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Synthetic methods for catalytically active polyaniline/platinum composites

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SYNTHETIC METHODS FOR CATALytically active POLYANILINE/PLATINUM COMPOSITES

by

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A thesis submitted in partial fulfillment
of the requirements for the

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SYNTHETIC METHODS FOR CATALYTICALLY ACTIVE POLYANILINE/PLATINUM COMPOSITES

is approved in partial fulfillment of the requirements for the degree of

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ABSTRACT

Synthetic Methods for Catalytically Active PANI/Pt Composites

by

Neloni Ranmali Wijeratne

Dr. David W. Hatchett, Examination committee Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas

Polyaniline (PANI) is an organic semiconductor, which has attracted great attention in fundamental science and industries over the past decade due to its conductivity and electrochemical properties. More recent studies have focused on insertion of noble metals into polyaniline, which influence the electronic and physical properties of the polymer. The metal also provides unique chemical properties, which can be utilized in catalytic and sensing applications. In this thesis, Pt incorporation was achieved using either PtCl$_6^{2-}$ or PtCl$_4^{2-}$ through electrochemical reduction into a PANI membrane, spontaneous reduction into a PANI membrane and by the direct chemical oxidation of aniline or oligomers. The electrochemical, chemical, and morphological properties of the PANI/Pt(IV) and PANI/Pt(II) composites were compared. Fourier-transform infrared spectroscopy (FTIR) and x-ray photoelectron spectroscopy (XPS) were used to examine chemical properties and chemical speciation of Pt in the materials. Scanning electron microscopy (SEM) was used to examine the formation of Pt particles and the overall morphology of the materials. Finally, conductivity measurements were used to
explore the influence of incorporating Pt particles on the electronic properties of the materials. The studies show that the three different synthetic methods produce PANI/Pt composites with different chemical compositions and electronic properties. The differences result from the overall oxidation state of the polymer and the interaction of nitrogen with the metallic Pt particles. The method of preparation influences the electrocatalytic oxidation of methanol and formic acid. Although, the electrochemically and chemically prepared PANI/Pt materials show some catalytic activity, they are not identical. PANI/Pt formed from the electrochemical reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$ shows enhanced catalytic activity relative to the other PANI/Pt composites. In addition, the catalytic activity of PANI/Pt prepared from the electrochemical reduction of PtCl$_4^{2-}$ is significantly enhanced relative to the PANI/Pt composite produced using PtCl$_6^{2-}$.
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INTRODUCTION

1.1 Introduction to Polyaniline

1.1.1 Background

Polyaniline is a conducting polymer with unique electrical and optical properties that have lead to its use in a variety of technological applications ranging from rechargeable batteries, sensors to corrosion inhibitors. It has the electronic properties of a semiconductor and, at the same time, the processing advantages of the mechanical properties of polymers. Among the electrically conductive polymers, polyaniline has been of particular interest because of its remarkable environmental stability, controllable electrical conductivity and high degree of processibility. The ability to use the material in various physical forms such as blends, films and wires has brought together scientists from different fields to achieve a common goal, controlling the electrical and mechanical properties of the polymer.

1.1.2 Characteristics of polyaniline

Polyaniline (PANI) is the product of the oxidative polymerization of aniline with a chain of alternating nitrogen atoms and benzene rings. The polyaniline chain consists of two principal repeating units, the completely reduced unit (benzenoid unit) and the completely oxidized unit (quinoid unit). The structure is shown in Figure 1.1.

The polymer is classified based on the overall oxidation state. The oxidation state of the polymer can be varied from the fully reduced state \((Y=0)\) to the fully oxidized state \((Y=1)\). Leucoemeraldine base (fully reduced), emeraldine base and pernigraniline base
(fully oxidized) are the main oxidation forms of PANI. The oxidation state of the polymer can be estimated by the ratio of the quinoid units to benzenoid units of the polymer. Generally, the Fourier transform infra red (FTIR) spectroscopy is used to calculate the oxidation state. The oxidation state of the polymer plays a major role in the conductivity of the polymer.

\[
\begin{array}{c}
\text{Reduced Form} \\
\begin{array}{c}
\text{NH} \\
\text{NH} \\
\text{Y}
\end{array}
\end{array}
\begin{array}{c}
\text{Oxidized Form} \\
\begin{array}{c}
\text{NH} \\
\text{N= =N} \\
\text{1-Y}
\end{array}
\end{array}
\]

Leucoemeraldine
Emeraldine
Pernigraniline

Figure 1.1 Chemical structure and Oxidized forms of Polyaniline

The commercially most important form of PANI is the emeraldine base. It consists of equal amounts of oxidized and reduced repeating units. The \(pK_a\) values attributed to the
protonated site (-NH$_2^+$-) of reduced unit and the protonated site (-NH$^+$=) of the oxidized unit have been determined by the Menardo and colleagues. The pK$_a$ values for -NH$_2^+$- and -NH$^+$= are 2.5 and 5.5 respectively. Either one or both of the nitrogen atoms can be protonated depending on the pH value of the doping acid and is called “doping”. The protonated form of the emeraldine base is called the emeraldine salt form. Dramatic changes in the electronic, optical, physical and chemical properties of the polymer accompanied by a major increase in the conductivity can be observed with proton doping. Emeraldine salt is the most conductive form of PANI at ~2-10 S/cm.

Environmental factors, such as surrounding atmosphere, humidity and the temperature can influence conductivity of polyaniline. However, the oxidation state and proton doping are main the parameters that influence conductivity.
Polyaniline has an extended π-conjugated system, formed from overlapping carbon p orbitals and the nitrogen sp³ orbitals to give an alternating single and double bond along the polymer chain. The most important feature of PANI as a conjugated polymer is its conversion into a conductive material through a process of proton doping. Doping generates mobile charge carriers that enable the electron to move freely along the polymer chain, which results in the flow of electric current. The proton doping of PANI and corresponding increase in the conductivity of PANI was first reported by MacDiarmid and colleagues in 1985. This new discovery leads to the classification and development of doped conducting polymers as a new class of organic polymers.

The oxidation state can also significantly influence the conductivity of the polymer. Fourier transform infrared (FTIR) spectroscopy is employed to determine the oxidation state of the polymer. Integrating the bands attributed to the quinoid and benzenoid units and calculating the ratio between them can be used to estimate the oxidation state of PANI. The ratio, R can be calculated as follows:

\[
\text{Oxidation State (R)} = \frac{\text{Area}_{\text{Quinoid}}}{\text{Area}_{\text{Benzenoid}}} = \frac{x}{1 - x}
\]

Emeraldine salt, the most conductive form of PANI has an oxidation state of 1. In other words the polymer to be optimally conductive it should have 1:1 ratio of quinoid to benzenoid units respectively.
1.1.3 Synthesis of polyaniline

Typically PANI is synthesized by oxidizing aniline monomer either electrochemically or chemically. The term PANI\(^C\) is usually employed to represent the chemically synthesized PANI and PANI\(^E\) for the electrochemically prepared PANI.

The significance of synthesizing PANI chemically is the ability to obtain the product in gram quantities. However, no control over the final oxidation state of the material makes chemical synthesis a non-homogeneous process. Experimentally, PANI\(^E\) attracts much more attention than PANI\(^C\), because of the fine control one can have over its final oxidation state and the purity of the final product.\(^{18,19}\) The main disadvantage of PANI\(^E\), is it can be produced in only minute quantities and also for it to be used in external devices it has to be removed from the electrode surface without destroying it.

PANI prepared by both chemically and electrochemically in acid is protonated and insoluble in most common organic solvents. The exception is n-methylpyrrolidone. To increase the solubility PANI can be deprotonated in NH\(_4\)OH or NaOH and dissolved directly into formic acid or acetic acid.\(^{19}\)

1.1.3.1 Chemical synthesis of PANI

The classical method of synthesizing PANI is direct chemical oxidation of aniline in an acidic medium by an oxidizing agent. Various oxidizing agents can be used in this process but the most common one used is ammonium persulfate \([(NH\(_4\))_2S\(_2O\_8\)].\(^{2,20}\) The final product is typically the emeraldine salt form of PANI. The emeraldine base can be synthesized by reacting the emeraldine salt with an ammonium hydroxide solution stripping the polymer of protons.

In recent years considerable amount of studies have been devoted to improve the mechanical properties of chemically prepared PANI.\(^{21}\) A study done by Smith colleagues have reported that using (NH\(_4\))\(_2\)S\(_2\)O\(_8\) or K\(_2\)Cr\(_2\)O\(_7\) at temperatures lower than 0°C, results in the formation of high molecular weight PANI. Mechanical strength and strength of
adhesion to a substrate can be improved by increasing the molecular weight of the polymer.

1.1.3.2 Electrochemical synthesis of PANI

Polyaniline is electrochemically synthesized by anodic oxidation on an inert electrode, typically Au or Pt. Cyclic voltammetry is the most commonly employed electrochemical technique to produce PANI. PANI films with desired thickness and oxidation state can be grown on the inert electrode by controlling the number of sweep segments and the final potential, respectively. Films that are produced by cyclic voltammetry, adhere more strongly to the electrode than films that are produced by applying a constant potential.

The mechanism for the electrochemical polymerization of aniline has been proposed by several groups. Mechanisms for anodic oxidation of aniline in acidic and alkaline mediums have also been reported. The initial step in the mechanism is pH independent, forming aniline radical cation from the oxidation of aniline. The subsequent coupling step after the formation of aniline radical is strongly dependent on the pH of the medium. In the acidic medium coupling take place in the head-to-tail manner and under the neutral and basic conditions it is in the head-to-head manner, resulting final product in different ratios. Genies and co-workers proposed the mechanism for the electropolymerization of aniline in acidic medium, while the studies in basic and neutral medium have been reported by Ohaska and group.

1.1.4 Applications of polyaniline

As an intrinsic conducting polymer, PANI is commercially significant due to its unique electrical properties and characteristics. Its applicability varies from energy storing devices like rechargeable batteries and photoelectrochemical cells to sensors. Superior transducing ability of PANI has lead to its use in microtubular biosensors and sensor arrays. The function of these sensors is to estimate glucose, urea and triglycerides concentrations.
PANI film based ammonia sensors has been fabricated in Russia to measure the ammonia content in the environment, in industrial, and agricultural applications. PANI electrode have a high selectivity towards ammonia even in the presence of other toxic gases such as nitrogen dioxide, methane, hydrogen sulfide and carbon monoxide and it operates at room temperature. The color changes associated with the change in oxidation state of PANI have made it possible for the polymer to be used in electrochromic display devices.

Adhesive property of PANI on solid substrates has enabled it to be utilized in anticorrosive and antistatic coatings. Electrically conductive salt form or an electrically nonconductive base form of PANI dissolved in an organic solvent can be
coated on iron or steel substrates to inhibit the corrosion.\textsuperscript{28} The base form of PANI is more preferable, due to its relatively high solubility in dimethyl sulfoxide, N-methylpyrrolidione and tetramethyl urea. Typically 1-200 \( \mu \text{m} \) thick PANI film is applied to the typical substrate.

In addition to these applications PANI has been used in light emitting devices\textsuperscript{29} and capacitors.\textsuperscript{30} Capacitors and light emitting devices have been prepared by sandwiching a dielectric materials such as paraffined paper or mica and emissive polymer layer between the two conducting PANI films respectively.\textsuperscript{9,30} Based on the studies done by Aghlara and group, use of thin PANI film instead of metal foils in the capacitors has increased the capacitance while still maintaining a smaller size and the shape that is easier to handle.

A novel feature of PANI is the ability to incorporate metal species into the polymer matrix, which enhances its properties as well as its industrial applicability which will be discussed in section 1.2.3. The species can be in the form of cationic species such as \( \text{Pd}^{2+} \), \( \text{Au}^{3+} \) and \( \text{Cu}^{2+} \) or anionic species such as \( \text{AuCl}_4^- \), \( \text{PtCl}_6^{2-} \) and \( \text{PdCl}_6^{2-} \).
1.2 Polyaniline/Metal composites

1.2.1 Introduction to Polyaniline/Metal composites

Insertion of noble metal species into a polymer matrix has been the focus of many studies recently. The relative ease of fabricating these materials and by incorporating specific binding sites that improves the selectivity and sensitivity in the polymer has lead to many potential applications. Electrochemically conductive polymers with dispersed metallic particles have been used for biosensors, electrochemical capacitors, protective coatings against corrosion and as an electrocatalyst. Interaction between the polymer and the metal influences the chemical properties of the polymer, imparting unique characteristics to the composite. In the case catalysis, the reactivity of the metals are often significantly enhanced. The polymer, also provides a high accessibility to the electrocatalytic center.

