions.

5.3.6 Attenuation of H_ads via oxide “blocking”

Close inspection of Figure 5.5 will reveal an interesting phenomena which occurs in HClO_4 and KOH at E < 0.5 V. For E_{ox} of 1.1 and 1.2 V, there is a subtle increase in ring current at E < 0.5 V for the oxide strip relative to the steady state scan. At E_{ox} of 1.3 V, the oxide strip and steady state ring current are essentially equal (E < 0.5 V), but at 1.4 V the oxide strip ring current dips very slightly below the steady state ring current. This is indicating that at lower E_{ox}, and hence, lower oxide coverages,
there is a slight increase in peroxide formation at potentials less than 0.5 V. At higher oxide coverages, peroxide formation is more attenuated, at least relative to the steady state ring current. This seems a bit counterintuitive at first glance, as it seems that more oxide should result in more peroxide formation at all potentials. However, we explain this feature by considering that for both HClO₄ and KOH, the presence of Hₐds during ORR is known to strongly facilitate peroxide formation at potentials < 0.4 V.³⁴, ³⁵, ⁴² It can be seen from Figure 5.3 that oxide is still being stripped off of the electrode at potentials < 0.5 V when Eₜₐ₉ > 1.2 V. Based on this, we can make the hypothesis that if oxide is still on the surface at E < 0.5 V, it will attenuate Hₐds and the resulting peroxide formation that Hₐds promotes. It follows that the opposite phenomena occurs when very little oxide is on the Pt surface, i.e when Eₜₐ₉ = 1.1 V. During the 1.1 V hold there is less oxide adsorbed and it is all essentially removed before the Hₐds region, resulting in a less inhibited Pt surface for Hₐds, marginally higher Hₐds coverage, and hence marginally higher peroxide formation (as compared to the steady-state CV which was scanned to 1.2 V, and has a thicker oxide).

5.3.7 Connections to anodic ORR sweep

One of the initial aims of this work was to better understand ORR inhibition during the forward (anodic) ORR sweep by utilizing information from the reverse sweep. Figure 5.7 shows the reverse (cathodic) ORR ½ wave potential vs qoxide. We were particularly interested in determining what amount of oxide should be present to obtain a ½ wave potential representative of the forward (anodic) sweep ORR. The
anodic sweep $\frac{1}{2}$ wave potential was found to be 0.897 V in HClO$_4$ and 0.852 V in KOH (Fig. 5.1 and 5.2). Using Figure 5.7, one can see that to achieve these $\frac{1}{2}$ wave potentials, $q_{\text{oxide}}$ must decrease to $-3.8 \times 10^{-4}$ C and $-3.6 \times 10^{-4}$ C in HClO$_4$ and KOH, respectively. These are certainly impossible values to achieve, but they dictate a very important principal: *The oxide film that inhibits the ORR during the anodic sweep is fundamentally different from the oxide film that inhibits the ORR during the cathodic sweep.* The two are not directly comparable, as completely different trends exist for each. As others have pointed out, the forward sweep ORR occurs on a Pt surface that is inhibited by a less compact and more reversible oxygenated species, usually believed to be OH$_{\text{ads}}$.\textsuperscript{3, 32, 34, 35, 42} Moreover, the oxide covered surface on the reverse sweep clearly catalyzes both H$_2$O$_2$ and H$_2$O formation from O$_2$ (see Fig. 5.5) at E > 0.6 V, while for the forward sweep at E > 0.6 there are negligible quantities of peroxide produced (see Ramaswamy et al.\textsuperscript{36}).

