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Electrochemistry of PANI/metal composites in basic solutions

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ELECTROCHEMISTRY OF PANI/METAL COMPOSITES IN BASIC SOLUTIONS

by

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Bachelor of Science
University of Nevada, Las Vegas
2008

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science in Chemistry

**Department of Chemistry
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**University of Nevada, Las Vegas
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THE GRADUATE COLLEGE

We recommend the thesis prepared under our supervision by

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December 2011

ABSTRACT

Electrochemistry of PANI/Metal Composites in Basic Solutions

by

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Polyaniline (PANI) has been extensively investigated due to its unique conductivity, which is primarily dependent on the oxidation state of the material and the solution pH. PANI is an insulator when it is oxidized, and the solution pH exceeds four. Numerous attempts to extend PANI's conductivity to neutral and alkaline environments have been unsuccessful. However, our previous study has demonstrated that PANI/Pd composite is conductive and catalytically active in a basic solution, pH \sim 12. Therefore, the conductivity and the electrochemical properties of PANI composites including PANI/Au, PANI/Pd and PANI/Pt were evaluated in basic solutions. The fundamental studies of PANI/metal composites were conducted to determine if the applications for the polymer could be extended to basic solutions that are traditionally precluded.

PANI/metal composites are produced electrochemically through the controlled uptake and reduction of metal anions including PtCl_4^{2-} , PdCl_4^{2-} , and AuCl_4^- using cyclic voltammetry. The deposition of metals into PANI was confirmed using the acid doping of the polymer, FTIR spectroscopy, and thermal gravimetric analysis (TGA). The acid doping study suggests that the metal species physically block proton-doping sites in the

polymer. FT-IR data indicates that a higher oxidation state is obtained for the polymer after the metal reduction. The TGA data also provides the measure of the approximate amount of metal in the polymer. The characterization data suggests that the conductivity should be diminished relative to the pristine polymer. However, all of the PANI/metal composites demonstrate catalytic activity for alcohols oxidation in basic solutions. The data indicate that the electrochemical responses and the conductivity of the composites are maintained at pH values that have typically produced insulating PANI. The results suggest that the metals act as solid-state dopants, which facilitates the continued conductivity of the polymer in basic solutions.

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CHAPTER 1

INTRODUCTION

1.1 Polyaniline (PANI)

1.1.1 PANI

Intrinsic conducting polymers (ICPs) have been used in numerous applications such as corrosion protection,¹ microelectronics,² and chemical sensing.³ ICPs, including polyacetylene, polythiophene, polypyrrole and polyaniline, are conjugated polymers, in which single and double bonds are alternated on the polymer chain providing high electron density. The polymers possess high electron density and the pristine forms have low conductivities, usually in the range of an insulator or a semiconductor.⁴ High conductivity of the polymers can be achieved through the reduction or oxidation of the polymers with the uptake of either an electron donor or acceptor. This process is called doping, changing the electrons density in the polymer backbone while providing charge mobility. The doped forms of the polymers have high conductivity, which can be comparable to metals. Among other ICPs, polyaniline (PANI) is unique because the conductivity can be achieved through either protonation or anion uptake in the polymer. In contrast to other polymers, PANI doped with protons does not change the number of the electrons on the polymer backbone. This unique conductivity sets PANI apart from other conducting polymers. In addition, the thermal stability and ease of synthesis make PANI one of the most studied conductive polymer systems.⁵

1.1.2 Conductivity of Polyaniline

PANI has variable conductivities depending on the doping level. The range of conductivity values can vary by $\sim 10^{10}$ based on the range of 10^{-9} to 10 S/cm.⁶ The

conductivity of the polymer depends on many factors including molecular weight, temperature, humidity, counterion doping, oxidation state, and proton doping.^{5,7}

Although all of these parameters can influence the conductivity of PANI, it is primarily dependent on the oxidation state and proton doping.

The general form of PANI consists of both reduced and oxidized units, which are provided in Figure 1.1. The reduced units contain two benzenoid rings with two amine groups, and the oxidized units contain one benzenoid ring, one quinoid ring, and two imine groups. Variations in the ratio of oxidized and reduced units within the polymer provide a wide range of different oxidation states for PANI. For example, leucoemeraldine is fully reduced form containing only benzenoid ring structures, while pernigraniline is the most oxidized form with two benzenoid and two quinoid structures. Some common forms of the polymer are provided in Figure 1.2. The emeraldine form of PANI has equal amount of reduced and oxidized units ($y = 0.5$), and is the most conductive in comparison to other oxidation states.⁸

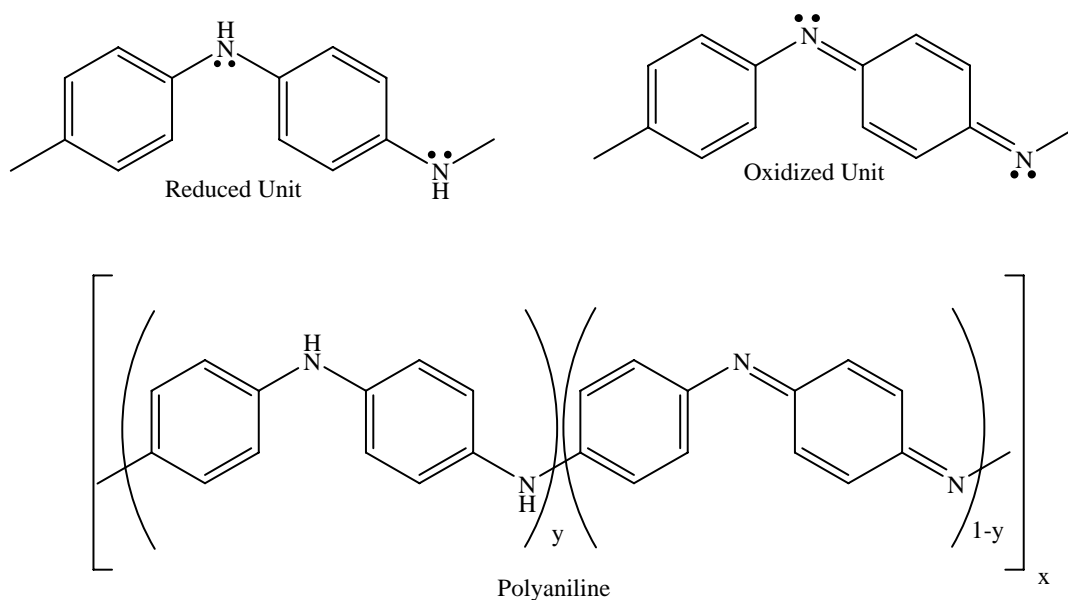


Figure 1.1: Polyaniline's units and its general form⁸

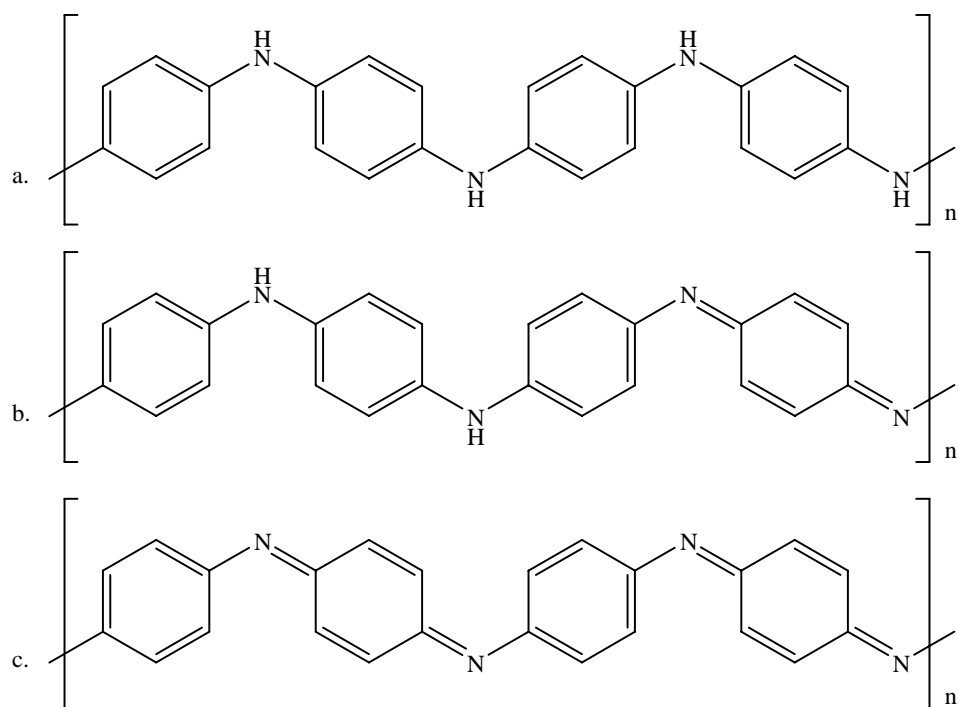


Figure 1.2: Common oxidation forms of polyaniline: a. Leucoemeraldine,
b. Emeraldine, c. Pernigraniline⁸

Numerous studies have evaluated the influence of pH on the conductivity of emeraldine, and have shown that it is related to proton doping at the nitrogen sites in the polymer.^{8,9,10} Specifically, the solution pH determines the percentage of nitrogen sites doped within the polymer. Previous studies have shown that the percentage of doping increases as the solution pH decreases below 4, and reaches a maximum at fifty percent when the solution pH is 2.⁹ In contrast, at high pH, the polymer is fully deprotonated, and the conductivity is lost regardless of the oxidation state of the material. The results indicate that the conductivity of PANI depends on both the solution pH, and the oxidation

state. The pK_a values (2.5 and 5.5) of the protonated amine and protonated imine doping sites¹¹ within the polymer are directly influenced by the solution pH. Doping of both units occurs when the $pH < 2.5$. At intermediate pH values, between 2.5 and 5.5 only the imine nitrogens are protonated. Finally, both the imine and amine nitrogen in the polymer are not protonated, and PANI becomes an insulator when the pH exceeds 4.⁷

“The polaronic model” has been used to explain the enhanced conductivity of PANI after proton doping.¹² The mechanism is based on the emeraldine form of PANI, proton doped at only fifty percent relative to the total nitrogen sites. The uptake of proton when the polymer exists in the emeraldine form leads to the highest conductivity based on doping the imine sites. The structure consists of a reduced unit and an oxidized unit with two positive charges at the nitrogens. The protonated emeraldine then undergoes a transition from a bipolaron (two positive charges on the imine nitrogens) to a polaron (two radical cations) with delocalized electron density along the polymer backbone. This rearrangement from the bipolaron to polaron is based on the fact that the charge distributes evenly across the polymer to stabilize the repulsion between the two positively charge imine nitrogens in the oxidized unit. The delocalization of electron density at the nitrogen sites in the polymer allows the flow of electrons along the polymer backbone. The mechanism of the polaronic model is demonstrated in Figure 1.3. This model explains the conductivity of PANI based solely on the oxidation state and proton doping. However, in the presence of non-acid dopants it is questionable whether the polaronic model is the relevant mechanism for the increased conductivity of PANI.

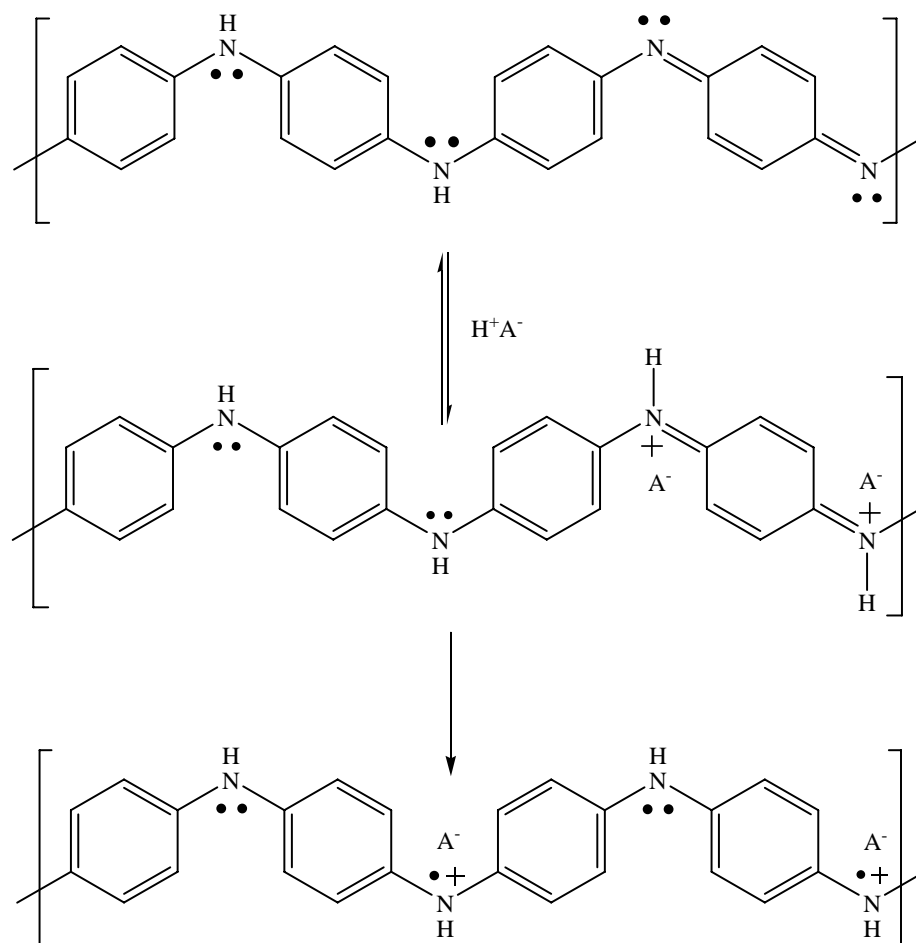


Figure 1.3: Emergence of conductivity based on the polaronic model.¹²

1.1.3 Synthesis

Polyaniline is synthesized using a variety of different methods. For example, there are literature reports that document chemical, electrochemical, gas-phase plasma, and enzymatic synthesis.^{5,7,13} The most common method is chemical synthesis, where PANI is produced through the direct oxidation of aniline with chemical oxidants such as ammonium persulfate, potassium dichromate, ceric sulfate, potassium ferricyanide, hydrogen peroxide, and potassium iodate.^{7,13} The oxidation of aniline is influenced by several factors such as concentration of oxidant, concentration of monomer, reaction

medium, duration of the reaction, and temperature.⁷ It is reported that when the molar ratio of the oxidant and the monomer is less than or equal to 1.15, an equal composition of oxidized and reduced units is obtained. The conductivity of the final product when proton doped is highest, which is consistent with the polaronic model. A higher amount of oxidant results in over oxidation of PANI, and reduces conductivity relative to the emeraldine.¹⁴ When the duration of the reaction is approximately 2 hours or greater, a constant yield is obtained based on the concentration of monomer indicating the complete reaction of monomer.¹⁴ Finally, the polymerization of aniline is also temperature dependent with variable reaction rate in the temperature range of 0 – 80°C. The rate of oxidation of the aniline monomer is the rate limiting step in the polymerization reaction, and can be precisely manipulated using temperature to influence polymer composition and speed of reaction.¹³