1.2.2 Synthesis of Polyaniline/Metal composites

PANI/metal composites can be synthesized by both direct chemical oxidation and electropolymerization. Chemical synthesis of PANI composites containing Au, Pt and Pd metal species involves direct chemical oxidation of the monomer using the corresponding metal salts such as AuCl₄⁻, PtCl₆²⁻ and PdCl₆²⁻ respectively. In the electrochemical synthesis metal species are introduced into the polymer during the oxidation of PANI.

1.2.2.1 Electrochemical synthesis of Polyaniline/Metal composites

The most popular method of dispersing microparticles of the metal into the polymer is electropolymerization. The electrochemical synthesis is a two-step process involving electrochemical polymerization of aniline at an inert electrode in the acidic medium followed by electrodeposition of the corresponding metal from a precursor salt, by either cyclic voltammetry or constant potential exhaustive electrolysis. Variety of transition metal complex anions in acidic mediums can be introduced into the polymer via these methods. Electropolymerization allows control of the thickness and homogeneity of the PANI film on the electrode surface. Strong adhesion to the substrate carrying current...
and resistance towards corrosion makes polyaniline an excellent candidate to be used in fabricating electrocatalytically active materials with dispersed metal particles. Several studies have been documented describing dispersion of Ag, Au, Pt, and Pd species in PANI. Chemical synthesis gives bulk amount of the composite.

The major drawback in this method is the difficulty in removal of the material from the electrode without causing any damage. This limits the use of the material on external devices.

1.2.2.2 Chemical synthesis of Polyaniline/Metal composites

Chemical synthesis of PANI/Metal composites has been attempted using various methods. The most common chemical method is direct oxidation of aniline by employing the corresponding noble metal species as the oxidizing agent in the acidic medium. As discussed in a previous section, the lack of control over the final oxidation state of the chemically synthesized composite still remains an issue.

1.2.3 Applications of Polyaniline/Metal composites

Polymer films with metal particles incorporated either during the film formation or electrodeposition on to the film influences the performance of the catalyst in certain electrochemical reactions that are of interest in fuel cells. High metal loadings with nano size particles enhances the catalytic activity of the metal. The large surface area of polyaniline allows high dispersion of metal particles that greatly reduces the amount of metal loading on the electrode and thereby significantly lowering the cost. Previous studies based on conventional methods of preparing metal catalyst demonstrate the difficulty of producing high catalytic activity of the metal.

The long-term goal of this research project is to develop PANI/Pt and PANI/Pd gas storage and catalytic materials both chemically and electrochemically. Highly dispersed Pt particles in PANI has been employed to activate various electrochemical reactions such as hydrogen oxidation, oxygen reduction, oxidation of small organic molecules such as methanol and oxidation of hydrazine.
The development of direct methanol fuel cells depends on fabrication of highly active electrodes for the electrocatalytic oxidation of methanol. Among the conjugated polymers, PANI with dispersed Pt particles have been particularly interesting because its potential range for conductivity is in the range of C₁ organic molecules oxidation. The formation of carbon monoxide, during the oxidation of organic molecules reduces the electrocatalytic activity of platinum greatly. The high dispersion of Pt particles in the modified electrode drastically reduces the poisoning effect of CO compared with the large Pt electrode, because of weak adsorption of CO on the dispersed platinum particles. The decrease in this chemisorbed species enhance the oxidation rate of MeOH. Based on the kinetic studies methanol electro-oxidation is first order with respect to methanol and main oxidation product is carbon dioxide.

\[
\text{H} - \text{C} - \overset{\text{O}}{\text{H}} + \text{H}_2\text{O} \rightarrow 6\text{H}^+ + \text{CO}_2 + 6\text{e}^-
\]

The potential of microbial fuel cells, as a means of generating electricity is becoming more promising with the discovery that marine sediments, sewage, sewage water and sludge can be used as the energy source. Use of fluorinated PANI, improves the tolerance of platinum against poisoning and therefore enhances the catalytic activity of platinum anodes in oxidation of hydrogen, produced by anaerobic microbial metabolism.

Electrocatalytic reduction of oxygen to hydrogen peroxide can be enhanced by increasing the area of the electrocatalyst reduction by electrodepositing Pt particles on a PANI film. Pt modified electrodes also play a major role in fuel cells, water electrolysis and electrosynthesis etc., where the electrocatalytic oxidation of hydrogen take place at the Pt particles.
PANI films with palladium incorporated are effective as an electrocatalyst in some hydrogenation reactions. As a host with π-bond conjugated system, PANI allows electronic charges to shuttle freely to the catalyst centers. Catalytic hydrogenation of 2-ethylanthraquinone (eAQ) is the key reaction in the anthraquinone method of industrial $\text{H}_2\text{O}_2$ production. Palladium catalyst supported on PANI is used in the hydrogenation stage because the smaller size of Pd particles in the composite promotes the formation of active quinines, which will yield $\text{H}_2\text{O}_2$ upon oxidation.

Palladium has the ability to absorb monolayers of hydrogen on its surface as well as absorb large quantities of hydrogen in its lattice. This unique property of palladium makes PANI/Pd composites an attractive choice of material for the chemical sensing of hydrogen and hydrogen-evolving materials. At room temperature, the metal has an unusual property of absorbing stoichiometrically up to nine molecules of hydrogen per one atom of palladium. In addition, the diffusion of hydrogen gas through a heated palladium allows purification of the hydrogen gas. This selective relationship between palladium and hydrogen and the ability of the metal to reversibly expel the hydrogen gas are possible justification for employing PANI/Pd industrially as a hydrogen fuel storage source.

Based on the work carried out by Lewis on palladium-hydrogen system, hydrogen absorption take place at the octahedral interstices of the face centered cubic (f.c.c.) palladium lattice without disrupting its metallic characteristics. Expansion of palladium lattice at high concentrations of hydrogen causes dimensional instability in the thick palladium films, which makes it a poor hydrogen sensor. Incorporation of Pd microparticles to the PANI matrix not only enhances the high and selective affinity for hydrogen but spatially separates and stabilizes the Pd clusters which will help to overcome the mechanical problems such as instability of palladium films.
1.3 Research Goals

The initial goal of this thesis project was to synthesis the PANI/Pt composite chemically and electrochemically and compare their properties. The composites were chemically and electrochemically synthesized under optimized conditions, followed by the characterization and comparison of the physical and chemical properties. The \textit{In-situ} uv/vis spectroscopic results based on previous study were employed to compare the mechanism for the formation of chemically synthesized polymer with the electropolymerization reaction mechanism of the electrochemically formed polymer. The influence of the metal on the proton doping and the oxidation state of the material was studied extensively using electrochemical doping, x-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy respectively.

Studying the influence of metal particles on the conductivity of PANI was an important part of this study because the next goal of this project was to study the catalytic applications of PANI/Pt composites that were chemically and electrochemically synthesized. The catalytic reactions of oxidation of methanol and oxidation of formic were studied. Images from the scanning electron microscopy were used to study the size and dispersion of metal particles on the polymer. The effect of oxidation state on the catalytic activity was also studied by means of FTIR spectroscopy.
1.4 References


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CHAPTER 2

EXPERIMENTAL

2.1 Introduction

The two typical methods for the synthesis of PANI are direct chemical oxidation of aniline using an oxidizing agent (i.e. peroxydisulfate) and anodic oxidation of aniline monomer at an inert electrode.\(^1\) The electrochemically and chemically prepared materials were characterized and compared using electrochemical and spectroscopic methods. The chemical properties of the material can be determined using Fourier transform infrared (FTIR) spectroscopy. X-ray photoelectron spectroscopy (XPS) can also be used to study the composition and speciation of the material indicating the final oxidation state of the metal in the composite. The reaction mechanism of the chemically and electrochemically prepared PANI/metal composite can be compared. Crystalline morphology and the distribution of the metal in the composites were examined by scanning electron microscope (SEM) images.

2.2 Chemicals

The synthesis of PANI using hexachloroplatinate as the precursor salt (PANI/Pt(IV)) was performed using aniline, \(C_6H_5NH_2\) (Aldrich, 99\%, 13293-4), tetrafluoroboric acid, \(HBF_4\) (Aldrich, 48\%, 20793-4), potassium hexachloroplatinate, \(K_2PtCl_6\) (Strem, 16921-30-5), and perchloric acid, \(HClO_4\) (Baker analyzed, 69-72\%, 9652-33). All solutions were prepared using 18.2 M\(\Omega\) cm water obtained from a Barnstead E-pure water filtration system.
PANI synthesis using tetrachloroplatinate as the precursor salt (PANI/Pt(II)) was carried out using N-Phenyl-1, 4-phenylenediamine, C\textsubscript{12}H\textsubscript{12}N\textsubscript{2} (Aldrich, 98%, 101-54-2), tetrafluoroboric acid, potassium tetrachloroplatinate, K\textsubscript{2}PtCl\textsubscript{4} (Alfa Aesar, 10025-99-7) HBF\textsubscript{4} (Aldrich, 48%, 20793-4) is used in the chemical synthesis, and perchloric acid, HClO\textsubscript{4} (Baker analyzed, 69-72%, 9652-33 is used in the electrochemical synthesis of PANI/Pt(II) composite.

The synthesis of pure PANI/HBF\textsubscript{4} was carried out using aniline, C\textsubscript{6}H\textsubscript{5}NH\textsubscript{2} (Aldrich, 99%, 13293-4), tetrafluoroboric acid, HBF\textsubscript{4} (Aldrich, 48%, 20793-4) and ammonium perxydisulfate (Mallinckrodt, 7277-54-0) as the oxidizing agent.

The catalytic reactions were carried out using methanol (EM Science, 67-56-1) and formic acid (Sigma, 88.1%, 64-18-6) in 1M H\textsubscript{2}SO\textsubscript{4} acid (Mallinckrodt, 96%, 7664-93-9) medium.

2.3 Synthesis

2.3.1 Chemical synthesis of PANI/Pt composites

PANI synthesis using hexachloroplatinate as the precursor salt (PANI/Pt(IV)) was generated in bulk quantity by direct chemical oxidation of 50.00 ml of 0.22 M aniline dissolved in 0.02 M HBF\textsubscript{4}, using 50.00 ml of 2.02 x 10\textsuperscript{-2} M K\textsubscript{2}PtCl\textsubscript{6} as the oxidizing agent. To ensure that all the PtCl\textsubscript{6}\textsuperscript{2-} was consumed, a 10:1 mole ratio of aniline to K\textsubscript{2}PtCl\textsubscript{6} was mixed. The weight of the PANI/Pt composite obtained in the chemical synthesis was influenced by the acid concentration. At higher concentration of acids, conversion of K\textsubscript{2}PtCl\textsubscript{6} to K\textsubscript{2}PtCl\textsubscript{4} takes place. K\textsubscript{2}PtCl\textsubscript{4} is not strong enough oxidizing agent to oxidize aniline to PANI. Previously completed studies from our laboratory indicated for highest yield of the chemical product, an optimum acid concentration of 0.02 M HBF\textsubscript{4} should be used.\textsuperscript{2}
Pure PANI/HBF₄ was synthesized using 0.20 M ammonium peroxydisulfate as the oxidizing agent. The chemical synthesis was carried out by mixing 0.22 M aniline in 1 M HBF₄ and 0.02 M (NH₄)₂S₂O₈ in 1 M HBF₄ in equal volumes.

To obtain the PANI/Pt composite using tetrachloroplatinate as the precursor salt PANI/Pt(II), 500.00 ml of 5 x 10⁻³ M N-phenyl-1,4-phenylenediamine dissolved in 0.02 M HBF₄ and 25.00 ml of 2.06 x 10⁻² M K₂PtCl₄ solutions were mixed in 5:1 molar ratio.

