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Block copolymer templated bimetallic nanoparticles for fuel cell applications

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BLOCK COPOLYMER TEMPLATED BIMETALLIC NANOPARTICLES
FOR FUEL CELL APPLICATIONS

By
Kyle Mikkelsen

Accepted in Partial Completion
Of the Requirements for the Degree
Master of Science

Kathleen L. Kitto, Dean of the Graduate School

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Kyle Mikkelsen

May 16, 2014
BLOCK COPOLYMER TEMPLATED BIMETALLIC NANOPARTICLES
FOR FUEL CELL APPLICATIONS

A Thesis
Presented to
The Faculty of
Western Washington University

In Partial Fulfillment
Of the Requirements for the Degree
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May 2014
Abstract

This study explored the use of a block copolymer, polystyrene-block-poly(4-vinylpyridine), as a template for the synthesis of platinum-gold bimetallic nanoparticles. The polymer forms spherical micelles in solution which can be cast onto a substrate and subsequently undergo film reconstruction in an orthogonal solvent. The film is then placed into an acidic bath containing varying ratios of K₂PtCl₆ and KAuCl₄ to load metals into the film. The nanoparticles are then formed by a reactive argon ion etch to remove polymer and reduce metal salts to a metal (0) state. The polymer selected had a polystyrene to poly(4-vinylpyridine) ratio of 3:1 to favor particle spacing on the surface and to attempt to control particle size and three different polymers were chosen to study. The polymer was analyzed by scanning force microscopy. The particles were analyzed by scanning force microscopy (SFM), transmission electron microscopy (TEM), x-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). Average particle size was found to be approximately 3 nm for all catalysts by TEM since they exceeded the detection ability of the SFM tips used. Bimetallic catalysts showed strong evidence for alloying by CV, XPS, and TEM. Composition of all catalysts was determined by XPS. The catalysts were tested for activity in the methanol oxidation reaction utilizing CV and the oxygen reduction reaction using a rotating ring-disk electrode (RRDE). The gold introduced into the particles showed evidence for resisting carbon monoxide poisoning common for pure platinum in the methanol oxidation reaction. In the case of the oxygen reduction reaction, gold appeared to increase the activity in a couple cases, but mostly it helped increase catalyst selectivity for the direct four electron conversion of oxygen to water over the production of peroxide as an intermediate.
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1. Introduction and Background

1.1 Energy Concerns

An increasing global population will continue to put strain on many resources necessary to maintain a healthy standard of living. Apart from the increasing demand for food, the largest issue will be the increase in demand for the energy required to cook our food, light our homes, and perform everyday tasks that are essential for life. This ever-increasing demand for energy will only amplify our reliance on fossil fuels if sustainable choices are not found, although current policy scenarios are projecting to reduce this dependency. This fact can be seen in Figure 1.1.\textsuperscript{1} The International Energy Agency projection indicates that by the year 2035, fossil fuels will still comprise over 75\% of our energy needs if no changes are made in policy. If changes are made, however, this number could drop to around 60\% under the 450 scenario, which would be a drastic set of changes to maintain the current levels of carbon dioxide (CO\textsubscript{2}) to 450 ppm.

This idea of maintaining CO\textsubscript{2} levels is not new. We have known for a long time that CO\textsubscript{2} levels are linked to the temperature of the earth and limiting them is important to prevent more climate change. Figure 1.2 displays data from the Vostok outpost in Antarctica.\textsuperscript{2} At this station, cores were taken from ice that has been undisturbed for hundreds of thousands of years. They then
used isotopic analysis to determine the temperature of the globe and the level of \( \text{CO}_2 \) in the atmosphere at the time that the cores formed naturally. It can be seen from the data that the level of \( \text{CO}_2 \) in the atmosphere and the temperature of the globe are directly related. Therefore, maintaining the levels of \( \text{CO}_2 \) to a safe limit to prevent more climate change is necessary.

![Graph showing correlation between atmospheric \( \text{CO}_2 \) and global temperature change.](image)

**Figure 1.2.** Vostok ice core data correlating atmospheric \( \text{CO}_2 \) to global temperature change. Reproduced with permission from the author.²

### 1.2 Energy Alternatives

There are many potential alternative energy options that must be explored to determine their efficiency and practicality. One potential alternative is biodiesel. Biodiesel is attractive because it can utilize current diesel engines, we already have the technology to make it, and it is considered carbon neutral since the carbon required to make the fuel was fixed from the atmosphere by plants.³ There are some drawbacks including potential competition with feed stocks, economic policy hindrances, and the potential of spreading genetically modified biomass species into natural habitat.⁴ Solar
power has always been an appealing option as well. More power from the sun hits the earth in one hour than humans will use in an entire year. The main issues are that the power from photovoltaic cells are not cost-competitive with that from fossil fuels and there is a lack of an efficient storage method for low illumination periods when there is insufficient solar flux on the cells or for electrical load compensation.

There are many types of energy storage available for electrical load management and they all have their pros and cons. Compressed air is promising but needs specific geographic locations to be implemented and most designs require fossil fuels. Batteries have extremely low power densities and generally low discharge rates. For higher discharge rates more money must be spent, but then a higher internal power loss mechanism occurs. Batteries are cheap and some require almost no maintenance, but have only 5-15 year lifetimes depending on operating temperatures and depth of discharge. Supercapacitors are promising due to their high power density and rapid discharge rates, but cost and low energy densities keep them from being a major player. Flywheels have also been of interest. They consist of a spinning rotor that is powered by an electromagnetic motor which acts as the generator when the power is to be recovered. They have long lifetimes and the fastest discharge rates, but flywheels are expensive and have self-discharge rates of around 20% capacity per hour.

Biological organisms have lasted for millennia without the help of fossil fuels for energy. They do this by storing energy chemically, such as in carbohydrates and fats. In principle, humanity may be able to store significant amounts of energy in a similar fashion. Hydrogen is the simplest molecule we could store energy with because it has the highest energy density per molecule. The energy density by weight of hydrogen is about three times that of gasoline or diesel, but the volumetric energy density is three times lower than natural gas at atmospheric pressure and requires high pressures to be competitive. Energy can be stored in alternative chemicals. Formic acid and methanol are candidates that are both liquids at room temperature which make them attractive since the requirement for high pressure storage is not needed. The higher volumetric energy density of formic acid and methanol exceed that of compressed air, batteries, supercapacitors, and flywheels. Formic acid is less toxic and volatile than methanol, but methanol has a higher energy density since
the carbon oxidation state is +4 for methanol versus +2 for formic acid. The plot in Figure 1.3 displays the energy density of some fuels based on density per unit volume versus per unit mass. The ideal case would be to the top right of the plot. So far gasoline is still the best fuel, although methanol is not far behind. The liquid hydrogen and compressed hydrogen values may seem quite low, but that is because the storage tanks required increase the weight to a point where it becomes an unattractive storage method. Hydrogen, formic acid, and methanol are all high energy density storage options, but what is the best way to extract the energy that is stored in these fuels?

1.3 Fuel Cells

The most promising form of energy production from a stored source is fuel cells, which will be the focus of this work and, more specifically, the catalysts inside the fuel cell. A typical gasoline engine converts chemical energy into mechanical energy at an efficiency of around 22%, whereas a fuel cell can convert chemical energy into electricity with an efficiency that is currently around 60%.
This makes fuel cells a major player in the renewable energy storage market. Fuel cell design is relatively simple, though many challenges still exist. A simple schematic is shown in Figure 1.4 for a hydrogen fuel cell, also known as a polymer electrolyte membrane fuel cell (PEMFC). PEMFCs can use a variety of fuels including formic acid (direct formic acid fuel cell, DFAFC) and alcohols (direct alcohol fuel cell, DAFC) instead of hydrogen. The cell consists of a polymer electrolyte, typically Nafion®, a sulfonated fluoropolymer. The polymer is sandwiched between two electrodes, which is usually carbon of some sort. The electrodes are coated with a catalyst to facilitate the necessary oxidation and reduction reactions. More detail will be given on the catalysts later. The fuel is introduced at the anode side (in the case of alcohol fuel cells, water is often also required). The fuel reacts with the catalyst to liberate protons and electrons. The protons pass through the polymer electrolyte membrane and the electrons pass through a circuit to do work. On the cathode side, oxygen from the air combines with the electrons and protons over the cathode catalyst to form water. A novel idea is to use this water on the anode side to reduce the volume of fuel required in DAFCs. Currently, the industry standard for PEMFCs is a platinum anode and cathode catalyst, which present the main problems with fuel cells.
1.4 Platinum as a Fuel Cell Catalyst

Besides cost, platinum as a fuel cell catalyst has two major downfalls. On the anode side, carbon monoxide (CO) from the oxidation of formic acid or methanol poisons the catalyst irreversibly which depletes the catalyst efficiency.\textsuperscript{18-20} In the case of ultrapure hydrogen this does not occur. Hydrogen is, however, isolated from the water gas shift reaction which inadvertently becomes contaminated with carbon monoxide.\textsuperscript{17, 21} The other issue with platinum lies on the cathode side. While finding a catalyst that is resistant to CO is important, platinum that is used for the cathode to perform the oxygen reduction reaction (ORR) has poor kinetics and does not have a high enough rate of reaction to keep up with the flux of protons and electrons from the anode.\textsuperscript{22-23} These sluggish kinetics coupled with the high price of platinum call for some advances to be made in fuel cell catalysis.

In order to reduce the amount of platinum, decrease catalyst poisoning, and increase the activity, many researchers have started synthesizing bimetallic Pt-M nanoparticles (NPs) where M is a second metal (M = Cr, Fe, Co, Ni, Cu, Zn, Ru, Pd, Sn, Os, Ir, Au).\textsuperscript{22, 24-41} These nanoparticles have been synthesized in a variety of methods which allow them to adopt different properties as well. Recently, a group used a modified polyol method (method which employs an alcohol rich polymer to stabilize the metals) to synthesize a palladium cored particle with a platinum shell (Pd@Pt) for use in the methanol oxidation reaction (MOR).\textsuperscript{27} Another route is to use surfactants to stabilize the particles. Ataee-Esfahani \textit{et al.} utilized this method to synthesize Au@Pt core-shell particles for utility in the MOR.\textsuperscript{40} A unique method employs a polymer with two different chains to constrain the particles and control the morphology at room temperature in order to synthesize the similar Au@Pt nanoparticles.\textsuperscript{24} Another method makes use of a two-step method in which one metal acts as a seed for the other metal in order to make Pt@Pd particles.\textsuperscript{41}

Some of the most cited papers surrounding bimetallic nanoparticles display some very exciting results. A paper published in \textit{Science} in 2007 synthesized a Pt\textsubscript{3}Ni(111) particle that displayed a 10 fold increase in activity over a pure Pt(111) face and a 90 fold increase in oxygen reduction activity over the most active pure platinum supported on carbon (Pt/C).\textsuperscript{22} Another well cited
example synthesized carbon nanotube membranes from an alumina template and then impregnated it with different metals and observed a highly ordered catalyst with increased performance. The direct fabrication of a catalyst on the carbon nanotube substrate was beneficial in that addition of carbon was not needed to implement it into a fuel cell. Some researchers have attempted even more complicated syntheses of trimetallic nanoparticles such as a gold core palladium shelled particle with an outer layer of platinum (Au@Pd@Pt).

1.5 Synthesis Background

The important attributes that a synthesis method should employ include the ability to control the size, shape, morphology, and composition of the nanoparticles being synthesized. If all of these can be done, a system can be synthesized to perform any reaction at increased activity and resistance to poisons and other interferences. A synthesis method will be presented which attempts to use a block copolymer templating method to accurately control the size, shape, morphology, and composition of bimetallic nanoparticles for utility in fuel cell reactions.

1.5.1 Micelle Theory

A block copolymer consists of different polymer chains that connect at a single terminus. The main attraction of block copolymers is that there are many combinations of different polymer chains to choose from allowing one to tailor the length of each chain very precisely, and subsequently control self-assembly. The theory of block copolymer self-assembly comes from a surfactant based model. In this model, the blocks of the copolymer are chosen such that the two are immiscible such as a hydrophilic head and a hydrophobic tail. The macromolecule can then be dissolved in a solvent that is selective of only one block, which will force it to assemble itself to maximize favorable interactions and minimize the unfavorable ones. It is this interaction that can be tailored to give many different shapes of micelles, which are aggregates of polymer chains that form different structures in the solid state. The volume of the head of the polymer chain will decrease upon dissolution in an orthogonal solvent, while the tail will interact favorably. To minimize the interactions of the head with the solvent, the chains will agglomerate into micelles. The micelle size
is dictated by minimizing the chain stretching of the corona, or exterior, while confining the core polymer chain entropy. Figure 1.5 displays a variety of solid state structures that can be formed by altering the polymer chain length and casting solvent for a diblock copolymer.\textsuperscript{48}

![Figure 1.5](image)

**Figure 1.5.** Solid state assemblies of a diblock copolymer consisting of different lengths of polymer A (white) and polymer B (black). Reproduced with permission from the author.\textsuperscript{48}

After a polymer solution is made with a diblock copolymer, the ability to form precisely controlled thin films is necessary. There are many laboratory techniques for making well defined thin films including spin coating and dip coating, though many more industrial techniques are available.\textsuperscript{49} The spin coating procedure is designed to give a monolayer thin film of polymer by rotating a substrate at high speeds (~500-4000 RPM) with a solution of polymer on top. The polymer is spread thin by the rotation of the substrate and dried at the same time by holding the rotation for some time. Dip coating is simply the act of dipping a substrate into a polymer solution. The polymer is coated onto the substrate in a uniform manner, although monolayer thickness is harder to achieve this way. The variety of coating procedures is not limited to these two, but the others options are for industrial scale use so it is unnecessary to delve further into them.