In addition to the conventional chemical oxidation of aniline other chemical synthetic methods have been used to produce PANI. The methods have been specifically developed to address the need for different physical and chemical properties of the polymer. For example, polymerization of aniline in organic solvents¹⁵ and sonochemical polymerization have been employed in the synthesis of PANI with higher solubility.^{16,17} The first method uses dodecylbenzenesulfonic acid aniline salt as a precursor in chloroform, and dichlorodicyanobenzoquinone as an oxidant. The polymer collected is a dark green suspension in chloroform, which can be precipitated by a mixture of methanol and acetone. In addition, ultrasound has been utilized during the oxidation of aniline using chemical oxidants to produce nanofibers. While the mechanism for PANI nanofibers formation is unknown, the result shows that the use of ultrasonication prevents

secondary PANI growth and agglomeration, and yields PANI nanofibers with high solubility.^{16,17} Finally, interfacial polymerization, has been utilized in the chemical synthesis of PANI.^{18,19} The polymer is produced at the interface of a polar phase (water, acids, and oxidants), and a non-polar phase (aniline and organic solvents). PANI nanofibers with a narrow diameter, and variable length from nanometers to micrometers were obtained. The interfacial polymerization is slow with a controllable reaction rate which allows PANI to form with defined nanostructures and a uniform distribution.¹⁸

Both enzymatic and gas-phase plasma polymerization have also been utilized in the synthesis of PANI.^{5,13,30-32} Enzymatic polymerization can be carried at room temperature, and neutral pH using hydrogen peroxide as an oxidant and horse radish peroxidase, or soybean peroxidase as catalysts.³⁰ The reaction depends on the catalytic activity of the enzymes, and the control over the process is lessened by the oxidation of aniline in the presence of peroxide. The PANI produced using this method is water soluble, with similar structure to chemical synthesized PANI.³³ However, the chain length of the polymer is much smaller than traditional chemical methods with lower degree of doping. Therefore, the polymer thermally degrades at lower temperatures in comparison to PANI produced from traditional chemical oxidants such as ammonium persulfate.³³ Gas-phase plasma polymerization is performed without chemical oxidants and solvents. The monomers are nebulized directly in the plasma stream.³¹ The monomers are ionized to form radical cations and the polymerization of PANI is initiated in the plasma.³² The resulting PANI residue is a clean product without traces of oxidants or solvents. However, the polymer is subjected to degradation due to the high energy

plasma, and is an insulator due to the lack of proton or anion doping of the final product.¹³

Alternatively, PANI can be synthesized electrochemically through the potential dependent anodic oxidation of aniline monomers at electrode surfaces. The electrode is typically an inert metal such as gold, platinum, palladium, and glassy carbon where the polymer nucleates. In addition, other non-traditional materials have been used as electrochemical substrates including stainless steel²⁰ and semiconductors.⁵ The electro-oxidation of aniline is usually carried in acidic electrolytes in order to maintain the conductivity during synthesis to produce an electroactive PANI film. Some electrolytes used in the synthesis include HCl,²¹ H₂SO₄,²² HClO₄,²³ and H₃PO₄,²⁴ and oxalic acid.²⁵ However, recently, electrochemical syntheses of PANI in acetonitrile with neutral pH and in alkaline have been reported, where the anodic oxidation of aniline is carried out in a solution of acetonitrile and LiClO₄.²⁶ The resulting PANI film had compact, globular structures, with good mechanical stability. The conductivity of PANI produced in acetonitrile is lower than PANI synthesized in traditional acidic solutions. Finally, the electropolymerization of aniline is also performed in alkaline solutions of KOH.²⁷ However, the PANI film is thin, and the synthesis terminates due to the lack of conductivity. The resulting material is soluble in acetone, but has not been characterized in detail.

There are three common electrochemical techniques that are utilized in PANI synthesis. Constant current utilizes a defined current density applied to an electrode that generates a sufficient oxidation potential to initiate polymerization. The PANI film is deposited at the electrode surface with the thickness related to the rate of reaction and

time the reaction was conducted. The current density is usually between 1- 10 mA/cm² to ensure a sufficient rate of reaction within the preset time.^{7,13} In contrast, the constant potential technique measures current as a function of a constant applied potential at the electrode. This method produces a PANI powder rather than a film that does not attached the electrode surface.²⁸ Finally, cyclic voltammetry can be utilized to cycle the electrode potential so the aniline monomer is electro-oxidized. Oxidation of aniline using this method produces PANI with each cycle until the desired quantity of polymer is reached on the electrode surface. The general mechanism of the electro-oxidation of aniline in acids is provided in Figure 1.4.²⁹

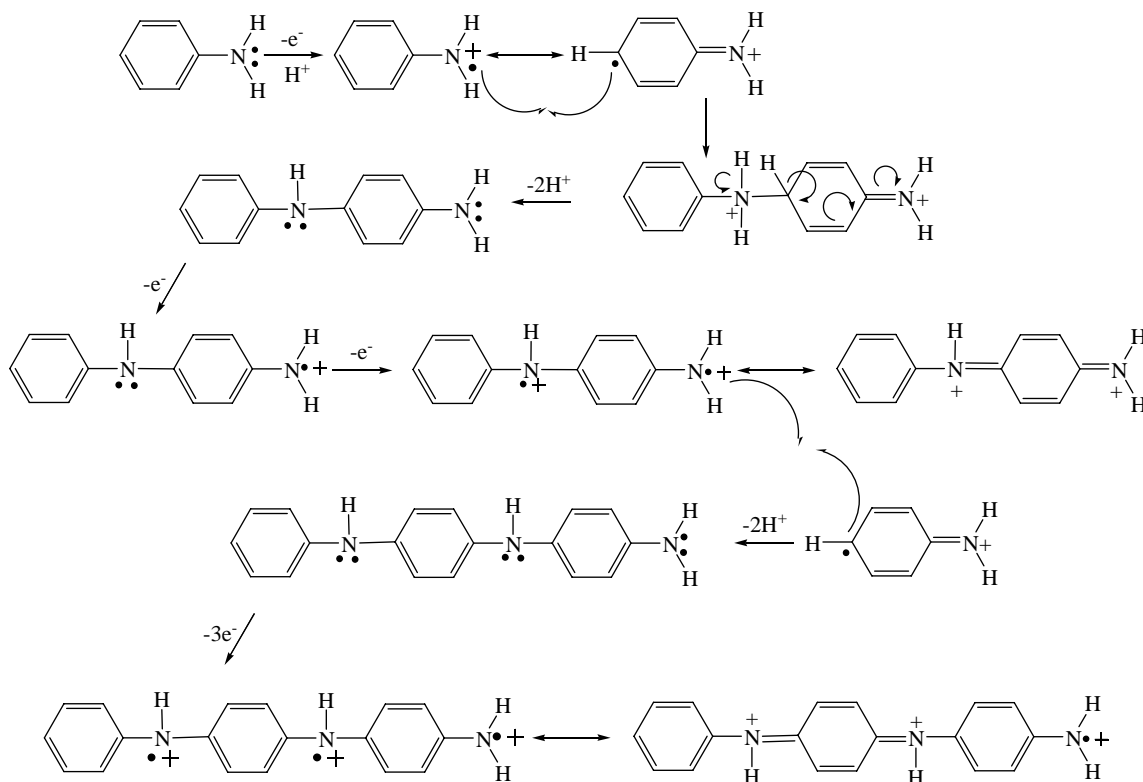


Figure 1.4: Electro-oxidation of aniline in an acid²⁹

Polymer synthesis is initiated through the formation of a radical cation at positive potentials. The polymer is sequentially deposited onto the electrode surface with each cycle at oxidizing potentials.²⁹ The film is cycled between oxidized and reduced states allowing the uptake of protons and anions to maintain charge neutrality and conductivity of the polymer. The number of the cycles can be varied in order to control the thickness of the film. The resulting PANI film is chemically bonded to the electrode surface, electroactive and homogenous in comparison to the other electrochemical techniques discussed previously.^{13,28} Electrochemical synthesis produces a more homogenous polymer because the oxidation of the monomer is carried out with no additional chemical oxidant. Therefore, the composition of oligomeric materials into the polymer matrix is minimized relative to PANI produced using chemical synthesis methods.⁷ The initiation and termination of the polymerization are also well-controlled electrochemically allowing the quantity and thickness to be precisely controlled using the applied potential. Cyclic voltammetry is employed to synthesize PANI films in this research to ensure that the polymer produced is homogenous and reproducible.

1.1.4 Applications

PANI is a diverse material which has been utilized in applications including batteries, electronics, and biological applications. Emeraldine base has been used to produce cathodes for batteries that have better recyclability compared to batteries with polyacetylene cathodes.³⁴ In addition, PANI and its derivatives have been utilized as coatings for metals such as iron and stainless steel to prevent corrosion.^{1,35,36} PANI is a promising material for electronic devices such as diodes or transistors because of the change in conductivity under the applied potential. Xing and co-workers have produced

a PANI diode which is currently being optimized for improved efficiency and reproducibility.³⁷ Moreover, PANI can be deposited on Au microelectrodes to produce high quality transistors.³⁸ The transistors exploit the properties of PANI which can be oxidized or reduced in response to electrical or chemical signals. When a potential is applied, it rapidly transfers charges in between the electrodes in an electrolyte producing switching time of less than 0.1 s.³⁸ In addition, since PANI can be doped/de-doped by acids and bases, it is a promising material for gas sensors.³ The detection of gases such as ammonia is based on the change in conductivity of PANI when it is exposed acidic or basic gases.³⁹ Moreover, incorporation PANI with other materials expanded its use to biological applications, which is typically excluded due to the high pH. For example, the modification of PANI with enzymes such as horse peroxidase,^{40,42} cytochrome c,⁴¹ glucose oxidase,⁴⁴ or single-stranded DNA⁴³ fabricates biosensors for detecting H₂O₂, glucose, and monitoring DNA hybridization, respectively.

1.2 PANI/metal composites

1.2.1 Introduction

The oxidation or reduction of PANI through electron donation or withdrawal makes the polymer sensitive to many chemical species. This limits the application of the pristine polymer because these interactions are indiscriminate. The oxidation/reduction of the polymer and electron donor/acceptor interactions often occur spontaneously without the ability to control the processes. Therefore, incorporating secondary components into PANI, such as metals, metal oxides or organic molecules into the polymer is often utilized to improve both selectivity and sensitivity for the targeted

chemical interactions. For example, nanoparticles or clusters of noble metals, including gold, palladium, and platinum provides the polymer with high surface area metal templates for chemical catalysis and sensing interactions. The combination of PANI and metal can also produce composites with novel and synergistic properties that are not originally present in each component.⁴⁵ More importantly, they provide selective surfaces for the withdrawal or donation of electron density through controlled interactions and chemically distinct reaction sites.

1.2.2 PANI/metal composites synthesis

Metal species can be introduced into PANI chemically or electrochemically. Chemical synthesis can be utilized to introduce metal nanoparticles into the polymer using ammonium persulfate to oxidize aniline to produce PANI. The polymer is then immersed in metal cations solutions. The cations are reduced spontaneously based on the high electron density associated with the polymer. The spontaneous reduction of the metal cations by the polymer results in the formation of PANI/metal composites.⁴⁶⁻⁴⁸ However, this method produces a more oxidized polymer with decreased conductivity as metal particles are reduced by the polymer. Metal particles can be also synthesized separately through the chemical reduction of metal cations. These preformed metal particles are then added to an aniline monomer solution; and a chemical oxidant, ammonium persulfate, is used to initiate the polymerization in the presence of metal.⁴⁹ The metal particles are trapped in the polymer matrix during the synthesis of PANI. This method generates a composite with nanosize particles uniformly distributed in the polymer.

An alternative method has been utilized to produce PANI/metal composites where the polymer and the metal are produced simultaneously through the oxidation/reduction of the aniline monomer in a solution containing metal precursors.⁵⁰⁻⁵³ The metallic anions/cations are utilized as an oxidizing agent for polymerization in the presence of an acid. The reduction of metal species to metal occurs while the polymer forms. The resulting composites have high metal loading while preserving PANI's properties. While all the chemical methods discussed can produce bulk quantities of composites, they have provided no direct control over the oxidation/reduction of both the polymer and the metal precursor when forming the composites. Electrochemical methods, however, can control the oxidation of the polymer, and the rate of reduction of metal cations or anions.

Electrochemical synthesis has been successfully used to synthesize PANI/metal composites. For instance, metal particles can be introduced into PANI film by co-deposition,^{54,55} or electrodeposition.^{56,57} In co-deposition, aniline oxidation and metal reduction occur at the same time at an electrode surface. The process is controlled by the applied potential of the electrode so that metal particles are embedded within the PANI film as it forms. The resulting composite contains mixed layers of metal and PANI.⁵⁴ On the other hand, electrodeposition of metal in PANI is achieved by reduction of metal precursor in the preformed polymer, which is obtained from the electro-oxidation of aniline. The metal is deposited in the polymer using either cation or anion doping through the normal the oxidation/reduction processes associated with the polymer. Because the applied potential controls the uptake and reduction of metal anions/cations in PANI, they are deposited at specific sites within the film. Moreover, the process can be

used to disperse the metal precursor uniformly in the polymer prior to the reduction of the species to metal.

While chemical synthesis provides bulk products, electrochemical synthesis only produces small quantities. However, the advantages of electrochemical synthesis offers far exceed the disadvantages. The process can be controlled precisely using the applied potential to ensure the quality of the polymer as well as to moderate the dispersion, size and quantity of metal particles in the polymer. Electrochemically synthesized PANI/metal composites have a uniform distribution of metal in the polymer matrix, and are more homogenous in comparison to composites produced chemically.⁵⁷ While chemical synthesis produces a uniform size of metal particles in the micrometer range which are encapsulated by the polymer as it forms,^{50,51} electrochemical methods can be used to produce metal particles in PANI with diameters ranging from nanometers to micrometers using the applied potential and the number of electrochemical cycles.⁵⁷ The metal surface area is also much higher for electrochemical methods because the polymer does not encapsulate the metal particles. Therefore, cyclic voltammetry was specifically utilized to produce the PANI/metal composites in all of the studies presented.

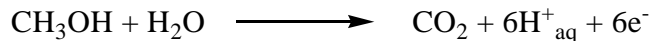
1.2.3 PANI/metal composite applications in basic solutions

PANI/metal composites have been used primarily in applications including catalysis and chemical sensing.^{58-61,63} The main goal is to maximize metal surface area for the chemical reactions and to minimize the contamination on the surface for the targeted applications. The use of bulk metal in catalysis and chemical sensing provides limiting metal surface area, with strong adsorption of species that poison the metal surface minimizing the reaction of species at the surface. The poisoning of the surface causes

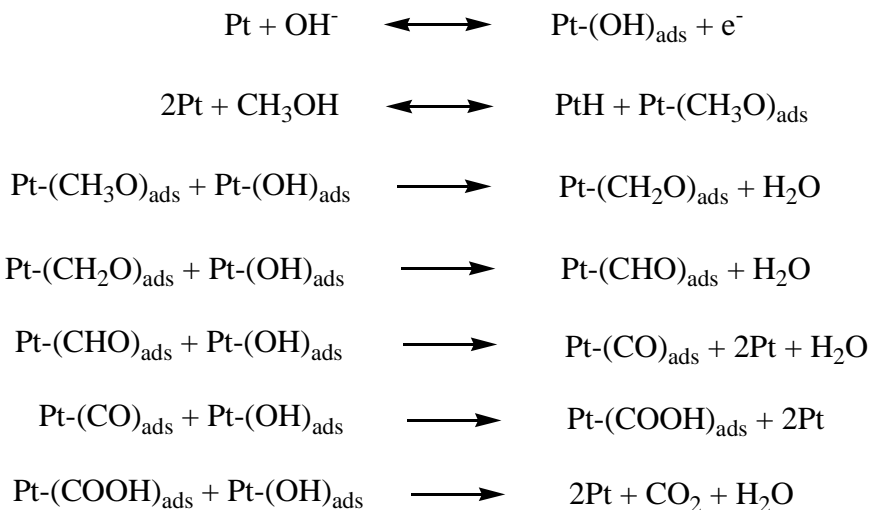
catalysis to be diminished since less of the metal surface is free for reaction. The PANI/metal composites often provide high surface areas with lower surface contamination or surface poisoning, and higher sensitivity than bulk metal surface.^{44,62} Traditionally, the applications of PANI have been limited to acidic environments with pH less than 4⁷ in order to maintain the conductivity. The same conditions are required for PANI/metal composites limiting the application of the material in basic based processes including batteries and fuel cell catalysis.