### 5.3.8 Mechanistic considerations

For an irreversible electron transfer reaction, such as the ORR, the rate of the reduction reaction (at sufficiently large overpotentials) can be described by the Butler-Volmer current-potential relationship,\textsuperscript{44}

$$|i| \approx i_o \exp \left( \frac{\alpha F \eta}{RT} \right)$$  \hspace{1cm} (5.3)

where $F$, $\eta$, $R$, and $T$ are Faraday’s constant, overpotential, gas constant and temperature, respectively. Unique to each catalyst system are $i_o$ and $\alpha$ which are
exchange current density and transfer coefficient, respectively. Exchange current density describes the inherent rate constant for the catalyst and transfer coefficient is a measure of the sensitivity of the reaction kinetics towards potential.\textsuperscript{45} If Equation 5.3 is applicable to the system under consideration, a linear relationship should exist between \( \ln i \) and \( \eta \); the slope of this linear relationship is defined as the Tafel slope, and it provides insight into the rate limiting step of the reaction (on the particular catalyst surface). Figure 5.8 shows mass-transport corrected Tafel plots obtained from ORR sweeps after oxide formation at 20 mV/s. We are confident that we are examining only ORR and not oxide removal with the Tafel plots, as the data from which the Tafel slopes are derived are corrected for background contributions, which includes oxide removal. At least two Tafel regions can be discerned from the data, with three regions potentially existing in alkaline electrolyte. To avoid introducing bias into the data by defining Tafel ranges via potential, we define the Tafel limits based on current density. The low current density (lcd) Tafel range is defined as spanning the range of potentials where the current is between 3% of the limiting current and where the Tafel line begins to deviate from linearity. The high current density (hcd) Tafel range is defined as spanning the range of potentials where the current is 90% of the limiting current and where the Tafel line begins to deviate from linearity. The middle Tafel region, if there is one, is defined as the span of linearity between the hcd Tafel region and the lcd Tafel region.
In both HClO₄ and KOH, the Tafel slopes of Pt/C after oxide formation decrease in the order of 1.1 V > 1.2 V > 1.3 V > 1.4 V (Figure 5.8, Table 5.2). The steady decrease observed in Tafel slope as \( q_{\text{oxide}} \) was increased lead us to believe that oxide coverage on the Pt surface plays a role in regulating the observed Tafel slope. To support this hypothesis, we will revisit a principal we presented earlier in the discussion. From Figure 5.4a, we know that there is a linear relationship between \( \ln i \) and \( q_{\text{oxide}} \). This is a unique relationship that allows us to make an important assumption: the Butler-Volmer current-potential relationship (Eq. 5.3) for our oxide coated Pt system can be modified as follows:

\[
|i| \approx i_o \exp \left(-k q_{\text{oxide}}\right) \exp \left(\frac{\alpha F |\eta|}{RT}\right) \tag{5.4}
\]

Or as

\[
|i| \approx i_o \exp \left(-\frac{\alpha F |\eta| k q_{\text{oxide}}}{RT}\right) \tag{5.5}
\]

where \(-k\) is a proportionality constant and represents the inverse correlation between current and \( q_{\text{oxide}} \). In essence, Eq. 5.4 states that \( q_{\text{oxide}} \) is only a constant which would not have any effect on the Tafel slope, while Eq. 5.5 states that \( q_{\text{oxide}} \) and \( \alpha \eta \) are intricately related, such that \( q_{\text{oxide}} \) will have an effect on the Tafel slope. We can probe the data to see which of these relationships apply. Figure 5.9 shows log \( i \) vs \( q_{\text{oxide}} \), this time for a range of \( \eta \). If Eq. 5.4 is valid, we expect to see the slope of the lines remain nearly constant as \( \eta \) is varied. If Eq. 5.5 is valid, we expect that the slope will change as \( \eta \) is varied. In Figure 5.9, two regions of data can be observed.
for both KOH and HClO$_4$—at low ORR overpotentials (0.9 to 0.84 V$_{RHE}$) the slope is changing, while at high overpotentials (0.82 to 0.78 V$_{RHE}$), the slope is relatively constant. This suggests that at low overpotentials the Tafel slope is highly dependent on oxide coverage, while at higher overpotentials the Tafel slope is less influenced by oxide coverage. This makes intuitive sense and provides some justification for other findings which suggest electrode coverage by oxygenated species plays an integral role in determining Tafel slope.$^{35}$