All the products were allowed to settle for 48 hours prior to vacuum filtering. The filtrate was washed extensively with ultra pure water and dried under ambient conditions. To remove the residual water in the samples they were dried in a vacuum oven at 80°C for 24 hours, prior to characterization measurements.

2.3.2 Electrochemical experiments

Electrochemical experiments were performed using the CHI660 electrochemical workstation with supplied electrochemical software. The synthesis was performed in a one-compartment cell using standard 3-electrode arrangement. The potential of the working electrode was measured against a Ag/AgCl reference electrode. The counter electrode was always a platinum sheet. The potential window used in each case was dependent on the fully developed voltammetric peaks of proton and anion doping. A scan rate of 10 mV/s was used to record all the cyclic voltammograms. Prior to running the electrochemical experiments all the solutions were degassed with nitrogen, to remove the oxygen.

The electrochemical synthesis of the polyaniline/metal composites were carried out in two steps. In the first step, polymer was grown onto the working electrode using 0.25 M aniline in 1 M HClO₄ and followed by electrodeposition of metal onto the polymer by dipping the working electrode into a 2.02 x 10⁻² M K₂PtCl₄ and 1 M HClO₄ in 1:1 volume ratio. The cyclic voltammograms for 20 scans were recorded at a scan rate of 10 mV/S. The number of scans and the scan rate was kept constant throughout all the
electrochemical experiments. The electrochemical synthesis of PANI/Pt(II) composite was carried out in the same manner employing K\textsubscript{2}PtCl\textsubscript{6}.

The process of producing the dipped PANI/Pt(IV) composite was accomplished in two steps. First step was to grow the PANI film in a gold disc electrode using 0.25 M aniline in 1 M HClO\textsubscript{4} solution. And in the second step platinum was incorporated into the polymer by immersing the PANI electrode in a solution containing 2.06 x 10\textsuperscript{-2} M K\textsubscript{2}PtCl\textsubscript{6} in 1 M HClO\textsubscript{4} overnight. The dipped PANI/Pt(II) composite was synthesized in the same manner substituting 2.06 x 10\textsuperscript{-2} M K\textsubscript{2}PtCl\textsubscript{4} in 1 M HClO\textsubscript{4} for the K\textsubscript{2}PtCl\textsubscript{6}.

For the characterization purpose electrochemical and dipped PANI/Pt composites were prepared using the same electrochemical apparatus described above. A platinum sheet or a mica/Au electrode was used as the working electrode for the electrochemical experiments. In the first step a thick layer of the polymer on the working electrode was produced. A scan rate of 10 mV/s was used to record the cyclic voltammograms for 300 scans. The deposition of the metal into the polymer was achieved by either cyclic voltammetry or by spontaneous reduction of Pt anion overnight to obtain the electrochemical and dipped PANI/Pt composites respectively. The final product was washed with copious amount of ultra pure water to remove the residual acid. It was then stripped off from the Pt sheet and vacuum dried for 24 hours prior to characterization. The electrochemical, chemical and dipped composites were characterized by using FTIR, XPS and SEM measurements.

The electrochemistry of the chemically prepared PANI/Pt composites were studied using a glassy carbon(GC) electrode coated with a thin layer of paraffin oil. The PANI/Pt composite was affixed to the GC electrode by pressing the powder to the electrode surface and tapping to remove the excess powder. The GC electrode coated with chemically prepared PANI/Pt composite was immersed in a solution of 1 M HClO\textsubscript{4} for one hour prior to performing the electrochemistry. The cyclic voltammmograms were obtained at a scan rate 10 mV/S in the potential range of 0.0 V to 0.85 V.
2.4 Catalytic Reactions of PANI/Pt composites

The electrocatalytic oxidations of methanol and formic acid were carried out in one-compartment cell using the same standard 3-electrode arrangement for all the experiments as previously described. Gold disc electrode was used as the working electrode during these studies.

2.4.1 Methanol Oxidation

The oxidation of methanol by electrochemically prepared and dipped PANI/Pt composites were performed by immersing the PANI/Pt electrodes in a solution containing 0.5 M methanol in 0.5 M H₂SO₄. A potential range of -0.15 V to 0.85 V was used at the scan rate of 10 mV/S to record all the cyclic voltammograms.

The oxidation of methanol by chemically prepared PANI/Pt composites were carried out using glassy carbon electrode coated with chemically prepared PANI/Pt composite. The GC electrode coated with PANI/Pt composite was immersed in a solution containing 0.5 M methanol in 0.5 M H₂SO₄ solution for one hour prior to running electrochemistry. The cyclic voltammograms were recorded in the range of 0.0 V to 0.85 V at a scan rate of 10 mV/S.

2.4.4 Formic acid oxidation

The oxidation of formic acid by all the PANI/Pt composites was performed in the similar way described above. The formic acid oxidation was carried out using a solution containing 0.5 M formic acid in 0.5 M H₂SO₄. The cyclic voltammograms were recorded at a scan rate of 10 mV/S.

All of the voltammetric responses corresponding to the proton doping prior to and after introducing the Pt and oxidation reactions were normalized against the first proton doping in 1 M HClO₄ before the incorporation of platinum. This allows a comparison of the number of active nitrogen sites in the polymer for proton doping in PANI membranes before and after the incorporation of platinum. In addition, the normalization also allows
comparison of the catalytic activity when different Pt incorporation methods such as electrochemical, spontaneous reduction and chemical were used.

2.4 Characterization

2.4.1 UV/VIS spectroscopy

The reaction mechanism for the chemically prepared PANI/metal composite can be presented and compared with the electrochemical reaction mechanism by employing uv/vis studies. The reaction mechanism for the chemically prepared PANI/Pt has been studied previously. In-situ UV/Vis spectroscopic data was used to monitor the depletion of reacting species and the subsequent formation of the PANI/metal composites.

All UV/Vis spectra were obtained using a StellerNet EPP 2000 fiber optic spectrophotometer equipped with a deuterium lamp and tungsten filament sources. Quartz cuvettes with a 1 cm path length were used to carry out all the UV/Vis measurements. The in-situ characterization of reactants and products was performed using the episodic data capture. The synthesis of PANI/Pt(IV) composite using hexachloroplatinate as the precursor salt was monitored using 1.50 ml of 0.05 M aniline in 0.2 M HBF$_4$ and 1.50 ml of 4.14 X 10$^{-2}$ M K$_2$PtCl$_6$, respectively.

2.4.2 FTIR spectroscopy

Fourier transform infrared spectroscopic data was employed to provide valuable measurements of the chemical composition of the PANI/metal composites and the pure polymer. The fingerprint region between 700 - 1600 cm$^{-1}$ of FTIR spectra is used to study the similarities and the differences between the chemical and electrochemical PANI/metal composites and the pure polymer. Integration of bands attributed to the oxidized unit and the reduced unit was used to estimate the oxidation state of the polymer. The oxidation state of the polymer plays a major role in the conductivity of the polymer.
FTIR measurements were obtained by BIO-RAD FTS 7000 spectrometer using a photoacoustic detector. A single point ATR crystal (Ge) was used to measure the electrochemically grown PANI/metal samples. Each sample was scanned 64 times with a resolution of 8 cm$^{-1}$.

2.4.3 X-ray photoelectron spectroscopy

X-ray Photoelectron spectroscopy of PANI/metal composites offers valuable information on the oxidation states of the metal species, chemical composition and the dopant level in the polymer.$^{1,3}$ X-ray Photoelectron spectroscopic measurements were collected by employing a surface science SSX-100 system with an Alkα x-ray source (1486.67eV) and a hemispherical electron analyzer. The powdered polyaniline/metal samples were mounted on a double-sided tape on a piece of aluminum foil. During the measurements pressure in the analysis chamber was maintained at $5 \times 10^{-9}$ Torr or lower.

2.4.4 Scanning electron microscope

Conductivity, mechanical properties and transport properties of the polymer drastically depend on the morphology of the polymer. The morphology of the polymer can be examined by SEM.$^{1,4}$ A scanning electron microscope (SEM) was employed to examine the distribution and the size of the metal particles in the polymer. SEM images were obtained by JEOL5600 electron microscope equipped with a backscattered detector. The samples were mounted on a carbon tape and measurements were taken with 15kV of electron acceleration voltage.

2.4.5 Conductance measurements

Conductance measurements were carried out to observe the effects of incorporating metal species into the polymer. The conductivity of chemically and electrochemically prepared polyaniline/metal composites were characterized via four-probe method. The materials were pressed into pellet with a 1.25 cm radius by three metric tons of pressure. Electrical contacts were made using a Cascade Microtech C4S-64/50 probe head with
Tungsten Carbide electrodes. The resistance of the four-point probe sheet was measured by HP 34401A Digital Multimeter connected to a Cascade Microtech CPS-05 probe station. During the measurements, constant pressure was maintained between the probe head and the substrate. Five measurements were taken at five different locations and then averaged.
2.5 References


CHAPTER 3

SYNTHESIS AND CHARACTERIZATION OF CHEMICALLY AND ELECTROCHEMICALLY PREPARED PANI/Pt COMPOSITES.

3.1 Introduction

The synthesis and characterization of PANI/Pt composites are the focus of this chapter. Specifically PANI/Pt membranes prepared with a pre-formed polymer electrode in solutions containing PtCl$_6^{2-}$ and PtCl$_4^{2-}$ will be compared to bulk PANI/Pt composites prepared using either PtCl$_6^{2-}$ or PtCl$_4^{2-}$ as the chemical oxidant. The synthesis, characterization, and a detail mechanism of formation for the chemically prepared PANI/Pt composite has been published previously.$^1$ The mechanism for the electrochemical uptake and reduction of Pt in PANI membranes will be presented and compared to the chemical system. Spectroscopic, electrochemical and imaging techniques will be used to characterize the chemical, electronic, and morphological properties of the materials.

3.2 Results and Discussion

3.2.1 Chemical formation of PANI/Pt composite

The synthesis of PANI is typically performed using a chemical oxidant such as peroxydisulfate in the presence of an acid. The solution parameters employed ensure that the polymer contains equal number of oxidized and reduced rings. In addition, the acid protonates the polymer ensuring high conductivity. The polymer is an insulator in its fully reduced form even with proton doping.$^2$ This demonstrates that proton doping alone
is not sufficient enough to ensure high conductivity. Rather, both proton doping and oxidation-state play a key role in the conductivity. The optimum synthetic conditions and mechanism for the chemically synthesized PANI/Pt composites have been extensively studied and documented. The optimized parameter for the PANI/Pt composite are significantly different than those used to chemically synthesize the polymer with a chemical oxidant. The optimum acid concentration for the PANI/Pt composite is significantly lower (0.02 M HBF$_4$) in comparison to the chemically prepared PANI (1 M HBF$_4$). There is evidence that under highly acidic conditions that PtCl$_6^{2-}$ is converted to PtCl$_4^{2-}$, which is not a strong enough oxidizing agent for the aniline monomer.

The reaction mixture of 1.5 ml of 0.2 M aniline and 1.5 ml of 4.4 x $10^{-3}$ M K$_2$PtCl$_6$ in 0.20M HBF$_4$ was monitored for 48 hours to study the mechanism of formation of the PANI/Pt composite. A mole ratio of 1:12 (K$_2$PtCl$_6$ to aniline) was used to ensure the complete reduction of PtCl$_6^{2-}$ during the reaction.

The uv/vis absorbance band for the aniline is centered at 254 nm. The oxidant PtCl$_6^{2-}$, has one band between 250 to 350 nm and a second at 454 nm. The band located in the spectral range of 250 to 350 nm is unresolved relative to the formation of the polymer and oligomeric material in the reaction. In addition, the second band at 454 nm is not resolved relative to the formation of PANI and oligomeric materials during the reaction. The emerging $\pi-\pi^*$ transition band of PANI can be observed at 320-360 nm and polaron-$\pi^*$ transition band of PANI at 440 nm. In addition, PANI has another absorbance band at 689 nm due to the polaron-$\pi$ transition. Therefore, it is difficult to monitor the PtCl$_6^{2-}$ band at 454 nm during the reaction. However, after filtering the PANI/Pt composite the spectral region encompassing the PtCl$_6^{2-}$ species is void of absorbance bands for the polymeric and oligomeric species. This allows the consumption of the Pt species to be measured.