### 1.5.2 Polymer-Metal Interactions

The use of a diblock copolymer to template metal nanoparticles is not new.\textsuperscript{24, 46-47, 50-56} Many researchers have utilized a diblock copolymer which contained a vinylpyridine-based (VP) repeat unit which is thought to be the important site at which the metal is bound to the polymer. Figure 1.6 displays the structure for poly(4-vinylpyridine) (P4VP) and poly(2-vinylpyridine) (P2VP), the two most commonly used pyridine repeat blocks used to template a metal nanoparticle. The pyridine ring is thought to interact with the metal in one of three major ways.\textsuperscript{57-58} If the media is neutral such that the nitrogen is not protonated and the dissolved metal of interest is in a neutral form, as in PdCl\textsubscript{2}, then
there is a metal-ligand interaction between the PdCl$_2$ and the pyridine. This is believed to be a fast interaction. If the pyridine is not protonated and the metal salt is an anion with a chlorine (PtCl$_6^{2-}$, PdCl$_4^{2-}$, AuCl$_4^-$, PtCl$_4^{2-}$), then the interaction takes place through a chlorine exchange on the anion for a pyridine. This is an equilibrium-based process and takes from hours to days. The last interaction takes place when the media is acidic enough to protonate the pyridine. To achieve this, either acidic forms of metal salts can be used (HAuCl$_4$ and H$_2$PtCl$_6$), or other salts (K AuCl$_4$ and K$_2$PtCl$_6$) can be dissolved in a dilute acid solution. In this case the pyridine is protonated to give pyridinium and the metal interacts through electrostatic interactions and hydrogen bonding providing an immediate equilibrium to be achieved.

1.5.3 Metal Formation from Micelles

After the polymer has been saturated with metal ions, it is necessary to reduce the metal into the corresponding metal (0) state to acquire metal particles. A variety of methods are commonly used to achieve the metal (0) oxidation state. One reduction technique involves the use of a chemical reducing agent such as ascorbic acid which donates electrons to the metal ion.$^{24}$ This can be done as a solution-phase reduction or by submerging a polymer coated substrate into the reducing agent. Another common approach is to use heat.$^{50,54}$ This is known as thermal decomposition and occurs when the polymer decomposes under high heat where the metal ions can act as electrophiles and become reduced by the breaking of the carbon-carbon bonds. This is similar
to the process of photoreduction that can be used as well.\textsuperscript{59} By this process, a block copolymer saturated with metal ions is subjected to intense ultraviolet radiation and the polymer is decomposed and donates excess electrons to the metal that is thereby reduced. This is attractive since high temperatures are not required. The standard hydrogen reduction is also available and is often used in industry.\textsuperscript{52} A stream of hydrogen gas is passed over or through the sample to be reduced while heating. The heat gives the system enough energy for the hydrogen to be broken down to reduce the metal ions. The last method discussed here employs a vacuum chamber to which a strong electromagnetic field can be applied. The sample is placed in the chamber and pumped down (~10 Pa) followed by the introduction of gas (Ar, O\textsubscript{2}, H\textsubscript{2}). The applied electromagnetic field ionizes the gas into its plasma phase which consists of cations and electrons that etch the polymer and reduce the metals, respectively. In the case of the O\textsubscript{2} plasma etch, the metal may end up with a protective oxide layer on it which may be desirable for certain reaction studies.\textsuperscript{55} In the case of the argon and hydrogen plasma etch, the metal is reduced to the lowest oxidation state.\textsuperscript{46, 56}

\textbf{Research Scope}

The goal of this research is to present research relevant the scientific community pertaining to block copolymer templated bimetallic nanoparticles and their applications to reactions within direct methanol fuel cells. In-depth studies will be displayed on catalyst synthesis and characterization including such techniques as: scanning force microscopy (SFM), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and cyclic voltammetry (CV) utilizing a rotating ring-disk electrode (RRDE). Detailed analysis is shown for the methanol oxidation reaction and the oxygen reduction reaction.
2. Experimental

2.1 Materials

Potassium tetrachloroaurate (K₂AuCl₄) and potassium hexachloroplatinate (K₂PtCl₆) were used as received from Fischer Scientific, Inc. Polystyrene-b-poly(4-vinylpyridine) (PS-b-P4VP) of block ratio ~3:1 was used as received from Polymer Source, Inc. Three polymers were specifically chosen: PS₁₃₉₂-b-P₄VP₄₇₁ (PDI = 1.07), PS₈₉₃-b-P₄VP₃₃₀ (PDI = 1.15), and PS₅₅₂-b-P₄VP₁₇₄ (PDI = 1.14) where the subscripts indicate the average number of repeat units for each respective chain. Indium tin oxide coated glass substrates (9-15 Ω/cm²) were acquired from Delta Technologies. Glassy carbon (GC) disk inserts (5 mm OD x 4 mm thick) were obtained from Pine Research Instrumentation. Silicon oxide (100 nm) coated silicon wafers were used as received from Virginia Semiconductors. Toluene (ACS Reagent Grade) was obtained from Macron Chemicals, vacuum distilled, and stored in an inert atmosphere prior to use. Sulfuric acid (H₂SO₄, 95.0 – 98.0 %) was used as received from Mallinckrodt. Anhydrous Methanol (99.9 %) was used as received from Fischer Scientific, Inc. Polystyrene (~150 kg/mol) was used as received from Fluka Analytical. Hydrofluoric acid (49 % in water) was used as received from Fischer Scientific.

2.2 Synthesis of Platinum-Gold Mono/Bimetallic Nanoparticles

2.2.1 Polymer Film Preparation

Platinum-gold (Pt-Au) nanoparticle synthesis follows a modified procedure as outlined by Aizawa et al. 60 ITO coated glass was cleaned by subsequent 10 minute sonication in dichloromethane, ultrapure water (18 MΩ), and isopropyl alcohol. Following sonication, the ITO is subjected to a 10 minute argon plasma cleaning step at ~ 10 Pa (Harrick Plasma, PDC 32G, 18W). Glassy carbon disks were subjected to polishing with 0.3 µm and 0.05 µm alumina suspensions on nylon and microfiber pads, respectively, for ~3 minutes each followed by a 15 minute plasma cleaning step. Block copolymer (PS-b-P4VP) films were prepared by first dissolving PS-b-P4VP in toluene (4 mg/mL) by heating overnight at 363 K. The solution was then filtered (Millipore syringe filters, PTFE,
0.45 µm). The filtered solution was then dispensed onto the substrate of interest and accelerated to a rotation of 3000 RPM for 60 seconds utilizing a Lite Laurell Spin Coater (WS-400B-6NPP).

2.2.2 Catalyst Synthesis from Polymer Templates
Films were then submerged into methanol for 10 minutes to allow the micelles to invert as displayed by Chai and Buriak. After drying with filtered air, the coated and inverted substrate is submerged in a bath containing varying ratios of K₂PtCl₆ and KAuCl₄ dissolved in 0.10 M H₂SO₄ which give a total metal ion concentration of 0.010 M. For this study, platinum to gold (Pt:Au) bath ratios of 100:0, 98:02, 95:05, 88:12, 50:50, and 0:100 were chosen. Following this step, the sample is rinsed with copious amounts of ultrapure water (18 MΩ) and dried with filtered air. The samples are finally subjected to a reactive argon ion etch for 15 minutes in the same chamber used for the cleaning steps mentioned previously. This step simultaneously removed the polymer template and reduced the metal salt(s) to a metal (0) particle form.

2.3 Instrumentation and Testing

2.3.1 Microscopy
Scanning force microscopy (SFM) was performed with a Digital Instrument Nanoscope IIIa multimode instrument operated in tapping mode. Conical silicon probes (Nanoscience Instruments) were utilized with resonant frequencies near 300 kHz. Transmission electron microscopy (TEM) was conducted on a Technai Osiris (FEI) scanning transmission electron microscope with an acceleration voltage of 200 keV and equipped with Analytical TWIN (A-TWIN) objective lenses integrated with a Super-X EDX detection system. Copper and nickel Tem grids (Structure Probe Inc., 500 mesh, Ted Pella Inc., 200/300 mesh) were coated with formvar (SPI) and carbon sputter coated (PELCO Carbon Evaporation Unit, 91520-91251) before use.

2.3.2 Elemental Analysis
X-ray photoelectron spectroscopy was carried out on a Sage 100 (SPECS) spectrometer operated at a pressure below 10⁻⁵ Pascals. All samples were analyzed with an unmonochromated Mg Kα X-ray
source operated at a power of 240 W at a take-off angle of 90°, resulting in a maximum probe depth of ~ 10 nm. The atomic concentrations were estimated by determining the integral intensities for specific elements and taking relative ratios of the peak areas using a Shirley background and fitting the peaks with 30 % Gaussian-Lorentzian components. High resolution analysis was performed on the platinum 4d (Pt 4d), gold 4d (Au 4d), and carbon 1s (C 1s) regions. All binding energies were corrected to the C 1s peak for the background hydrocarbon component (C-C/C-H) at 284.6 eV.$^6$

2.3.3 Electrochemical Analysis

Electrochemical analysis was carried out on either a PARSTAT 2273 (Princeton Applied Research) or a Wavedriver 20 bipotentiostat (Pine Research Instrumentation). Three electrode setups consisted of a silver/silver chloride reference electrode (Ag/AgCl), a platinum wire counter electrode, and ITO coated glass bearing the particles of interest as the working electrode. Rotating ring-disk electrochemistry (RRDE) was performed utilizing the previously mentioned bipotentiostat and a rotating ring-disk electrode (Pine Research Instrumentation, AFMSRCE). The reference electrode was Ag/AgCl and the counter was a coiled platinum wire. The first working electrode was a 5 mm wide glassy carbon disk coated with the particles of interest. The second working was a platinum ring with an inside diameter of 6.5 mm and an outside diameter of 7.5 mm that was embedded in the electrode and concentric with the disk, but not touching. All voltammograms are reported relative to a ferricyanide calibrated Ag/AgCl electrode.

Steady-state cyclic voltammetry (CV) plots were obtained with a three electrode setup in 0.10 M H$_2$SO$_4$ purged with nitrogen (Praxair, >99%) at room temperature. A scan rate of 0.10 V/s was used for ten sweeps between -0.25 and 1.40 V. Kinetic electrochemical studies were completed with the rotating ring-disk electrode in oxygen (Praxair, >99%) saturated 0.10 M H$_2$SO$_4$ with constant bubbling during experiments to keep the oxygen concentration constant. The RRDE study was divided into two steps. First, the disk is potentiostatically held at -0.20 V for one hour at 2000 RPM to stabilize the catalyst. Secondly, five linear sweep voltammograms were obtained between 1.00 V and -0.30 V at the glassy carbon disk while holding the platinum ring at a constant 1.00 V. The first sweep was done at 400 RPM followed by the next four at increasing intervals of 400 RPM until the final sweep at 2000 RPM.

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3. Synthesis and Characterization

3.1 Film Preparation and Characterization

For this study, three different polystyrene-b-poly(4-vinylpyridine) polymers were chosen; PS$_{1392}$-b-P4VP$_{471}$, PS$_{893}$-b-P4VP$_{330}$, and PS$_{552}$-b-P4VP$_{174}$, where the subscripts indicate the average number of repeat units for each respective polymer segment. These particular block copolymers were selected since spherical micelles are afforded from self-assembly in toluene.$^{62-63}$ A schematic displaying the micelle formation upon toluene dissolution is displayed in Figure 3.1. The pyridine functionality was selected as this group is well established for pH controlled protonation and binding metal ions.$^{57}$

![Schematic of PS-b-P4VP forming micelles upon solvation in toluene.](image)

**Figure 3.1.** Schematic of PS-b-P4VP forming micelles upon solvation in toluene.

Once the polymer is dissolved in toluene (4 mg/mL), the solution can be cast onto a substrate using a spin coater to give the thin films shown in Figure 3.2 a, c, and e. After casting thin films, a kinetically trapped configuration of micelles populates the substrate surface. The micelle consists of a polystyrene outer shell, or corona, due to the favorable interactions with toluene and a poly(4-vinylpyridine) core due to the unfavorable reaction with the hydrophobic casting solvent. It can be seen in the figure that the micelles have a spherical morphology and a quasi-hexagonally close packed orientation on the surface. Analysis of the scanning force microscopy images was performed
Figure 3.2. SFM images of polymer films made from different PS-b-P4VP block copolymers as cast from toluene (a, c, e) and the corresponding inverted films (b, d, f) displayed on ITO coated glass substrate. a-b) PS<sub>552</sub>-b-P4VP<sub>174</sub>  c-d) PS<sub>893</sub>-b-P4VP<sub>330</sub>  e-f) PS<sub>1392</sub>-b-P4VP<sub>471</sub>. All images shown are 2 µm by 2 µm and have been flattened and had the height scale adjusted for optimum viewing.

to determine the height, periodicity, and full width at half the maximum (FWHM) by the method shown in Figure 3.3 and the results are displayed in Table 3.1. After the film has been prepared, a “priming” step is required to expose poly(4-vinylpyridine) chains from the cast micellar film and, hence, allow for access to the pyridine ring for binding the metal salt(s) of interest.<sup>57-58</sup> The priming step is achieved by inverting the kinetically isolated morphology of the film. Inversion takes place when the film is immersed in a solution of a hydrophilic nature such as methanol or water. This
causes the core to favorably interact with the solvent and the corona to interact unfavorably. This causes the poly(4-vinylpyridine) core to maximize the surface area of interaction with the solvent and, after drying the film, form toroids on the surface of the substrate as seen in Figure 3.2 b, d, and f. Since the polystyrene does not interact favorably with the inverting solvent, it acts as a web of immobile vitrified strands that immobilize the P4VP chains and allow for the retention in the areal uniformity of the sample. The priming was experimentally found to allow for more reproducibility in loading metal ions in the PS-b-P4VP films.

