Electrochemical Studies Of Nanoscale Composite Materials As Electrodes In Direct Alcohol Fuel Cells

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ELECTROCHEMICAL STUDIES OF NANOSCALE COMPOSITE MATERIALS
AS ELECTRODES IN PEM FUEL CELLS

by

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Major Professors: Diego J. Diaz and Lei Zhai
ABSTRACT

Polymer electrolyte membrane fuel cells (PEMFCs) have recently acquired much attention as alternatives to combustion engines for power conversion. The primary interest in fuel cell technology is the possibility of 60% power conversion efficiency as compared to the 30% maximum theoretical efficiency limited to combustion engines and turbines. Although originally conceived to work with hydrogen as a fuel, difficulties relating to hydrogen storage have prompted much effort in using other fuels. Small organic molecules such as alcohols and formic acid have shown promise as alternatives to hydrogen in PEMFCs due to their higher stability at ambient conditions. The drawbacks for using these fuels in PEMFCs are related to their incomplete oxidation mechanisms, which lead to the production of carbon monoxide (CO). When carbon monoxide is released in fuel cells it binds strongly to the platinum anode thus limiting the adsorption and subsequent oxidation of more fuel. In order to promote the complete oxidation of fuels and limit poisoning due to CO, various metal and metal oxide catalysts have been used.

Motivated by promising results seen in fuel cell catalysis, this research project is focused on the design and fabrication of novel platinum-composite catalysts for the electrooxidation of methanol, ethanol and formic acid. Various Pt-composites were fabricated including Pt-Au, Pt-Ru, Pt-Pd and Pt-CeO$_2$ catalysts. Electrochemical techniques were used to determine the catalytic ability of each novel composite toward the electrooxidation of methanol, ethanol and formic acid. This study indicates that the novel composites all have higher catalytic ability than bare Pt electrodes. The increase in catalytic ability is mostly attributed to the increase in CO poison tolerance and promotion of the complete oxidation mechanism of methanol, ethanol and
formic acid. Formulations including bi- and tri-composite catalysts were fabricated and in many cases show the highest catalytic oxidation, suggesting tertiary catalytic effects. The combination of bi-metallic composites with ceria also showed highly increased catalytic oxidation ability. The following dissertation expounds on the relationship between composite material and the electrooxidation of methanol, ethanol and formic acid. The full electrochemical and material characterization of each composite electrode is provided.
for my beautiful wife
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<td>CV</td>
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<tr>
<td>DAFC</td>
<td>Direct Alcohol Fuel Cell</td>
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<td>Copper Underpotential Deposition</td>
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<tr>
<td>UPD</td>
<td>Underpotential Deposition</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Spectroscopy</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Proton Exchange Membrane Fuel Cell</td>
</tr>
<tr>
<td>DFAFC</td>
<td>Direct Formic Acid Fuel Cell</td>
</tr>
<tr>
<td>MWCNT</td>
<td>Multiwalled Carbon Nanotube</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon Nanotube</td>
</tr>
<tr>
<td>ECA</td>
<td>Electrochemically Active Surface Area</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene Oxide</td>
</tr>
<tr>
<td>i</td>
<td>Current</td>
</tr>
<tr>
<td>j</td>
<td>Current density</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------</td>
</tr>
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<td>$i_{pa}$</td>
<td>Peak Anodic Current</td>
</tr>
<tr>
<td>$i_{pc}$</td>
<td>Peak Cathodic Current</td>
</tr>
<tr>
<td>$j_{pa}$</td>
<td>Peak Anodic Current Density</td>
</tr>
<tr>
<td>$j_{pc}$</td>
<td>Peak Cathodic Current Density</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage/Potential</td>
</tr>
<tr>
<td>PSS</td>
<td>Polystyrene Sulfonic Acid</td>
</tr>
<tr>
<td>AA</td>
<td>Acetic Acid</td>
</tr>
<tr>
<td>AAL</td>
<td>Acetaldehyde</td>
</tr>
<tr>
<td>ED</td>
<td>Ethane-1,1-diol</td>
</tr>
</tbody>
</table>
CHAPTER 1. BACKGROUND