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During the chemical synthesis of PANI/Pt(IV), increases in the intensity of the bands between 320 nm and 400 nm and the emergence of new band at 689 nm are indicative of the formation of polymer. Furthermore, formation of polymer is accompanied by an increase in the baseline absorbance due to the formation of platinum colloids in solution. The band at 347 nm is attributed to the initial formation of short chain units of the polymer, which occurs due to the reduction of metal species and oxidation of aniline. The formation of soluble short chain oligomers is followed by the emergence of the long chain polymer with uv/vis absorbance centered at 689 nm. Once the reduction of PtCl$_6^{2-}$ ceases at around 20 hours, the reaction of oligomeric species leads to the continued formation of long chain polymer. The emergence of the polymer in solution is accompanied by a decrease in solubility and eventual precipitation of the PANI/Pt composite.

Based on the UV/vis spectroscopic data polymer initiation and subsequent reaction mechanism can be presented. There are two possible pathways for the chemical formation of PANI/Pt using PtCl$_6^{2-}$. The first possible mechanism involves the reduction PtCl$_6^{2-}$ to Pt(0) in one step. The second involves a two-step reduction process in which PtCl$_6^{2-}$ is reduced to the intermediate PtCl$_4^{2-}$ which reacts with only oligomeric species in the solution. The two-step process is supported on uv/vis data that showed no product is formed when aniline and PtCl$_4^{2-}$ are mixed. However, when PtCl$_4^{2-}$ was mixed with the dimer, n-phenyl-1,4-phenylenediamine, the polymer reaction was initiated and the PANI/Pt composite is formed. The two-step mechanism is presented in Figure 3.1.

The conversion of aniline to the radical cation is terminated when all of PtCl$_6^{2-}$ is reduced to PtCl$_4^{2-}$. This is supported by constant absorbance for the oligomeric species and the continued increase in absorbance band at 689 nm. This trend in the absorbance is indicative of the conversion of short chain oligomers to long chain polymer. The overall chemical reaction for the reduction of PtCl$_6^{2-}$ can be presented using the following
reaction. The products shown represent the building blocks for the polymer formation in solution.

\[
\begin{align*}
\text{PtCl}_6^{2-} & + 2 \text{NH}_3^- & \rightarrow & 2 \text{NH}_2^+ + \text{PtCl}_4^{2-} + 2\text{HCl} \\
\text{PtCl}_4^{2-} & + 2 \left[ \text{NH}_3^- \right]_n & \rightarrow & 2 \left[ \text{NH}^- \right]_n + \text{Pt}(0) + 2\text{HCl}
\end{align*}
\]

\[
\text{PtCl}_4^{2-} + 2 \text{NH}_3^- \not\rightarrow \text{No Reaction}
\]

Figure 3.1 Mechanism of formation for chemically prepared PANI/Pt composite

The uv/vis data also provides information regarding the interaction of the emerging polymer and the colloidal Pt formed in solution. As the solubility limit of the polymer is exceeded the precipitation occurs and a dramatic loss in uv/vis signal is observed at 689 nm. In addition, the absorbance shifts back to the baseline. This suggests that there is significant interaction between the Pt colloids in solution and the polymer. This is consistent with the nucleation of the polymer on noble metal surfaces such as Pt and Au during electrochemical oxidation of the monomer documented previously. Therefore, both the nucleation of the polymer onto the Pt particles in solution and the continued growth of the long chain polymer units play a role in the decreased solubility and precipitation of the PANI/Pt composite.

3.2.2 Electrochemical formation of PANI/Pt composite

The traditional method of incorporating metal into the polymers is through the electrochemical reduction of ionic metal species into a priori PANI membrane. A more
homogeneous polymer metal composite can be obtained from the electrochemical synthesis by controlling the oxidation state of the material using the applied potential. The controlled uptake and dispersion of PtCl$_6^{2-}$ is also possible using the known doping behavior of the polymer and the applied potential. In contrast, very little control over the final oxidation state or dispersion of Pt is possible in the chemical system.

The normal doping of PANI in acidic solutions requires that protons to be taken up during the reduction of the polymer and anions during the oxidation. The uptake of protons and anions ensures charge neutrality in the polymer membrane. The uptake of metallic anions is much different than that of typical anions from acid. When reversing from an oxidation potential to a reduction potential, anions from acid are expelled from the membrane. However, metallic anions are not expelled from the membrane during this process. Rather, the reduction of the metallic anion in the membrane occurs. For example, the reduction of AuCl$_4^-$, PtCl$_4^{2-}$, PtCl$_6^{2-}$ in PANI have all been documented previously.$^6$ The reduction of hexachloroplatinate to metallic platinum occurs through the oxidation of the polymer. The electrochemical reduction of hexachloroplatinate occurs at the amine nitrogen, which contains a lone pair of electrons. In the process, portions of the benzenoid units are converted to the quinoid units as electrons are removed from the nitrogen groups. The process increases the oxidation state of the electrochemically synthesized Pt composite in comparison to the a priori PANI membrane or chemically produced PANI which traditionally have equal numbers of oxidized and reduced units.$^7$

The general electrochemical reduction of PtCl$_6^{2-}$ by PANI is presented in Figure 3.2.

The reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$ are presented in Figure 3.3. For comparison, a Pt disc electrodes immersed in a PtCl$_6^{2-}$ and PtCl$_4^{2-}$ are also presented. The cyclic voltammograms in Figure 3.3a and 3.3b show the electrochemical response of bare Pt electrodes in the Pt anion solutions. The two voltammograms were used to identify the reaction potentials for the reduction of the anions and other electrochemical reactions that
occur over the potential range studied. The cyclic voltammograms presented in Figures 3.3c and 3.3d represent the first voltammetric cycle of the PANI membrane electrodes immersed in PtCl$_6^{2-}$ and PtCl$_4^{2-}$, respectively. For reference, the normal doping waves for

\[
\text{PtCl}_6^{2-} + 2\text{e}^- \rightarrow \text{PtCl}_4^{2-} + 2\text{Cl}^- \quad E_{1/2} = 0.46\text{V} \quad \text{vs. Ag/AgCl}
\]

\[
\text{PtCl}_4^{2-} + 2\text{e}^- \rightarrow \text{Pt}(0) + 4\text{Cl}^- \quad E_{1/2} = 0.535\text{V} \quad \text{vs. Ag/AgCl}
\]

proton and anion uptake in a PANI membrane are observed between -0.2 V to 0.80 V vs. Ag/AgCl in the absence of PtCl$_6^{2-}$ and PtCl$_4^{2-}$. The three voltammetric waves A, B and C are common to all electrodes for the reduction of both PtCl$_6^{2-}$ and PtCl$_4^{2-}$.

The three voltammetric waves do not all represent the reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$. The reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$ to Pt(0) occurs between 0.535 V and 0.46 V vs. Ag/AgCl based on previously published standard reduction potentials. The half wave potential for the reduction of Pt(IV)/Pt(II) and Pt(II)/Pt(0) are presented below:

Figure 3.2 Electrochemical reduction of PtCl$_6^{2-}$ by PANI
The experimental conditions used in our studies were not standard conditions and therefore, the potentials are shifted in the voltammetric response to more positive potentials between 0.63 to 0.53 V vs. Ag/AgCl. This region is denoted using the letter A. The reduction of both PtCl₆²⁻ and PtCl₄²⁻ are encompassed by the voltammetric range associated with A. The voltammetric waves noted by B and C correspond to formation of PtO⁹ and the adsorption of protons to form hydrogen⁹,¹⁰ respectively, at metallic Pt surfaces in the PANI membrane. In general, the formation of PtO takes place between 0.4 - 0.2V vs. Ag/AgCl. The reactions for oxide formation is given:

\[
\begin{align*}
Pt + H_2O & \rightarrow Pt-(OH)_{ads} + H^+ + e^- \\
Pt-(OH)_{ads} & \rightarrow PtO + H^+ + e^- 
\end{align*}
\]

The formation of Pt-H occurs typically below 0.0 V vs. Ag/AgCl.¹¹ The adsorption/desorption of hydrogen occurs through a two step process in which hydrogen is weakly adsorbed followed by stronger adsorption at the Pt surface.¹² The voltammetric waves for the adsorption processes are observed at potentials between 0.2 V to -0.1 V vs. Ag/AgCl. The reduction of protons on platinum⁵ are presented below:

\[
\begin{align*}
H^+_{(aq)} + e^- + Pt & \rightarrow Pt-(H)_{ads} \\
2Pt-(H)_{ads} & \rightarrow H_2 + 2Pt 
\end{align*}
\]

In Figures 3.3c and 3.3d, the voltammetric waves for the uptake of ClO₄²⁻, PtCl₆²⁻, and PtCl₄²⁻ are indistinguishable appearing at \( E = 0.768 \) V vs. Ag/AgCl in the voltammetry for the PANI membranes. However, the expulsion of ClO₄²⁻ is resolved relative to PtCl₆²⁻ and PtCl₄²⁻ reduction at \( E = 0.733 \) V vs. Ag/AgCl. The emergence of a second voltammetric wave, A, between \( E = 0.63 - 0.53 \) V vs. Ag/AgCl, encompasses the reduction of PtCl₆²⁻, and PtCl₄²⁻ to Pt(0). The calculated difference in the reduction
Figure 3.3 Cyclic voltammogram of a and b are Pt disc electrodes immersed in a solution containing 2.06 x 10^{-2} M K_2PtCl_4 in 1 M HClO_4 and 2.06 x 10^{-2} M K_2PtCl_6 in 1 M HClO_4 respectively, c and d are PANI film grown on a disc electrode immersed in a solution containing 2.06 x 10^{-2} M K_2PtCl_4 in 1 M HClO_4 and 2.06 x 10^{-2} M K_2PtCl_6 in 1 M HClO_4 the respectively. Scan rate v=10 mV/s and electrode area=0.015 cm^2
potential for the Pt(IV)/Pt(II) and Pt(II)/Pt(0) redox couples (0.08 V) suggests that the
two step reduction is contained within the broad voltammetric wave observed in the
potential range between 0.63 V to 0.53 V vs. Ag/AgCl. The absence of cathodic current
on the reverse scan implies that the reduction of PtCl\textsubscript{6}\textsuperscript{2-}, and PtCl\textsubscript{4}\textsuperscript{2-} to Pt (0) are
irreversible.

The voltammetric response for waves B and C are observed at E = 0.342 V and E =
0.210 V vs. Ag/AgCl for the PANI electrode in PtCl\textsubscript{6}\textsuperscript{2-} for the formation of platinum
oxide\textsuperscript{9} and the weak hydrogen adsorption\textsuperscript{9,10} respectively. The PANI film immersed in
PtCl\textsubscript{4}\textsuperscript{2-} the B and C waves are located at E = 0.355 V and E = 0.130 V vs. Ag/AgCl
respectively indicating that the hydrogen adsorption slightly different in PANI/Pt
composites. Similar voltammetric responses can be observed for the reduction of PtCl\textsubscript{6}\textsuperscript{2-},
and PtCl\textsubscript{4}\textsuperscript{2-} at Pt electrodes. For comparison, the potentials for waves B and C in the
voltammetric response for the Pt electrodes immersed in PtCl\textsubscript{6}\textsuperscript{2-} are located at E = 0.284
V and E = 0.084 V vs. Ag/AgCl. These values shift to E = 0.230 V and E = 0.052 V vs.
Ag/AgCl for Pt disc electrode immersed in PtCl\textsubscript{4}\textsuperscript{2-}.

Figure 3.4 presents the cyclic voltammometric response of the acid doping of PANI
electrodes, uptake and reduction of PtCl\textsubscript{6}\textsuperscript{2-}, and PtCl\textsubscript{4}\textsuperscript{2-} at the same membrane, followed
by the second acid doping of the electrodes. The bottom voltammograms represent, the
characteristic anion and proton uptake/expulsion waves for a PANI membrane in acid. at
The uptake and expulsion of protons in the PANI membranes are clearly resolved and can
be observed at half-wave potentials of E\textsubscript{1/2} = 0.113 V and 0.121 V vs. Ag/AgCl in the
cyclic voltammograms. The corresponding potentials for the uptake of the anion are also
similarly appearing at E = 0.74 V and E = 0.755 V for the PANI membrane in the acid
solution.