**Table 3.1.** SFM measurements of as cast polymer images. Measurements are not corrected for tip convolution.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>PS_{1392-171} b-P4VP</th>
<th>PS_{893-330} b-P4VP</th>
<th>PS_{952-174} b-P4VP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height</td>
<td>26 (2.9)</td>
<td>16 (3.1)</td>
<td>14 (2.5)</td>
</tr>
<tr>
<td>Periodicity</td>
<td>101 (7.8)</td>
<td>60 (11)</td>
<td>63 (7.9)</td>
</tr>
<tr>
<td>FWHM</td>
<td>54 (4.9)</td>
<td>32 (3.5)</td>
<td>35 (4.7)</td>
</tr>
</tbody>
</table>

**3.2 Particle Synthesis**

Once the polymer had been primed for loading, the metal salt(s) of interest can be loaded into the polymer. This is done by simply immersing the film into a solution, or bath, that is acidic and
contains the metal ions intended for defining the nanoparticle catalyst composition. The poly(4-vinlypyridine) segments of the micelle core are protonated by the acidic solution to produce positively

**Figure 3.4.** Schematic of the electrostatic and hydrogen binding of the core of the PS-b-P4VP with PtCl$_6^{2-}$ and AuCl$_4^{-}$.

**Figure 3.5.** SFM image of a cast PS$_{1392}$-b-P4VP$_{471}$ polymer film after inversion and loading with platinum salt.
charged pyridinium units throughout the pyridinium chain. The pKa of the pyridine is reported to be 4.5. The Henderson-Hasselbalch equation can be used to determine the amount of pyridine that would be protonated in the solution that this research uses to load the metal ions. The 0.10 M H₂SO₄ solution had a pH of 1.24 and therefore the ratio of base to acid is ~0.00055 which correlates to less than half of one percent of the polymer is left as pyridine, while the rest would be in the pyridinium state. Anions in solution subsequently populate the pyridinium environment to screen neighboring particles.

Figure 3.6. SFM images of nanoparticles synthesized from polymer templates. Particles are from one of six platinum and gold (Pt:Au) immersion baths: a) 100:0, b) 98:02, c) 95:05, d) 88:12, e) 50:50, and f) 0:100. All images shown are 2 μm by 2 μm, have been flattened, had the height scale adjusted for optimum viewing, and are displayed on ITO coated glass substrate.
cationic charges in these chains. In the case of K₂PtCl₆ and KAuCl₄, platinate and aurate anions electrostatically bind to pyridinium-rich sites and load the films with inherent platinum and gold. It can be seen from the schematic in Figure 3.4 that the ionic charge is dispersed throughout the interior of the polymer chains. Hydrogen-bonding and ligand displacement are also possible interaction mechanisms of pyridinium with PtCl₆²⁻ and AuCl₄⁻ but are known to be kinetically slower processes.⁵⁸ An SFM image of a PS₁₃₉₂-b-P₄VP₄₇₁ polymer film that has been loaded with platinum salt is displayed in Figure 3.5. The image shows similar characteristics to the inverted film shown in Figure 3.2f, but the micelles appear to be swollen and more textured indicating that the metal has indeed loaded into the film. Table 3.2 displays the different bath ratios chosen of platinum to gold to obtain a variety of metal compositions.

![Figure 3.7](image)

**Figure 3.7.** SFM image of clean ITO coated glass. Image is 2 µm by 2 µm and has been flattened and had the height scale adjusted for optimum viewing.

After the polymer film has been loaded with metal ions, it can then be subjected to a reactive argon ion etch procedure to produce nanoparticles. In this procedure, the sample is placed into a chamber filled with ~0.2 torr argon. A strong electromagnetic field is applied to ionize the argon gas into an argon plasma consisting of Ar⁺(g) and e⁻. The argon plasma is known to physically etch organic films and to reduce metal ions to their metal (0) oxidation state.⁵³,⁵⁶ The result of the argon ion etch is a reduced nanoparticle array on the surface of the substrate. Figure 3.6 displays compositionally tuned PtₓAuₑ₀₀₋ₓ nanoparticle arrays created from compositionally tuned platinate and aurate immersion baths. All other SFM images are available in appendix II. The SFM images show well-spaced nanoparticles with approximately uniform size and a quasihexagonal packing array. Any
additional smaller particles scattered about the main array correspond to the topography set by the polycrystalline indium-tin oxide (ITO) substrate. An SFM image of ITO coated glass used as a substrate for images is displayed in Figure 3.7 for comparison. Note the size of the scale bar compared to the images containing particles.

3.3 Particle Characterization

3.3.1. Scanning Force Microscopy

Scanning force microscopy was performed on the nanoparticles as synthesized from six compositionally tuned immersion baths as shown in Figure 3.5. Analysis of the images was performed to determine the height, periodicity, and full width at half maximum (FWHM) and the results are displayed in Table 3.2. The values in the table are obscured by the scanning tip convolution and fail to assess further details within the resulting clusters of nanoparticles created for a single P4VP domain (see TEM section). This misconception is due to the resolution limit of an SFM tip. Since the tip had a diameter of 8 nm it was unable to resolve individual particles within a cluster and caused them to appear to be a single particle. The periodicity value determined by SFM, however, is appropriate for assessing the population of nanoparticle clusters on the surface (see below).

Table 3.2. SFM measurements of six compositions of nanoparticles synthesized from three different polymer sizes. Measurements are not corrected for tip convolution.

<table>
<thead>
<tr>
<th>Bath Pt:Au mole ratio</th>
<th>Dimension</th>
<th>$PS_{(n)}$-$b$-$P4VP_{(m)}$ diblock copolymer templatea and SFM measured dimensionsb in nm (Standard Deviation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$PS_{1392}$-$b$-$P4VP_{471}$</td>
</tr>
<tr>
<td>100:0</td>
<td>Height</td>
<td>11 (2.0)</td>
</tr>
<tr>
<td></td>
<td>Periodicity</td>
<td>100 (13)</td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td>55 (4.3)</td>
</tr>
<tr>
<td>98:02</td>
<td>Height</td>
<td>11 (2.6)</td>
</tr>
<tr>
<td></td>
<td>Periodicity</td>
<td>100 (25)</td>
</tr>
<tr>
<td></td>
<td>FWHM</td>
<td>Height</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>--------</td>
</tr>
<tr>
<td>95:05</td>
<td>54 (5.6)</td>
<td>12 (1.9)</td>
</tr>
<tr>
<td></td>
<td>24 (2.1)</td>
<td>10 (1.5)</td>
</tr>
<tr>
<td></td>
<td>28 (4.3)</td>
<td>9 (1.2)</td>
</tr>
<tr>
<td>88:12</td>
<td>12 (2.2)</td>
<td>8 (1.5)</td>
</tr>
<tr>
<td></td>
<td>9 (1.8)</td>
<td>66 (8.5)</td>
</tr>
<tr>
<td></td>
<td>100 (16)</td>
<td>50 (11)</td>
</tr>
<tr>
<td>50:50</td>
<td>15 (2.8)</td>
<td>10 (3.1)</td>
</tr>
<tr>
<td></td>
<td>9 (1.1)</td>
<td>70 (13)</td>
</tr>
<tr>
<td></td>
<td>70 (13)</td>
<td>48 (5.2)</td>
</tr>
<tr>
<td>0:100</td>
<td>16 (2.7)</td>
<td>11 (1.4)</td>
</tr>
<tr>
<td></td>
<td>8.1 (0.81)</td>
<td>70 (11)</td>
</tr>
<tr>
<td></td>
<td>23 (3.8)</td>
<td>70 (11)</td>
</tr>
</tbody>
</table>

**a-** n and m represent the average number of repeat units respectively.

**b-** Average of 15 particles.

### 3.3.2 Transmission Electron Microscopy

Transmission electron microscopy was performed on selected samples to analyze the size and morphology of the samples. Selected catalysts displayed activity towards one or both of the reactions required to run a fuel cell effectively. Samples were prepared on silicon oxide passivated silicon wafer as per methods described above. To transfer the array, an over-coating of the nanoparticle array with polystyrene homopolymer was conducted and used to capture relieved nanoparticles from a dissolved substrate. The film carried with it the particles that were synthesized and was subsequently captured on a formvar coated and carbon sputter coated TEM grid. This method effectively captured the particles, but likely compromises the array periodicity due to inadvertent distortion of the transfer layer during lift-off and physical transfer of the TEM grids. TEM images can be seen in **Figure 3.8** along with particle diameter histograms. It can be seen from the histograms that the particle diameter distributions were narrow and displayed Gaussian character. The inconsistency in cluster spacing can readily be seen in the TEM images below where some
Figure 3.8. TEM images of particle synthesized from the 88:12 Pt:Au bath from polymers: a) PS\textsubscript{1392}-b-P4VP\textsubscript{471}, c) PS\textsubscript{893}-b-P4VP\textsubscript{330}, and e) PS\textsubscript{552}-b-P4VP\textsubscript{174}. The corresponding particle diameter histograms are shown adjacent to the image (b, d, f). Images are taken at a magnification of 39 kX and an accelerating voltage of 200 keV.
clusters have moved around from the ideal quasihexagonal close packed pattern and in some cases the individual particles have migrated during the film transfer step, but the catalyst should not move around during electrochemical testing. Only select images and histograms are displayed. All others are available in appendix III. A table of measurements taken from TEM images is shown in Table 3.3.

The images revealed that the catalysts are not a single particle as previously indicated by SFM, but are clusters of particles of a smaller diameter. The TEM has revealed the smaller size of the particles which is beneficial since smaller catalyst size increases activity due to a higher surface area.65 Looking at the data in Table 3.3 we can see that all of the particle diameters are statistically similar since the range including the error bars on all of them overlap. Previous results for chemical reduction of metal-loaded arrays have indicated that the strength of the reducing agent influences the nucleation rate and affects the ultimate size and number of nanoparticles created from a block copolymer domain.66

Table 3.3. Measurements taken from TEM images quantifying average particle diameter and average number of particles per cluster.

<table>
<thead>
<tr>
<th>Bath Pt:Au mole ratio</th>
<th>Dimension</th>
<th>PS_{1392-n}b-P4VP_{471}</th>
<th>PS_{893-n}b-P4VP_{330}</th>
<th>PS_{552-n}b-P4VP_{174}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Particle Width</td>
<td>2 (1.0)</td>
<td>2.2 (0.68)</td>
<td>1.8 (0.46)</td>
</tr>
<tr>
<td></td>
<td>Particles per Cluster</td>
<td>25 (2.6)</td>
<td>13 (1.9)</td>
<td>30 (3.4)</td>
</tr>
<tr>
<td>100:0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>98:02</td>
<td>Particle Width</td>
<td>3.0 (0.56)</td>
<td>2.8 (0.51)</td>
<td>3.0 (0.64)</td>
</tr>
<tr>
<td></td>
<td>Particles per Cluster</td>
<td>16 (1.9)</td>
<td>14 (2.3)</td>
<td>17 (2.6)</td>
</tr>
<tr>
<td>95:05</td>
<td>Particle Width</td>
<td>3.0 (0.59)</td>
<td>3.1 (0.55)</td>
<td>2.9 (0.58)</td>
</tr>
<tr>
<td></td>
<td>Particles per Cluster</td>
<td>18 (1.2)</td>
<td>15 (2.9)</td>
<td>15 (1.9)</td>
</tr>
<tr>
<td>88:12</td>
<td>Particle Width</td>
<td>2.9 (0.79)</td>
<td>3.2 (0.65)</td>
<td>3.8 (0.70)</td>
</tr>
<tr>
<td></td>
<td>Particles per Cluster</td>
<td>23 (3.0)</td>
<td>15 (2.2)</td>
<td>13 (2.4)</td>
</tr>
</tbody>
</table>

a- n and m represent the average number of repeat units respectively.
High resolution imaging and elemental mapping was acquired for the 88:12 Pt:Au by bath catalyst synthesized with PS1392-b-P4VP471. The results are displayed in Figure 3.9 with Figure 3.9a displaying the high-angle annular dark-field image of two clusters of particles. The image in Figure 3.9b shows the elemental map for platinum overlaid onto the dark field image. The platinum appears to be evenly dispersed throughout the particles and relatively no signal shows up in the background.