We turn our attention back to Eq. 5.5 to show that (at least for low overpotentials) the Tafel slope should decrease as $q_{oxide}$ is increased. We can use information from the best fit lines (Figure 5.9b, KOH) at low overpotentials ($E \geq 0.84$ V) to model the effect of $q_{oxide}$ on current. The low overpotential KOH data from Figure 5.9b is given again in Figure 5.10a, where each overpotential can be fit as an exponential having the following parameters

$$|i| = A \exp (k|\eta|q_{oxide}) = A \exp (b q_{oxide})$$  \hspace{1cm} (5.6)

where $A$ is a pre-exponential factor. It can be shown that the pre-exponential factors for all overpotentials in Figure 5.10a can be fit to an exponential having a dependence on $\eta$ (see Figure 5.10b) such that

$$A (A \text{ cm}^2\text{Pt}^{-2}) = 2.09 \times 10^{-7} \exp (21.7 |\eta|)$$  \hspace{1cm} (5.7)

where it can be shown that
21.7 = \frac{aF}{RT} \quad (5.8)

which is equivalent to the Butler-Volmer exponential for an electron transfer occurring at 298K with an $\alpha \approx 0.55$ (first electron rate limiting step). Therefore, the pre-exponential factor, $A$ can be written as

$$A \left( A \text{ cm}^{-2} \text{ m}^{-2} \right) = 2.09 \times 10^{-7} \exp \left( \frac{aF}{RT} |\eta| \right) \quad (5.9)$$

The term in the exponential in Eq. 5.6 (Figure 5.10a) is multiplied by $q_{oxide}$ and

$$b = k|\eta| \quad (5.10)$$

It can be shown for the overpotentials given in Figure 5.10a that the linear dependence of $b$ on $\eta$ has a non-zero intercept (see Figure 5.10c), meaning that the proposed exponential in Eq. 5.6 will become

$$|i| = A \exp \left[ (22125|\eta| - 9475)q_{oxide} \right] \quad (5.11)$$

Finally, combining Eq. 5.11 with Eq. 5.9, it can be shown that for low overpotentials

$$|i| = i_0 \exp \left( \frac{aF}{RT} |\eta| \right) \exp (k_1|\eta|q_{oxide}) \exp (-k_2 q_{oxide}) \quad (5.12)$$

There are 4 terms in Eq. 5.12; the first of which defines exchange current density, or the current passed in the system at the equilibrium potential (and no oxide coverage); for the system described here, this value is 0.2093 $\mu$A cm$^{-2}$Pt. The second term defines the dependence of current density on Butler-Volmer electrode kinetics (the $\alpha$ of 0.55 suggests that the rate determining step for Pt/C is the first electron transfer$^{45, 46}$) The third term defines the relationship between $q_{oxide}$ and $\eta$, with $k_1$
being the proportionality constant, whose magnitude is equal to 22125 V⁻¹ C⁻¹ for our system. This third term explains the dependence of the Tafel slope on qoxide. The final term defines the inverse dependence of current on oxide coverage. It has a proportionality constant, k₂, which in our system is equal to 9475 C⁻¹.