Integration of voltammetric waves associated with proton/anion uptake and expulsion
provides an estimate of the number of active sites in the 3-D polymeric membranes.

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Figure 3.4 Cyclic voltammograms of a PANI electrode Bottom, immersed in 1 M HClO₄ without Pt, Middle, in a solution containing 2.06 x 10⁻² M K₂PtCl₆ in 1 M HClO₄ (Left), and 2.06 x 10⁻² M K₂PtCl₄ in 1 M HClO₄ (Right), Top. Immersed in a 1 M HClO₄ after incorporation of PtCl₆²⁻ (Left) and PtCl₄⁷⁻ (Right)
Generally, the proton doping takes place at the imine and amine nitrogens in the polymer based on the pKa of the polymer and the dopant acid. However the reduction of PtCl₆²⁻ blocks the nitrogen sites within the 3-D polymer matrix reducing the uptake of protons and anions. Area covered by the voltammetric waves for proton and anion doping provides an estimate of the total charge passed during the uptake and expulsion of the two ionic species. The wave area was estimated by integrating the waves using the CHI660 software. Proton doping is resolved relative to the Pt electrochemistry limiting the error of the estimate. However, the voltammetric waves for anion uptake and expulsion are not resolved and are not used in the calculations. Table 3.1 provides the charge associated with the first and second proton doping and the reduction of proton doping associated with uptake and reduction of PtCl₆²⁻ and PtCl₄²⁻.

<table>
<thead>
<tr>
<th>Composite</th>
<th>PANI 1ˢᵗ proton doping, Q (C/cm²)</th>
<th>PANI 2ⁿᵈ proton doping Q (C/cm²)</th>
<th>% Difference in after incorporation of Pt</th>
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<tr>
<td>PANI/Pt (IV)</td>
<td>4.73×10⁻²</td>
<td>2.54×10⁻²</td>
<td>46</td>
</tr>
<tr>
<td>PANI/Pt (II)</td>
<td>3.54×10⁻²</td>
<td>1.63×10⁻²</td>
<td>54</td>
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</tbody>
</table>

The data in Table 3.1 shows that there is a significance decrease in the charge associated with the uptake/expulsion of protons. Lone pair electron densities in the nitrogen sites of the polymer are reduced by the reduction of PtCl₆²⁻/PtCl₄²⁻ and formation of Pt particles at nitrogen sites. The data suggest that the proton doping sites are blocked by the reduced Pt particles. It is important to note that after the first scan, the polymer contains metallic Pt particles within the polymer matrix. Further reduction of PtCl₆²⁻ or PtCl₄²⁻ can occur at nitrogen sites within the polymer or at the newly created Pt surfaces.

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Therefore, each subsequent scan does not decrease the proton doping proportionately in comparison to the first voltammetric scan.

3.2.3 Spontaneous reduction of Pt anion into the polymer

The previous section was focused on the electrochemical uptake and reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$. However, the formation of the PANI/Pt(IV) and PANI/Pt(II) composites can also be achieved through the spontaneous reaction of the polymer while immersing in solution containing PtCl$_6^{2-}$ and PtCl$_4^{2-}$. When PANI electrodes are immersed in solutions of PtCl$_6^{2-}$ and PtCl$_4^{2-}$ the anions are spontaneously reduced based on the inherent electron density of the polymer membrane. The reduction is believed to proceed at nitrogen sites with lone pair electrons. The cyclic voltammograms for the dipped PANI electrodes are presented in Figure 3.5.

The characteristic proton/anion doping prior to the immersion and spontaneous reduction of PtCl$_6^{2-}$ and PtCl$_4^{2-}$ is presented at the bottom of Figure 3.5 The characteristics anion and proton uptake/expulsion waves in 1M HClO$_4$ are well resolved for the both PANI membranes and they are located at $E_{1/2} = 0.764$ V and $E_{1/2} = 0.115$ V vs. Ag/AgCl respectively. Integration of the proton uptake/expulsion waves indicate that each electrode has approximately the same number of active amine and imine sites.

A significantly smaller reduction in the proton doping of each membrane is observed after immersing in PtCl$_6^{2-}$ and PtCl$_4^{2-}$ in comparison to the electrochemical reduction. This is consistent with the spontaneous reduction of Pt particles at the PANI membrane surface and subsequent blocking of active nitrogen sites in the material. Platinum was incorporated into the polymer by spontaneous reduction at the point of contact of the anion and polymer. This data supports the reduction of Pt at mainly surface sites with minimal permeation into the 3-D polymer membrane. Thus, reducing proton doping at the surface rather than the bulk of the polymer.

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Figure 3.5 Cyclic voltammetry of PANI electrodes immersed in a solution of 1 M HClO$_4$.

Bottom: Electrochemically formed PANI membranes. Top: PANI membrane electrodes after incorporation of Pt using PtCl$_6^{2-}$ (left) and PtCl$_4^{2-}$ (right).
Table 3.2 - Proton Doping Charge Integration

<table>
<thead>
<tr>
<th>Composite</th>
<th>PANI 1\textsuperscript{st} proton doping, Q (C/cm\textsuperscript{2})</th>
<th>PANI 2\textsuperscript{nd} proton doping Q (C/cm\textsuperscript{2})</th>
<th>% Difference in after incorporation of Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>PANI/Pt (IV)</td>
<td>3.16x10\textsuperscript{-2}</td>
<td>2.58x10\textsuperscript{-2}</td>
<td>18</td>
</tr>
<tr>
<td>PANI/Pt (II)</td>
<td>2.8x10\textsuperscript{-2}</td>
<td>2.08x10\textsuperscript{-2}</td>
<td>26</td>
</tr>
</tbody>
</table>

3.2.4 Electrochemistry of chemically prepared Platinum composites

The electrochemical and spontaneous reduction of PtCl\textsubscript{6}\textsuperscript{2-} and PtCl\textsubscript{4}\textsuperscript{2-} result in a decrease in proton doping due to Pt particles blocking the electroactive sites in the polymer. The interaction between Pt and nitrogen groups in the polymer is not fully understood. For electrochemical reduction to take place, a certain degree of electrostatic interaction is implied. Similarly, in the case of the chemical formation of PANI/Pt the nucleation of the polymer on Pt implies that there is a significant interaction between the polymer and the Pt particles. The electrochemical response for the chemically prepared PANI/Pt composite was studied using a glassy carbon electrode coated with a thin layer of paraffin oil followed by a thicker layer of PANI/Pt composite. The electrode was then cycled in a solution of 1M HClO\textsubscript{4}. The background current of a uncoated glassy carbon electrode and a glassy carbon/PANI/Pt composite electrode are presented in Figure 3.6.

The characteristics anion and proton uptake/expulsion peaks for the composite can be observed indicating that electroactive sites within the PANI/Pt composite are not completely blocked. However, the peak shape clearly shows that the doping is minimized relative to pure PANI (not shown).\textsuperscript{13} In addition, to the normal proton/anion doping waves, two additional weakly resolved voltammetric waves can be observed in the potential range from 0.30 to 0.65 V vs. Ag/AgCl. These two waves are consistent with the oxidation/reduction of trapped oligomeric materials in the polymer matrix. They
Figure 3.6 Cyclic voltammetry of glassy carbon electrodes immersed in a solution of 1 M 
HClO₄. Bottom: Glassy Carbon with no PANI/Pt. Top: Glassy Carbon with chemically 
prepared PANI/Pt.
are also observed if the polymer is over-oxidized during the degradation process of long chain PANI.\textsuperscript{13}

3.2.5 FTIR spectroscopy of PANI/Pt composites

FTIR spectroscopy was used to examine how the incorporation of Pt particles influences the chemical properties of the polymer. Specifically, the method will be used to examine the chemical signature and oxidation state of all the PANI/Pt composites produced. The oxidation state of each polymer is obtained by integration of the quinoid and benzenoid units in the polymer based on the following structure and formula:

\[
Oxidation \text{ State (R)} = \frac{\text{Area}_{\text{Quinoid}}}{\text{Area}_{\text{Benzenoid}}} = \frac{x}{1-x}
\]

The fingerprint region between 700-1600 cm\textsuperscript{-1} provides information regarding the characteristics bands attributed to the polymer. For example, the characteristics IR absorption bands for PANI can be identified at 1500 cm\textsuperscript{-1} and 1600 cm\textsuperscript{-1} for the aromatic benzene ring stretches, 1315 cm\textsuperscript{-1} for C-N stretching absorption, and 830 cm\textsuperscript{-1} for C-H out-of-plane bending mode.\textsuperscript{14} The similarities and the disparities in the FTIR spectra for the pure PANI/HBF\textsubscript{4}, electrochemical, dipped, and chemical PANI/Pt composites generated by PtCl\textsubscript{6}\textsuperscript{2-} or PtCl\textsubscript{4}\textsuperscript{2-} are presented in the Figures 3.7, 3.8, and 3.9, respectively.
The characteristics bands for the quinoid and benzenoid rings structures are located at 1597 cm\(^{-1}\) and 1512 cm\(^{-1}\) respectively for PANI/HBF\(_4\) before Pt incorporation. In contrast to PANI/HBF\(_4\), the bands attributed to the quinoid and benzenoid rings in the electrochemically prepared PANI/Pt(IV) composite, have shifted to higher energies of 1631 cm\(^{-1}\) and 1522 cm\(^{-1}\) respectively. A significant 23 cm\(^{-1}\) shift from 832 cm\(^{-1}\) to 855 cm\(^{-1}\) in the out-of-plane C-H bond can be observed in the PANI/Pt(IV) composite, as compared to the pure PANI/HBF\(_4\). This may be due to the higher electron density the PANI/Pt composite through the valance band of the Pt metal. The most notable disparity can be observed for the C-N stretch when comparing the PANI/Pt(IV) composite with emeraldine salt form of PANI. The characteristic band at 1334 cm\(^{-1}\) of PANI/HBF\(_4\) has shifted to 1365 cm\(^{-1}\) in the composite. This 31 cm\(^{-1}\) shift to higher energy is an indicative of direct influence of the Pt particles and loss of electron density at the nitrogen heteroatom in the polymer. The reduction of the Pt species occurs at the expense of the lone pair electrons at the nitrogen groups, reducing the electron density within the polymer. The ratio of oxidized and reduced units in the polymer obtained through integration results in a value of 3.19 for PANI/Pt(IV). The value indicates that there are more oxidized units than reduced units in the polymer.

A similar response can be observed for the electrochemically prepared PANI/Pt(II) composite. The characteristics quinoid and benzenoid bands have shifted to higher energies and they are located at 1613 cm\(^{-1}\) and 1522 cm\(^{-1}\) respectively. In addition, the IR bands for C-N bond and out-of-plane C-H bond at 1347 cm\(^{-1}\) and 848 cm\(^{-1}\) are also consistent with the results observed for PANI/Pt(IV). In comparison, the ratio of oxidized versus reduced units in the polymer provides a ratio of R = 2.32. This value is again consistent with more oxidized units in PANI/Pt(II) and comparable to PANI/Pt(IV). The value might be slightly lower due to the lower electron density required to reduce PtCl\(_4^{2-}\) in comparison to PtCl\(_6^{2-}\) in the polymer.
Figure 3.7 FTIR spectra of a. Pure PANI/HBF$_4$ electrochemically prepared a. PANI/Pt(IV) and b. PANI/Pt(II) composites.
Significant changes in the FTIR spectra for dipped PANI/Pt(IV) and PANI/Pt(II) indicate that the reduction and interaction of Pt with the PANI membrane is much different than that for electrochemically produced PANI/Pt composites. Specifically the benzenoid and quinoid band show a significant reduction in intensity relative to the other bands in the finger print region. The ratio of oxidized and reduced units for these two materials was not calculated due to the diminished signal. The quinoid, benzenoid N-H bond and out-of-plane C-H shift to higher frequency consistent with the reduction of Pt. However, the FTIR band for the quinoid structure splits into two distinct bands located at 1629 cm\(^{-1}\) and 1573 cm\(^{-1}\) indicating that the Pt changes the ability to polarize the quinoid ring structure in the composites. The IR band for the benzenoid ring is located at 1504 cm\(^{-1}\) in both dipped composites. The C-N bond in PANI/Pt(IV) and PANI/Pt(II) can be observed at 1357 cm\(^{-1}\) and at 1343 cm\(^{-1}\) respectively, indicative of the difference in electron densities required to reduce the two species. The shifts in the out-of-plane C-H bonds towards higher energies further confirm the energy required to polarize the C-H bonds within the quinoid structure are different when Pt is present.