Figure 3.9. TEM and EDX results for two clusters of the 88:12 Pt:Au by bath catalyst synthesized with PS1392-b-P4VP471 displaying: a) high angle annular dark field image b) elemental EDX map for platinum c) elemental EDX map for gold d) EDX spectra showing the Lα lines used for quantification e) line scan performed on two particles f) line scan spectra for Pt and Au.
The elemental map image for gold is shown in Figure 3.9c and displays a similar trend where the gold appears evenly distributed throughout the particles with little to no signal in the background. The elemental maps show strong evidence for a Pt-Au bimetallic alloy phase. The EDX spectrum is displayed in Figure 3.9d and shows the peaks that were used to determine the percent platinum and gold for these clusters. The overall image was analyzed to give Pt\textsubscript{54}Au\textsubscript{42} while examination of individual particles ranged from Pt\textsubscript{54}Au\textsubscript{46} to Pt\textsubscript{58}Au\textsubscript{42}. These values align well with the XPS data presented later in the chapter and the variance in composition between individual particles would explain any deviation. Figure 3.9f displays a line scan performed on the particles shown in Figure 3.9e. The results indicate that the core of the particle is richer in gold than the exterior signifying a core-shell morphology with a platinum rich shell.

3.3.3 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was carried out on all combinations of three polymers and six baths to give 18 different catalysts. A set of spectra for the PS\textsubscript{1392-b-P4VP\textsubscript{471}} polymer are shown in Figure 3.10 with an overall low standard deviation of 2.29. All other spectra are available in appendix IV. The spectra were fit using a 30 % Gaussian-Lorentzian fit and by constraining the areas of the overlapped peaks to the lone peaks. For example, in the green trace the platinum 4d 3/2 was constrained to be 0.66 times the area of the 4d 5/2 peak due to the rules of spin orbit splitting. The same would be done in that spectra for the gold peaks. The gold 4d 5/2 peak would be constrained to be 1.5 times the area of the lone 4d 3/2 peak. The areas of the platinum and gold peaks were obtained to give a percent platinum relative to gold ratio and vice versa. The results of the composition determination are shown in Table 3.4.

The data in Table 3.4 displays the binding energy of the platinum and gold peaks for the catalysts synthesized with PS\textsubscript{1392-b-P4VP\textsubscript{471}}. The values for gold increase as platinum is introduced and the values for platinum decrease as gold is introduced to the system. According to literature, this is indicative of an alloy which is due to the effects of charge transfer due to alloy formation.\textsuperscript{67} This correlation and affirmation by literature lends good evidence that a platinum gold alloy was formed for each catalyst in this series.
Figure 3.10. XPS spectra of catalysts made from PS$_{1392}$-b-P4VP$_{471}$ with the six immersion baths used for the study. The pure platinum spectra is shown at top (blue) with decreasing platinum by bath content until pure gold at bottom (red). The platinum and gold 4d 5/2 and 4d 3/2 peaks are displayed and all binding energies are corrected to 284.6 eV.\textsuperscript{61}
Table 3.4. Particle composition as determined by XPS.

<table>
<thead>
<tr>
<th>Bath Pt: Au mole ratio</th>
<th>PS_{1392-b-P4VP_{471}}</th>
<th>PS_{893-b-P4VP_{330}}</th>
<th>PS_{552-b-P4VP_{174}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>100:0</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>98:02</td>
<td>62</td>
<td>84</td>
<td>83</td>
</tr>
<tr>
<td>95:05</td>
<td>59</td>
<td>80</td>
<td>67</td>
</tr>
<tr>
<td>88:12</td>
<td>47</td>
<td>62</td>
<td>63</td>
</tr>
<tr>
<td>50:50</td>
<td>23</td>
<td>47</td>
<td>35</td>
</tr>
<tr>
<td>0:100</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

a- n and m represent the average number of repeat units respectively.

Table 3.5. Fitted XPS peak positions for the platinum and gold 4d 5/2 and 5d 3/2.

<table>
<thead>
<tr>
<th>Catalyst Composition</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Au 4d 3/2</td>
</tr>
<tr>
<td>Pt_{100}Au_{0}</td>
<td>N/A</td>
</tr>
<tr>
<td>Pt_{62}Au_{38}</td>
<td>353.34</td>
</tr>
<tr>
<td>Pt_{59}Au_{41}</td>
<td>352.88</td>
</tr>
<tr>
<td>Pt_{47}Au_{53}</td>
<td>352.52</td>
</tr>
<tr>
<td>Pt_{23}Au_{77}</td>
<td>352.90</td>
</tr>
<tr>
<td>Pt_{0}Au_{100}</td>
<td>352.60</td>
</tr>
</tbody>
</table>

a- n and m represent the average number of repeat units respectively.

3.3.4 Cyclic Voltammetry

Cyclic voltammetry can give insights into the chemical nature of a catalyst by analyzing how it reacts with species in solution and by analyzing the resulting curve data. The voltammograms in Figure 3.11 were obtained by cycling the catalysts synthesized with PS_{1392-b-P4VP_{471}} between -0.25 and 1.40 V vs Ag/AgCl until a “steady-state” was achieved in nitrogen purged 0.10 M H_{2}SO_{4}. All other CVs with the other two polymer sizes are available in appendix V. A steady-state occurs when there
Figure 3.11. Steady-state voltammograms of six catalysts synthesized with $\text{PS}_{1392-b-\text{P4VP}}_{471}$ with different. Voltages are reported relative to Ag/AgCl.

is no change between subsequent cycles, indicating that the catalyst is no longer evolving its surface or internal structure. From the CV's we can see the character of pure platinum nanoparticles on the first plot and pure gold nanoparticles on the lowest plot with the varying compositions shown in between. With the varying platinum and gold compositions it is easy to see the varying platinum and gold character. Since the CV is surface sensitive it can give insights into the surface composition of the nanoparticles. The $\text{Pt}_{62}\text{Au}_{38}$ catalyst shows slight gold characteristic by a broader anodic peak near 1.0 V and a small gold hydroxide reduction peak near 0.75 V. This trend is seen for all the bimetallic catalysts. This indicates that the surface is alloyed and populated by both platinum and gold due to the fact that the platinum hydroxide reduction peak near 0.25 V and the gold hydroxide reduction peak near 0.75 V shift as the composition is varied. If they were phase separated, we
would expect to see the peaks in the same position as the pure particles. This aligns well with literature which has reported the same phenomena.\(^6^7\)

![Voltammogram of Pt\(_{100}\)Au\(_{0}\) catalyst by XPS made with PS\(_{1392}\)-b-P4VP\(_{471}\) displaying the hydrogen desorption peaks that were integrated to calculate ECSA.](image)

The character of platinum is defined by the platinum anodic oxidation and cathodic reduction peaks around 1.0 V and 0.3 V respectively along with the anodic hydrogen adsorption peaks and cathodic hydrogen desorption peaks near -0.25 V. The hydrogen ad/desorption peaks can be very helpful in the analysis of the surface area of the platinum since the area of the peak is proportional to the amount of hydrogen that can adsorb to the surface. The amount of hydrogen on the surface is then proportional to the number of catalytically active sites available to undergo catalysis. It is readily noticeable that the Pt\(_{23}\)Au\(_{77}\) and Pt\(_{0}\)Au\(_{100}\) have no hydrogen peaks with which to calculate the electrochemically active surface area (ECSA) and therefore they will not be considered.

To obtain the ECSA values it is necessary to use a combination of techniques besides CV. TEM and SFM can be employed by taking measurements made from the images and outlining a model to determine the surface area of a particle and the XPS compositional data can be used to determine the amount of the surface that is platinum. Equation 1 is the generic equation that is used to calculate ECSA.\(^6^8\)

\[
\frac{H_{ads} \, (C)}{cm^2} \times \frac{mass \, Pt \, (g)}{cm^2} \times \frac{2.10 \, C}{m^2} = ECSA \left( \frac{m^2}{g \, Pt} \right)
\]

The numerator represents the area of the hydrogen desorption peaks as shown in Figure 3.12.\(^1^7\) The right hand portion of the denominator is a constant, but the left hand portion we
do not have yet. To get this value of the mass of platinum per square centimeter of electrode area we must combine a couple techniques. Using the diameter of a nanoparticle as measured from TEM along with the average number of particles per cluster, the mass of metal per cluster can be obtained

\[
\frac{4\pi}{3} \left( \frac{\text{Diameter (cm)}}{2} \right)^3 \times \frac{\text{Particles}}{\text{Cluster}} \times \text{PtAu Density} = \frac{\text{Mass Alloy (g)}}{\text{Cluster}}
\]

as seen in equation 2 where the density was found from a reference based on the composition of the particle.\(^6\) This result is the mass of metal in each cluster of particles. This outcome can then be combined with the periodicity from SFM. The periodicity, if applied correctly, can be expanded infinitely outward in a hexagonal array to give the number of clusters in a specific area. This combined with the mass of the alloy per cluster can result in the mass of alloy per electrode area as

\[
\frac{2}{\sqrt{3} \times \text{Periodicity}^2} \times \frac{\text{Mass Alloy (g)}}{\text{Cluster}} = \frac{\text{Mass Alloy (g)}}{\text{Electrode Area (cm}^2)}
\]

seen in equation 3. This value tells us how much catalyst was on the surface of the electrode that was used in the reaction, but the desired quantity relates to the amount of active surface area, which is directly related to platinum as the active site. Therefore, we can combine this with a mass platinum value as determined by XPS, which tells what percentage of the catalyst is platinum, and thus result in a value of mass platinum per electrode area which is seen in equation 4. This value, when plugged back into equation 1, allows us to determine the electrochemically active surface area of a catalyst by plugging in the relevant parameters for a specific catalyst. The ECSA is an important metric for a catalyst because it gives a numerical representation of the amount of surface platinum that is actively being utilized by a nanoparticle to perform a specific reaction. With platinum being so expensive, it is important to know if it is being utilized to the maximum potential. The ECSA values for the catalysts that have appreciable hydrogen desorption peaks are displayed in Table 3.6. From this data we can see that the pure platinum catalyst has the highest ECSA as we would expect due to the fact that the entire surface is composed of platinum. The value decreases as gold is added. This is also expected due to the fact that the gold is partially populating the surface of the catalyst causing less platinum active sites to be available.
Table 3.6. ECSA values as determined by CV, TEM, SFM, and XPS for all catalysts that displayed hydrogen desorption peaks.

<table>
<thead>
<tr>
<th>PS(<em>{(n)})-b-P4VP(</em>{(m)}) diblock copolymer template(^a), Catalyst composition Pt(_{100-x})Au(_x), and ECSA values in m(^2) / g Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS(<em>{1392})-b-P4VP(</em>{471})</td>
</tr>
<tr>
<td>Pt(_{100})Au(_0)</td>
</tr>
<tr>
<td>676</td>
</tr>
<tr>
<td>Pt(<em>{62})Au(</em>{38})</td>
</tr>
<tr>
<td>444</td>
</tr>
<tr>
<td>Pt(<em>{59})Au(</em>{41})</td>
</tr>
<tr>
<td>324</td>
</tr>
<tr>
<td>Pt(<em>{47})Au(</em>{53})</td>
</tr>
<tr>
<td>198</td>
</tr>
</tbody>
</table>

\(^a\) n and m represent the average number of repeat units respectively.

\(^x\) approximation of the fraction of platinum in particle by XPS.
4. Methanol Oxidation Reaction

4.1 Background and Theory

The methanol oxidation reaction (MOR) is an essential process in direct methanol fuel cells (DMFCs), a type of DAFC. A scheme for a DMFC is shown in Figure 4.1. The MOR takes place on the anode side of a DMFC where aqueous methanol is introduced and reacted across the catalyst layer to liberate protons and electrons. The protons pass through the polymer electrolyte membrane while the electrons pass through an external circuit to do work. Ideally, carbon dioxide is the anode byproduct whereas water is that of the cathode. The cathode reaction will be discussed in a later chapter. Currently, industrial applications involving fuel cells rely upon platinum particle catalysts as the primary choice for the anode material. The drawbacks to utilizing platinum are the high cost and propensity to become poisoned with carbonaceous impurities. A reaction scheme is displayed in Figure 4.2 which displays the possible routes that the oxidation of methanol over platinum can take.