1.2.3.1 Catalysis

PANI/metal composites have been utilized as catalysts for the electro-oxidation of small organic molecules. Methanol oxidation is a simple way to assess the composites' catalytic activity. The oxidation of methanol generates six electrons, which make it a promising fuel. The reaction is usually carried in acidic electrolytes. However, a drawback of acids is the strong adsorption of anions to the catalyst surface (poisoning). Although this is often minimized as the metal particle diameter is decreased, the use of neutral/basic electrolytes has been shown to minimize the poisoning of the metal catalyst surface in comparison to acidic environments.⁶⁸ For example, Pt is an efficient catalyst for primary alcohols in acid solutions. However, the efficiency of the process decreases as the surface is poisoned with species such as CO_{ads}. However, when the same reaction is carried at high pH, the reaction's efficiency increases because of the desorption of CO from the Pt surface in basic solutions.⁶⁹ Other metals, including Au and Pd, can also be utilized for catalysis in basic solution because the metal surfaces can be regenerated at high pH to minimize the influence of poisoning.⁷⁰ Methanol is oxidized in a basic solution through the following reaction.⁶²



The mechanism of methanol oxidation in a basic solution using Pt as a catalyst with additional reactions for the regeneration of the metal surface is provided. The role of hydroxide in cleaning the Pt metal surface is addressed in the last five reactions with the final reaction provided a path to clean the Pt surface.⁶²



1.2.3.2 Chemical sensing

In addition to catalysis, PANI composites are also used for chemical sensing. For instance, incorporated gold particles within a PANI matrix can be utilized in biological applications. The use of PANI in biological applications is typically excluded due to the loss of PANI's conductivity in neutral or basic pH. Therefore, the pH requirements of PANI make it largely incompatible with the study of biologically active systems that would denature under highly acidic conditions. Au surfaces are widely utilized in biological sensing because it can be modified with biologically relevant species using thiol linkages for applications including bio-, and immuno-sensing.⁶⁴ There are a few examples where biologically active molecules have been affixed to PANI and used in solutions at neutral pH. For example, Yang et al. has reported that PANI/Au can be used

as a matrix to immobilize microperoxidase, which is a potential H_2O_2 sensor.⁶³ Moreover, glucose oxidase is included within a PANI and Au composite in order to fabricate a glucose sensor.⁴⁴ The limitations of the application of PANI in biological sensor applications can be moderated when the polymer is electroactive at pH values consistent with biological systems. Therefore, there is a need to produce PANI that remains conductive under any pH condition.

1.3 Research Goals

There have been many attempts to extend PANI's conductivity to neutral and alkaline environment using acidic groups such as sulfonate^{65,66} or polyelectrolytes.⁶⁷ These researches modify the nitrogen sites or substitute the ring with organic molecules, which will convert to the conductive form of PANI in hydroxide solutions. Recently, PANI modified with metal polyelectrolytes is found to be electroactive in neutral environment, and utilized for biological applications.⁶⁰ However, in each case PANI must be either chemically modified or chemical species must be entrapped to provide the conductivity. In contrast, there are very few studies that concentrate on the conductivity of PANI/metal composites in basic environment. In these systems the metal will be utilized as the dopant rather than proton or anions species. Our previous study has demonstrated that PANI/Pd is conductive and catalytically active in a basic solution, pH ~ 12. Since PANI is oxidized and deprotonated, these results suggest that the metal may provide the same delocalized charges at nitrogen sites, which is observed in the polaronic model. Therefore, PANI doped with gold and platinum should demonstrate a similar behavior. This project presents the preparation and characterization of PANI/Au, PANI/Pd and

PANI/Pt composites. The conductivity and the electrochemical properties of these composites in specific will be evaluated to determine whether they can be used in basic solutions which will allow the material to be utilized uniformly in solutions of both high and low pH.

CHAPTER 2

EXPERIMENTAL

2.1 Introduction

The polymerization of aniline and the deposition of metal in the film are performed electrochemically using cyclic voltammetry. The oxidation state of the polymer before and after metal deposition, the composition, and the conductivity of the PANI/metal composites are evaluated separately using various characterization methods. The methods include thermal gravimetric analysis (TG), electronic conductivity, Fourier transform infrared spectroscopy (FT-IR), and coulometric methods to measure the charge associated with the proton doping of the polymer. Finally, the PANI/metal composites are specifically studied for their electrochemical and catalytic activity in basic solutions containing primary alcohols.

2.2 Chemicals

PANI is synthesized using aniline 99% (Aldrich Chemical Company, 13, 293-4) and perchloric acid 69 – 72% (JT Baker, 9652-33). Aniline is distilled prior to using. Metal compounds used are Potassium tetrachloroaurate (III) 98+% (Strem Chemicals, 93-7906), Potassium tetrachloropalladate (II) 99% (Strem Chemicals, 46-2126), and Potassium tetrachloroplatinate (II) 99.9% (Strem Chemicals, 78-1970).

2.3 Electrochemical synthesis of PANI/metal composites

PANI and PANI/metal composites (PANI/Au, PANI/Pd, and PANI/Pt) were synthesized using a CHI 760C potentiostat. The current was measured as a function of

the applied potential, which was cycled within a predetermined potential range. The current was plotted against the applied potential to give the corresponding cyclic voltammogram. The experiments were performed using an electrolytic cell containing three electrodes. The reference electrode was an Ag/AgCl electrode filled with 3M KCl, the counter electrode was a Pt sheet with surface area at least ~ 1.5 greater than the area of the working electrode. A glassy carbon (GC) disk electrode with 3 mm in diameter (0.0707 cm^2) was used as the working electrode. The GC electrode was used rather than common working electrodes including Au, Pd or Pt to ensure that the working electrode surface does not contribute to the oxidation of primary alcohols in the presence of the deposited metal. The glassy carbon electrode was polished between experiments using fine alumina powder (CH Instruments, Inc, 1, 0.3, and 0.05 micron), sonicated in ethanol, and finally washed with ultra-pure water. The cell was purged with nitrogen gas for ten minutes prior to the experiment in order to degass the solution, and to ensure that oxidation/reduction processes associated with oxygen were minimized.

A PANI film was deposited electrochemically on an electrode using 0.25M aniline in 1M HClO₄ solution prior to the metal deposition. The electrode was cycled between -0.20 V and 0.85 V at the scan rate of 0.01 V/s for 20 cycles. The PANI film was washed with ultra-pure water to remove residual acid from the electrode surface. The electrode was then immersed in a metal salt solution, 5mM KAuCl₄, 5mM K₂PdCl₄, or 5mM K₂PtCl₄ for metal deposition poised at 0.85 V to ensure the spontaneous reduction of the metal species did not occur. The metal anions were then reduced in the polymer using 10 potential cycles from 0.85 V to -0.20 V at a scan rate of 0.01 V/s. The electrode was then

removed from the metal solution, and washed with ultra-pure water to remove residual surface metals.

The PANI/metal composites were also deposited on a gold mica working electrode for FTIR measurements. The flat gold substrates provide a usable surface for FTIR microscopy after the PANI/metal composite is formed. The gold mica working electrode was prepared by evaporating gold on mica with 3000Å of thickness. Bulk quantities of PANI/metal composites were produced on Pt sheet electrodes, and delaminated for TG analysis and conductivity measurement. Sequential deposition of polymer and metal using the methods outlined above were utilized to produce thick PANI/metal composites (~1 mm) on the Pt sheet. The film was rinsed with ultrapure water to remove excess metal anions from the polymer surface, and dried in air for 48 hours prior to characterization.

2.4 Characterization

2.4.1 Acid doping

The polymer was electrochemically doped with 1M HClO₄ before and after the metal deposition denoted as the first and second acid doping, respectively. All experiments were performed using a CHI 760C potentiostat. The experimental set-up was identical to the synthesis of polymer and the composites. The electrode was cycled in the acid solution at a scan rate of 0.01 V/s. For statistical analysis three trials were performed for each composite. The voltammetric waves associated with the proton doping and expulsion were integrated to obtain the charge passed for the processes prior to and after metal reduction.

2.4.2 Infrared Spectroscopy

Fourier Transform – Infrared Spectroscopy (FT-IR) is performed to determine the chemical composition of the PANI/metal composite relative to pristine PANI. The goal is to identify chemical functional groups that are influenced by the introduction of metal into the polymer. FT-IR is also utilized to determine the oxidation states of PANI, and the composites.⁷¹ The spectra were obtained using a BIORAD Digilab FTS 7000 Fourier Transform – Infrared spectrometer with UMA 600 microscope. The spectral range utilized was from 700 and 4000 cm^{-1} . Each sample was scanned 128 times with spectral resolution of 8 cm^{-1} .

2.4.3 Thermal gravimetric analysis

Thermal gravimetric analysis (TGA) can provide information about the thermal properties of the polymer, and the amount of metal incorporated.^{72,73,74} The method provides a precise measurement of the weight change of the PANI/metal composite as the temperature is elevated. The mass loss of the composites can be related to the loss of moisture and degradation of organic components of the polymer. The metals do not volatilize under the thermal conditions applied, and remain unperturbed. Therefore, the method provides a direct measure to the percent mass of metal in the composite relative to the organic components. The TG measurements were performed using the Netzsch STA 449 C instrument. The samples were loaded in aluminum oxide crucibles and heated from 25 °C to 1200 °C. A baseline measurement was performed in order to correct for buoyancy, and to ensure the reproducibility of the measurements. Each sample (PANI, PANI/Au, PANI/Pd and PANI/Pt) was measured three times for statistical

analysis. Air was used as both protective gas and purge gas with flow rates of 20 mL/min and 50 mL/min, respectively.

2.4.4 Conductivity measurement

The conductivity of PANI and the composites was measured using a four-point probe. For the measurements, a current is passed through the two outer probes, and the voltage drop between two inner probes is measured. The resistance is obtained using Ohm's law $V = IR$, where the potential and current from the measurement are used to obtain R , the resistance. The same amount of each composite, approximately 0.030 g, was pressed into 0.8 cm in diameter pellet with Tetragon Scientific Delta-Press to ensure reproducibility of the sample preparation. The Cascade Microtech C4S 4-point probe attached to a CPS Probe Station is used for the conductivity measurement. Alessi C4S 4-Point Probe Head 64/5 2383, made of Tungsten carbide is used for the contacts with the samples. The Agilent 34401A Multimeter, which records the resistance measurements, is connected to the probe station. Each sample was measured at least at five different contact points on the pellet. The value of resistance is then used to calculate the conductivity of the material based on following equations:

$$R = \frac{\rho \times l}{A}$$

$$A = \pi r^2$$

$$\rho = \frac{1}{\sigma}$$

where R is the resistance, l is the thickness of the pellet, A is the surface area, r is the radius, ρ is the resistivity, and σ is the conductivity.

2.5 Electrochemistry of PANI/metal composites in basic solutions

The electroactivity of PANI/metal composites was studied in basic solutions with pH approximately 14, which normally ceased the electroactivity of PANI and results in loss of conductivity. All electrochemical studies were performed with the CHI 760C potentiostat with the same 3-electrode set-up as previous experiments. The GC working electrode was coated with the composites prior to the experiments.

2.5.1 Electroactivity of PANI/Au in sodium hydroxide

This experiment was designed to determine the activity of the composite in an extremely basic solution with pH approximately 14. PANI/Au and a gold disk electrode were cycled in 1M NaOH solution between -0.4 V and 0.75 V at a scan rate of 0.01 V/s. The current was normalized versus the geometric electrode area.

2.5.2 Electro-oxidation of alcohols

The catalytic activity of PANI/metal composites was probed for the electrochemical oxidation of primary alcohols in basic solutions for comparison to bulk metals. In addition, the oxidative processes were used to examine the conductivity of the composites at high pH. The composites were examined in solutions containing 1M methanol in 1M KOH. The composites were cycled between -0.60 V and 0.20 V at a scan rate of 0.01 V/s. Au, Pd, and Pt disk electrodes were also examined under the same conditions for comparison to the composite materials. In addition, PANI/Au, and Au disk electrode were examined for the oxidation of 1-propanol in 1M KOH, where the potential was cycled from -0.4 V to 0.5 V at a scan rate of 0.01 V/s. The current responses were normalized versus the geometric electrode areas for direct comparison. The results will be examined in chapter 3 and 4.

CHAPTER 3

ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF PANI/METAL COMPOSITES

3.1 Introduction

PANI and PANI composites are electrochemically synthesized using cyclic voltammetry. The materials are then characterized in detail using different methods including FT-IR spectroscopy, thermal gravimetric (TG) analysis, and electrochemical proton doping of the polymer. FT-IR spectroscopy shows how metal reduction affects the structure and oxidation state of the polymer relative to the pristine material. The TGA data provides the weight composition of PANI versus the metal component, and the influence of the metal on the thermal properties of the polymer relative to pure PANI. Finally, the proton doping provides information about the free nitrogen sites before and after metal deposition providing a measure of the loss of active sites due to metal physically blocking these sites. Moreover, the conductivity of PANI and its composites is measured using four point probe to determine how the introduction of metals influences the electrical properties of PANI.