Current Energy Crisis

In recent years a massive effort has been directed toward answering questions related to the international energy crisis. Due to the limited supply of fossil fuels, the debate about sustainable sources of energy has moved to the top of the agenda in political, economic, and social circles. In terms of the demand for fossil fuels, “Peak oil” is the period when the maximum rate of petroleum extraction is reached, after which the rate of production enters terminal decline. US domestic oil production arguably plateaued in 1970 and global production of conventional crude oil arguably reached this plateau in 2005.¹ The depletion of fossil fuels combined with increasing demand for energy, has dramatically increased the global prices of petroleum products. In the coming years this trend will continue and the most significant impact will be related to the availability and price of liquid fuel for transportation. Due to the unique nature of the current energy crisis resulting from global depletion of petroleum sources, the US Department of Energy (DOE) in the Hirsch report states that “The problems associated with world oil production peaking will not be temporary, and past ‘energy crisis’ experience will provide relatively little guidance.”²

While the outlook for fossil fuels may be grim, scientists around the world have made incredible discoveries related to alternative energy sources. Electrochemical technology is an ongoing area of research which has shown significant promise in the production of stationary and mobile energy reserves, while maintaining sustainability and its environmental friendliness. With the threat of fast depletion of fossil fuels (petroleum, coal and natural gas) and the green house
effect caused by burning them, world leaders are forced to seek and develop more efficient energy conversion devices as regenerative power sources to save the world’s valuable natural resources. Electrochemical devices, such as batteries, fuel cells and supercapacitors are set to replace current thermal-based technologies as alternative power systems.

**Fuel Cells**

Fuel cells are device that convert chemical energy from a fuel (most commonly hydrogen) into electricity through the chemical reaction with oxygen or another oxidizing agent. First discovered in the mid 19th century by Christian Friedric Schobein, fuel cells are among the oldest electrical energy conversion technologies. Fuel cell research however, lacked motivation during the first 100 years of their discovery since fossil fuels were abundant and inexpensive. As electrical energy became more popular at the beginning of the 20th century, more effort was devoted to the development of electrical energy conversion systems such as electrical generators. Due the depletion of fossil fuels, much interest has shifted to the development of fuel cell technology. Fuel cells have shown particular promise due to fuel flexibility, low emission of pollutants, high energy efficiency, and their application to stationary and mobile tasks.\(^1\)\(^-\)\(^5\) This is in stark contrast to conventional combustion based engines which are severely limited by their Carnot efficiency. Fuel cells however, are not limited by the Carnot maximum, and near theoretical efficiencies can be achieved by using intelligently engineered electrochemical devices.\(^6\) A comparison between a few different electrical systems and their efficiencies is shown in figure 1.
As can be seen, fuel cells have the potential for much more efficient energy conversion than other currently used systems. With the addition of heat recovery systems, certain types of fuel cells are currently reaching efficiencies of nearly 85%. This is in contrast to combustion engines and turbines with a maximum 30% theoretical efficiency. Like batteries, single fuel cells can be combined in series to create a stack with cumulative power output. Stacks can thus be sized according to power demands for specific applications. Renewable energy from wind, water and sun are increasingly becoming more popular, but these energy sources are not reliable sources of energy due to irregular power output. However, the combination of these energy sources with hydrogen (or other fuels) in co-operation with fuel cells could provide a viable system for future power generation. Current research and development of new fuel cell materials will help to address the challenges in developing commercial fuel cells.

*Fuel Cell Comparison.* There are a variety of fuel cells which are at different stages of production and have different applications. The six major types of fuel cells are categorized
based on their electrolyte. Table 1 lists the six major types of fuel cells as well as their attributes and applications.