A unique property of this analysis is that we are able to extract a single exchange current density which is independent of any surface coverage, which we will call the absolute exchange current density. In most ORR literature, ‘exchange current’ is extrapolated to be the amount of current passed at the equilibrium potential. However, most reports of ORR exchange current densities do not consider that the surface is actually partially oxidized, especially at lower overpotentials during the reported forward scans. To illustrate this, we measured the ‘exchange current’ for the low overpotential forward scan KOH data given in Figure 5.8 (measured from projected i at 1.2 V using line of best fit from log i vs. E plot). We found the exchange current density to be 7.64 × 10⁻⁹ A cm⁻² Pt, which is roughly 30 times lower than that of the ‘absolute exchange current’ we calculated for Pt (2.09 × 10⁻⁷ A cm⁻² Pt). This is because the ‘exchange current’ density calculated from the forward sweep also contains a contribution from surface coverage of oxygenated species (namely OHads). Our experimental methods and analysis have permitted us to deconvolute this term to show that regardless of the quantity of oxide on the Pt surface, the absolute exchange current for Pt in 0.1 M KOH remains constant at 2.09 × 10⁻⁷ A cm⁻² Pt.
Figure 5.11 presents the experimentally obtained Tafel plots (log i vs. η) of the ORR with Pt oxide layers formed at $E_{ox}$ of 1.1, 1.2, 1.3 and 1.4 V for 40 s, respectively. The dotted lines in Figure 5.11 represent the data calculated from Eq. 5.12, using the $q_{oxide}$ formed at the corresponding $E_{ox}$ for 40 s (Table 5.1), and assuming $i_0$, $k_1$ and $k_2$ of 0.209 μA cm$^{-2}$, 22125 V$^{-1}$ C$^{-1}$ and 9475 C$^{-1}$, respectively, for ORR in KOH. Figure 5.11 shows that Eq. 5.12 can accurately predict the Tafel slope for the low current density/low overpotential region. The data provide very strong evidence that the measured ORR Tafel slope is highly dependent on the presence of oxygenated surface species and should not be mistaken for a change in rate-limiting step. The modeled α value of 0.55 is very good indication of a 1 electron-transfer rate limiting step. An identical equation with different constants can be modeled for the Pt/C system in 0.1 M HClO$_4$. We believe this analysis can be validated for all other Pt-based catalyst systems.

We performed a similar treatment of the data for high overpotentials (in 0.1 M KOH), where the current shows little interdependence between overpotential and $q_{oxide}$. As a result, the observed current can be described with only the 1$^{st}$, 2$^{nd}$, and 4$^{th}$ terms from Eq. 5.12 (with different constants, of course). Interestingly enough, the 2$^{nd}$ term, which is related to Butler-Volmer electrode kinetics is different for high overpotentials. This time, instead of an α of ca. 0.5, α is observed to be ca. 0.78, suggesting the possibility of emergence of a “chemical” rate limiting step. It can be
shown with Figure 5.6 that peroxide formation in KOH begins to occur at potentials 
< 0.85 V (\(\eta > 0.35\) V). On this basis, we believe that at low overpotentials (\(\eta \leq 0.35\) V) the ORR proceeds via an inner-sphere electron transfer while at high overpotentials (\(\eta > 0.35\) V), the ORR proceeds via a mixed inner-sphere/outer sphere reaction. Given the fact that the oxide reduction proceeds very slowly at low overpotentials, we can rationalize that in this regime, O\(_2\) is adsorbed to both oxide “sites” and “active Pt sites”, but it undergoes ORR only on the active Pt sites (inner-
sphere), leading to the observed \(\alpha\) of ca. 0.5. When the system is pushed further away from equilibrium (e.g. higher overpotentials), there is sufficient driving force for the ORR to occur on both “active Pt sites” and on “oxide sites” (outer-sphere). This hypothesis is corroborated by the decreased absolute exchange current density in the higher current density range. If ORR were truly occurring on a more pristine (active) Pt surface at higher overpotentials, the exchange current would reflect that (as it does for the high overpotential regime of the forward sweep \(7 \times 10^{-8}\) A, compared to \(8 \times 10^{-9}\) A for low overpotential regime of forward sweep). Instead, for the reverse sweep, the absolute exchange current is higher at low overpotentials (\(2 \times 10^{-7}\) A for low OP and \(8 \times 10^{-9}\) A for high OP), indicating that ORR is probably proceeding on a more active surface. This argument is valid even if ORR on an oxide site does not result in a ‘chemical’ rate limiting step, but only in a shift in symmetry coefficient from 0.5 to 0.78. Symmetry coefficient can be crudely defined as the fraction of energy that is used to get the electron over the energy “barrier”. It is intuitive that on an oxide surface, the greater physical separation
between adsorbed oxygen and active catalyst results in a higher fraction of energy required to push the electron over the energy barrier.