The electrochemically and dipped PANI/Pt composites demonstrate that Pt influence the polymer through the conversion of benzenoid to quinoid units and changes in polarizability of nitrogen groups within the polymer. The FTIR spectra for the chemically formed PANI/Pt composites are examined for comparison with the electrochemically and spontaneously formed PANI/Pt composites. The chemical synthesis of PANI/Pt composites should show significant differences in the ratio of oxidized and reduced units due to the fact that polymer does not have to reduce either PtCl\(_6^{2-}\) or PtCl\(_4^{2-}\) after formation. Rather, the reduction of the two species is tied to the oxidative polymerization of PANI. The nitrogen groups in the polymer should also be influenced differently due to the difference in oxidation-state (i.e., the polymer is more reduced in comparison to the electrochemically generated PANI/Pt composites). The
Figure 3.8 FTIR spectra of PANI membranes immersed in solutions of a. PtCl₆²⁻ and b. PtCl₄²⁻.
calculated ratio of oxidized versus reduces units for the chemically prepared composites are $R = 0.71$ for PANI/Pt(IV) and $R = 0.69$ for PANI/Pt(II). The ratios indicate that there are more reduced units than oxidized units in the chemically prepared composites.

The IR spectra for the chemically prepared composite and PANI/HBF$_4$ are comparable to the electrochemically and spontaneously prepared PANI/Pt composites. The IR bands associated with the aromatic ring stretching, quinoid and benzenoid rings shift to lower energies for the both chemically prepared PANI/Pt(II) and PANI/Pt(IV) composites. The difference is likely due to higher electron density in the chemically prepared composites. For reference the quinoid and benzenoid bands appear between 1588 - 1589 cm$^{-1}$ and 1493 - 1504 cm$^{-1}$ for the two chemically prepared composites. Furthermore, significant shift of the C-N moiety and the out-of-plane C-H bond towards lower energies of 1311 - 1316 cm$^{-1}$ and 819 - 827 cm$^{-1}$ also verifies the change in the chemical nature of the chemically prepared composites. The shifts to lower energy are a direct result of the synthetic method used and the overall interaction of Pt particles with nitrogen groups in the polymer. In contrast to the electrochemical and spontaneously prepared PANI/Pt composites, the IR band for the characteristic N-H stretching is at a much higher intensity in the chemically prepared PANI/Pt composites. In addition, the N-H band and aromatic C-H bands$^1$ are superimposed on each other in the region of 2600 cm$^{-1}$ and 3600 cm$^{-1}$. Presence of ring overtones in the region of 1700 cm$^{-1}$ and 2400 cm$^{-1}$ can be observed in the chemically synthesized PANI/Pt composites that are not observed in other composites. The ring overtones observed at 1952 cm$^{-1}$ and 2322 cm$^{-1}$ are indicative of the formation of amine salts in chemically prepared PANI/Pt composites.

3.2.6 XPS analysis of PANI/Pt composites.

The binding energy data of XPS spectra provides information regarding the oxidation state of species in a given material. The XPS spectra for the electrochemical, dipped and
Figure 3.9 FTIR spectra of chemically prepared a. PANI/Pt(IV) and b. PANI/Pt(II) composites
chemical composites prepared using PtCl$_6^{2-}$ or PtCl$_4^{2-}$ are presented in figure 3.10, 3.11, and 3.12 respectively.

The presence of metallic platinum in PANI/Pt composites generated either from PtCl$_6^{2-}$ or PtCl$_4^{2-}$ can be confirmed using the two Pt$^{4f}$ bands located at 71.2 eV and 73.9 eV. These values are in agreement with the previously reported energies for Pt(0). It is worth noting that the Pt$^{4f}$ bands in the dipped composites are more pronounced than in for the electrochemically or chemically prepared PANI/Pt composites, due to the presence of Pt particles at the surface of the polymer in the dipped composite. This result is consistent with the fact that XPS is a surface technique. Furthermore, the presence of Pt$^{4d}$ bands at the binding energies of 314.4 and 331.6 eV is also an indicative of metallic platinum. The absence of bands at 73.9 eV for the Pt(II)$^{4f}$ and 77.8 eV for Pt(IV)$^{4f}$ confirms that the only species of Pt present in the PANI/Pt composites are metallic platinum.

Identification of dopant anions is based on the presence of Cl in each sample. Two Cl$_2^p$ bands at 198.7 eV and 207.7 eV attributed to the Cl$^-$ from PtCl$_6^{2-}$ or PtCl$_4^{2-}$ and ClO$_4^{2-}$ from HClO$_4$ can be observed for the electrochemically prepared and dipped PANI/Pt composites. The Cl$_2^s$ bands for both Cl$^-$ and ClO$_4^{2-}$ species are located at the 270.6 eV and 278.6 eV respectively. There is only one band for Cl$_2^p$ or Cl$_2^s$ for the chemically prepared PANI/Pt(IV) and PANI/Pt(II). The Cl$^-$ is present in the PANI/Pt composite as a result of the reduction of PtCl$_6^{2-}$ or PtCl$_4^{2-}$. Therefore, the XPS confirms the reduction of the two species.

3.2.7 Scanning electron microscope images of PANI/Pt composites

The previous studies using X-ray photoelectron spectroscopic data indicates that the Pt metal is the only species present in all PANI/Pt composites. However, previous characterization of the PANI/Pt composites provides no information regarding Pt surface distribution or particle size. SEM is a surface technique that is typically used to study
Figure 3.10 X-ray photoelectron spectra of electrochemically prepared a. PANI/Pt(IV) b. PANI/Pt(II)
Figure 3.11 X-ray photoelectron spectra of PANI membranes immersed in solutions of a. $\text{PtCl}_6^{2-}$ and b. $\text{PtCl}_4^{2-}$. 

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Figure 3.12 X-ray photoelectron spectra of chemically prepared a. PANI/Pt(IV) b. PANI/Pt(II)

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morphology and domain size of Pt particles. However, the dispersion of Pt particles within the polymer matrix cannot be observed directly because the method provides only surface images.

SEM images for the electrochemically prepared PANI/Pt(IV) and PANI/Pt(II) composites are presented in the figure 3.13. Typically, Pt particles in the electrochemically synthesized composites are much smaller than the particles in the chemical composites. The particle size does not change significantly for the PANI/Pt composite generated from either PtCl$_6^{2-}$ or PtCl$_4^{2-}$. Pt particles on the order of ~100 nm to 1 μm in diameter are observed for the PANI/Pt(IV) and PANI/Pt(II) composites. It is not possible to determine the dispersion of the Pt particles in the material. However, the porous architecture of the polymer provides high surface area for the metal particles to be dispersed.

The SEM images of dipped PANI/Pt composites presented in figure 3.14, also confirm the presence of metallic platinum. The distribution of platinum particles are at the surface and the distribution is not uniform as observed in the electrochemically prepared PANI/Pt composites. The distribution of the particles is likely due to energetic differences in the material at the point of contact after the reduction of the PtCl$_6^{2-}$ or PtCl$_4^{2-}$. In fact, the particle diameter for the dipped PANI/Pt(IV) and Pt(II) composites is less than 200nm, with a more uneven distribution on the surface.

For comparison, the SEM images of the chemically fabricated PANI/Pt composites are presented in figure 3.15 and 3.16. The particles are much larger than those in electrochemical and dipped composites. The particles are approximately 1μm in diameter in the both chemically prepared PANI/Pt(IV) and PANI/Pt(II) composites. A more uniform surface distribution of particles in the polymer can be observed.
Figure 3.13 SEM images of electrochemically prepared a. PANI/Pt(IV) at x 20000 magnification and b. PANI/Pt(II) at x 20000 magnification.
Figure 3.14 SEM images of dipped a. PANI/Pt(IV) at x 20000 magnification and b. PANI/Pt(II) at x 14000 magnification.

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Figure 3.15 SEM image of chemically prepared PANI/Pt(IV) composite a. x 1000 magnification and b. x 4300 magnification
Figure 3.16 SEM image of chemically prepared PANI/Pt(II) at x 3700 magnification.
3.2.8 Electronic Resistivity/Conductance of the PANI/Pt composites

Emeraldine salt is the most conductive form of PANI with an equal number of oxidized units and reduced units and high degree of proton doping. The emeraldine salt has a theoretical oxidation state of $1.0$, indicative of equal number of oxidized and reduced units. In addition, the synthetic conditions are sufficiently acidic to allow full proton doping of the polymer. The high degree of proton doping increases the number of free charge carriers in the polymer, which enables the electrons to flow freely along the polymer chain.\(^{17}\)

The four-point probe method was used to measure the conductivity of the PANI/HBF\(_4\), chemically and electrochemically synthesized PANI/Pt composites. The conductance of the pure polymer without Pt is $9.0 \pm 10\% \text{ S/cm}$ is in consistent with the previously reported values of $2-10 \text{ S/cm.}^{18}$ The higher conductivity of PANI/HBF\(_4\) is due to the equal number of oxidized and reduced units and higher degree of proton doping. In contrast, conductivities of the chemically and electrochemically prepared PANI/Pt composites are $1.1 \times 10^{-7} \text{ S/cm}$ and $6.6 \times 10^{-3} \text{ S/cm}$ respectively. The decrease in the conductivity of the chemically produced PANI/Pt is due to the reduced number of charge carriers in the polymer and reduced oxidation state. Formation of amine salt and the isolation of charge in the ammonium groups within the polymer contribute to the decrease in charge carriers. In addition, the higher number of reduced units in the polymer also play a key role in decreasing the conductivity of the chemically prepared PANI/Pt composite.

The conductivity of the electrochemically prepared PANI/Pt composite is lower than that of the emeraldine salt. The incorporation of platinum particles also reduces the proton doping by 52\% physically blocking the proton from accessing the active nitrogen sites. In addition, the increased number of oxidized units in the polymer also diminishes the conductivity.
3.3 References


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4.1 Introduction

Although PANI is a conductive polymer, it does not display any catalytic activity without the incorporation of platinum metal. The dispersion of platinum particles in polyaniline facilitates electrocatalytic reactions such as the oxidation of methanol, formic acid and formaldehyde. These reactions are important in the development of fuel cells.\textsuperscript{1,2} The 3-D polymer has high surface area to allow uniform dispersion of Pt metal particles into the polymer. The high dispersion increases the overall catalytic surface area available to the system. Furthermore, high dispersion reduces the amount of platinum loading required to obtain catalytic activity, which lowers the cost of production of the material.\textsuperscript{3}

The catalytic reaction of methanol at Pt surfaces proceeds by a multi-electron oxidative process where several products or intermediates are formed.\textsuperscript{4,5} Laborde \textit{et al.} have proposed a mechanism for the oxidation of methanol at a platinum modified polyaniline electrode in acidic medium. The mechanism was based on data obtained from electrochemically modulated infrared reflectance spectroscopy (EMIRS).\textsuperscript{1} In the proposed mechanism methanol oxidation can take place through dual pathways. The first path proceeds through direct formation of CO\textsubscript{2} through a reactive intermediate such as formaldehyde or formic acid. In the first step methanol is adsorbed and converted to (CH\textsubscript{2}O)\textsubscript{ads}. Subsequently, it leads to the formation of reactive intermediates such as (CHO)\textsubscript{ads} and (OH)\textsubscript{ads}. Oxidation of these reactive intermediates can proceed either
directly to carbon dioxide or through indirect pathway via (CO)\text{ads} to carbon dioxide (CO\textsubscript{2}).