**Table 1. The six major types of fuel cells**

<table>
<thead>
<tr>
<th>Name</th>
<th>Operating Temperature</th>
<th>System Output</th>
<th>Efficiency</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen PEMFC</td>
<td>50-100</td>
<td>&lt;250 kW</td>
<td>50-60%</td>
<td>Portable Power, Transportation</td>
</tr>
<tr>
<td>DAFC</td>
<td>60-90</td>
<td>1-100 W</td>
<td>50-60%</td>
<td>Portable Power, Transportation</td>
</tr>
<tr>
<td>Alkaline FC</td>
<td>90-100</td>
<td>10-100 kW</td>
<td>60-70%</td>
<td>Military, Space</td>
</tr>
<tr>
<td>Phosphoric Acid FC</td>
<td>150-200</td>
<td>50-1000 kW</td>
<td>80-85%</td>
<td>Distributed Generation</td>
</tr>
<tr>
<td>Molten Carbonate FC</td>
<td>600-700</td>
<td>&lt;1000 kW</td>
<td>85%</td>
<td>Large Distributed Generation</td>
</tr>
<tr>
<td>Solid Oxide FC</td>
<td>650-1000</td>
<td>5-3000 kW</td>
<td>85%</td>
<td>Large Distributed Generation</td>
</tr>
</tbody>
</table>

When heat recovery systems are used, fuel cells can obtain efficiencies up to 85%. PAFCs, MCFCs and SOFCs are all primarily used for stationary power applications while PEMFCs and DAFCs are used for smaller power applications such as vehicles and even electronics. PAFCs, MCFCs and SOFCs all operate based on solution phase electrolytes which typically make them very heavy. PEMFC and DAFC have a solid electrolyte (PEM) and are therefore more advantageous to use in transportation devices and small electronics. The solid polymer membrane limits corrosion from electrolyte solutions and removes the need to contain and circulate a liquid. Other advantages for PEMFCs and DAFCs are their ability to quickly startup and operate at low temperatures, which is essential for applications in vehicles and small devices. The disadvantages for using either of these fuel cells, is the high cost of production related to the need for Pt as an electrode catalyst.
Proton exchange membrane fuel cells (PEMFCs) are a type of fuel cell which uses a membrane to separate the chemical oxidation and reduction reaction in order to generate an electrical current. PEMFCs are named for the membrane that separates the anode from the cathode. A typical PEMFC is shown in figure 2.

![Figure 2. PEMFC with hydrogen fuel](image)

As can be seen there are three main components, the anode, cathode and polymer electrolyte membrane (PEM). The electrodes in PEMFCs are usually constructed from Pt or Pt composites. The PEM acts as a separator, preventing gas crossover and mixing. The membrane is composed of a polymer capable of conducting protons through an aqueous network. Much research has been dedicated to the study of different polymer materials for PEMFCs, and currently the best performing polymer membrane is made with Nafion®. When hydrogen is used as the fuel and oxygen is used as the oxidant, the following half cell reactions occur in the PEMFC:

Anode half reaction
\[ H_2 \rightarrow 2H^+ + 2e^- \quad E^0 = 0 \text{ V} \quad (1.1) \]

Cathode half reaction

\[ \frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad E^0 = 1.23 \text{ V} \quad (1.2) \]

Overall reaction

\[ H_2 + \frac{1}{2} O_2 \rightarrow H_2O \quad E_{cell} = 1.23 \text{ V} \quad (1.3) \]

These reactions take place at the anode and cathode respectively. Immediately following the anodic half cell reaction, protons are conducted through the membrane to react at the cathode. Simultaneously, electrons are forced around the circuit to do electrical work which completes the redox process by promoting the reduction of oxygen to water.

**PEMFC Efficiency Limitations.** High energy efficiency and power density in PEMFCs are a direct function of the thermodynamics, porous electrode kinetics, materials for membranes and reactant mass transfer. PEMCs utilize the free energy of a chemical reaction to generate electrical energy. The Gibbs free energy in a chemical reaction is related to the cell voltage via the following:

\[ \Delta G = -nFE \quad (1.4) \]

where \( \Delta G \) is the change in Gibbs free energy of a reaction, \( n \) is the number of electrons involved with the redox reaction, \( F \) is Faraday’s constant and \( E \) is the cell voltage. Current in a fuel cell is directly related to the electron transfer rate as shown in the following:

\[ I = \frac{E}{R} \quad (1.5) \]

where \( I \) is current produced, \( E \) is the cell voltage and \( R \) is the cell resistance. The Typical I-V curve of a PEMFC is shown in figure 3.
Only Gibbs energy can be converted into electrical energy. The theoretical voltage \( E^{th} \) is derived by rearranging equation 1.4 to give the following:

\[
E^{th} = \frac{-\Delta G}{2F}
\]  