### 5.3.9 Origin of different Tafel regions

The 3rd Tafel region observed for KOH in Figure 5.8 (at E < 0.8 V\textsubscript{RHE}) and Table 5.2 is quite intriguing. We can say with some degree of certainty that it is a real phenomena and not an artifact of how we measured the Tafel slopes. Classical Tafel analysis would suggest that a slope anywhere near 120 should be the result of a slow 1st electron transfer. However, in the ORR community it is commonly believed that slopes > 120 mV/dec are undoubtedly linked to a new rate determining step\textsuperscript{46}. Due to the very overt change in Tafel slope occurring for the Pt/C catalyst at $E_p$ of 1.3 and 1.4 V, we are inclined to believe that the rate determining step has changed. We will not speculate further on the nature of that change in this work. However, we are very interested in what caused the change in Tafel slope.

Figure 5.12a shows the total quantity of $q_{oxide}$ remaining at the first and second Tafel slope switch in KOH. The changes in Tafel slope could be easily rationalized if they occurred when a certain amount of oxide was remaining on the surface, but this is not the case. The shift in Tafel slope occurs when different amounts of oxide are remaining for different amounts of initially deposited oxide films. Figure 5.12b shows the fraction of total $q_{oxide}$ remaining when the Tafel slope changes. Again, there is no specific fraction of $q_{oxide}$ remaining which leads to a change in Tafel slope.
We believe these results may illustrate a deeper concept in oxide growth and removal. Take for example, Figure 5.10 where different $q_{\text{oxide}}$s and their resulting ORR activities are given at a variety of overpotentials. Clearly it can be seen from the 2 overlapping data points at $\sim$0.7 mC that $q_{\text{oxide}}$ is the determining factor for the magnitude of ORR activity at a variety of different overpotentials. These two overlapping data points happen to have the same $q_{\text{oxide}}$, but one oxide was grown at 1.3 V for 60 seconds and the other at 1.4 V for 10 s. This suggests that oxide growth always proceeds in the same manner—regardless of whether it was formed with long times or high potentials. As shown in the inset of Figure 5.8, these two data points have identical Tafel slopes and changes. This indicates that as long as a constant quantity of oxide is formed on the electrode it will be removed the same way. However, if different quantities of oxide are formed on the electrode they will not be removed in the same manner. Different oxide films will exhibit a path-dependent ‘memory effect’ whereupon their entire reduction process is predicated upon an intricate balance between the initial amount of oxide that was present and the electrode potential (which is the driving force for reduction). This rationalizes why there is no ‘magic’ quantity of remaining oxide (Figure 5.12) that is required to spur a change in the ORR Tafel slope—these changes are dependent on the initial quantity of oxide. Differences during oxide reduction lead to differences in the local environment of active ORR sites which could lead to a change in ORR mechanism. Though we have only analyzed results in KOH because of the more obvious changes
in Tafel slope, we see no reason why this explanation does not apply to measurements in HClO₄, perhaps on a smaller scale. This hypothesis is in agreement with recent in operando X-ray absorption studies of oxide formation by Redmond et al. which showed that oxide removal and oxide formation do not proceed along the same (or even reverse) pathway.²⁶