3.2 Electrochemical synthesis of PANI and PANI/metal composites

3.2.1 Electrochemical synthesis of PANI

The synthesis of PANI was achieved at a GC working electrode that was cycled in a solution containing 0.25M aniline in 1M perchloric acid (HClO_4) for 20 cycles at a scan rate of 0.010 V/s. The starting potential for PANI synthesis was 0 V and the scanning direction was initially positive to facilitate the oxidation of the aniline monomer. The

electrolyte utilized for the synthesis of PANI was 1 M perchloric acid, which produced smooth films at relatively fast growth rates when comparison to other acidic electrolytes such as HCl, H₂SO₄, and HNO₃.⁷⁵ The oxidation of aniline to anilium cations is followed by the sequential increase in surface nucleation of PANI during subsequent cycles.⁷ Figure 3.1 shows the polymerization of aniline on GC electrode in solutions containing 0.25 M aniline in 1 M HClO₄. The voltammogram shows the growth of the polymer in addition to two distinct electrochemical processes: (A, A') and (B, B'), which correspond to protons/anions uptake and expulsion. The corresponding half-wave potential for each reversible redox process is calculated as follow:⁷⁶

$$E_{1/2} = \frac{E_{pa} + E_{pc}}{2}$$

The half wave potentials are $E_{1/2} = 0.080$ V and $E_{1/2} = 0.726$ V for the proton, and anion vs. Ag/AgCl, respectively. When the potential is scanned in the negative direction PANI can be reduced and becomes the electron-rich leucoemeraldine. The change in oxidation state results in an uptake of protons (peak A) to maintain charge neutrality in the system. When the potential is reversed, protons are expelled from the polymer, as the electrostatic charge becomes more positive (peak A'). As the potential is scanned to more positive potentials, PANI is oxidized and becomes electron-deficient. The uptake of ClO₄⁻ anions (peak B) neutralizes the electrostatic positive charge of the more oxidized polymer. The expulsion of anions (peak B') occurs when the applied potential is reversed and scanned to more negative potentials. The increase in current during this process corresponds to an increase in thickness of PANI as it nucleates on the electrode surface and previously deposited polymer. Finally, an oxidation/reduction process at ~0.426 V emerges with each sequential scan becoming more apparent as the thickness of

the polymer increases. The voltammetric waves can be attributed to the formation of over oxidized short chain oligomeric materials that are trapped in the polymer matrix.

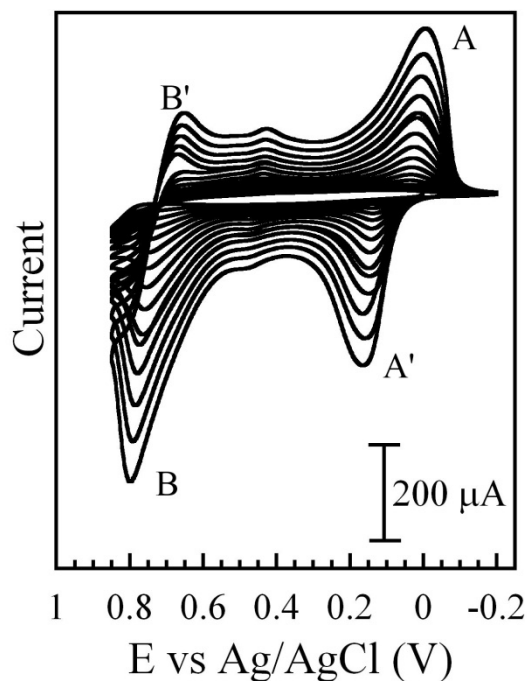


Figure 3.1: Cyclic voltammetry response of a 0.0707 cm² glassy carbon electrode in 0.25M aniline in 1M HClO₄ at 0.01 V/s scan rate

3.2.2 Electrochemical synthesis of PANI/metal composites

The proton/anion doping behavior of PANI can be utilized to introduce novel chemical species into the polymer, specifically, metal anions to be dispersed in the polymer using the normal doping characteristics of the polymer. The deposition of metal species in PANI is achieved through anion doping. The uptake of metal anions (AuCl₄⁻, PdCl₄²⁻, and PtCl₄²⁻) occurs at the positive potential when the polymer is oxidized. However, the metal anions are not expelled from the polymer during the negative scan. Rather, they are reduced into the polymer as the potential is scanned to more negative

values. The metal particles are dispersed in the polymer based on the electrostatic interaction of the polymer with the corresponding metal anions. The deposition of metal was carried in a solution containing 5mM KAuCl_4 , K_2PdCl_4 , or K_2PtCl_4 . The reduction processes are provided below:⁸²



Figure 3.2 shows the reduction of AuCl_4^- to Au (0) in PANI. The metal anions are brought in at approximately 0.70 V. The reduction of AuCl_4^- starts at approximately 0.50 V, and becomes more prominent at 0.326 V. The reduction is accompanied by the expulsion of Cl^- ions based on the equation provided. The subsequent scans show a decrease in anion uptake, which suggests that the nitrogen sites in the polymer become less available as more metal is deposited in PANI. The shift of the anion uptake peak to more positive potentials with each scan implies that the process is less thermodynamically favorable. The anions have to penetrate deeper within the polymer to reach the free nitrogen sites as these sites become blocked by Au metal reduction.

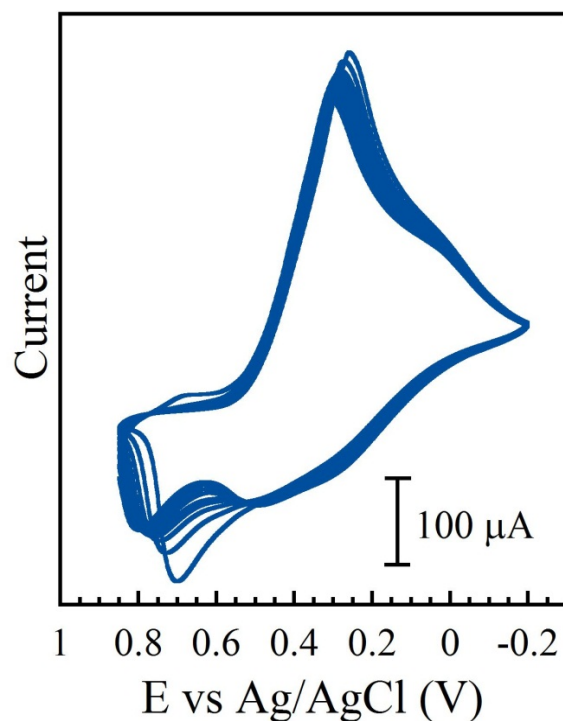


Figure 3.2: Cyclic Voltammetry Response of gold deposition on a 0.0707 cm^2 PANI coated GC working electrode at 0.01 V/s scan rate

Figure 3.3 presents the deposition of palladium into PANI. The anion uptake occurs at approximately the same potential as gold, 0.65 V . However, the anodic peak current increases with each scan rather than decreasing like gold. There is no potential shifting observed in this case. The result suggests that palladium might interact differently with the polymer than gold. Specifically Pd deposition may be more favorable at existing Pd deposits rather than the polymer causing an increase in the current as the Pd surface area increases. The reduction of palladium initiates at 0.55 V as the potential is scanned to more negative potentials, and the cathodic peak potential for the reduction of palladium is observed at 0.116 V . The reduction peak of palladium is broader when compared to gold suggesting that the reduction may be occurring at both polymer and Pd metal sites. In

addition, the broad band encompasses the region for the expulsion of Cl^- anions which may contribute to the broad voltammetric wave.

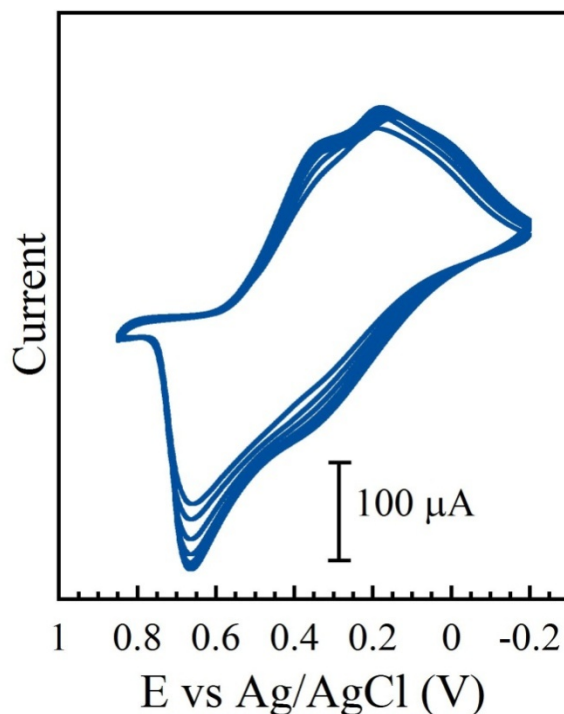


Figure 3.3: Cyclic Voltammetry Response of palladium deposition on 0.0707 cm^2 PANI coated GC working electrode at 0.01 V/s scan rate

Figure 3.4 shows the deposition of platinum particles into PANI. The anion uptake occurs approximately at 0.65 V , which is in agreement with gold and palladium. However, the uptake of platinum anions shows no noticeable decrease increase in current with each voltammetric cycle. There is also very little shift in potential in comparison to Au or Pd reduction. The data suggests that the Pt precursor and the deposited Pt interact with the polymer differently than both Au and Pd species. When the potential is scanned to more negative potentials, the Pt anions are reduced to metallic Pt, which is

accompanied by the expulsion of Cl^- anions. The reduction of Pt is initiated at approximately 0.50 V, and the peak potential of the reduction is observed at 0.350 V.

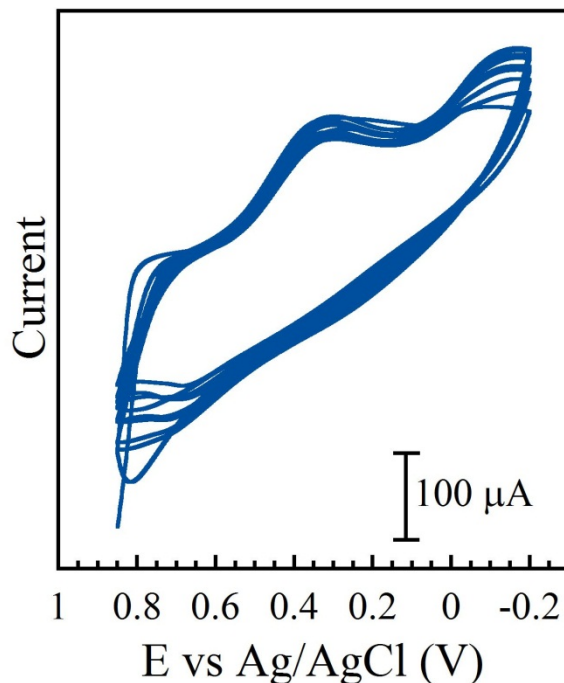


Figure 3.4: Cyclic Voltammetry Responses of platinum deposition on 0.070 cm² PANI coated GC working electrode at 0.01 V/s scan rate

The reduction of metal anions into PANI is initiated and occurs at lower reduction potentials comparing to the literature values in all cases, which implies that the reduction of metal anions is actually less thermodynamically favorable in these experimental settings. The re-oxidation of the metals does not occur because it is embedded in the polymer, and the chemical species required are not available internally to facilitate the formation of the metal anions on the reverse scan. The electrostatic interaction of the metal anions with the polymer results in a loss of activity at nitrogen sites after metal reduction. Metal anions are reduced into the polymer by the amine nitrogens resulting in

a point of contact between the two species.⁵⁰ The polymer becomes more oxidized in the process because the oxidation of the nitrogen sites is not chemically reversible. Negatively charged species (anion doping) are retained in the polymer matrix to compensate for the change in oxidation state of the polymer. Therefore, the resulting composites contain an oxidized PANI with direct chemical linkages between the polymer and the metal.

3.3 Characterization

3.3.1 Acid doping

The oxidation state of the polymer changes as the potential is varied. The change in oxidation state results in an uptake or expulsion of either protons or anions to maintain the charge neutrality in the polymer matrix. Perchloric acid ($pK_a = -7$) was specifically used to dope the polymer because the perchlorate anions (ClO_4^-) and amine groups have strong interactions when compared to other anions from acids such as HCl, H_2SO_4 , or H_3PO_4 . Specifically, perchlorate anions are able to form hydrogen bonds with hydrogen atoms within the aromatic rings of PANI. In addition, they are electron-donors; therefore, they stabilize the quinoid structures within the polymer.⁷⁶

The proton doping of the polymer was performed in 1M $HClO_4$. The doping prior to the metal reduction, which is designated as 1st acid doping, is typically the proton doping of PANI on a GC working electrode. The proton doping after the metal reduction, 2nd acid doping, is the doping of PANI/metal composites in the acid solution. These processes are shown in Figure 3.5, 3.6 and 3.7. The oxidation/reduction processes associated with proton/anion uptake and expulsion can be identified in the voltammetry.

The half-wave potential values of each composite for 1st and 2nd acid doping are presented in Table 1. After metal reduction, the protons peaks of 2nd acid doping shift to more positive potential. The shift in potential implies that the uptake and expulsion of protons is achieved more easily. The anions peaks of 2nd acid doping, on the other hand, shift to more negative potentials, which implies that more energy required for the anions expulsion. This could be due to the metal blocking nitrogen sites in the polymer which would likely influence the interaction of positive and negative ions in the polymer with free nitrogen groups. In addition, the metal physically blocks the nitrogen sites; therefore, the anions have to diffuse further within the polymer.

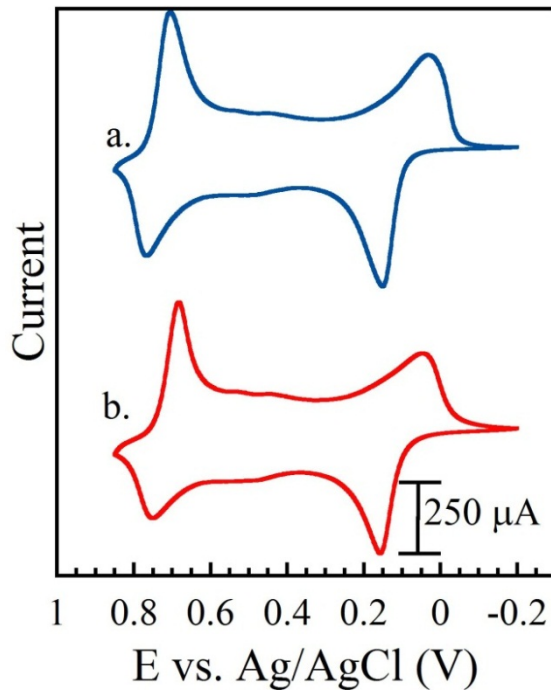


Figure 3.5: Acid doping of PANI/Au composites on a 0.0707 cm² GC working electrode in 1M HClO₄ (a) 1st acid doping and (b) 2nd acid doping

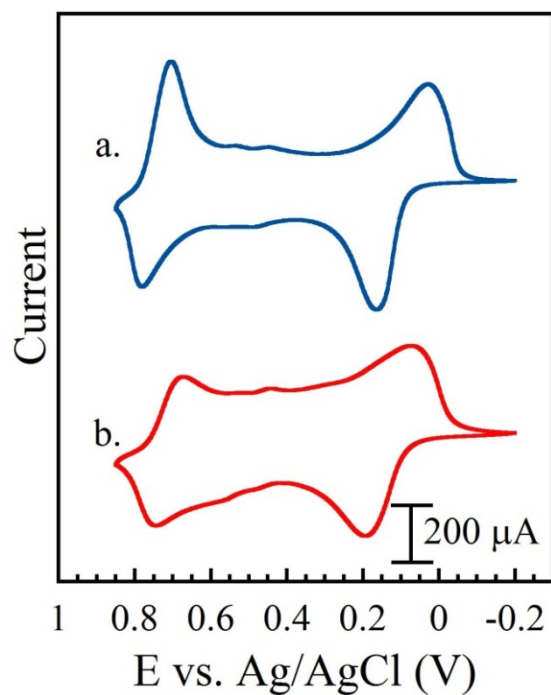


Figure 3.6: Proton doping of PANI/Pd composite on a 0.070 cm^2 GC working electrode in 1M HClO_4 (a) 1st acid doping and (b) 2nd acid doping

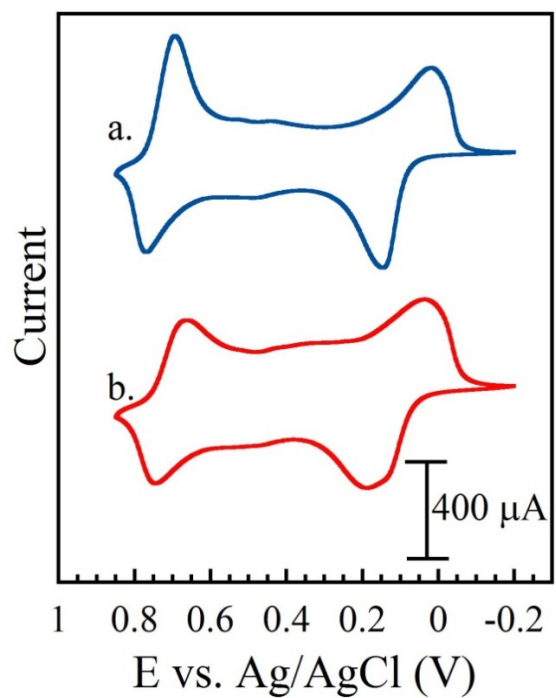


Figure 3.7: Proton doping of PANI/Pt composite on a 0.070 cm² GC working electrode in 1M HClO₄ (a) 1st acid doping and (b) 2nd acid doping

The corresponding decrease in current and charge for proton and anion doping is observed after the introduction of metals. It is an indication that reduction produces metal particles that physically block nitrogen sites, therefore blocking both proton and anion uptake. Integration of the charge (Q) associated with proton expulsion before and after metal reduction is used to determine the reduction in active nitrogen sites in the polymer. The charge integration for each composite is presented in Table 2.