(1.6)

The theoretical cell voltage of a PEMFC is limited by many competing factors as seen in figure 3. The open circuit voltage (OCV) losses are caused by voltage given from internal currents when the external circuit is broken. These processes account for about 20% of the total losses. These voltages are primarily related to parasitic half-reactions such as the oxidation of platinum...
linked to the presence of impurities, like carbon monoxide (from the steam reforming process). Other internal currents are caused by gas cross-over through the membrane. At lower current densities, losses are primarily related to the activation of electrochemical reactions. These losses are minimized by addition of Pt/composite catalysts as shown in figure 4.

![Reaction path](image)

**Figure 4. Activation energy required in PEMFCs**

As can be seen, when a catalyst is used in the Pt electrodes, the activation energy is lowered thus increasing the kinetics of the oxidation reactions. The activation energy is related to current through the Arrhenius equation which displays a logarithmic dependence of current on activation energy and temperature.

The linear portion seen in figure 3 is usually attributed to ohmic losses in the fuel cell membrane because of protonic resistance. The flow of protons through the Nafion® membrane is greatly affected by the water concentration. At high current density, a distinct drop in the voltage can be seen and is caused by mass transport limitations usually linked to the lack of
reactive gases at the electrodes or electrode flooding. It has been the effort of much research to address one or more of these losses by designing catalytic electrode materials, better polymer membranes and constructing intelligently designed fuel cell apparatus.

**DAFCs and DFAFCs.** Although originally conceived to work with hydrogen as a fuel, the challenges presented by the handling and storage of hydrogen have sparked interest in using alternative materials for fuels such as formic acid, borohydrides, as well as many other small organic molecules including sugars, ethers, and aldehydes. Among these molecules, alcohols have received increased recent attention as alternative fuels for PEMFCs. In particular, direct alcohol fuel cells (DAFCs) (which do not require the use of a fuel reformer) are equipped to operate with methanol as a fuel, creating the direct methanol fuel cell (DMFC). A typical DMFC is shown below.

![Direct Alcohol Fuel Cell with methanol](image)

**Figure 5. Direct Alcohol Fuel Cell with methanol**
Figure 5 shows the DMFC with membrane (red) and electrodes (grey). The basic function of the fuel cell is accomplished by feeding the anode with a methanol/water solution and oxygen from air supplied to the cathode. The simplified process involves the oxidation of methanol to carbon dioxide at the anode and the reaction of oxygen with protons to form water at the cathode. In this process the electrons generated from the alcohol oxidation process are isolated as a current and can be used as a power source.

In addition to methanol many other fuels have been tested in PEMFCs including ethanol and formic acid. Each of these fuels performs differently in a PEMFC and can give various power outputs. Table 2 shows a list of different fuels and parameters related to them.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Qualified Power</th>
<th>Working Temperature</th>
<th>Production Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>0.1 – 100 W</td>
<td>60 - 90 °C</td>
<td>Commercial/Research</td>
</tr>
<tr>
<td>Ethanol</td>
<td>&lt; 50 W</td>
<td>60 – 90 °C</td>
<td>Research</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>&lt; 0.14 W</td>
<td>&lt; 40 °C</td>
<td>Commercial/Research</td>
</tr>
</tbody>
</table>

Each fuel has a variety of drawbacks. For alcohols and formic acid these drawbacks are primarily related to the incomplete oxidation of these fuels and resulting byproducts. The byproduct of incomplete methanol oxidation is carbon monoxide (CO). Ethanol and formic acid also form CO due to incomplete oxidation mechanisms but they have shown many more byproducts which lead to a decrease in predicted voltage and current. CO production is a particular problem in PEMFCs since it binds strongly to the Pt anode. Figure 6 shows carbon monoxide being produced by the incomplete oxidation of methanol. The CO binds strongly to the Pt anode preventing methanol from reacting at the surface.
Once sufficient concentrations of CO bind to the Pt, and the fuel is unable to reach the surface of the anode, the electrode is said to be “poisoned” and high overpotentials are required to remove the adsorbed CO. These high overpotentials decrease the overall efficiency of the fuel cell.