5.4 Conclusions

In this work, a comprehensive analysis of the effects of Pt oxide films on the oxygen reduction reaction at pH extremes was presented. The study is particularly unique because all experimental data was obtained using the same catalyst, so all results are directly comparable and errors stemming from systematic variations during catalyst preparation are mitigated. A possible mechanism of oxide growth during potential holds was proposed. In alkaline, Pt was found to form a much stronger bond to oxygen than in acid, but interestingly, the Pt surface in acid appears to have a larger affinity towards PtOₓ as it is able to host a much larger density of oxide. The formation of thicker oxides leads to increases in absolute peroxide formation, but interestingly, in alkali, peroxide formation seems to be better facilitated by a thinner, and more hydrated oxide layer than a thicker PtOₓ layer. Lower ORR activity in alkaline media is thought to be linked to the strength of the Pt-O bond and the outer-sphere ORR mechanism which is believed to proceed in alkaline conditions. The ORR was found to be inhibited differently during the forward ORR sweep than the
reverse ORR sweep, which provides evidence for the widely accepted place-exchange model whose effects cannot be observed during the ORR in the forward sweep. The mechanism of the ORR in acid and base was thoroughly discussed and decreases in Tafel slope as thicker oxides were grown on the surface were shown be consistent with a theoretical calculation. On the basis of this study, it is proposed that the initial amount of oxide deposited may play the biggest role in determining the mechanistic pathway of the ORR. The analysis described herein provides a detailed look at effects of oxide on the ORR, which will become especially useful as researchers begin to look for new ORR catalysts which can be operated at higher and higher fuel cell voltages, and hence in the potential range where it is difficult to isolate oxide formation/reduction processes from the oxygen reduction reaction.

5.5 References


5.6 Figures & Tables

Figure 5.1: Pt/C Catalyst electrochemical signature in HClO₄ and KOH before and after experimentation: (a,c) Ar-saturated electrolyte and (b,d) O₂-saturated electrolyte.

Conditions: 298 K, 20 mV/s, 1600 RPM
Figure 5.2: Effect of increasing time of oxidation (t_ox) on (a,c) oxide reduction and (b,d) background subtracted ORR polarization curves (reverse scan) in HClO₄ and KOH. Oxide formation potential is 1.2 V. (a,c) Ar-saturated electrolyte and (b,d) O₂-saturated electrolyte. Conditions: 298 K, 20 mV/s, 1600 RPM
Figure 5.3: Effect of increasing oxidation potential ($E_{ox}$) on (a,c) oxide reduction and (b,c) background subtracted ORR polarization curves (reverse scan) in HClO$_4$ and KOH. Oxide formation time is 40 s at each potential. (a,c) Ar-saturated electrolyte and (b,d) O$_2$-saturated electrolyte. Conditions: 298 K, 20 mV/s, 1600 RPM
Figure 5.4: Relationship between $q_{oxide}$ and (a) mass-transport corrected ORR current (0.9 V) and (b) oxide-stripping peak overpotential in 0.1 M HClO$_4$ and 0.1 M KOH. The linearity of the lines illustrates that an identical oxide can be grown via increases in time or potential. ORR measured in O$_2$ saturated electrolyte. All data derived from cathodic scans of CVs measured at 20 mV/s, 298 K and 1600 RPM. †Peak potential = 1.23 – peak overpotential.
Figure 5.5: Peroxide formation (measured from ring electrode current) as a function of oxide formation potential in 0.1 M HClO$_4$ and 0.1 M KOH. As oxide gets thicker, there is a higher absolute quantity of peroxide formed. Oxide formation time is 10 s at each potential. All data derived from ORR cathodic disk electrode scans measured at 20 mV/s, 298 K and 1600 RPM.
Figure 5.6: Peroxide formation (measured from ring electrode current) in 0.1 M KOH normalized to (a) quantity of oxide on electrode before reduction ($q_{\text{oxide}}$) and (b) quantity of oxide remaining on electrode during reduction. Peroxide formation facilitated more by thinner oxide layer. All data derived from ORR cathodic disk electrode scans measured at 20 mV/s, 298 K and 1600 RPM.
Figure 5.7: ORR $\frac{1}{2}$ wave potential as a function of $q_{\text{oxide}}$ in 0.1 M HClO$_4$ and 0.1 M KOH. Equations of the best-fit lines are also given. All data derived from background-corrected ORR cathodic scans measured at 20 mV/s, 298 K and 1600 RPM.
Figure 5.8: Tafel plot of ORR current for different oxide formation potentials in (a) 0.1 M HClO₄ and (b) 0.1 M KOH. Forward scan and steady-state reverse Tafel data also shown. All oxide formation potentials held for 40 s. All data derived from background and mass-transport corrected ORR cathodic scans measured at 20 mV/s, 298 K and 1600 RPM. Inset shows Tafel plot of ORR current for similar oxide layers grown with different conditions.
Figure 5.9: ORR current as a function of oxide quantity for various overpotentials in (a) 0.1 M HClO₄ and (b) 0.1 M KOH. Slope of line of best fit included. At all potentials $\geq 0.84$ V the slope is different, while at potentials $< 0.84$ the slope is relatively constant. This indicates that at low overpotentials the Tafel slope is highly dependent on oxide coverage while at high overpotentials the Tafel slope is less influenced by oxide coverage.
Figure 5.10: (a) ORR current as a function of oxide quantity for low overpotentials in 0.1 M KOH. Equation of best fit exponential included. Modified from Figure 9, except y-axis is not logarithmic. (b) shows dependence of pre-exponential constant ‘A’ on overpotential ($\eta$). (c) shows dependence of proportionality constant ‘b’ on overpotential.