\begin{align*}
\text{Pt} + (\text{CH}_3\text{OH})_{\text{sol}} &\rightarrow \text{Pt-(CH}_3\text{OH)}_{\text{ads}} \\
\text{Pt-(CH}_3\text{OH)}_{\text{ads}} &\rightarrow \text{Pt-(CH}_2\text{O)}_{\text{ads}} + 2\text{H}_\text{aq}\text{+} + 2\text{e}^- \\
\text{Pt-(CH}_2\text{O)}_{\text{ads}} &\rightarrow \text{Pt + (CH}_2\text{O)}_{\text{sol}} \\
\text{Pt-(CH}_2\text{O)}_{\text{ads}} &\rightarrow \text{Pt-(CHO)}_{\text{ads}} + \text{H}_\text{aq}\text{+} + \text{e}^- \\
\text{Pt + H}_2\text{O} &\rightarrow \text{Pt-(OH)}_{\text{ads}} + \text{H}_\text{aq}\text{+} + \text{e}^- \\
\text{Pt-(CHO)}_{\text{ads}} + \text{Pt-(OH)}_{\text{ads}} &\rightarrow 2\text{Pt} + \text{CO}_2 + 2\text{H}_\text{aq}\text{+} + 2\text{e}^- \\
\text{Pt-(CHO)}_{\text{ads}} + \text{Pt-(OH)}_{\text{ads}} &\rightarrow \text{Pt + Pt-(COOH)}_{\text{ads}} + \text{H}_\text{aq}\text{+} + \text{e}^- \\
\text{Pt-(CHO)}_{\text{ads}} + \text{Pt-(OH)}_{\text{ads}} &\rightarrow \text{Pt + Pt-(CO)}_{\text{ads}} + \text{H}_\text{aq}\text{+} + \text{e}^- \\
\text{Pt-(CO)}_{\text{ads}} + \text{Pt-(OH)}_{\text{ads}} &\rightarrow 2\text{Pt} + \text{CO}_2 + \text{H}_\text{aq}\text{+} + \text{e}^- \\
\text{Pt-(CO)}_{\text{ads}} + \text{Pt-(OH)}_{\text{ads}} &\rightarrow \text{Pt + Pt-(COOH)}_{\text{ads}} \\
\text{Pt-(COOH)}_{\text{ads}} &\rightarrow \text{Pt + CO}_2 + \text{H}_\text{aq}\text{+} + \text{e}^- 
\end{align*}

Figure 4.1 The proposed mechanism for methanol oxidation on platinum modified polyaniline electrode in acidic medium by Laborde et al.\textsuperscript{1}

The oxidation of methanol at Pt surfaces results in the formation of CO. The CO can remain chemisorbed at the surface of the Pt reducing active catalytic sites.\textsuperscript{1,6} Poisoning is a term that is used to identify the diminished catalytic activity and cell efficiency due to CO adsorption at Pt surfaces. The results of Laborde et al. demonstrate that the poisoning caused by the (CO)\text{ads} can be minimized by increasing dispersion of platinum particles in the PANI film. Electrochemical uptake and reduction of PtCl\textsubscript{6}\textsuperscript{2-} and PtCl\textsubscript{4}\textsuperscript{2-} can be used to increase dispersion of Pt particles in the PANI membrane. In addition, the particle diameter plays a key role in the dispersion based on steric repulsion and Pt particle
interaction within the membrane. Although the incorporation of Pt in PANI is the focus of this chapter, optimization of particle diameter was not considered. In general, the catalytic activity of a bulk Pt electrode is sufficiently less than highly dispersed Pt. The ability to increase catalytic activity is based on increasing the rate of reaction for the rate-determining step, adsorption of methanol. In addition the high surface area of dispersed Pt and porosity of the PANI film increases the diffusion rate of methanol into the PANI/Pt composite by minimizing diffusion barriers.

The reaction pathway for formic acid is much like the mechanism proposed for methanol. It has been suggested that the catalytic oxidation of formic acid can also take place through two separate pathways. The pathways are presented in Figure 4.2. In the first pathway oxidation of formic acid can take place through a direct path to CO$_2$ via the reactive intermediate Pt-COOH. The indirect path proceeds through the Pt-CO intermediate. Osawa et al have suggested that the decomposition of adsorbed formate will give CO$_2$.

![Figure 4.2 Dual-path mechanism for formic acid oxidation](image)

The objective of our study was to identify how the method of incorporating platinum particles in PANI influences the catalytic activity. In this chapter the electrochemical,
dipped and chemical PANI/Pt composites are compared using the known catalytic reactions of methanol and formic acid in acidic solutions. In the case of electrochemical and dipped sample preparation the number of active proton doping sites were similar so that a direct comparison of the doping and catalytic response was possible. To compare amount of proton doping and catalytic activity in each case, all of the voltammetric responses were normalized against the PANI proton doping in 1 M HClO₄ prior to introducing Pt.

4.2 Results and Discussion

The oxidation of methanol and formic acid were carried out at electrodes produced from electrochemically, spontaneously, and chemically formed PANI/Pt composites. In this chapter, the composites prepared using PtCl₆²⁻ will be denoted as PANI/Pt (IV) and PtCl₄²⁻ will be denoted as PANI/Pt (II).

4.2.1 Catalytic Reactivity of PANI/Pt Composites

The catalytic oxidation of methanol is presented in Figure 4.3. The voltammograms show ten cycles in the catalytic reaction. The catalytic reaction results in a negative current response in both the forward and reverse voltammetric scans. An identical voltammetric response was observed in the oxidation of formic acid. The oxidation of methanol and formic acid occurs in the forward and reverse scans regardless of electrode polarization, which is indicative of catalytic reactions. In addition, the forward and reverse scans for the catalytic oxidation of methanol and formic acid have different thermodynamic potentials. This indicates that the COads is formed at the Pt surface during methanol and formic acid oxidation. The difference in potentials is consistent with strong adsorption and plays a major role in the catalytic reaction. The CO formed is considered as a poisoning species because it blocks the catalysis sites in the platinum composites.
Figure 4.3 Cyclic voltammograms of electrochemically prepared PANI/Pt(II) electrode immersed in a solution containing 0.5 M methanol in 0.5 M H$_2$SO$_4$. 

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The cyclic voltammetry for the catalytic oxidation of methanol and formic acid by PANI/Pt(IV) and PANI/Pt(II) are presented in Figures 4.4 and 4.5. The Pt was introduced into polymer by electrochemical reduction, spontaneous reduction, and direct chemical synthesis. The cyclic voltammetry from the oxidation of methanol and formic acid by electrochemically formed PANI/Pt(IV) membrane appears in the top left of figure 4.4. The oxidation of methanol is initiated at ~0.35 V vs. Ag/AgCl and reaches a maximum current density at a potential of 0.64 V vs. Ag/AgCl. Previous studies\(^1,10\) have shown that the potential for methanol oxidation at Pt electrodes was ~0.64 V vs. Ag/AgCl which is consistent with our data. As stated previously the oxidation of methanol and formic acid oxidation results in the strong chemisorption of CO at the Pt surface. The adsorption of CO reduces the catalytically active sites in the PANI/Pt composites and pushes the potential to more negative values. In Figure 4.4 the current maximum for the reverse scan is observed at 0.56 V vs. Ag/AgCl. The potential difference between the forward and reverse scan is 0.08 V. The difference in potentials is indicative of the degree of poisoning by CO. However, the difference in potential is also due to the fact that at more positive potentials CO formed is oxidized to CO\(_2\) which is displaced from the Pt surface renewing activity at previously blocked sites.\(^1\) Therefore higher methanol oxidation can be observed in the positive sweep. Furthermore, the high dispersion of Pt particles in the electrochemically prepared PANI/Pt composites reduces the degree CO adsorption at Pt sites in comparison to bulk Pt surfaces.\(^1,6\) The shift to a more positive potential in the positive sweep indicates that the oxidation of methanol and formic acid is thermodynamically more favorable with lower free energy, \((\Delta G = -nF\Delta E_{\text{re}})\)

In the formic acid oxidation proton expulsion peak at \(E = 0.25\) V vs. Ag/AgCl can be resolved and it is followed by oxidation of formic acid at \(E = 0.65\) V vs. Ag/AgCl. The oxidation of formic acid displays a wider voltammetric wave at \(E = 0.40\) V vs. Ag/AgCl in the forward (negative potential) sweep. The Integration of the formic acid oxidation
Figure 4.4 Cyclic voltammograms showing the oxidation of methanol or formic acid in solutions containing either 0.5 M MeOH or 0.5 M HCO₂H in 0.5 M H₂SO₄. Left Top: electrochemically prepared PANI/Pt(IV) electrode, Right Top: dipped PANI/Pt(IV) electrode. Bottom: Chemically prepared PANI/Pt(IV).

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peaks for the positive and negative sweep indicates that the highest oxidation occurs during the negative sweep. This observation is opposite of what was reported in previous studies. The studies by Laborde and et al. indicate the highest formic acid oxidation is observed during the positive sweep. The difference in results of this study may be due to the higher pH used in our studies. The formation of formate ion is the rate-determining step in the formic acid oxidation. Low pH in the medium inhibits the deprotonation of formic acid to form formate ion. Subsequently, adsorption of formate ion would be slowed. However, as the potential moves from positive to negative during the negative sweep, H⁺ uptake by PANI enhances the formation of formate ion. Therefore, higher formic acid oxidation can be observed in the negative sweep.

The voltammetric responses for the oxidation of methanol and formic acid can be observed for the dipped PANI/Pt(IV) composites in Figure 4.4 top right. Although the voltammetric responses for the dipped electrodes are similar they are strikingly different than the oxidation of methanol and formic acid at electrochemically prepared PANI/Pt(IV) electrodes. We do not observe catalytic activity for the dipped, spontaneously reduced PANI/Pt composite electrodes. The characteristic proton expulsion peak at E = 0.25 V vs. Ag/AgCl is clearly visible in both methanol and formic acid solution with the absence of current due to the oxidation of methanol and formic acid. The proton uptake and expulsion is also observed in both the methanol and formic acid solutions. This maybe due to the fact reduction of PtCl₆²⁻ has been limited to the surface limiting dispersion. Limiting the dispersion of Pt in the PANI membrane increases the susceptibility of the Pt surfaces to poisoning from CO adsorption. It is likely that this CO adsorption in these samples has poisoned the surface eliminating catalytic activity. The results are consistent with surface exposed Pt in the spontaneously dipped PANI/Pt composites.

The electrochemical response of PANI/Pt(IV) produced from the chemical synthesis is presented at the bottom of Figure 4.4. In contrast to the electrocatalytic activity
observed for the electrochemically prepared PANI/Pt(IV) composite, the chemically prepared composites shows little catalytic activity. The voltammetric wave at $E = 0.48$ V vs. Ag/AgCl observed during the positive sweep corresponds to the oxidation of methanol and formic acid. Additionally, the methanol and formic acid oxidation potential have shifted to a more negative potentials in comparison to the electrochemically prepared PANI/Pt(IV). This indicates the oxidation of methanol and formic acid by chemically prepared PANI/Pt(IV) is less spontaneous. A more significant observation involves the complete loss of catalytic activity for the negative sweep. To understand the decrease in catalytic activity of the chemically prepared composites, the mechanism of formation of the material must be considered. In contrast to either the electrochemical or dipped PANI/Pt composites, the chemical formation proceeds through nucleation and growth of PANI on pre-formed Pt particles in solution. The active catalytic sites are blocked by polymer nucleation on the Pt surface. This is consistent with the known passivation of metal surfaces by PANI.  

The data in Figure 4.4 suggest that the method of platinum incorporation influences the catalytic activity of PANI/Pt composites. The differences arise from the dispersion of Pt into the polymer matrix. Higher dispersion limits the chemisorption and poisoning of the Pt surface by CO. In addition, the nucleation and growth of the polymer on preformed Pt surfaces limits the catalytic activity through passivation.