Table 1: The half-wave potential values of 1st and 2nd acid doping of PANI composites

	PANI/Au		PANI/Pd		PANI/Pt	
	H ⁺	ClO ₄ ⁻	H ⁺	ClO ₄ ⁻	H ⁺	ClO ₄ ⁻
1 st doping	0.092 V	0.737 V	0.096 V	0.743 V	0.082 V	0.732 V
2 nd doping	0.101 V	0.717 V	0.132 V	0.710 V	0.112 V	0.703 V

Table 2: Charge integration of proton expulsion for 1st and 2nd acid doping of PANI composites

	PANI/Au	PANI/Pd	PANI/Pt
1 st doping	4.435 × 10 ⁻³ C	3.846 × 10 ⁻³ C	3.987 × 10 ⁻³ C
2 nd doping	3.548 × 10 ⁻³ C	2.092 × 10 ⁻³ C	2.525 × 10 ⁻³ C

The average decrease of charge for the proton expulsion is $20\% \pm 1$, $46\% \pm 4$, and $37\% \pm 3$ for composites with Au, Pd, and Pt, respectively. These results indicate that approximately 20% of the nitrogen sites within the PANI/Au, 46% within PANI/Pd, and 37% within Pt are blocked by the metal particles for these samples. The percentages are influenced by the number of cycles employed, and can be controlled by increasing or decreasing the number of metal reduction cycles.

3.3.2 FT-IR

While the proton uptake/expulsion provides information regarding the interaction of the reduced metals with the nitrogen groups in the polymer, FTIR spectroscopy can be used to qualitatively evaluate changes in functional groups including benzenoid, quinoid, imine, and amine moieties. FTIR spectroscopy was used to evaluate the PANI/metal composites chemical composition relative to pristine PANI. The goal is to correlate changes in chemical functional groups as a function of metal uptake into the polymer matrix. Specifically, oxidation/reduction of the ring structures and changes in the nitrogen functional group bands are expected with the reduction of metal into the polymer. Figure 3.9 presents the spectra of PANI and its composites. Characteristic absorption bands ($\pm 5 \text{ cm}^{-1}$) are presented in Table 3. The band at $800 - 860 \text{ cm}^{-1}$ corresponds to the out-of-plane (oop) bending of C-H bond within the aromatic rings.⁷⁷ The uptake of metal into the polymer causes this band to shift to a higher wavenumber. This might be due to the influence of metal particles at the nitrogen sites. The large relative shift in energy for the PANI/Au composite indicate the gold particles may influence the electron density in the polymer in comparison to palladium and platinum. The intensity of this band also increases in all PANI/metal composites in comparison to

the pristine polymer. Benzenoid units are oxidized in the polymer during the reduction of the metal precursors. The intensity of oop C-H band is likely influenced indirectly by this process. It is possible that metals deposited at nitrogen sites in close proximity to the aromatic hydrogens influencing the intensity of the band. The C=N stretching of the quinoid rings is observed at 1126 cm^{-1} for PANI.⁷⁸ A shift to higher energy (1142 cm^{-1}) is observed on all the PANI composites. C-N stretching is observed at 1302 cm^{-1} for PANI,⁷⁶ and at slightly higher energy for all PANI composites. The metal interaction with nitrogen sites directly influences the vibration of C=N, and C-N bonds. PANI is oxidized to a higher oxidation state as metals are reduced in the film. Therefore, the presence of metals and higher oxidation states causes the shift of this band to higher energy.

While aromatic C-H stretching bands at 3000 cm^{-1} are not influenced by the introduction of metals, the N-H stretching band of secondary amines at 3300 cm^{-1} diminishes when metals are reduced in the polymer. The electrochemical responses suggest that the metal particles are deposited at the nitrogen sites, and oxidize the amines. The change in intensity of the N-H bands in the FTIR is consistent with the electrochemical data that indicate the reduced metals physically block the nitrogen sites of the polymer.

Table 3: FT-IR absorption bands of PANI and PANI/metal composites

	PANI	PANI/Au	PANI/Pd	PANI/Pt
Oop C-H bending	827 cm ⁻¹	842 cm ⁻¹	827 cm ⁻¹	825 cm ⁻¹
C=N stretching	1126 cm ⁻¹	1142 cm ⁻¹	1142 cm ⁻¹	1142 cm ⁻¹
C-N stretching	1302 cm ⁻¹	1316 cm ⁻¹	1306 cm ⁻¹	1309 cm ⁻¹
Aromatic C=C (Benzenoid)	1481 cm ⁻¹	1497 cm ⁻¹	1492 cm ⁻¹	1489 cm ⁻¹
Aromatic C=C (Quinoid)	1565 cm ⁻¹	1578 cm ⁻¹	1574 cm ⁻¹	1566 cm ⁻¹

The characteristic benzenoid and quinoid unit bands of polyaniline are observed at 1481 and 1565 cm⁻¹, respectively.⁷⁹ The band at 1481 cm⁻¹ is attributed to the aromatic C-C stretching vibration. The band at 1565 cm⁻¹ is attributed to the conjugated C=C stretching of quinoid units. The spectra of PANI/Au, PANI/Pd (II), and PANI/Pt (II) show a shift to higher energy for these two bands, which is indicative of a change in electron density for the polymer. This suggests that all three metals withdraw electrons from nitrogen groups in the polymer, and shift the bands associated with the primary and secondary functional groups to a higher energy. The results are consistent with the shift to higher energy for the C-C and C-N stretching bands as noted earlier. The characteristic bands for benzenoid (~1500 cm⁻¹) and quinoid (~1590 cm⁻¹) can be used to qualitatively estimate the polymer oxidation state based on the changed in intensity of the bands. The integrated areas associated with these two bands can be used to calculate the

ratio (R) of quinoid and benzenoid units providing a measure of the change in oxidation state of the polymer before and after metal reduction. It is presented in Figure 3.8.

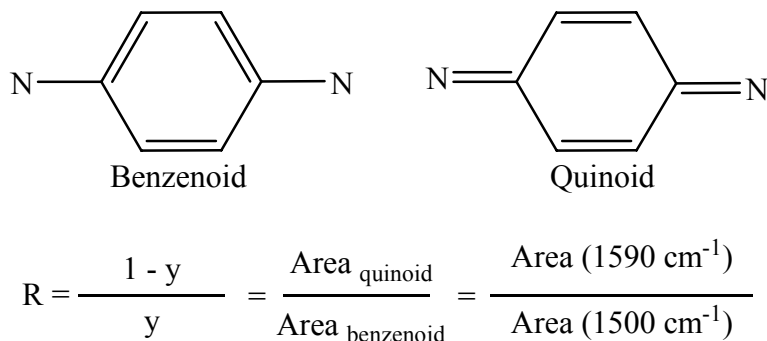


Figure 3.8: PANI units and R ratio of benzenoid and quinoid units

A calculated R ratio for electrochemical PANI is 1.04, which indicates that the polymer contains approximately equal amount of benzenoid and quinoid units. On the other hand, the R ratios for PANI/Au, PANI/Pd, and PANI/Pt are 2.54, 1.32, and 1.26, respectively. The ratios suggest that there is relatively higher amount of quinoid than benzenoid units, and the polymer is oxidized as metal reduction occurs in comparison to pristine polymer. The R ratio of PANI/Au is much higher compared to PANI/Pd or PANI/Pt, which indicates that the polymer is more oxidized for PANI/Au. These results, however, do not correlate with the acid doping data, which showed that only 20% of nitrogen sites are blocked by Au particles, in comparison to 46% in PANI/Pd and 37% in PANI/Pt. This is probably due to a relatively strong interaction between the polymer and Au particles when compared to other metals. Specifically, Au may withdraw more electron density from the polymer; thereby oxidizing it to form more quinoid units.

Further studies will be conducted to determine that relationship between the doping and specific metals as it correlates with blocking of nitrogen sites.

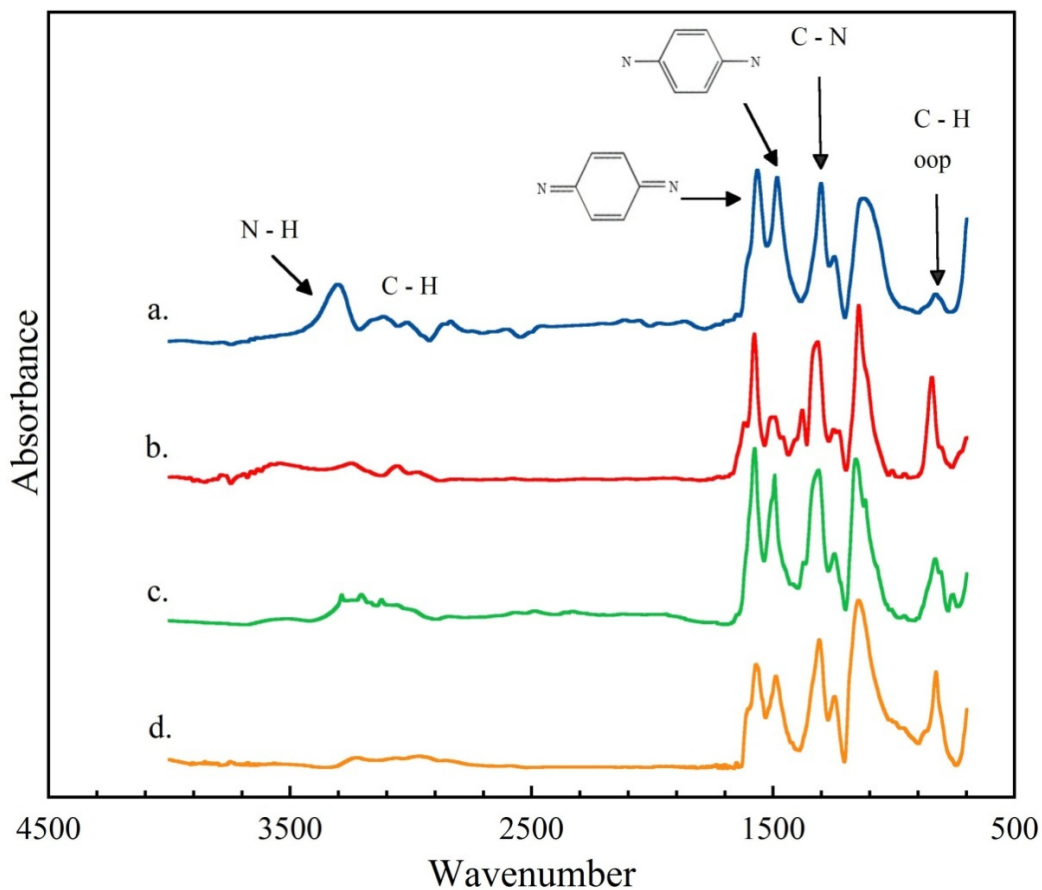


Figure 3.9: FT-IR spectra of PANI and PANI/metal composites (a) PANI, (b) PANI/Au, (c) PANI/Pd, and (d) PANI/Pt

3.3.3 Thermal gravimetric analysis

Thermal gravimetric analysis can provide qualitative information about the composites and their compositions including the thermal properties of the polymer and the amount of metal incorporated. The analysis provides a measurement of the polymer and metal composition based on the mass change as a function of temperature. The

largest mass loss corresponds to the thermal degradation and loss of the polymer component as water and CO₂ gas in air atmosphere. The metals do not evaporate under the thermal conditions employed and are retained. Therefore, the percentage mass of metal in the composite is the final value obtained in the measurement. The thermal degradation of PANI and its composites are presented in Figure 3.10.

The thermal degradation of acid doped PANI occurs in three stages. The first stage with 7% mass loss is associated with the loss of water in the polymer below 100 °C.⁸⁰ The second stage occurs between 100 °C to 320 °C, which is attributed to the loss of anions ClO₄⁻ in the polymer. Finally, the decomposition of the polymer backbone begins at the temperature above 320 °C, and ends at 620 °C. Overall, the electrochemical PANI yields a mass loss of 98.9% ± 0.8, which is consistent with the full thermal degradation and loss of the organic material in the measurement.

The thermal degradation of PANI/metal composites follows a similar trend because the polymer component must go through the same thermal degradation cycle. Therefore, the water loss occurs at below 100 °C accounting for 3 – 4% mass loss of the composites. The excess anions such as residual ClO₄⁻ and Cl⁻ from the reduction of metal anions (AuCl₄⁻, PdCl₄²⁻, and PtCl₄²⁻) are off gassed as the temperature increases. The degradation of the polymer of the composites occurs at 50 °C lower than the degradation temperature of pure PANI suggesting that the metal influences the structure and thermal stability of PANI.⁸¹ The final temperature observed for the complete loss of polymer varies among the composites with the degradation of PANI/Au, and PANI/Pd at 530 °C, and 515 °C, respectively. The degradation of PANI/Pt is completed at a much higher temperature of 670 °C. A slight increase in mass for PANI/Pd is observed after the

degradation of the polymer at approximately 600 °C. This could be probably due to the formation of PdO since the TGA experiments were carried in air atmosphere. The mass percentages of composition of metal that remains after the degradation of the polymer for PANI/Au, PANI/Pd and PANI/Pt are approximately $17.7 \pm 6.6 \%$, $20.9 \pm 0.8 \%$, and $16.6 \pm 1.2 \%$, respectively.