\[ \eta = 1.23 \text{ V} - E \text{ (V)} \]
Figure 5.11: Tafel plot of ORR current (low current density regime) for different oxide formation potentials in 0.1 M KOH. Tafel data predicted by Eq. 5.12 is indicated by dotted lines. All experimental data derived from background and mass-transport corrected ORR cathodic scans measured at 20 mV/s, 298 K and 1600 RPM.
Figure 5.12: (a) Quantity of remaining oxide when Tafel slope changes in 0.1 M KOH. (b) Fraction of total oxide that remains when Tafel slope changes. Data shown as a function of $q_{oxide}$, but $E_{ox}$ given for reference. All $E_{ox}$ held for 40 s. 1st Tafel slope change is defined as the shift from low to middle/high current density. 2nd Tafel slope change is defined as shift from middle to high current density (only observed for $E_{ox}$ of 1.2, 1.3 and 1.4 V).
Table 5.1: Summary of effects of oxide formation time and potential.

<table>
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<tr>
<th>Electrolyte</th>
<th>Potential held (V)</th>
<th>Duration held (s)</th>
<th>Oxide stripping peak potential (V)</th>
<th>ORR Activity @ 0.9 V (i) (mA cm(^{-2}))</th>
<th>(q_{\text{oxide}}) (mC)</th>
<th>(\frac{q_{\text{oxide}}(t_1 \text{ or } E_1)}{q_{\text{oxide}}(t_2 \text{ or } E_2)})</th>
<th>(\frac{i(t_2 \text{ or } E_2)}{i(t_1 \text{ or } E_1)})</th>
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Table 5.2: Summary of reverse scan Tafel slopes from Figure 5.8

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<th>Electrolyte</th>
<th>Potential held (V)</th>
<th>Tafel slope low current density (mV/dec)</th>
<th>Tafel slope middle/high current density (mV/dec)</th>
<th>Tafel slope high current density (mV/dec)</th>
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List of References

Chapter 1 References

1. CO₂Now. Atmospheric CO₂ from Mauna Loa Observatory. <http://co2now.org/>


4. APMEX. Precious Metal Spot Prices. <www.apmex.com>


159


Chapter 2 References


**Chapter 3 References**


Chapter 4 References


28. Wakisaka, M., Morishima, S., Hyuga, Y., Uchida, H. & Watanabe, M. Electrochemical behavior of Pt–Co(111), (100) and (110) alloy single-crystal electrodes in 0.1 M HClO4 and 0.05 M H2SO4 solution as a function of Co content. *Electrochem. Commun.* 18, 55-57 (2012).


**Chapter 5 References**