For comparison to PANI/Pt(IV) the oxidation of methanol and formic acid by the electrochemically prepared PANI/Pt(II) composites is presented in Figure 4.5. The voltammetric responses for PANI/Pt(II) composites produced using electrochemical, spontaneous reduction and chemically are similar to the electrochemical response for PANI/Pt(IV) shown in Figure 4.4. The oxidation of methanol and formic acid by the electrochemically prepared PANI/Pt(II) are presented in the top left of figure 4.5. The methanol oxidation by the electrochemically prepared PANI/Pt(II) is initiated at $E = 0.35$ V vs. Ag/AgCl and reaches its maximum at $E = 0.60$ V vs. Ag/AgCl. The methanol oxidation...
Figure 4.5 Cyclic voltammograms showing the oxidation of methanol or formic acid in solutions containing either 0.5 M MeOH or 0.5 M HCO₂H in 0.5 M H₂SO₄. Left Top: electrochemically prepared PANI/Pt(II) electrode, Right Top: dipped PANI/Pt(II) electrode. Bottom: Chemically prepared PANI/Pt(II).
oxidation is observed at $E = 0.53$ V vs. Ag/AgCl in the negative sweep. In contrast, the formic acid oxidation by the electrochemically prepared PANI/Pt(II) starts at $E = 0.45$ V vs. Ag/AgCl. The formic acid oxidation can be observed at $E = 0.65$ V vs. Ag/AgCl. In addition proton expulsion peak also can be observed at $E = 0.25$ V vs. Ag/AgCl in the positive sweep. Again, low formic acid oxidation can be observed in the positive sweep as seen in the formic acid oxidation by the electrochemically prepared PANI/Pt(IV). During the negative sweep a wide voltammetric wave can be observed for the formic acid oxidation at $E = 0.45$ V vs. Ag/AgCl. Due to the ease of formation of formate ion in the negative sweep higher formic acid oxidation can be observed.

The oxidation of methanol and formic acid by the dipped PANI/Pt(II) composites are presented at the top right of Figure 4.5. In comparison to the electrochemical PANI/Pt(II) composites the dipped PANI/Pt(II) composites does not exhibit any catalytic activity. The proton expulsion peak shifts to more positive potential of $E = 0.25$ V and $E_{1/2} = 0.20$ V vs. Ag/AgCl during the methanol and formic acid catalysis respectively. These voltammometric responses indicates there is little catalytic activity in the dipped PANI/Pt(II) composites.

The cyclic voltammetric responses for the methanol and formic acid oxidation by chemically prepared PANI/Pt(II) composite are presented at the bottom cyclic voltammograms of figure 4.5. In comparison, with the dipped PANI/Pt(II) composites, the chemically prepared composites exhibit more catalytic activity, confirmed by the presence of voltammometric wave at $E = 0.58$ V vs. Ag/AgCl for both methanol and formic acid oxidations. However, the catalytic activity observed in the chemically prepared PANI/Pt(II) composites it is less prominent in comparison to the electrochemically prepared composite. The absence of methanol and formic acid oxidation peak in the negative sweep is a significant observation that verifies the diminished catalytic activity in the chemical composites. The lower oxidation potentials in the positive sweep for methanol and formic acid oxidation suggest that the oxidations

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are less spontaneous than observed in the electrochemically prepared PANI/Pt(II) composites.

Considering all the electrochemical data, we can state that the catalytic activity of electrochemical composites is very high in comparison to the other methods of PANI/Pt preparation. The high catalytic activity may be due to the high and uniform dispersion of platinum particles in the PANI film obtained for the electrochemical reduction of PtCl\textsubscript{6}\textsuperscript{2-} and PtCl\textsubscript{4}\textsuperscript{2-}.

4.2.3 Comparison of PANI/Pt(IV) and PANI/Pt(II) composites.

In the previous section platinum incorporation methods change the catalytic activity of the PANI/Pt composites. The electrochemical incorporation of platinum into the polymer shows the highest catalytic activity. In this section, a direct comparison between the materials produced from PtCl\textsubscript{4}\textsuperscript{2-} to PtCl\textsubscript{6}\textsuperscript{2-} is performed. Figures 4.6 and 4.7 present the oxidation of methanol and formic acid carried out with PANI/Pt composites generated from PtCl\textsubscript{4}\textsuperscript{2-} and PtCl\textsubscript{6}\textsuperscript{2-}.

The voltammetric response for both methanol and formic acid oxidation by electrochemically prepared PANI/Pt(II) shows highest catalytic activity as compared to PANI/Pt(IV). Integration of methanol and formic acid oxidation during the positive sweep, for both electrochemically prepared PANI/Pt(IV) and PANI/Pt(II) composites (bottom Figure 4.6 and 4.7) provides an estimate of the total reaction using the charge passed for methanol and formic acid oxidation. Table 4.1 provides the charge associated with oxidation of methanol and formic acid by electrochemically prepared PANI/Pt(IV) and PANI/Pt(II) composites. In addition the percent difference between the oxidation of methanol and formic acid at PANI/Pt(IV) and PANI/Pt(II) is provided.
Figure 4.6 Oxidation of methanol by electrochemically, dipped and chemically prepared PANI/Pt(IV) and PANI/Pt(II) composites.
Figure 4.7 Oxidation of formic acid by electrochemically, dipped and chemically prepared PANI/Pt(IV) and PANI/Pt(II) composites.
Table 4.1- Charges associated with the methanol and formic acid oxidation

<table>
<thead>
<tr>
<th></th>
<th>Electrochemically prepared PANI/Pt(IV) Q (C/cm²)</th>
<th>Electrochemically prepared PANI/Pt(II) Q (C/cm²)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH oxidation</td>
<td>4.212 x 10⁻¹</td>
<td>9.76 x 10⁻¹</td>
<td>56</td>
</tr>
<tr>
<td>HCOOH oxidation</td>
<td>3.78 x 10⁻¹</td>
<td>1.527</td>
<td>75</td>
</tr>
</tbody>
</table>

The table 4.1 indicates that the oxidation of methanol and formic acid is significantly higher when the PANI/Pt composite was produced from PtCl₄²⁻. This is likely due to the fact that the two electron reduction of PtCl₄²⁻ requires less electron density from the polymer minimizing the oxidation state of the polymer in comparison to PANI/Pt(IV). In addition, the particles in the PANI/Pt(IV) composite have larger diameters between 200 nm to 1μm compared to the particles in the PANI/Pt(II) composite (100nm to 500 nm). Smaller and more highly dispersed particles are more effective in the oxidation of methanol and formic acid. The higher surface area, lower oxidation state of the polymer and the lower adsorption of CO at the more highly dispersed, smaller Pt particles contribute to the high catalytic activity in PANI/Pt(II). In contrast to the electrochemical composites there is no significant difference in the voltammetry observed for dipped PANI/Pt samples. Neither composite shows catalytic activity. Finally, chemically prepared PANI/Pt displays trends consistent with the electrochemically prepared PANI/Pt composites. Although the chemical composites exhibit far less catalytic activity in comparison to the electrochemical materials, the PANI/Pt(II) composite shows greater catalytic activity in comparison to PANI/Pt(IV).
4.4 References


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CHAPTER 5

CONCLUSIONS

The goal of this thesis project was to perform the synthesis of PANI/Pt(IV) and PANI/Pt(II) composites electrochemically, through spontaneous reduction and oxidative polymerization of aniline and oligomers using PtCl₆²⁻ and PtCl₄²⁻. The electrocatalytic activity of PANI/Pt composite materials was examined for methanol and formic acid oxidation. The electrochemical, chemical and morphological properties of the PANI/Pt composites were also compared.

In the electrochemical synthesis, platinum modified PANI films were fabricated through the uptake and reduction of PtCl₆²⁻ or PtCl₄²⁻. The reduction of PtCl₆²⁻ and PtCl₄²⁻ occurs at amine nitrogens in the polymer producing imine groups in the process. This is confirmed using FTIR spectroscopy by integrating the number of quinoid and benzenoid units, which showed a higher oxidation state of the polymer as compared to the emeraldine salt form of PANI. In addition, there is a significant decline in the anion and proton doping with the introduction of platinum into the polymer. The nitrogen sites in the polymer have been blocked by the reduction of the Pt particles at nitrogen sites. The oxidation state of the polymer and the degree of proton doping play a key role in the conductivity of the composite. Therefore, the incorporation of Pt to the polymer diminishes the conductivity of the electrochemically prepared PANI/Pt(IV) by a factor of 10³ as compared to the PANI membrane without Pt. Similarly, decrease in the proton doping and absence of the 1:1 ratio in the oxidized to reduced units in the dipped PANI/Pt(IV) and PANI/Pt(II) composites suggests that the conductance of these composites is less than that of the PANI membrane without Pt.
In comparison, the chemically prepared PANI/Pt(IV) and PANI/Pt(II) have much lower oxidation states of 0.71 and 0.69. In addition, the lack of free charge carriers in the chemically prepared PANI/Pt(IV) composite also contributes to the decrease in the conductivity. Specifically, the ammonium salt formed reduces the ability of the polymer to shuttle electron density through the polymer chain. This is likely due to the localization of electron density at the lone pair electrons through the protonation of the nitrogen groups. The conductance of PANI/Pt(IV) composite is reduced by a factor of $10^7$ as compared to the PANI without Pt.

The XPS results indicate the electrochemical, spontaneously reduced, and chemical composites contain fully reduced metallic platinum. There was no Pt(IV) and Pt(II) observed in any of the samples. The SEM images of the chemically and electrochemically fabricated composites indicate that the Pt particles are uniformly dispersed at the surface. The decreases in proton doping observed for these samples (~50%) also implies that the particles are dispersed into the polymer matrix. This hypothesis is based on the fact that the surface alone does not contain 50% of the total electroactive sites. The results from the characterization techniques indicate both PtCl$_6^{2-}$ and PtCl$_4^{2-}$ are can be used to electrochemically prepare PANI/Pt composites. The spontaneous reduction and formation of PANI/Pt using preformed polymer membranes dipped in solution containing PtCl$_6^{2-}$ and PtCl$_4^{2-}$ is also possible. However, the results indicate that dispersion is minimized by reduction of the Pt species at the surface of the electrode. Finally, PtCl$_6^{2-}$ and PtCl$_4^{2-}$ can be used as the oxidizing agent to initiate polymerization of PANI using either aniline or oligomers.

The comparison of electrocatalytic oxidation of methanol and formic acid was carried out on the materials produced using the three synthetic methods. This study indicates the electrocatalytic activity of methanol and formic acid at platinum particles can be influenced by the method of synthesis and Pt reduction or dispersion. The electrochemical incorporation shows the greatest catalytic activity relative to the other
PANI/Pt composites. The platinum composites fabricated by spontaneous reduction and chemical synthesis using either PtCl\textsubscript{6}\textsuperscript{2-} or PtCl\textsubscript{6}\textsuperscript{2-} as the oxidizing agent shows very little catalytic activity towards methanol and formic acid oxidation. The same trend in catalytic activity is observed for PANI/Pt prepared from the direct chemical oxidation using PtCl\textsubscript{6}\textsuperscript{2-} and PtCl\textsubscript{4}\textsuperscript{2-}. Comparison of the electrochemically reduced PANI/Pt using PtCl\textsubscript{4}\textsuperscript{2-} and PtCl\textsubscript{6}\textsuperscript{2-} also show different catalytic activity in the oxidation of methanol and formic acid.

The PANI/Pt composites produced from PtCl\textsubscript{4}\textsuperscript{2-} has enhanced catalytic activity relative to PtCl\textsubscript{6}\textsuperscript{2-}. The difference is likely due to the difference in electron density required for the full reduction of PtCl\textsubscript{6}\textsuperscript{2-} versus PtCl\textsubscript{4}\textsuperscript{2-}. In addition the Pt particle diameters in the PANI/Pt composite produced from the electrochemical reduction of PtCl\textsubscript{4}\textsuperscript{2-} are smaller. Smaller particle size allows much higher catalytic surface area to be achieved. The reduction of proton doping for the two composites is similar. The oxidation state of the two composites is significantly different with PANI/Pt(IV) having a higher oxidation state of R = 3.19 as compared to R = 2.32 for PANI/Pt(II). It is likely that the oxidation of methanol and formic acid is influenced by the loss of electron density in the polymer.
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