![Figure 4.1. Schematic of a direct methanol fuel cell utilizing a polymer electrolyte membrane.](image-url)
Figure 4.2. Reaction scheme for the methanol oxidation reaction displaying possible routes of reaction: 1) incomplete oxidation to formyl species, 2) preferred oxidation to carbon dioxide, and 3) catalytic poisoning by incomplete oxidation to carbon monoxide.70-71

Ideally, the oxidation goes to completion, as shown in reaction 2 of Figure 4.2, where the carbon dioxide is formed and would immediately desorb. Upon incomplete oxidation of hydrocarbons, like methanol, platinum forms carbon monoxide instead of carbon dioxide as seen in reaction 3 of the scheme. The carbon monoxide molecule may bind irreversibly to the platinum atoms which would reduce the effective catalyst area and thus the activity of the catalyst.18-20 Other reaction products are possible upon incomplete oxidation, such as formate and other formate-like intermediates, which are undesirable as well but generally do not bind to platinum surface site as irreversibly as carbon monoxide. To increase platinum nanoparticle resistance to poisoning by carbon monoxide, formate, and other carbonaceous impurities, we added a second metal, gold, to the catalyst on the premise that the higher electronegativity of gold would weaken the platinum-carbon bond seen in CO poisoning.72-73

4.2 Reaction Mechanism

Without utilizing in situ infrared technology or some type of mass spectrometry it is difficult to determine the actual oxidation pathway for methanol at a platinum-based electrode.74 There are
Figure 4.3. Reaction mechanism for the decomposition of methanol over a metal catalyst. Shown above are the CO pathway (top after split) and the non-CO pathway (bottom after split) involving formic acid as an intermediate.\textsuperscript{75}

thought to be two dominant routes by which the platinum-catalyzed methanol oxidation reaction can proceed.\textsuperscript{70-71} The first, seen in Figure 4.3 (top), shows the reaction proceeding through an adsorbed carbon monoxide intermediate. Both processes begin by dissociatively adsorbing the methanol into an \( \text{M-CH}_2\text{-OH} \) (where M is the metal) species followed by subsequent dehydrogenation to give \( \text{M-CH}_2\text{-O-M} \). At this point, adsorbed \( \text{M-CH}_2\text{-OH} \) can be further reacted by the \( \text{M-CO} \) route or the \( \text{M-formic} \) route. The CO pathway is generally undesired due to the propensity for platinum to become irreversibly poisoned by the adsorbed CO.\textsuperscript{18-20} The CO pathway forms an \( \text{M-CO} \) species while the non-CO pathway forms formic acid by reacting with a nearby hydroxyl group from a dissociatively adsorbed water to form \( \text{M-CHO-OH} \). The \( \text{M-CO} \) also combines with a hydroxyl produced from a neighbor metal atom capable of activating water to give \( \text{CO}_2 \) with concurrent dehydrogenation. The formic acid species also undergoes dehydrogenation to give \( \text{CO}_2 \). In both processes six protons and six electrons are liberated and result in \( \text{CO}_2 \) ultimately being released, but in the CO pathway, it is possible that the metal-carbon bond is too strong and the carbon monoxide will not react further. This causes the reactive site on the metal to be occupied indefinitely and the catalyst loses activity. It was recently discovered using DFT calculations that, upon adding gold to a platinum catalyst, the reaction can proceed preferentially via the formic acid route.\textsuperscript{75}
4.3 Metric for Analysis

A typical methanol oxidation curve acquired with a standard 3-electrode cyclic voltammetry study is shown in Figure 4.4. The forward anodic peak, labeled $I_f$, is commonly attributed to the oxidation of methanol. The reverse peak, labeled $I_b$, is usually attributed to the oxidation of poisons such as CO and other incompletely oxidized species.$^{70-71,73,75}$ Recently, experiments coupling electrochemical techniques with mass spectroscopy propose that the reverse peak and forward peak liberate similar molecular fragments but likely differ by the rate of reaction and mechanism.$^{76}$ A commonly used metric for comparing the resistance to carbonaceous poisoning for MOR catalysts is the ratio of the $I_f/I_b$ since favorable reaction mechanisms are represented by $I_f$ while less desirable mechanisms are represented by $I_b$. Similarly, a high activity catalyst will have a high peak $I_f$ current and a high $I_f/I_b$ ratio, which lends itself to a high amount of methanol turnover as indicated by $I_f$ and low amount of poison produced as indicated by a low $I_b$.

![Figure 4.4. Typical methanol oxidation cyclic voltammogram displaying the forward and reverse anodic peaks commonly seen in this type of reaction for a Pt$_{100}$Au$_0$ catalyst synthesized with PS$_{1392}$-$b$-P4VP$_{471}$. Voltage reported relative to Ag/AgCl at 100 mV/s.](image)
4.4 Results and Discussions

The methanol oxidation reaction was run on all the catalysts synthesized for this study. This includes all permutations of the six immersion baths combined with the three different sized polymers. The steady-state cyclic voltammograms for all six catalysts made with the PS$_{1392}$-b-P4VP$_{471}$ polymer are displayed in Figure 4.5. The cyclic voltammograms for the rest of the catalysts tested are located in appendix V. The plots display a trend that is to be expected as we lower the platinum content. The pure platinum catalyst at the top of the set shows the highest forward peak, but also the highest reverse peak. As more gold is introduced, the forward and reverse peaks lose intensity though not in equivalent amounts. This indicates that the introduced gold permits activation of bound carbon monoxide and results in nanoparticle catalysts that are more resistant to poisoning. The exchange of a platinum atom for one of gold compromises the population of highly active

![Figure 4.5. Steady-state cyclic voltammograms of catalysts synthesized from the six immersion baths used for this study and the PS$_{1392}$-b-P4VP$_{471}$ polymer. Voltages are displayed versus Ag/AgCl at a scan rate of 100mV/s and the inset displays Pt: Au bath ratio.](image-url)
Table 4.1. Forward and reverse peak current values normalized to platinum mass. The $I_f/I_b$ ratio is also reported below.

<table>
<thead>
<tr>
<th>Peak Values</th>
<th>PS$<em>{1392}$-$b$-P4VP$</em>{471}$</th>
<th>PS$<em>{893}$-$b$-P4VP$</em>{330}$</th>
<th>PS$<em>{552}$-$b$-P4VP$</em>{174}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt$<em>{100}$Au$</em>{0}$</td>
<td>Pt$<em>{100}$Au$</em>{0}$</td>
<td>Pt$<em>{100}$Au$</em>{0}$</td>
</tr>
<tr>
<td>$I_f$ (A/g Pt)</td>
<td>1224</td>
<td>295</td>
<td>577</td>
</tr>
<tr>
<td>$I_b$ (A/g Pt)</td>
<td>670</td>
<td>195</td>
<td>323</td>
</tr>
<tr>
<td>$I_f/I_b$</td>
<td>1.82</td>
<td>1.70</td>
<td>1.48</td>
</tr>
</tbody>
</table>

|             | Pt$_{62}$Au$_{38}$          | Pt$_{83}$Au$_{17}$          | Pt$_{83}$Au$_{17}$          |
| $I_f$ (A/g Pt) | 473                        | 342                        | 922                        |
| $I_b$ (A/g Pt) | 198                        | 168                        | 482                        |
| $I_f/I_b$    | 2.29                      | 2.05                       | 1.28                       |

|             | Pt$_{59}$Au$_{41}$          | Pt$_{80}$Au$_{20}$          | Pt$_{67}$Au$_{43}$          |
| $I_f$ (A/g Pt) | 343                        | 82                         | 221                        |
| $I_b$ (A/g Pt) | 137                        | 39                         | 117                        |
| $I_f/I_b$    | 2.33                      | 1.2                        | 1.36                       |

|             | Pt$_{47}$Au$_{53}$          | Pt$_{82}$Au$_{38}$          | Pt$_{63}$Au$_{37}$          |
| $I_f$ (A/g Pt) | 157                        | 37                         | 58                         |
| $I_b$ (A/g Pt) | 11                         | 10                         | 8                          |
| $I_f/I_b$    | 1.27                      | 2.66                       | 2.63                       |

$a$- n and m represent the average number of repeat units respectively.

$x$- approximation of the fraction of platinum in particle by XPS.

platinum catalysis sites and results in a reduced $I_f$. The values for $I_f$, $I_b$, and $I_f/I_b$ are displayed in

Table 4.1. The values in the table are corrected to amperes per gram of catalyst (interpreted through ECSA). This figure of merit assesses the Pt$_x$Au$_{100-x}$ nanoparticle series with respect to platinum content providing insight into platinum utilization. We can determine if it is cost effective to lower the amount of platinum or not by evaluating these numbers. From the table values it is apparent that the
pure platinum catalyst results in the highest current produced per gram of platinum on the surface. The fact remains that the incorporation of gold has increased the I/I₀ ratio which indicates that the gold helps reduce the carbon-based poisons, namely carbon monoxide, that plague platinum catalysts by occupying active sites and reducing activity. While the current may not be as high for a platinum-gold sample versus a pure platinum sample, the current will remain stable over a longer period of time. This would give the fuel cell a better longevity than it had previously seen utilizing current catalyst technology.
5. Oxygen Reduction Reaction

5.1 Background

The oxygen reduction reaction (ORR) occurs at the cathode of most polymer electrolyte membrane fuel cells. The schematic displayed in Figure 5.1 is the same one shown previously for the methanol oxidation reaction. The difference now is that we want to focus our attention to the right side of the representation to examine what is happening at the cathode. The cathode of the direct methanol fuel cell (DMFC) is being flooded with protons and electrons from the catalytic breakdown of methanol along with oxygen from the input air. The cathode catalyst uses these ingredients to catalytically reduce oxygen into water. The current standard for use in the oxygen reduction reaction on the cathode side of polymer electrolyte membrane fuel cells is particulate platinum.\textsuperscript{17} The issues with platinum for this purpose are the cost of platinum, the slow kinetics with regards to the oxygen reduction reaction, and reducing the amount of peroxide that can be produced as a byproduct of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic.png}
\caption{Schematic of a direct methanol fuel cell utilizing a polymer electrolyte membrane.}
\end{figure}
incomplete reduction. A reaction scheme is shown in Figure 5.2 that displays the possible routes.

![Reaction Scheme](image)

**Figure 5.2.** Reaction scheme for the oxygen reduction reaction. Not shown are the transfer of protons and electrons.

that the oxygen reduction reaction can take. Generally, the platinum catalyst simply cannot keep up with the flux of protons and electrons from the anode side and any peroxide produced can damage system components vital to keeping the cell running properly (i.e. carbon electrode support, Nafion® polyelectrolyte membrane, etc.). Gold has recently been shown to help stabilize platinum nanoparticles against dissolution and help kinetics such that water is the main product of the reaction. This section of the paper will demonstrate the use of platinum-gold nanoparticles for the oxygen reduction reaction with favorable results.

### 5.2 Utilizing RRDE for Oxygen Reduction

The rotating ring-disk electrode is commonly used to evaluate the kinetics of the oxygen reduction reaction. The design of the experimental setup for this reaction is relatively simple. A motor, or rotator, is utilized to stir an electrolyte solution that is saturated with oxygen. The motor is designed such that there is minimal electrical noise generated as to not interfere with the voltammograms being recorded. An example of the setup used in these experiments is shown in Figure 5.3. From the image at right, it can be seen that the solution is continuously purged with oxygen to ensure that the concentration of bulk oxygen stays a constant. The white part at the end of the shaft is made of Teflon and contains the disk and the ring as seen in Figure 5.4. Due to the
laminar flow of the solution, upon stirring, the reactive species first hit the disk in the center and any side products or intermediate species are then swept to the disk to be “detected”. The disk contains

Figure 5.3. Images of the RRDE setup showing the rotator (left) and electrochemical cell (right).

the catalyst of interest which can be applied by the standard polymer templating technique utilized previously. The ring was chosen to be platinum since this makes it easy to detect peroxide for reasons that will be seen later.

The advantages to stirring the solution during electrochemical testing may not be readily apparent. During a standard cyclic voltammetry experiment, the solution is static and, therefore, the rate of reaction cannot be determined since the reaction is limited to the rate at which the reactive
species can diffuse to the catalyst surface to react. By stirring the solution, the diffusion limitation can be removed and the kinetics of a catalyst can be effectively studied. Typically, a single sweep, known as linear sweep voltammetry, is performed. Since the working electrode is constantly being flooded with reactant, one can imagine that a cyclic sweep would be useless since the reverse sweep would follow the same line trace as the forward sweep. It is also necessary to perform these reactions at multiple rotation rates to allow for kinetic measurements to see how the rate of reaction changes with increased access to reagent.

An RRDE experiment was performed on all eighteen catalysts produced by the three different polymer sizes chosen for this study coupled with six different immersion baths. An example linear sweep voltammogram stack is shown in Figure 5.5 for pure platinum synthesized with PS_{1392-b-P4VP}_{471}. Experiments were performed in 0.10 M H_2SO_4 purged continuously with oxygen. A platinum coil was used as a counter electrode and voltages are reported versus Ag/AgCl. The voltage at the disk was scanned from 1.0 V to -0.25 V at 5 mV/s scan rate while the platinum ring was held at 1.0 V to oxidize peroxide without reacting any water in the solution. The initial rotation rate was 400 RPM and was ramped up in 400 RPM increments up to 2000 RPM. The catalysts were pretreated in the same cell by holding the disk potentiostatically at -0.20 V for one hour at 2000 RPM. This allows for the catalysts to condition and come to equilibrium. From the plots in Figure 5.5
we can see that the disk current becomes more negative upon increasing rotation rate, as expected due to the increased amount of reactant species available, but it seems to have a maximum at 1600 RPM since the 1600 and 2000 RPM traces overlap. This indicates that we have reached the kinetic maximum of the catalyst since it cannot produce anymore current. We must delve deeper into the kinetics behind this reaction in order to determine the mechanism by which the reaction is proceeding.

![Graph](image)

**Figure 5.5.** RRDE plot for Pt$_{100}$Au$_0$ by XPS synthesized with PS$_{1392}$-b-P4VP$_{471}$ at 5 mV/s displaying the disk current (bottom) and the ring current (top) both plotted versus the applied disk potential. The ring was held at 1.0 V and all voltages are reported versus Ag/AgCl.