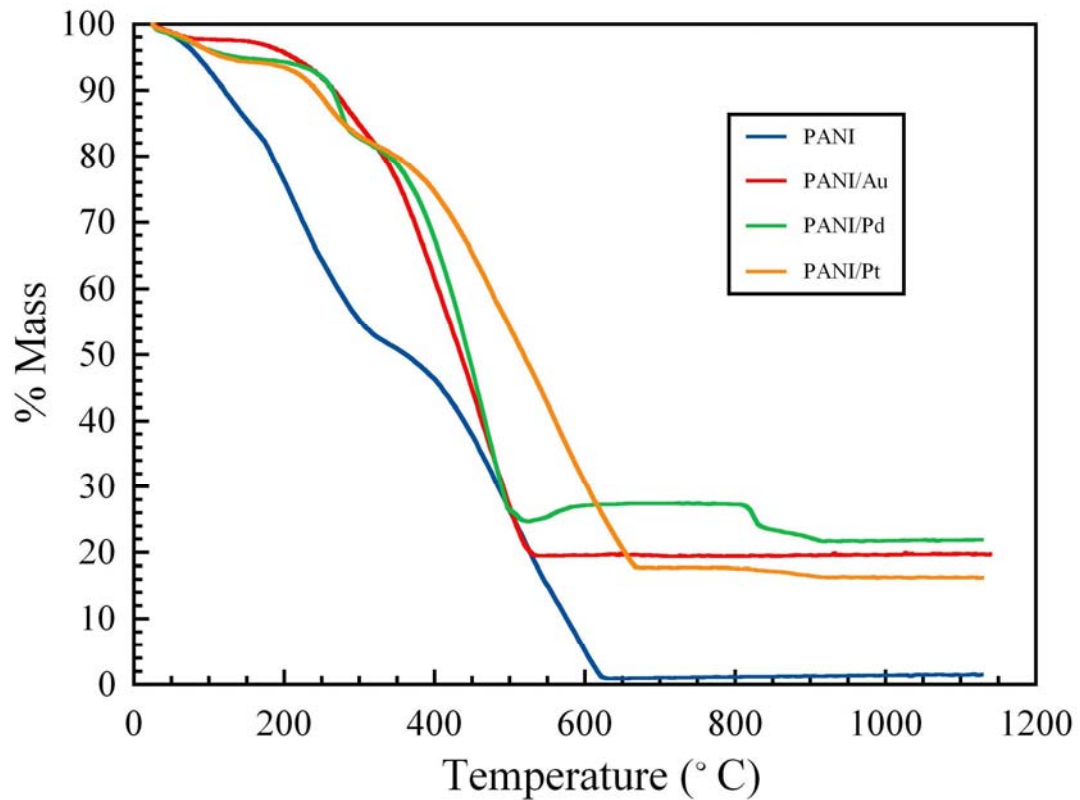


Figure 3.10: Thermal degradation of PANI and PANI composites

3.3.4 Conductivity

The conductivity of PANI and PANI composites was measured using a four-point probe to determine the influence of the metals on the polymer electronic properties.

PANI and its composites were synthesized electrochemically, and then pressed into

pellets with 0.4-cm radii, and approximately 0.05-cm thickness for the four-point probe measurements. The conductivity has been previously reported for doped PANI (2-10 S/cm).⁵⁰ The experimental conductivity of PANI and PANI/metal composites were calculated from the measured resistances base on the previously presented equations. The conductivity values, σ , of PANI and PANI composites are presented in Table 4. Among the composites, PANI/Au has a higher measured conductivity relative to PANI/Pd and PANI/Pt. This data correlates with the acid doping data, which shows that there are more nitrogen sites available in PANI/Au composites after the metal reduction. However, according to FT-IR data, PANI/Au has the highest R ratio, which suggests that the polymer is more oxidized for this composite, and hence should be less conductive. A possible explanation of this behavior is that Au particles might interact with polymer differently than Pd and Pt to delocalize the charges in the composites, and make it more conductive. The measured conductivity of electrochemically synthesized PANI is 2.0 ± 0.2 S/cm, which is in agreement with the literature.⁵⁰ Although PANI composites have higher conductivity values than an insulator, they are significantly lower than the value of pure PANI. The results are consistent with a higher oxidation state of PANI after metals are reduced into the polymer. In addition the metal reduction was not performed in acid solutions and no additional acid doping was conducted with the PANI/metal composites used in the conductivity experiments. Therefore, the values represent the inherent conductivity of the polymer/metal composites. However, the values for all three composites are significantly higher than the values obtained for the undoped emeraldine, which has the reported value in the range of $10^{-10} - 10^{-8}$ S/cm.^{6,7} The data suggests that in spite of the reduced proton doping and increase in oxidation state that the reduced

metal may contribute to maintaining the conductivity of the polymer in the absence of acid doping.

Table 4: Conductivity values of PANI and PANI/metal composites

PANI	PANI/Au	PANI/Pd	PANI/Pt
2.0 ± 0.2	0.66 ± 0.05	0.023 ± 0.002	0.157 ± 0.005
S/cm	S/cm	S/cm	S/cm

3.4 Conclusion

Metal nanoparticles were incorporated into PANI utilizing cyclic voltammetry. The presence of metals and their influence on the polymer was confirmed by electrochemical, FT-IR and TG data. The acid doping study suggests that all metals were reduced into the polymer and interacted with the nitrogen sites. The study also showed the loss of proton and anion doping after metal reduction, which confirmed that the metals physically blocked the nitrogen sites based on decreasing proton/anion doping. Spectroscopic data confirmed that the polymer changed to a higher oxidation state after the metal reduction. In addition, TG data provided the approximate amount of metal in the composites, which can be adjusted by varying the reduction cycles during the synthesis. The presence of metals also influences PANI's thermal and electrical properties. The TGA data suggested that PANI/metal composites were less thermally stable than pristine PANI due to the presence of metal at the nitrogen sites, which acted as dopants. Finally, while

PANI/metal composites were less conductive than pure PANI, they showed higher conductivity values than an undoped emeraldine base.

CHAPTER 4

ELECTROCHEMISTRY OF PANI/METAL COMPOSITES IN BASIC SOLUTIONS

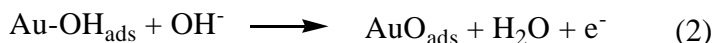
4.1 Introduction

Metals including Pt and Pd are often used as catalysts for methanol oxidation. However, strong adsorption of species at the catalyst surface is a significant issue with these materials in acidic solutions, which reduces catalytic efficiency. Basic solutions have recently been explored as an alternative to acidic solutions for methanol oxidation. Surface reactions in basic solutions that suppress poisoning possibly increase the catalytic efficiency relative to the same metals in acidic solutions.⁸³ The uptake and dispersion of metal nanoparticles in a polymer supporting matrix can also reduce the adsorption of poisonous species on the catalyst surfaces.⁸³ However, the mechanism for reduced poisoning at metal surfaces in PANI composites has not been determined. The oxidation of methanol on PANI/metal composites has higher catalysis efficiency and less poisoning relative to bulk metal surface. In addition, the conductivity of PANI/metal composites is demonstrated in basic solutions. Traditionally PANI conductivity is lost in basic solutions due to the deprotonation of polymer. However, catalysis is observed for all PANI/metal composites. The results suggest that PANI/metal composites can be used at any pH, extending the possible applications of the polymer into areas traditionally precluded.

4.2 Electroactivity of PANI/Au in hydroxide

The interaction of a gold surface with OH⁻ ions has been examined recently.^{84,85} The adsorption of OH⁻ at Au surfaces is initiated at approximately -0.356 V according to

equation 1, and increases as the potential is scanned more positive.⁸⁴ The formation of AuO occurs at a potential > 0.294 V according to equation 2.⁸⁵



The Au surface can be reconditioned as the potential is reversed to more negative values, where AuO is reduced. The desorption of OH^- ions completes at a potential -0.356 V.⁸⁵ Figure 4.1 presents cyclic voltammograms of PANI/Au composite, and a gold disc electrode in 1M NaOH solution (pH ~ 14). The electrode was cycled between -0.4 V and 0.75 V at a scan rate of 0.01 V/s. The current responses have been divided by the geometric area of the electrode for direct comparison. The cyclic voltammogram of the Au electrode is shown in Figure 4.1a. The current response is attributed to an interaction between the gold surface and hydroxide ions. The formation of AuO is observed at 0.326 V vs. Ag/AgCl as the potential is scanned positively, which agrees favorably with the literature values for the surface processes. When the potential is reversed, AuO is reduced back to Au at 0.075 V. The small cathodic current observed at approximately -0.150 V might be due the reduction of a monolayer AuO, and the desorption of OH^- ions. The electrochemistry shown is indicative of the reactions at Au surfaces. The polymer acts as a conductive template which allows surface reactions at Au surface embedded in PANI. The anodic current is observed at 0.308 V, which corresponds to the formation of AuO on the Au particles' surfaces. The oxidation of the gold surface of PANI/Au composite occurs at a less positive potential comparing to the Au disc electrode. The result indicates that the oxidation of the gold surface is more thermodynamically favorable at the Au disc electrode. On the other hand, the reduction of AuO, and the

desorption of OH⁻ ions occur at more positive potentials, 0.087 V and -0.131 V, on the PANI/Au composite. It implies that the reduction of AuO is achieved under more thermodynamically favorable conditions. In addition the current density indicates the surface area on the PANI/Au composite is higher when compared to the surface area of the gold disc electrode. An integration of the charge density associated with the reduction of AuO on the metal surface presented in Table 5 shows an increase of 71% for the PANI/Au composite in comparison with the gold disc electrode for the same geometric areas. The above results correspond to the surface interaction between Au nanoparticles in the composite and OH⁻ ions in the solution, which occurs at the surface of the composites. In order to receive the current responses at the electrode surface, the electrons must be shuttled from those metal surfaces, through the inner PANI chains, to the electrode surfaces. When the composites are immersed in basic solutions, therefore PANI is deprotonated, and should lose its conductivity. However, the polymer maintains its conductivity and electrons are still transferred along the PANI chains to reach the electrode surface during the oxide formation/reduction. The study of PANI/Au in a basic solution suggests that metal must contribute to delocalizing electron density in the polymer, enhancing the conductivity in solutions with pH values greater than 4.

Table 5: Charge densities of negative scans (cathodic peak) for PANI/Au and Au disc electrode in 1M NaOH

Au disc	PANI/Au
$8.535 \times 10^{-4} \text{ C/cm}^2$	$2.992 \times 10^{-3} \text{ C/cm}^2$

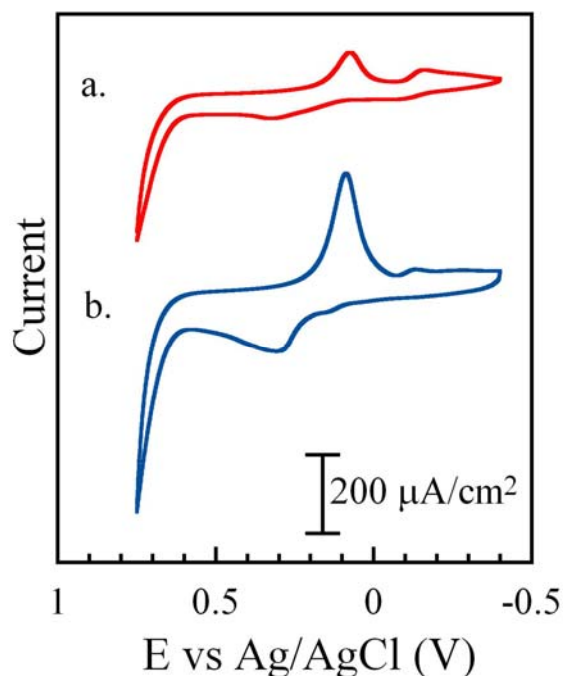


Figure 4.1: Cyclic voltammetry responses of gold in 1M NaOH at a scan rate of 0.01 V/s
 (a) Au disc electrode $d = 2$ mm (steady-state), (b) PANI/Au on GC electrode $d = 3$ mm
 (steady-state)

4.3 Electro-oxidation of alcohols

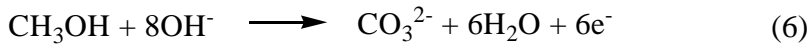
4.3.1 Electro-oxidation of methanol

Recent literatures have shown that an absence of oxides on Au surface makes it a promising catalyst for methanol oxidation.^{64,70,86} Previous studies examine the electrocatalytic activity of Au, and show that the nanoparticles which have a rough surface with different crystallographic orientations exposed exhibit a high activity in basic solutions.^{64,70,87,88} The poisoning effect on the Au surface has been attributed to adsorption of CO during methanol oxidation at the metal surface, which blocks further oxidation. CO can be electrochemically reduced at metal surfaces at high positive potentials greater than 0.544 V. The possible mechanism for the reactions is presented

below. However, previous studies show that the poisoning is reduced during the oxidation of methanol in basic solutions.^{84,88}



In the study of Borkowska et al. methanol oxidation on Au surface in a basic solution occurs in two independent regions according to the following the equations:⁸⁸



The formation of formate ions (equation 5) occurs at potentials more negative of the formation of AuO monolayer at potential at 0.294 V. The formation of carbonate ions (equation 6) occurs at far more positive potentials greater than 0.294 V, which is unlikely due to the formation of AuO. The applied potential (-0.6 V to 0.2 V) suggest that methanol was oxidized according to equation 5. Borkowska and co-workers suggested a pH-dependent mechanism for this reaction, where $\bullet\text{CH}_2\text{OH}$ is a radical that continues to react with hydroxide ion based on the following reactions.⁸⁸

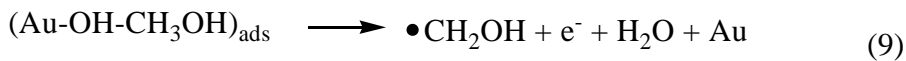
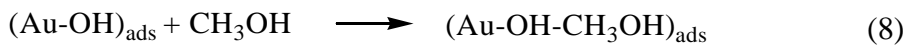
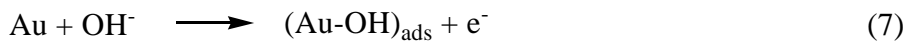


Figure 4.2 presents the cyclic voltammetry responses of a gold disc electrode and PANI/Au composite in a 1M CH₃OH in 1M KOH solution. The electrodes were cycled between -0.6 V and 0.2 V at a scan rate of 0.01 V/s. Figure 4.2a presents the current

response of the Au disc electrode in the CH₃OH solution. The result shows no methanol oxidation process, but rather an adsorption/desorption process of OH⁻ anions on the gold surface. An anodic peak is detected at approximately -0.15 V, which might be attributed to the adsorption of OH⁻ anions on the Au surface, which starts at 0.356 V as stated previously. As the potential is scanned towards more positive values, the Au surface is covered with more OH⁻ ion. However, there is no complete formation of AuO since the potential ends before the oxide formation potential 0.294 V. When the potential is reversed towards the negative values, a cathodic peak is observed at approximately -0.2 V. This peak corresponds to the desorption of OH⁻ anions, which was observed earlier at -0.015 V. At further positive potentials, the current response decreases and flattens at approximately 0.3 V, which might be due to a complete desorption of OH⁻.⁸⁵