*Pt/metal Bimetallic Catalysts for the Electrooxidation of Methanol.* Methanol presents as a good fuel choice due to its high energy density (compared to hydrogen) low operating temperatures, relatively quick start-up time and rapid response to load changes.\(^{12-15}\) While DMFCs address the need to move away from fossil fuel dependency, they present several challenges; many of which are derived from the anode. The best performing anode material for the electrochemical oxidation of methanol is carbon supported platinum, however limitations of Pt as a catalyst include the following: high overall cost, slow dynamics of methanol oxidation, corrosion of the carbon substrate, and poisoning of the electrode surface.\(^{16-19}\) The multistep oxidation of methanol on Pt proceeds as follows:

---

**Figure 6.** Poisoning of Pt anode by CO from the incomplete oxidation of methanol
Methanol adsorption and dehydrogenation

\[ \text{CH}_3\text{OH} \rightarrow \text{Pt}--\text{COH}_{\text{ads}} + 3\text{H}_{\text{ads}} \]  

(1.7)

Oxidation of Pt--COH_{ads}

\[ \text{Pt}--\text{COH}_{\text{ads}} + 3\text{OH}_{\text{ads}} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \]  

(1.8)

Ionization of H_{ads} (current producing step)

\[ 3\text{H}_{\text{ads}} \rightarrow 3\text{H}^+ + 3\text{e}^- \]  

(1.9)

Anodic formation of more OH_{ads} species

\[ 3\text{H}_2\text{O} \rightarrow 3\text{OH}_{\text{ads}} + 3\text{H}^+ + 3\text{e}^- \]  

(1.10)

Under certain conditions the anodic Pt--COH_{ads} are transformed to Pt--CO_{ads} which are extremely difficult to oxidize and therefore “poison” the electrode surface. Therefore, many research groups have studied bimetallic catalysts in order to reduce concentration of Pt (lower cost) and improve methanol oxidation kinetics.\textsuperscript{20-24} One such catalyst that has been widely studied is Pt/Ru.\textsuperscript{13,25-33} The effect of Pt/Ru is thought to decrease CO poisoning by the introduction of Ru--OH sites which promote the conversion of Pt--COH_{ads} to CO\textsubscript{2} (equation 1.8) rather than CO.\textsuperscript{33,34} Other bimetallic electrodes have also been studied including Pt/Au composites. Since CO will not bind strongly to Au, results from Pt/Au electrode studies show much improved methanol oxidation kinetics when compared to bare Pt.


\textit{Pt/metal Bimetallic Catalysts for the Electrooxidation of Ethanol.} Ethanol is also an interesting candidate for DAFCs since it possesses all the benefits of methanol while also being inexpensive, non-toxic, and “green” (since it can be produced from biomass).\textsuperscript{35-37} The catalytic oxidation of ethanol is far more complicated than that of methanol due to the C-C bond which
results in reaction intermediates and products not seen in methanol oxidation. Ethanol oxidation on Pt is generally believed to follow two parallel reactions as shown in the following:\(^{36}\):

Complete oxidation of ethanol to form \(\text{CO}_2\):

\[
\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}_2 + 12\text{e}^- 
\]

(1.11)

Incomplete oxidation of ethanol to form various products:

Acetaldehyde (AAL)

\[
\text{CH}_3\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + 2\text{H}^+ + 2\text{e}^- 
\]

(1.12)

Ethane-1,1-diol (ED)

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH(OH)}_2 + 2\text{H}^+ + 2\text{e}^- 
\]

(1.13)

Acetic acid (AA)

\[
\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + 4\text{H}^+ + 4\text{e}^- 
\]

(1.14)