### 5.3 Kinetics of the Reaction

The foundation of the kinetics for the oxygen reduction reaction were laid by Damjanovic *et al.* in 1966 and further expanded upon by that same group in the next year. In this derivation, it
was determined that one could calculate three rate constants by using the disk and ring simultaneously as shown in Figure 5.6 where “bulk” indicates a dissolved species and “ads” indicates a surface adsorbed species. The most desirable reaction pathway for oxygen reduction would be the four electron reduction pathway with rate constant $k_1$ due to the lack of a possibility for peroxide to be formed and undergo possible later reactions with fuel cell components. Therefore, it is desirable to have this rate as high as possible. If the catalyst proceeds via the alternative peroxide pathway, it is desirable to have $k_3$ much higher than $k_2$ such that any peroxide that may be produced would be rapidly converted to water. This would eliminate a large amount of peroxide that would otherwise make its way into the bulk of the solution where it can perform further side reactions. The disk can be utilized to determine $k_1$ and $k_3$ since the catalyst is required to reduce $O_2$ or $H_2O_2$ into water and the ring will not be affected by this since it is held at an oxidizing potential. The disk can be used to determine $k_2$ which tells us how much peroxide is being generated. This is simple since the ring is at an oxidizing potential such that peroxide will be oxidized, but water nor oxygen can be oxidized. Utilizing the derivation set forth we can utilize equations 5 – 7 to determine $k_1$, $k_2$, and $k_3$.

$$k_1 = \frac{S_2Z_1(I_1N - 1)}{(I_1N + 1)}$$  \hspace{1cm} (5)

$$k_2 = \frac{2S_2Z_1}{(I_1N + 1)}$$  \hspace{1cm} (6)

$$k_3 = \frac{S_1Z_2N}{(I_1N + 1)}$$  \hspace{1cm} (7)
Where \( S_2 \) is the slope of \( \ln(I_d/I_0) \) versus the inverse square root of the rotation rate \( (\omega^{-1/2}) \) in RPM. In this equation, \( I_d \) is the disk limiting current and \( I_0 \) is the disk current at a specific potential. The disk limiting current is defined as being the point at which the disk electrode has reached its limit such as platinum has in Figure 5.5 near -0.15 V. \( S_1 \) and \( I_1 \) are defined as the slope and intercept of \( \ln(I_d/I_0) \) versus \( \omega^{-1/2} \), respectively, where \( I_R \) is the ring current. The constant, \( N \), is a geometric factor known as the collection efficiency which is defined by the dimensions of the disk and ring relative to one another and is specific to each RRDE assembly. For this assembly, \( N \) is 0.2555. This correlates to 25.55% of molecules generated at the disk reaching the ring to be “detected”. For equations 5-7, \( Z_1 \) and \( Z_2 \) are defined as 0.62\((D_{O_2})^{2/3}v^{-1/6}\) and 0.62\((D_{H_2O_2})^{2/3}v^{-1/6}\), respectively, where \( D_{O_2} \) and \( D_{H_2O_2} \) are the diffusion coefficients of oxygen and peroxide, respectively, and \( v \) is the kinematic viscosity of water. For this study, \( D_{O_2} \), \( D_{H_2O_2} \), and \( v \) have been chosen as 1.9x10^{-5} \text{ cm}^2\text{s}^{-1}, 1.18x10^{-5} \text{ cm}^2\text{s}^{-1}, \) and 0.00997 \text{ cm}^2\text{s}^{-1}, respectively.\(^{86-88}\) For more details behind this analysis, see appendix VII.

5.4 Results and Discussion

This analysis was carried out on all catalysts synthesized for this study. The RRDE plots for six catalysts synthesized with the PS_{1392-b-P4VP_{471}} polymer are shown in Figure 5.7, all other RRDE plots can be seen in appendix VI. From the plots, it is apparent that the Pt_{23}Au_{77} and Pt_{0}Au_{100} catalysts synthesized with PS_{1392-b-P4VP_{471}} do not exhibit a limiting disk current and, therefore, cannot be analyzed by this kinetic method. Since the pure gold does not show much catalytic activity, as seen by the depth of current the disk reaches, and the Pt_{23}Au_{77} never reaches a plateau indicating a large overpotential, these catalysts may have other significant limitations. To evaluate the rates of reaction for the different catalysts, it is necessary to first compare \( k_1 \), \( k_2 \), and \( k_3 \) to each other within a single catalyst, as seen in Figure 5.8, and then compare \( k_1 \), \( k_2 \), and \( k_3 \) between the different catalysts to measure the effectiveness of adding gold to a platinum nanoparticle catalyst, as seen in Figure 5.9.
Figure 5.7. RRDE plot for catalysts synthesized with PS\textsubscript{1392-b-P4VP\textsubscript{471}} at 5 mV/s displaying the disk current (bottom) and the ring current (top) both plotted versus the applied disk potential. The catalysts are displayed as a)-f) Pt\textsubscript{100}Au\textsubscript{0}, Pt\textsubscript{62}Au\textsubscript{38}, Pt\textsubscript{59}Au\textsubscript{41}, Pt\textsubscript{47}Au\textsubscript{53}, Pt\textsubscript{23}Au\textsubscript{77}, and Pt\textsubscript{0}Au\textsubscript{100} by XPS, respectively. The ring was held at 1.0 V and all voltages are reported versus Ag/AgCl.

All catalysts in Figure 5.8 were made with PS\textsubscript{1392-b-P4VP\textsubscript{471}}. In Figure 5.8a the kinetic parameters $k_1$, $k_2$, and $k_3$ for the Pt\textsubscript{100}Au\textsubscript{0} catalyst are displayed. The four electron pathway, $k_1$, is the prevalent reaction by an order of on average 1.5 over the peroxide generating pathway, $k_2$. The
Figure 5.8. Kinetic parameter plots of $k_1$, $k_2$, and $k_3$ for a) Pt$_{100}$Au$_0$, b) Pt$_{62}$Au$_{38}$, c) Pt$_{59}$Au$_{41}$, and d) Pt$_{47}$Au$_{53}$ by XPS synthesized with PS$_{1392}$-b-P4VP$_{471}$. Voltages are reported versus Ag/AgCl and the y-axis is on a log$_{10}$ scale.

ability of this catalyst to react peroxide to water by the four electron mechanism does not change much over the voltage range presented and, up until ~0.25 V, it is dominant over the peroxide formation route. This pure platinum catalyst will be the metric to which we compare the other catalysts in order to determine if the addition of gold has allowed for enhanced activity or increased rate by the four electron route. The plot in Figure 5.8b displays the kinetic parameters for the Pt$_{62}$Au$_{38}$ catalyst. We can see that this catalyst reduced oxygen with kinetic parameters and mechanism similar to the pure platinum nanoparticle where the direct four electron process dominates and the peroxide-consuming rate is higher than the peroxide-producing route (up until ~0.25 V). Qualitatively, it appears that $k_1$ is higher than $k_2$ by a larger amount than in the case of the
pure platinum. The catalyst in Figure 5.8c displays the kinetic parameters for the Pt$_{59}$Au$_{41}$ catalyst. This catalyst shows many similar traits to the ones discussed thus far. The biggest difference of note is that $k_3$ dominates over $k_2$ for a wider potential range in comparison to other catalysts ($k_3 > k_2$ up until ~0.11 V). This indicates that this catalyst would be better at reacting any peroxide produced before it could escape the catalyst vicinity. The kinetic parameters for the Pt$_{47}$Au$_{53}$ catalyst are displayed in Figure 5.8d. This catalyst also shows enhanced peroxide suppression up until ~0.13 V, but the decreased difference between $k_1$ and $k_2$ indicates that this catalyst would be inferior to the Pt$_{62}$Au$_{38}$ catalyst due to the higher rate of peroxide production.

**Figure 5.9.** Logarithmic plots comparing kinetic parameters between Pt$_{100}$Au$_0$, Pt$_{62}$Au$_{38}$, Pt$_{59}$Au$_{41}$, and Pt$_{47}$Au$_{53}$ by XPS synthesized with PS$_{1392}$-$b$-P4VP$_{471}$. a) $k_1$ b) $k_2$ c) $k_3$ d) $k_1/k_2$
Comparing \( k_1 \), \( k_2 \), and \( k_3 \) between the different catalysts can give more insight into which catalyst executes the oxygen reduction reaction by the preferred four electron route. The plots can be seen in Figure 5.9 along with a plot displaying the relationship of \( k_1/k_2 \). This ratio can give an indication as to how selective a catalyst is for the four electron process versus the peroxide route due to the desire for \( k_1 \) to have a higher rate than \( k_2 \).\(^{87}\) The rest of the kinetic parameters calculated for PS\(_{693}\)-b-P4VP\(_{330}\) and PS\(_{952}\)-b-P4VP\(_{174}\) are displayed in appendix VII. The plot in Figure 5.9a displays \( k_1 \) for the catalysts analyzed in the previous paragraph. Most notably, the Pt\(_{62}\)Au\(_{38}\) catalyst has the highest \( k_1 \) at most potentials indicating the highest conversion of oxygen through the four electron route. The next highest \( k_1 \) is pure platinum. Looking at \( k_2 \) in Figure 5.9b, the Pt\(_{62}\)Au\(_{38}\) catalyst is still the highest, which, in this case, means that it is producing peroxide at the fastest rate. The best catalyst in this case is the Pt\(_{59}\)Au\(_{41}\) followed by Pt\(_{47}\)Au\(_{53}\). Looking at \( k_3 \) in Figure 5.9c reveals relatively no difference between these catalysts, but the Pt\(_{59}\)Au\(_{41}\) and Pt\(_{47}\)Au\(_{53}\) catalysts do outperform the other two in this case. This is a good sign indicating an increased peroxide removal mechanism. The largest indicator of catalytic activity and selectivity can be seen in Figure 5.9d. The Pt\(_{59}\)Au\(_{41}\) catalyst has around a threefold increase in selectivity for the direct four electron process over pure platinum and the Pt\(_{62}\)Au\(_{38}\) shows almost a twofold increase.

Examining all the data at hand, it can be concluded that the addition of gold has, in the case of the Pt\(_{62}\)Au\(_{38}\) catalyst, increased the activity and four electron oxygen reduction selectivity and, in the case of the Pt\(_{59}\)Au\(_{41}\) catalyst, greatly increased the selectivity for the four electron oxygen reduction reaction while compromising overall activity. Another metric we can examine to determine which catalyst is better is the overpotential applied to get the reaction to turn on. The standard reduction potential for oxygen to water is 0.893 V versus Ag/AgCl and any extra voltage that need be applied is considered overpotential.\(^{88}\) This is extra work to get the reaction to occur, so any reduction in this is advantageous because more voltage can be extracted from a fuel cell with a catalyst that has a low overpotential.\(^{88}\) The question is how to find out at what voltage the reaction turns on for these catalysts? Examining the plots in Figure 5.8 it is apparent that the kinetic parameters begin to show up around 0.55 V. This is due to the constants being undefined before this point due to the log scale. It can be inferred that the beginning of these plots corresponds to the turn-on voltage for these
catalysts since this is the point at which the reduction of oxygen begins to take place according to the relationships defined in equations 5 – 7. The overpotentials are plotted together in Figure 5.10. The catalyst with the lowest overpotential is the Pt₅₉Au₄₁ catalyst and the Pt₆₂Au₃₈ catalyst is very similar to the pure platinum only being lower by 80 µV. This indicates that the Pt₅₉Au₄₁ catalyst is superior in many ways to the pure platinum displaying a lower overpotential, higher selectivity for the four electron conversion of oxygen to water over peroxide production, a higher $k_3$ indicating a faster peroxide to water turnover rate, but a lower current value is produced by this catalyst. The Pt₆₂Au₃₈ catalyst boasts some similar qualities. It is superior in selectivity for the four electron process over platinum, but not against the Pt₅₉Au₄₁, has a similar overpotential to platinum, a higher $k_3$, and an increased current produced.

Table 5.1 provides containing the relevant kinetic parameters useful for comparing these catalysts to one another for the oxygen reduction reaction. The parameter $(k_1 \text{ Pt}_{x} \text{Au}_{100-x}) / (k_1 \text{ Pt}_{100}\text{Au}_0)$ has been used to determine what the maximum ratio is for the direct four electron conversion of oxygen to water versus the pure platinum catalyst. This means that the Pt₁₀₀Au₀ catalysts will all have values of 1.00 and anything higher indicates a higher conversion overall, while anything lower indicates a lower conversion rate relative to pure platinum. It is noteworthy that many of the Pt₅Au₁₀₀-x bimetallic catalysts have a higher average conversion rate for the four electron
The next parameter in the table is the maximum $k_1/k_2$ value which indicates how selective the catalyst is for the direct four electron process over the two electron process that produces harmful peroxide. The values for this parameter vary greatly between polymer sizes and catalyst compositions. Catalysts of note are the $\text{Pt}_{59}\text{Au}_{41}$ synthesized with $\text{PS}_{1392-}b\text{-P4VP}_{417}$ with a $k_1/k_2$ ratio of 12.88 versus 5.17 of $\text{Pt}_{100}\text{Au}_0$ made with the same polymer. The $\text{Pt}_{60}\text{Au}_{20}$ and $\text{Pt}_{62}\text{Au}_{38}$ synthesized with $\text{PS}_{893-}b\text{-P4VP}_{330}$ have a conversion selectivity of 11.66 and 12.05, respectively, versus 9.12 of the pure platinum made with the same polymer. The plateau values for the $k_3$ parameter were all very similar and slight differences can be determined by examining the average plateau values reported in the table. The overpotential values reported showed two catalysts that had lower overpotentials versus pure platinum: the $\text{Pt}_{59}\text{Au}_{41}$ synthesized with $\text{PS}_{1392-}b\text{-P4VP}_{471}$, and the $\text{Pt}_{62}\text{Au}_{38}$ synthesized with $\text{PS}_{893-}b\text{-P4VP}_{330}$. This would allow for a higher voltage to be obtained from the fuel cell run with this catalyst since less energy is required to get the reaction to proceed over pure platinum.
Table 5.1. Kinetic parameters for different Pt:Au catalysts made with diblock copolymer templates in performing the oxygen reduction reaction.