In contrast to the Au disc electrode, methanol oxidation is observed at the PANI/Au composite in solutions containing 1M CH₃OH and 1M KOH. Figure 4.2b shows the steady-state cyclic voltammetry response of PANI/Au, and Figure 4.2c shows the complete 20 cycles of PANI/Au between -0.6 – 0.2 V with a scan rate of 0.01 V/s. The composite shows two voltammetric waves, which are associated with the oxidation of methanol. When the potential is swept towards the positive values (positive scan), methanol is oxidized at -0.133 V vs Ag/AgCl. When the potential is reversed towards the negative values (negative scan), methanol is oxidized at -0.121 V vs Ag/AgCl. The potential difference might be due to the poisoning of the metal surface. However, the potential difference is relatively small ~ 12 mV, which agrees with previous literatures that poisoning effect isn't significant in our system. The current density during the positive scan is significantly larger than during the negative scan. The charge density is

integrated for both current peaks for comparison, and presented in Table 6. The charge density during the negative scan decreases approximately 79% when compared to the positive scan. The process is minimized based on the adsorption of OH⁻ anions at Au, which results in the the formation of AuO on the surface during the positive scan. Although the formation of AuO typically occurs at 0.294 V as stated above, Figure 4.2a shows that there the oxidation of Au-OH_{ads} to form AuO occurs during the positive scan. When the potential is reversed towards the negative values, AuO is reduced at approximately -0.2 V. The AuO must be partially reduced to observe methanol oxidation during the negative scan. Therefore, the charge density observed for the negative scan is significantly diminished during the positive scan. While Au disc electrode shows no catalytic activity for methanol oxidation, PANI/Au can perform as a catalyst for the reaction with less poisoning and relatively high efficiency. The catalytic activity observed in PANI/Au might be due to a smaller size of the particles, and their surface morphology. In addition, the solution pH, and the dispersion of Au particles in the polymer decreases the poisoning effect and increases the catalysis efficiency.⁸³

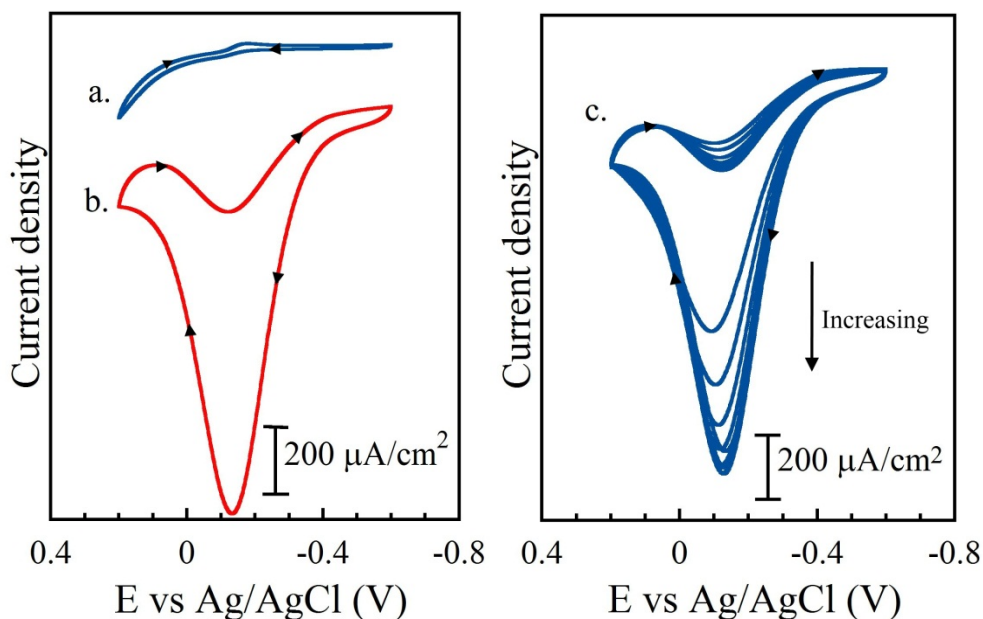
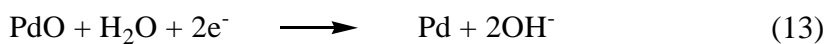
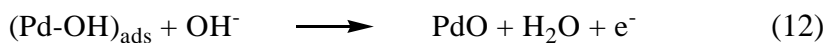
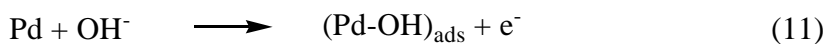


Figure 4.2: Cyclic voltammetry responses of gold in 1M CH₃OH in 1M KOH at a scan rate of 0.01 V/s (a) Au disc electrode d = 2 mm (steady-state), (b) PANI/Au on GC electrode d = 3 mm (steady-state), and (c) PANI/Au (complete 20 cycles)

Methanol oxidation at Pd surface can be compared to Au surfaces. While OH⁻ ions enhance methanol at the Au surface, the adsorption of OH⁻ ions on the Pd surface simply generates an oxide, PdO. The oxide then inhibits the adsorption of methanol and decreases the catalysis efficiency. The formation of PdO occurs at ~ -0.25 V (equation 12) during the positive scan and is reduced back to Pd at potential less than -0.38 V (equation 13) based on the following reactions.⁸⁹



The proposed mechanism of methanol oxidation at Pd surface is presented below (equation 14 – 17). The oxidation of methanol occurs with the formation of CO on the Pd surface. Further reactions of adsorbing CO on Pd with oxygen and OH⁻ will remove the species from the metal surface, and regenerate the metal. Possible reactions are according to equation 18 – 20.⁷⁴

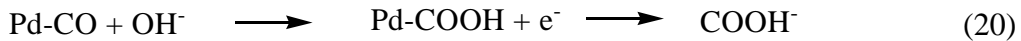
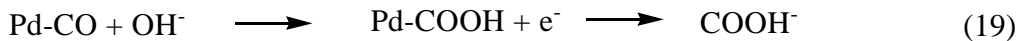
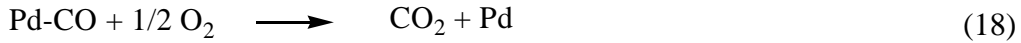
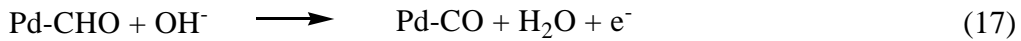
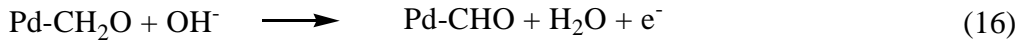
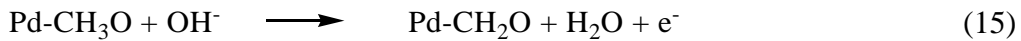
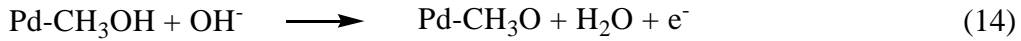


Figure 4.3a shows the electrochemical responses of a Pd disc electrode in 1M CH₃OH in 1M KOH solution. During the positive scan, methanol is oxidized on a clean Pd surface at -0.216 V. The adsorption of OH⁻ ions also occurs during the positive scan, and oxidizes the metal surface partially. A second anodic current is observed at -0.296 V during the negative scan, which is attributed to the oxidation of methanol and other adsorption intermediate species on Pd.⁹⁰ The difference in potential, 80 mV, corresponds to the poisoning effect, which is the formation of PdO and adsorption of CO on Pd surface. In addition, the anodic peak during the negative scan has a smaller current density than the first anodic peak. Charge densities associated with the two anodic peaks are integrated, and presented in Table 6. A 78% reduction in charge density shows that

the catalysis efficiency on the Pd electrode surface decreases during the negative scan due to the surface poisoning.

Figure 4.3b and 4.3c presents the cyclic voltammetry responses of PANI/Pd composite in the methanol solution. The oxidation of methanol occurs at -0.229 V during the positive scan, and at -0.299 V during the negative scan. The potential difference between the two peak potentials for PANI/Pd is 70 mV, which is slightly smaller comparing to the Pd disc electrode. The result indicates that PANI/Pd is less subjected to the poisoning effect, which might be due to the dispersion of the metal particles in the polymer. In addition, methanol oxidation occurs at a more negative potential on PANI/Pd composite comparing to the Pd disc electrode, which implies that the process is less thermodynamically favorable on PANI/Pd. However, the current density of PANI/Pd composite is much higher than the current density of the Pd disc electrode. The integrated charge densities for the anodic peaks during the positive scan and the negative scan are $Q = -7.279 \times 10^{-2} \text{ C/cm}^2$, and $Q = -2.141 \times 10^{-2} \text{ C/cm}^2$, respectively. The oxidation of methanol on PANI/Pd during the positive scan is increased by $\sim 77\%$ comparing to the oxidation on Pd electrode. This is due to the increasing surface area of PANI/Pd comparing to Pd disc electrode.

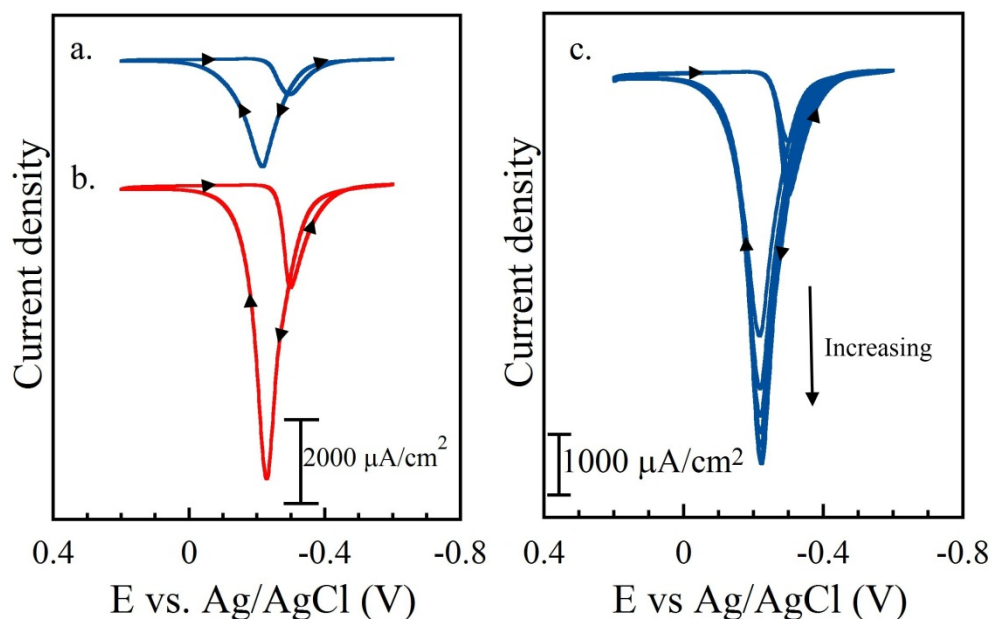


Figure 4.3: Cyclic voltammetry responses of palladium in 1M CH₃OH in 1M KOH at a scan rate of 0.01 V/s (a) Pd disc electrode d = 3 mm (steady-state), (b) PANI/Pd on GC electrode d = 3 mm (steady-state), and (c) PANI/Pd (complete 20 cycles)

Pt is considered one of the most efficient catalysts for methanol oxidation in basic solutions.⁵⁹ One of the main concerns for using Pt is the poisoning on the metal surface. Chemical species such as OH⁻ ions and even the reactant, CH₃OH, adsorbs on the metal surface, or reacts with each other to lowers the catalysis efficiency.⁹² At lower potentials, CH₃OH and OH⁻ ions accumulate on the Pt surface, and generate CO.⁶² Moreover, adsorption of OH⁻ ions increases as the potential increases, and results in the formation of oxides at potential values greater than 0.8 V.⁶⁹ Recent literatures have suggested of dispersing Pt particles in a polymer matrix and basic solutions in order to alleviate the poisoning effect on the metal surface.⁶² Therefore, PANI/Pt was examined for its electrocatalytic activity for methanol oxidation in a basic solution.

The oxidation of methanol on the Pt surface yields different products depending on the applied potential range.⁹¹ At lower potentials < 0.5 – 0.6 V, the oxidation of methanol generates carbonate ions.⁹² At higher potentials, the reaction yields formate ions. The general equations for both products are presented below. A possible mechanism for the reaction was presented in chapter 1.⁶²

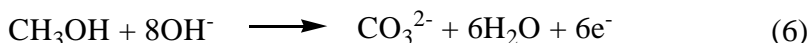


Figure 4.4 shows the electrochemical responses of PANI/Pt composite and a Pt disc electrode in a 1M CH₃OH in 1M KOH solution. The electrodes were cycled between -0.6 V and 0.2 V at a scan rate of 0.01 V/s. Figure 4.4a shows the current response of the Pt disc electrode with two anodic peak currents. When the potential is scanned towards the positive values, an anodic peak current is observed at -0.291 V, which corresponds to the oxidation of methanol on a clean Pt surface. In addition, the adsorption of CH₃OH and OH⁻ ions on the metal surface generates other intermediate species, which aren't completely oxidized during the positive scan. When the potential is reversed towards the negative values, the peak potential during the negative scan shifts to a more negative value, -0.362 V. This peak is attributed to the oxidation of methanol in addition to the removal of adsorbed products on the Pt surface.^{93,94} The potential difference (~ 71 mV) indicates that the metal surface is poisoned with CO or other intermediate species. These species must be removed prior to the oxidation of methanol. It requires more energy (more negative potentials) to remove these species. Therefore, the methanol oxidation occurs at a more negative potential. The current density during the negative scan is smaller than during the positive scan. The charge densities for two anodic peaks are used

to evaluate the catalysis efficiency between the positive and negative scan (Table 6). A 67% reduction in charge density shows that the poisoning on the metal surface decreases its catalytic activity.

Figure 4.4b and 4.4c show the cyclic voltammetry response of PANI/Pt composite for methanol oxidation. The oxidation of methanol during the positive scan on PANI/Pt occurs at -0.237 V, which is less negative comparing to the Pt disc electrode. The result implies that methanol oxidation is more thermodynamically favored on PANI/Pt composite. This might be due to a different surface structure on Pt particles in the composite. Smaller Pt particle with more defects have higher affinity for OH⁻ ions, and enhance the catalytic activity.⁹² The peak potential during the negative scan is -0.320 V, which is also less negative comparing the Pt disc electrode. However, the higher potential difference (83 mV) between the positive and negative scan of PANI/Pt comparing to the Pt disc electrode indicates that the poisoning effect is more pronounced on the composite. This probably is due to a higher affinity of Pt particles for OH⁻ ions, which generates more intermediate species and blocks the metal surface. The charge density during the positive and negative scan is $-2.066 \times 10^{-1} \text{ C/cm}^2$ and $-8.163 \times 10^{-2} \text{ C/cm}^2$, respectively. PANI/Pt exhibits greater charge density than the Pt disc electrode. The charge density during the positive scan of PANI/Pt increases 100% comparing to the Pt disc electrode. This is due to the higher surface area of PANI/Pt composite.