The complete oxidation of ethanol yields \(12\text{e}^-\) while the incomplete oxidation produces \(2\text{e}^-\) (for AAL and ED) and \(4\text{e}^-\) (for AA). It has been shown that little \(\text{CO}_2\) is produced in the oxidation of ethanol, leading researchers to believe that the primary mode of ethanol oxidation is through the incomplete oxidation mechanism.\(^{36,38-42}\) Addition of Ru, Au, and other transition metals has shown to increase the catalytic ability of Pt catalysts toward the oxidation of ethanol which could be the result of \(\text{–OH}_{\text{ad}}\) species promoting the formation of AA (\(4\text{e}^-\) compared to \(2\text{e}^-\) for AAL and ED). More studies are needed to understand the exact mechanism of bimetallic catalysts toward alcohol electrooxidation.\(^{43,44}\)

\textit{Pt/metal Bimetallic Catalysts for the Oxidation of Formic Acid.} Direct Formic Acid Fuel Cells (DFAFCs) have also captured attention as possible alternatives. There are a variety of advantages to using formic acid rather than methanol as a fuel. Methanol has been found to be a
toxic substance, but dilute formic acid is on the US Food and Drug Administration list of food additives that are generally recognized as safe. In addition, formic acid has been shown to have two orders of magnitude smaller crossover flux through the Nafion® membrane than methanol. Lower crossover flux allows the use of more concentrated formic acid solutions in the DFAFCs. Formic acid also has a higher electronic motive force than either hydrogen or methanol PEMFCs. Challenges in using formic acid in fuel cells are primarily related to the byproducts of incomplete oxidation at the anode. These byproducts (such as CO) poison the electrode and decrease overall performance. The oxidation of formic acid on platinum is believed to proceed via two possible pathways shown below:

Direct Pathway

HCOOH + Pt → Pt + CO₂ + 2H⁺ + 2e⁻ (1.15)

Indirect Pathway

HCOOH + Pt → Pt—CO + H₂O (1.16)
Pt + H₂O → Pt—OH + H⁺ + e⁻ (1.17)
Pt—CO + Pt—OH → 2Pt + CO₂ + H⁺ + e⁻ (1.18)

In the direct pathway, formic acid is converted entirely into CO₂ in a 2 electron process. The indirect pathway, however, leads to the production of CO which can poison the surface of fuel cell electrodes. Similar to alcohol oxidation kinetics, anodes in DFAFC anodes have been designed using platinum composited with ruthenium and gold to limit CO formation by providing M—OH groups through the indirect pathway (1.18). However, to promote the direct oxidation (1.15) of formic acid and limit the production of CO, many researchers have employed catalytic materials to be used as DAFC anodes. While the mechanism is still not well understood.
understood, platinum/palladium anodes have been shown to increase the oxidation kinetics of formic acid through the direct oxidation mechanism.

**Nanoceria in DAFC Catalysts**

Metal oxides have also been widely studied in Pt-composite electrodes for fuel cells in order to increase catalytic activity. One metal oxide that has been generating a great deal of attention is ceria (CeO$_2$). CeO$_2$ has shown a great ability to store and release oxygen (oxygen carrying capacity) with little distortion of the lattice, which is due to the cerium atom’s ability to reversibly undergo the oxidation/reduction processes from Ce$^{4+}$ to Ce$^{3+}$. The oxidation of alcohols and formic acid with Pt/ceria catalysts is generally believed to proceed similar to that of Ru, with the production of CeO$_2$—OH$_{ads}$ species which decrease CO$_{ads}$ species on the surface of the Pt electrode; however the mechanism is not well understood.

When ceria is presented in the nanoscale (nanoceria), the catalytic ability has shown to increase, most likely due to the high surface area which offers a large number of oxygen vacancies and enhanced mobility of these vacancies. Nanoceria is typically synthesized from the oxidation of cerium cations in aqueous solutions. When the pH of these solutions is increased by the addition of a base, ceria is formed. Figure 7 is the Pourbaix diagram of cerium in water which indicates the pHs and potentials ceria formation is thermodynamically favorable.
Substrates for Metal/Metal Oxide Composites