<table>
<thead>
<tr>
<th>Kinetic Parameters</th>
<th>PS_{1392}^{n-b}-P4VP_{471}</th>
<th>PS_{893}^{n-b}-P4VP_{330}</th>
<th>PS_{552}^{n-b}-P4VP_{174}</th>
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<tr>
<td>Average $k_1/(k_1-100Pt)$</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
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<tr>
<td>max $k_1/k_2$</td>
<td>5.17</td>
<td>9.12</td>
<td>8.39</td>
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<td>$k_3$ plateau (cm s$^{-1}$)</td>
<td>0.0083</td>
<td>0.0093</td>
<td>0.0104</td>
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<tr>
<td>Overpotential (V)</td>
<td>0.3425</td>
<td>0.3323</td>
<td>0.3425</td>
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<table>
<thead>
<tr>
<th></th>
<th>Pt$<em>{62}$Au$</em>{38}$</th>
<th>Pt$<em>{83}$Au$</em>{17}$</th>
<th>Pt$<em>{83}$Au$</em>{17}$</th>
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<tr>
<td>Average $k_1/(k_1-100Pt)$</td>
<td>1.34</td>
<td>0.97</td>
<td>1.21</td>
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<td>max $k_1/k_2$</td>
<td>7.63</td>
<td>8.16</td>
<td>7.90</td>
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<tr>
<td>$k_3$ plateau (cm s$^{-1}$)</td>
<td>0.0089</td>
<td>0.0090</td>
<td>0.0106</td>
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<td>Overpotential (V)</td>
<td>0.3425</td>
<td>0.3325</td>
<td>0.3677</td>
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<th>Pt$<em>{80}$Au$</em>{20}$</th>
<th>Pt$<em>{87}$Au$</em>{43}$</th>
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<tr>
<td>Average $k_1/(k_1-100Pt)$</td>
<td>0.71</td>
<td>1.30</td>
<td>2.37</td>
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<tr>
<td>max $k_1/k_2$</td>
<td>12.88</td>
<td>11.66</td>
<td>4.59</td>
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<tr>
<td>$k_3$ plateau (cm s$^{-1}$)</td>
<td>0.0095</td>
<td>0.0101</td>
<td>0.0083</td>
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<tr>
<td>Overpotential (V)</td>
<td>0.3274</td>
<td>0.3324</td>
<td>0.3979</td>
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<th>Pt$<em>{82}$Au$</em>{38}$</th>
<th>Pt$<em>{83}$Au$</em>{37}$</th>
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<tr>
<td>Average $k_1/(k_1-100Pt)$</td>
<td>0.90</td>
<td>1.10</td>
<td>1.56</td>
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<td>max $k_1/k_2$</td>
<td>5.10</td>
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<td>$k_3$ plateau (cm s$^{-1}$)</td>
<td>0.0098</td>
<td>0.0100</td>
<td>0.0090</td>
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<tr>
<td>Overpotential (V)</td>
<td>0.3626</td>
<td>0.3173</td>
<td>0.4331</td>
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</table>

* $n$ and $m$ represent the average number of repeat units respectively.

* $x$-approximation of the fraction of platinum in particle by XPS.
6. Conclusions

To our knowledge, this research represents the first published successful synthesis of platinum-gold bimetallic nanoparticles from a block copolymer templating procedure. The catalysts synthesized were subjected to electrochemical testing for activity towards the methanol oxidation reaction and the oxygen reduction reaction which are two vital reactions for fuel cell operation. Well organized polystyrene-\-b\-poly(4-vinylpyridine) films were cast onto multiple substrates demonstrating the flexibility of using a polymer templating technique. The polymer selected allowed for well controlled periodicity on the surface of the substrate to prevent agglomeration of particles. Utilizing immersion baths, the precise control over particle composition was displayed and confirmed by XPS. An argon ion plasma reduction technique was employed to reduce the metal ions and etch the polymer template. It is believed that altering the reduction technique would allow for control over size of nanoparticles in a cluster created from a P4VP micelle core. The particle measurements were ultimately obtained by TEM characterization leading to all particles being roughly 3 nm in diameter with a narrow distribution. Cyclic voltammetry was the final characterization technique and revealed a high electrochemically active surface area and varying platinum and gold character in the bimetallic samples. The CV result and the TEM-EDX line scan analysis along with the literature comparison to the XPS binding energy shifts, leads to the idea that a platinum-gold alloy was formed for each of the bimetallic nanoparticles synthesized.

The testing for enhanced activity in the methanol oxidation reaction revealed that the addition of gold did not increase the activity, but did increase the tolerance to carbonaceous poisons that poison the surface of the catalyst and deplete performance which has been shown to be true in the literature.\textsuperscript{72-73, 90-91} The catalysts were cycled fifty times and all catalysts came to a steady-state within that time. The $I_f$, or forward peak, and $I_b$, or backward peak, were compared to see how the tolerance varied between catalysts. The forward peak is thought to be the main oxidation of methanol into carbon dioxide, protons, and electrons, and the reverse peak is thought to be the oxidation of carbonaceous impurities and byproducts left behind. Ultimately, the platinum-gold alloy
particles allowed for a higher tolerance to poisoning and still allowed for the methanol oxidation reaction to run successfully.

The oxygen reduction reaction was studied for all catalysts presented. The rotating ring-disk electrode assembly allows for the elimination of the diffusion limitation provided by standard static cyclic voltammetry. This allows for kinetic parameters to be determined and for byproducts of intermediates to be detected at the ring that is concentric with the disk. The ring was chosen to be platinum for this study with a glassy carbon disk where the catalyst was deposited. The catalyst was subjected to a one hour potentiostatic treatment to allow for catalyst stabilization. The samples were then run through a linear sweep voltammetry experiment at 400 RPM up to 2000 RPM in 400 RPM increments. During these runs, the ring was being held at 1.0 V to allow for the oxidation of any peroxide formed as an unwanted byproduct, but not oxidize any other important species. From the kinetic analysis it was determined that the Pt\textsubscript{62}Au\textsubscript{38} and Pt\textsubscript{59}Au\textsubscript{41} catalysts outperformed the pure platinum catalyst. The Pt\textsubscript{62}Au\textsubscript{38} catalyst displayed enhanced selectivity for the four electron conversion straight to water over platinum, a similar overpotential to platinum, a higher $k_3$, and an increased overall reduction current. The Pt\textsubscript{59}Au\textsubscript{41} catalyst is improved in many ways compared to pure platinum displaying a lower overpotential, higher selectivity for the four electron transformation of oxygen to water over peroxide production, a higher $k_3$ indicating a faster peroxide to water turnover rate, but a lower current value is produced by this catalyst. Overall, the introduction of gold into platinum nanoparticles has shown beneficial effects toward the oxygen reduction reaction compared to pure platinum nanoparticles.

Fuel cells are quickly becoming viable alternative for the future clean-energy economy.\textsuperscript{9, 15-16} The need has arisen for advancements in catalyst technology to decrease the cost and increase the lifetime of these cells.\textsuperscript{17} Bimetallic nanoparticles have emerged as a major player in the advancement of fuel cell technology throughout the world.\textsuperscript{28-39} The results of this thesis indicate that the addition of gold to a platinum nanoparticle can help increase the catalysts resistance to carbon monoxide poisoning, but this does not lend itself to increasing activity due to the surface platinum decreasing upon gold addition. Additionally, the addition of gold to a platinum system has displayed much enhanced selectivity for the direct four electron process of oxygen reduction to water along
with a couple catalysts exhibiting lower overpotentials over pure platinum. These advancements bode well for the future of fuel cell technology. The ease by which a bimetallic can be synthesized from this method will also make it easier to discover new and even better catalysts to further improve current technologies.
References
Appendices

Appendix I. Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Units (if any)</th>
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<tbody>
<tr>
<td>µm</td>
<td>micrometer</td>
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</tr>
<tr>
<td>µV</td>
<td>microvolt</td>
<td></td>
</tr>
<tr>
<td>Ag/AgCl</td>
<td>silver/silver chloride reference electrode</td>
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</tr>
<tr>
<td>Ar</td>
<td>argon</td>
<td></td>
</tr>
<tr>
<td>Ar^+</td>
<td>positive argon ion</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
<td></td>
</tr>
<tr>
<td>Au 4d</td>
<td>4d orbitals of the gold atom</td>
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</tr>
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<td>Au@Pd@Pt</td>
<td>gold core with palladium middle shell and platinum outer shell</td>
<td></td>
</tr>
<tr>
<td>Au@Pt</td>
<td>gold core with a platinum shell</td>
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<tr>
<td>C 1s</td>
<td>the 1s orbital of the carbon atom</td>
<td></td>
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<tr>
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<td>coulomb</td>
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<tr>
<td>cm</td>
<td>centimeter</td>
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</tr>
<tr>
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<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
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</tr>
<tr>
<td>DAFC</td>
<td>Direct alcohol fuel cell</td>
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</tr>
<tr>
<td>DFAFC</td>
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<tr>
<td>DFT</td>
<td>density function theory</td>
<td></td>
</tr>
<tr>
<td>D_{H₂O₂}</td>
<td>diffusion coefficient of peroxide in water</td>
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<tr>
<td>DMFC</td>
<td>direct methanol fuel cell</td>
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<td>D_{O₂}</td>
<td>diffusion coefficient of oxygen gas in water</td>
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<tr>
<td>e⁻</td>
<td>electron</td>
<td></td>
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<td>ECSA</td>
<td>electrochemically active surface area</td>
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<td>energy dispersive x-ray analysis</td>
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<tr>
<td>FWHM</td>
<td>full width at half the maximum</td>
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<tr>
<td>g</td>
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<td>k₁-100Pt</td>
<td>rate constant, k₁, but specifically for the pure platinum catalyst</td>
<td>cm s⁻¹</td>
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rate constant for the two electron conversion of oxygen to peroxide \( \text{cm s}^{-1} \)
rate constant for the two electron conversion of peroxide to water \( \text{cm s}^{-1} \)
kiloelectron volt \( \text{keV} \)
kilogram \( \text{Kg} \)
thousand times, often referring to a magnification \( \text{kX} \)
liter \( \text{L} \)
laser ablation \( \text{LA} \)
magnesium \( \text{Mg} \)
milligram \( \text{mg} \)
megajoules \( \text{MJ} \)
milliliter \( \text{mL} \)
millimeter \( \text{mm} \)
generic symbol denoting a metal \( \text{M} \)
molarity \( \text{mol} \)
methanol oxidation reaction \( \text{MOR} \)
millivolt \( \text{mV} \)
collection efficiency \( \text{N} \)
nickel \( \text{Ni} \)
nanometers \( \text{nm} \)
nanoparticles \( \text{NPs} \)
oxygen gas or dioxygen \( \text{O}_2 \)
oxygen reduction reaction \( \text{ORR} \)
osmium \( \text{Os} \)
poly(2-vinylpyridine) \( \text{P2VP} \)
poly(4-vinylpyridine) \( \text{P4VP} \)
palladium \( \text{Pd} \)
palladium core with a platinum shell \( \text{Pd@Pt} \)
polydispersity index \( \text{PDI} \)
polymer electrolyte membrane \( \text{PEM} \)
polymer electrolyte membrane fuel cell \( \text{PEMFC} \)
parts per million \( \text{ppm} \)
polystyrene-\text{block}-poly(4-vinylpyridine) \( \text{PS-}b\text{-P4VP} \)
platinum \( \text{Pt} \)
platinum core with a platinum shell \( \text{Pt@Pd} \)
platinum supported by carbon \( \text{Pt/C} \)
ratio of platinum to gold \( \text{Pt:Au} \)
platinum core with a palladium shell \( \text{Pt@Pd} \)
a three to one platinum to nickel catalyst displaying a (111) \( \text{(hkl)} \) miller indices face \( \text{Pt}_3\text{Ni}(111) \)
polytetrafluoroethylene \( \text{PTFE} \)
rotations per minute \( \text{RPM} \)
rotating ring-disk electrode \( \text{RRDE} \)
scanning force microscopy \( \text{SFM} \)
standard deviation \( \text{STD} \)
transmission electron microscopy \( \text{TEM} \)
volt \( \text{V} \)
vinylpyridine \( \text{VP} \)
watt \( \text{W} \)
defined as \( 0.62x(D_{\text{O}_2})^{2/3}xV^{1/6} \) \( \text{cm s}^{-1/2} \)
defined as \( 0.62x(D_{\text{H}_2\text{O}_2})^{2/3}xV^{1/6} \) \( \text{cm s}^{-1/2} \)
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<td>( \Omega )</td>
<td>ohms</td>
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<tr>
<td>( \omega )</td>
<td>RPM</td>
<td>( \text{revolutions minute}^{-1} )</td>
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Appendix II. Scanning Force Microscopy Images