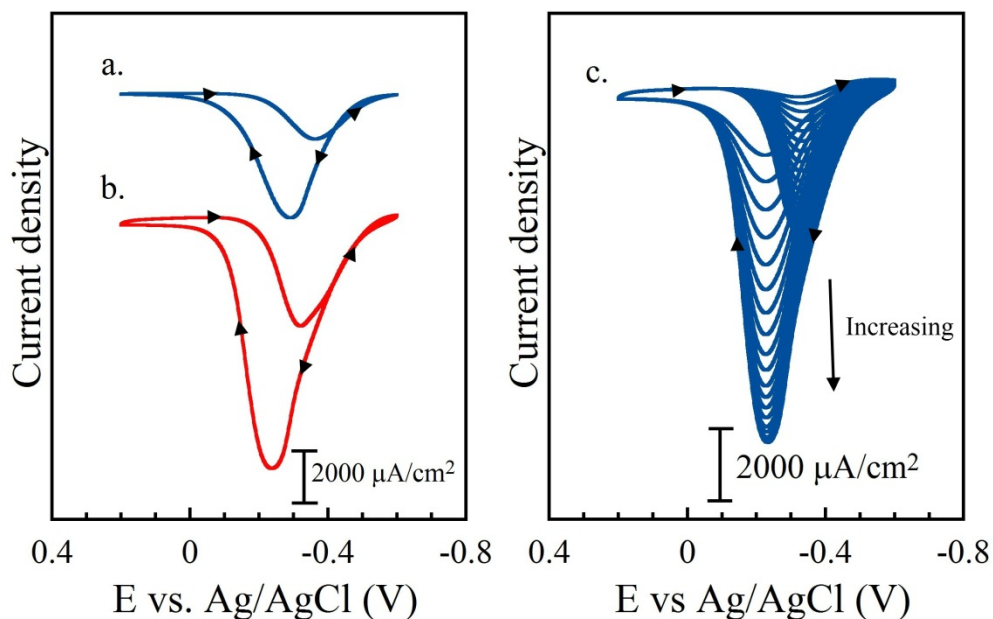


Figure 4.4: Cyclic voltammetry responses of platinum in 1M CH₃OH in 1M KOH at a scan rate of 0.01 V/s (a) Pt disc electrode d = 2 mm (steady-state), (b) PANI/Pt on GC electrode d = 3 mm (steady-state), and (c) PANI/Pt (complete 20 cycles)

Table 6: Charge densities of PANI/metal composites and corresponding disc electrodes for methanol oxidation

	PANI/Au	PANI/Pd	Pd disc	PANI/Pt	Pt disc
Positive scan	-2.195×10^{-2} C/cm ²	-7.279×10^{-2} C/cm ²	-4.102×10^{-2} C/cm ²	-2.066×10^{-1} C/cm ²	-1.032×10^{-1} C/cm ²
Negative scan	-4.634×10^{-3} C/cm ²	-2.141×10^{-2} C/cm ²	-9.076×10^{-3} C/cm ²	-8.163×10^{-2} C/cm ²	-3.424×10^{-2} C/cm ²

PANI/metal composites exhibit higher electro-catalytic activity in comparison to bulk metals. PANI/Pd and PANI/Pt have higher charge density than the corresponding bulk electrodes. This is due to a greater surface area that the composites possess. The Au disc electrode shows no catalytic activity for methanol oxidation. However, methanol oxidation is observed at PANI/Au. The oxidation of methanol during the positive scan at PANI/Au occurs at a less negative potential (-0.133 V) comparing to other composites (-0.237 V and -0.229 V). It indicates that methanol oxidation is more thermodynamically favorable on Au. In addition, the potential difference between the positive and negative scan for PANI/Au composite is the smallest comparing to other composites and bulk electrodes. The results imply that the poisoning at Au surface is less pronounced than Pd or Pt surface.

4.3.2 Electro-oxidation of 1-propanol

In previous literatures, the electro-oxidation of 1-propanol has been studied at Pd and Pt surfaces. There are relatively few examples of catalysis at Au surfaces. Therefore, the catalytic activity of PANI/Au and Au disc electrode was examined in a solution of 1M 1-propanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$) in 1M KOH using cyclic voltammetry. The electrodes was examined between -0.4 V and 0.5 V with the scan rate of 0.01 V/s. Figure 4.5 shows the electrochemical responses of PANI/Au and a gold disc electrode for comparison in the propanol solution. Figure 4.5a shows the oxidation of propanol on a gold disc electrode. The cyclic voltammogram is similar to methanol oxidation with two anodic peaks. When the potential is scanned towards the positive values, 1-propanol is oxidized at 0.160 V with the integrated charge density $Q = -4.497 \times 10^{-2} \text{ C/cm}^2$. On the reversed scan 1-propanol is oxidized at -0.005 V with $Q = -9.315 \times 10^{-3} \text{ C/cm}^2$. The high potential

difference and a 79% reduction in charge density indicate that the metal surface is poisoned; therefore, the potential shifts to more negative values. Figure 4.5b and 4.5c show 1-propanol oxidation on a PANI/Au composite electrode. Table 7 presents the charge densities of PANI/Au and the Au disc electrode for comparison. The oxidation of 1-propanol occurs at more positive potentials on a PANI/Au composite electrode comparing a gold disc electrode, which potential that 1-propanol oxidation is more thermodynamically favorable on PANI/Au composites. However, the potential difference between the two anodic peaks of PANI/Au is much higher than the gold disc electrode, 240 mV. PANI/Au also has a lower charge density in comparison to the gold electrode. The oxidation of propanol on PANI/Au during the positive scan is decreased by ~ 39% comparing to the Au disc electrode. The results imply that PANI/Au is more susceptible to poisoning, and has lower catalysis efficiency than the Au disc electrode. It might be due to the differences in surface structures of Au particles and Au electrode, which need to be studied further in details in addition to the reaction mechanism.

Table 7: Charge densities of PANI/Au composite and Au disc electrode for 1-propanol oxidation

	Au disc	PANI/Au
Positive scan	$-4.497 \times 10^{-2} \text{ C/cm}^2$	$-2.752 \times 10^{-2} \text{ C/cm}^2$
Negative scan	$-9.315 \times 10^{-3} \text{ C/cm}^2$	$-6.249 \times 10^{-3} \text{ C/cm}^2$

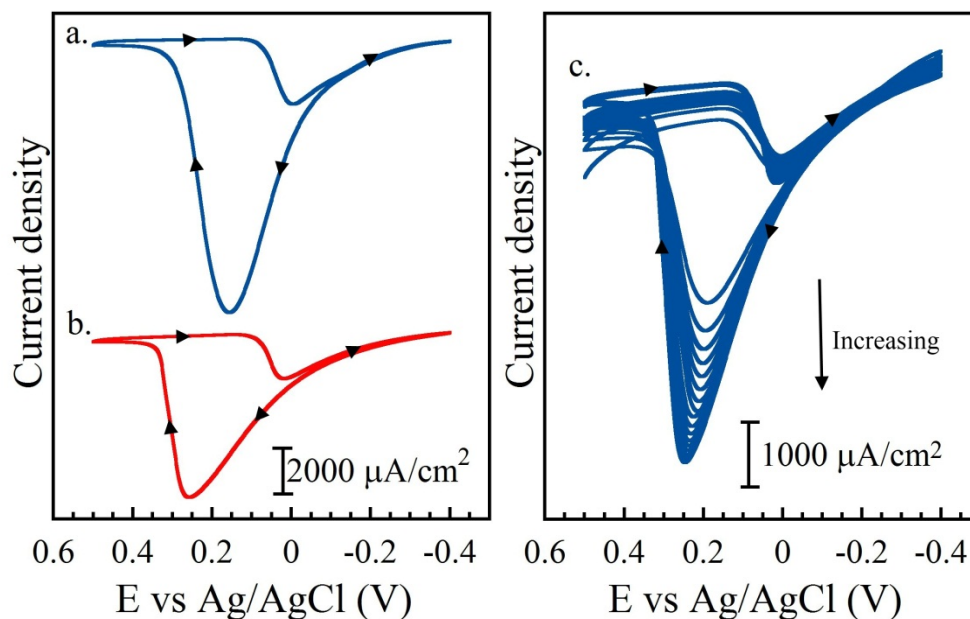


Figure 4.5: Cyclic voltammetry responses of gold in 1M $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ in 1M KOH at a scan rate of 0.01 V/s (a) Au disc electrode $d = 2$ mm (steady-state), (b) PANI/Au on GC electrode $d = 3$ mm (steady-state), and (c) PANI/Au (complete 20 cycles)

4.4 Conductivity of PANI/metal composites in basic solutions

All experiments were conducted in basic solutions, with $\text{pH} \sim 14$. PANI typically becomes an insulator due to the high oxidation state and the loss of proton doping. Therefore, PANI/metal composites were expected to show no electrochemical responses. However, PANI/metal composites remained conductive, and exhibited catalytic activity in basic solutions. The interactions of metal nanoparticles and the solutions ions (alcohols and OH^-) occur at the composites' surfaces. The charges must be shuttled from the composites' surfaces through the insulating polymer to the electrodes' surfaces in order to produce electrochemical responses. The presence of metal particles might contribute to the enhanced conductivity. Metals are deposited at the nitrogen sites;

therefore, they may act as a solid dopant, which can delocalize the charges on the polymer, and maintain the conductivity in the absence of proton doping.

4.5 Conclusion

While the Au electrode shows no catalytic activity for methanol oxidation, PANI/Au exhibits a relatively good catalytic activity with a small potential difference between forward and reverse scans, which indicates that the poisoning is not pronounced on the Au surface. Therefore, PANI/Au is a promising electrocatalyst for methanol oxidation. Both PANI/Pd and PANI/Pt have greater charge densities than the corresponding disc electrodes, which suggest that PANI/Pd and PANI/Pt have higher surface areas comparing to bulk metals. PANI/Pd has less poisoning on the metal surface comparing to the Pd disc electrode. It might be due to the OH⁻ ions and PANI, which suppress the poisoning on the metal surface.⁸³ In addition, the preliminary data also presents the catalytic activity of PANI/Au and Au for 1-propanol oxidation. Further studies are needed to evaluate the reaction in detail. Finally, the presence of metal particles in PANI maintains its conductivity in basic solution, which suggests that PANI/metal composites can be used for any application previously precluded in basic solutions.

CHAPTER 5

CONCLUSIONS and SUMMARY

Conductive PANI/metal composites were prepared using electrochemical methods. Proton doped PANI was produced electrochemically using cyclic voltammetry. PANI/metal composites were produced through the controlled uptake and reduction of metal anions including AuCl_4^- , PdCl_2^{2-} , and PtCl_2^{2-} . The uptake and dispersion of the metal precursors into the polymer occurs as the amine nitrogen sites become oxidized in order to maintain charge neutrality. Reduction of the species occurs as the potential is cycled to more negative values causing the nucleation of metal onto the polymer. Proton doping was examined to determine the loss of electrochemical activity associated with the reduction of metal at the amine nitrogen groups. A significant reduction in proton doping was observed for all three composites indicating that the metal physically blocked the nitrogen sites. The average decrease in proton doping for PANI/Au, PANI/Pd and PANI/Pt was 20%, 46%, and 37%, respectively. These values were produced using identical methods indicating that each metal has a different affinity for the polymer. The FT-IR data for each composite indicates that the uptake and reduction of the metal precursors occurs at the expense of the polymer. Therefore, the polymer is more oxidized relative to the starting materials. In addition, bands associated with the nitrogen functional groups in the polymer shift to higher energy consistent with the intrinsic linkage of the polymer and metal, and an increase in the oxidation state of the polymer. The value of R, the ratio of quinoid and benzenoid units, can be used to estimate the change in oxidation state for PANI before and after the metal reduction. The pristine PANI had a value of $R \approx 1$, while all PANI/metal composites had $R > 1$, which indicates

a higher degree of oxidation through the formation of quinoid units at the expense of fully reduced benzenoid units. The formation of PANI/metal composites also influences the polymers thermal properties as the oxidation state increases. For example, the thermal degradation of PANI/metal composites started at lower temperatures when compared to pristine polymer. The uptake and reduction of the metals decrease the thermal stability of the polymer through higher oxidation states and increased thermal diffusion relative to the pristine polymer. The thermal measurements were also used to estimate the mass loading of metal through the thermal evaporation of the organic polymer leaving the metal as the final product. The metal content for each composite was 17.7%, 20.9%, and 16.6% for PANI/Au, PANI/Pd and PANI/Pt, respectively. The data suggests that in spite of the differences in proton doping observed for each polymer, the overall metal content is similar in the composites. Finally, PANI/metal composites were examined for their electrical properties. The measured conductivity of PANI is approximately 2.0 S/cm. In contrast, PANI/Au, PANI/Pd, and PANI/Pt had lower conductivities of 0.66, 0.023, and 0.157 S/cm, respectively. While these values are lower comparing to PANI's, they are significantly higher than the conductivity associated with insulating emeraldine base ($10^{-10} - 10^{-8}$ S/cm). The data indicates that the conductivity is maintained in spite of the increased oxidation and blocking of the amine nitrogens in the polymer. PANI/metal composites maintain the conductivity of the polymer regardless of increasing oxidation state and decreasing proton doping.

The proton doping conductivity model for the polymer would suggest that catalysis in basic solutions would be prohibited. However, the conductivity values suggest that PANI/metal composites can be used for the catalytic oxidation of methanol in basic

solutions. All of the PANI/metal composites examined in basic solutions containing methanol demonstrated catalytic activity with higher charge densities and less poisoning relative to the bulk metal catalyst surfaces. The difference in catalytic activity can be attributed to shielding by the polymer and a reduction of surface adsorption as metal particle dimension is reduced. In addition higher efficiencies can be attributed to a higher overall surface area of the metal nanoparticles in the polymer in comparison to bulk metal electrode with the same geometric area. Therefore, the three dimensional polymer provides a template for both the dispersion and reduction of metal particles size increasing the overall active surface area for catalysis.

Catalysis at Au surfaces has not been widely explored and relatively few examples exist in the literature because the metal is easily poisoned during common oxidative processes. Particle dimension plays a critical role and PANI/Au composites exhibited good catalytic activity for methanol oxidation. While the measured charge density of PANI/Au was lower than both PANI/Pd and PANI/Pt, the oxidation of methanol was not observed at bulk Au. In addition the potential difference for the forward and reverse voltammetric scan was smallest for PANI/Au which implies the composite was the least poisoned by the adsorption of intermediate species. PANI/Au also exhibited good catalytic activity for 1-propanol oxidation. While the preliminary data suggest that PANI/Au is a potential catalyst for the oxidation of alcohols and fuel cells, further studies are needed to evaluate the properties of PANI/Au in more detail. Furthermore, the conductivity of PANI/Au in a basic solution suggests that it can be used in place of Au for biological applications with pH values of 7 or higher. The use of PANI as a biosensor

template has typically been precluded due to the high pH required to minimize denaturing of biologically relevant species.

All catalytic experiments were carried in basic solutions with an approximate pH of 14, which normally would cease PANI's activity and result in loss of current responses. However, the results showed that the electrochemical responses for all of the composites were maintained at pH values that have traditionally produced an insulating form of the polymer. The data suggested that the formation of linkages between the metal and polymer might be critical in maintaining the high conductivity in basic solutions. The conductivity of the polymer in acidic solutions has been previously attributed to delocalized charge at the nitrogen groups in the polymer which allow the shuttle of electrons through the aromatic polymer. Therefore, it is likely that metal uptake and physical blocking of nitrogen sites in the polymer occurs through the formation of intrinsic linkages with the polymer. These linkages allow the metal to act as a solid state dopant delocalizing the charge at nitrogen groups in the polymer to maintain the conductivity of the composite without proton doping.

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