Figure II.1. SFM images of catalysts synthesized with PS\textsubscript{893-b-P4VP\textsubscript{330}. a)-f) are Pt\textsubscript{100}Au\textsubscript{0}, Pt\textsubscript{84}Au\textsubscript{16}, Pt\textsubscript{80}Au\textsubscript{20}, Pt\textsubscript{62}Au\textsubscript{38}, Pt\textsubscript{47}Au\textsubscript{53}, and Pt\textsubscript{0}Au\textsubscript{100}, respectively.
Figure II.2. SFM images of catalysts synthesized with PS$_{552}$-b-P4VP$_{174}$. a)-f) are Pt$_{100}$Au$_0$, Pt$_{83}$Au$_{17}$, Pt$_{67}$Au$_{33}$, Pt$_{63}$Au$_{37}$, Pt$_{35}$Au$_{65}$, and Pt$_0$Au$_{100}$, respectively.
Appendix III. TEM images and Particle Diameter Histograms
Figure III.1. TEM images of: a) \( \text{Pt}_{100}\text{Au}_0 \) b) \( \text{Pt}_{62}\text{Au}_{38} \) c) \( \text{Pt}_{59}\text{Au}_{41} \) and d) \( \text{Pt}_{47}\text{Au}_{53} \) synthesized with PS_{1392}-b-P4VP_{471} along with corresponding histograms to the right of each image.
Figure III.2. TEM images of: a) Pt$_{100}$Au$_{0}$ b) Pt$_{84}$Au$_{16}$ c) Pt$_{80}$Au$_{20}$ and d) Pt$_{62}$Au$_{38}$ synthesized with PS$_{893}$-b-P4VP$_{330}$ along with corresponding histograms to the right of each image.
Figure III.3. TEM images of: a) Pt$_{100}$Au$_0$ b) Pt$_{83}$Au$_{17}$ c) Pt$_{67}$Au$_{33}$ and d) Pt$_{63}$Au$_{37}$ synthesized with PS$_{552}$-b-P4VP$_{174}$ along with corresponding histograms to the right of each image.
Appendix IV. XPS Data

Figure IV.1. XPS data for PS₉₉₃-b-P4VP₃₃₀ beginning with pure platinum at the top (blue) with decreasing amounts down to pure gold at the bottom (red).
Figure IV.2. XPS data for PS$_{592}$-$b$-P4VP$_{174}$ beginning with pure platinum at the top (blue) with decreasing amounts down to pure gold at the bottom (red).
Appendix V. Cyclic Voltammetry

Figure V.1. Steady-state voltammograms of catalysts synthesized with PS_{893}-b-P4VP_{330} in 0.10 M H_{2}SO_{4} purged with nitrogen. Voltage is reported versus Ag/AgCl.
Figure V.2. Steady-state voltammograms of catalysts synthesized with PS<sub>893</sub>-b-P4VP<sub>330</sub> in 2.0 M methanol in 0.10 M H<sub>2</sub>SO<sub>4</sub> purged with nitrogen. Voltage is reported versus Ag/AgCl.
Figure V.3. Steady-state voltammograms of catalysts synthesized with PS_{552-\text{b}-P4VP_{174}} in 0.1 M H2SO4 purged with nitrogen. Voltage is reported versus Ag/AgCl.
Figure V.4. Steady-state voltammograms of catalysts synthesized with PS_{552-b-P4VP_{174}} in 2.0 M methanol in 0.10 M H$_2$SO$_4$ purged with nitrogen. Voltage is reported versus Ag/AgCl.
Appendix VI. RRDE Data

**Figure VI.1.** RRDE plot for catalysts synthesized with PS$_{893}$-b-P4VP$_{330}$ at 5 mV/s displaying the disk current (bottom) and the ring current (top) both plotted versus the applied disk potential. The catalysts are displayed as a)-f) Pt$_{100}$Au$_0$, Pt$_{84}$Au$_{16}$, Pt$_{80}$Au$_{20}$, Pt$_{62}$Au$_{38}$, Pt$_{47}$Au$_{53}$, and Pt$_0$Au$_{100}$ by XPS, respectively. The ring was held at 1.0 V and all voltages are reported versus Ag/AgCl.
Figure VI.2. RRDE plot for catalysts synthesized with PS_{552-b-P4VP}_{174} at 5 mV/s displaying the disk current (bottom) and the ring current (top) both plotted versus the applied disk potential. The catalysts are displayed as a)-f) Pt_{100}Au_{0}, Pt_{83}Au_{17}, Pt_{67}Au_{33}, Pt_{63}Au_{37}, Pt_{35}Au_{65}, and Pt_{0}Au_{100} by XPS, respectively. The ring was held at 1.0 V and all voltages are reported versus Ag/AgCl.
Appendix VII. ORR Kinetic Data

Figure VII.1. Kinetic parameter plots of $k_1$, $k_2$, and $k_3$ for a) Pt$_{100}$Au$_0$, b) Pt$_{84}$Au$_{16}$, c) Pt$_{80}$Au$_{20}$, and d) Pt$_{62}$Au$_{38}$ by XPS synthesized with PS$_{893}$-b-P4VP$_{330}$. Voltages are reported versus Ag/AgCl and the y-axis is on a log$_{10}$ scale.
Figure VII.2. Kinetic parameter plots of $k_1$, $k_2$, and $k_3$ for a) Pt$_{100}$Au$_0$, b) Pt$_{83}$Au$_{17}$, c) Pt$_{67}$Au$_{33}$, and d) Pt$_{63}$Au$_{37}$ by XPS synthesized with PS$_{552}$-b-P4VP$_{174}$. Voltages are reported versus Ag/AgCl and the y-axis is on a log$_{10}$ scale.
Figure VII.3. Logarithmic plots comparing kinetic parameters between Pt$_{100}$Au$_0$, Pt$_{84}$Au$_{16}$, Pt$_{80}$Au$_{20}$, and Pt$_{62}$Au$_{38}$ by XPS synthesized with PS$_{893}$-$b$-P4VP$_{330}$. a) $k_1$ b) $k_2$ c) $k_3$ d) $k_1/k_2$
Figure VII.4. Logarithmic plots comparing kinetic parameters between Pt\textsubscript{100}Au\textsubscript{0}, Pt\textsubscript{83}Au\textsubscript{17}, Pt\textsubscript{67}Au\textsubscript{33}, and Pt\textsubscript{63}Au\textsubscript{37} by XPS synthesized with PS\textsubscript{552}-b-P4VP\textsubscript{174}. a) k\textsubscript{1} b) k\textsubscript{2} c) k\textsubscript{3} d) k\textsubscript{1}/k\textsubscript{2}
Figure VII.5. Plots of $I_0/I_R$ versus $\omega^{-1/2}$ at selected voltages (inset) near 0.50 V, 0.45 V, 0.40 V, 0.35 V, 0.30 V, and 0.25 V for a) Pt$_{100}$Au$_0$, b) Pt$_{62}$Au$_{38}$, c) Pt$_{59}$Au$_{41}$, and d) Pt$_{47}$Au$_{53}$ synthesized with PS$_{1392}$-b-P4VP$_{471}$. 
Figure VII.6. Plots of $I_0/I_R$ versus $\omega^{-1/2}$ at selected voltages (inset) near 0.50 V, 0.45 V, 0.40 V, 0.35 V, 0.30 V, and 0.25 V for a) Pt$_{100}$Au$_{0}$, b) Pt$_{84}$Au$_{16}$, c) Pt$_{80}$Au$_{20}$, and d) Pt$_{62}$Au$_{38}$ synthesized with PS$_{893}$-b-P4VP$_{330}$. 
Figure VII.7. Plots of $I_D/I_R$ versus $\omega^{-1/2}$ at selected voltages (inset) near 0.50 V, 0.45 V, 0.40 V, 0.35 V, 0.30 V, and 0.25 V for a) Pt$_{100}$Au$_0$, b) Pt$_{83}$Au$_{17}$, c) Pt$_{67}$Au$_{33}$, and d) Pt$_{63}$Au$_{37}$ synthesized with PS$_{552}$-b-P4VP$_{174}$. 
Figure VII.8. Plots of \( \frac{I_d}{(I_d-I)} \) versus \( \omega^{1/2} \) at selected voltages (inset) near 0.50 V, 0.45 V, 0.40 V, 0.35 V, 0.30 V, and 0.25 V for a) Pt100Au0, b) Pt62Au38, c) Pt59Au41, and d) Pt47Au53 synthesized with PS1392-b-P4VP471.
Figure VII.9. Plots of \( \frac{I_a}{(I_a-I_d)} \) versus \( \omega^{1/2} \) at selected voltages (inset) near 0.50 V, 0.45 V, 0.40 V, 0.35 V, 0.30 V, and 0.25 V for a) Pt\textsubscript{100}Au\textsubscript{0}, b) Pt\textsubscript{84}Au\textsubscript{16}, c) Pt\textsubscript{80}Au\textsubscript{20}, and d) Pt\textsubscript{62}Au\textsubscript{38} synthesized with PS\textsubscript{893}-b-P4VP\textsubscript{330}.
Figure VII.10. Plots of $I_d/(I_d-I_0)$ versus $\omega^{1/2}$ at selected voltages (inset) near 0.50 V, 0.45 V, 0.40 V, 0.35 V, 0.30 V, and 0.25 V for a) Pt$\text{100}$Au$\text{0}$, b) Pt$_{83}$Au$_{17}$, c) Pt$_{67}$Au$_{33}$, and d) Pt$_{63}$Au$_{37}$ synthesized with PS$_{552}$-b-P4VP$_{174}$. 

Appendix VIII.I Kinetic Theory Background

The kinetic theory for this study done on the ORR using the RRDE is quite old and matured dating back to the 1960’s. The basis for this analysis is that by comparing what is detectable on the disk to what is detected on the ring, there can be an understanding about what the rate of a specific, yet simplified, reaction mechanism is. The main points for this study are to find the slope and intercept of the plot of \( I_D/I_R \) versus the inverse square root of the rotations rate and to find the slope of \( I_d/(I_d-I_D) \) versus the inverse square root of the rotation rate. The equations from chapter 5 have

\[
k_1 = \frac{S_2Z_1(I_1N - 1)}{(I_1N + 1)} \tag{5}
\]

\[
k_2 = \frac{2S_2Z_1}{(I_1N + 1)} \tag{6}
\]

\[
k_3 = \frac{S_2Z_2N}{(I_1N + 1)} \tag{7}
\]

been provided for reference. The slope of the first plot required should give some insight into the amount of peroxide being formed since it incorporates the ring current into the equation, while the intercept gives an idea of what the theoretical ratio of water to peroxide formation would be at an infinite rotation rate. This would help determine the fraction of all products that is peroxide, hence the denominator of all the equations incorporates this along with the collection efficiency which corrects for the inability of the ring to come into contact with all of the produced peroxide. In the second plot of \( I_d/(I_d-I_0) \) versus \( \omega^{-1/2} \) the slope is indicative of the rate at which water is produced since it is taking a ratio of the disk limiting current to the difference between the current at a voltage and the limiting current. In the equation for \( k_1 \) this slope can be seen in the numerator interacting with what appears to be the fraction of products produced that are not peroxide, giving rise to \( k_1 \) the direct reduction of oxygen to water. In \( k_2 \) this slope can also be seen, but since it is for oxygen to peroxide, it would not include that same \( I_1N-1 \) parameter that \( k_1 \) utilized to correct for the amount of peroxide production. The equation for \( k_3 \) is self-explanatory due to utilizing the slope that relates water to peroxide production along with a collection efficiency correction factor as seen in other parts that include peroxide detection factors. The factors of \( Z_1 \) and \( Z_2 \) were defined earlier as \( 0.62(D_{O2})^{2/3}v^{-1/6} \) and \( 0.62(D_{H2O2})^{2/3}v^{-1/6} \), respectively, where \( D_{O2} \) and \( D_{H2O2} \) are the diffusion coefficients of oxygen and
peroxide, respectively, and \( \nu \) is the kinematic viscosity of water. For this study, \( D_{\text{O}_2} \), \( D_{\text{H}_2\text{O}_2} \), and \( \nu \) have been chosen as \( 1.9 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \), \( 1.18 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \), and \( 0.00997 \text{ cm}^2\text{s}^{-1} \), respectively. It is easy to understand why these parameters were necessary to determine the rate of reaction of oxygen and peroxide. In \( Z_1 \) the speed at which oxygen can move through water is corrected for, and that is why this factor is seen in \( k_1 \) and \( k_2 \). The reason that \( Z_2 \) is seen in \( k_3 \) is because it is a correction for how quickly peroxide can diffuse through water, and \( k_3 \) is the only rate that deals with the reaction of peroxide. Ultimately, this is a relatively simple, yet effective, tool for analyzing the kinetics of a catalyst for the ORR utilizing RRDE.\(^{86-88}\)
References


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