While the metal/metal oxide bifunctional catalysts have a major impact on alcohol oxidation kinetics in DAFCs, the support material for these composites is also important.\textsuperscript{34, 72-75} Compared to bulk metal catalysts, supported catalysts show higher activity and stability. Many supports have been studied for applications in fuel cells.\textsuperscript{74-83} Essential requirements of potential support materials include high surface area, conductivity, stability and low cost. Carbon materials have traditionally been the primary support material for anode catalysts in PEMFCs, due to their relative stability in acidic and basic media, good electric conductivity and high specific surface area. It has been shown that carbon supported materials can have strong
influence on the properties of metal nanoparticles including the following: size, size distribution, stability and morphology. Such parameters can affect the catalytic abilities of composite materials in such a way to increase performance, mass transport, electrochemical surface area (ECA) and corrosion resistance. The optimization of carbon support material is very important to the development of catalysts for PEMFCs. A variety of carbon support materials have been studied including carbon black, graphite, carbon nanotubes and most recently graphene. In this work both MWCNTs and graphene were studied as supports for metal nanoparticle composite electrodes.

Multiwalled Carbon Nanotubes. Due to their high electrical conductivity and surface area, multiwalled carbon nanotubes present as excellent candidates for fuel cell electrode supports and many studies have shown enhanced catalytic ability for the oxidation of alcohols when using MWCNTs as the support for composite catalysts.\textsuperscript{79-82} These studies have shown that MWCNTs are superior to carbon black as catalyst supports in PEMFCs. Reports show that MWCNT supported catalysts can give a 10% higher fuel cell voltage and twice the power density than those supported on carbon black.\textsuperscript{15, 84} It has also been shown that lower Pt loadings are required in MWCNT composites compared to other supports to achieve similar performance. This has the potential to significantly lower the amount of Pt necessary for catalysts and therefore lower production costs.

Graphene. Graphene is also an interesting candidate for applications in fuel cell composite electrodes. Its high conductivity and surface area make it ideally suited for electrochemical catalysis. Graphene is a flat monolayer of a hexagonal network of carbon atoms. Due to its thinness, mechanical strength, transparency, conductivity and high surface area,
Graphene has recently become the focus of intense research efforts for many applications including DAFCs, supercapacitors, sensors, and transistors. Although predicted not to exist for thermodynamic reasons, Geim et al. produced a single atomic layer of graphene by mechanically exfoliating graphite with adhesive tape. Since then, it has been a topic of interest to develop a means to easily produce single layers of graphene. Research has led to a variety of ways to produce graphene including the reduction of graphene oxide shown in figure 8.

Figure 8. Electro-Reduction of Graphene Oxide

Graphene oxide (GO) is a unique molecule which is best described as a sheet of graphene containing a variety of functional groups including hydroxyl, epoxy and carbonyl. GO can easily be produced from the oxidation of graphite through Hummer’s method; a technique which includes exfoliating and oxidizing graphite with the combination of strong acids and oxidizing
agents.\textsuperscript{86} GO is a useful precursor to graphene since it is easily dispersed in water.\textsuperscript{87-89} The reduction of GO usually proceeds from the addition of hydrazine to aqueous suspensions of GO. The removal of polar functional groups causes the reduced graphene to precipitate from solution where it can be isolated by filtration or centrifugation.\textsuperscript{90,91} Recently many research groups have also started investigating the electrochemical reduction of GO.\textsuperscript{92-95} Studies have shown that graphene films can be formed on the surface of electrodes by the electrochemical reduction of GO. When sufficiently negative potentials are applied, the reduced graphene deposits on the surface of a working electrodes forming multiple layers of graphene. These films can be used as supports for metal nanoparticles in PEMFCs.\textsuperscript{93,94,96-98}

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CHAPTER 2. EXPERIMENTAL

Chemicals and Materials

All aqueous solutions were prepared with triply distilled water with 18 MΩ/cm resistivity (Barnstead B-Pure). Formic acid (Fisher Anhydrous, ACS Reagent grade), ethanol (Fisher Anhydrous, ACS Reagent grade) and methanol (Fisher Anhydrous, ACS Reagent grade) were used to prepare 1.0 M solutions in 0.5 M H₂SO₄ (Fisher ACS Reagent grade), which functioned as the supporting electrolyte. High-purity nitrogen gas (N₂) was obtained from Air Liquide and bubbled through formic acid and alcohol solutions to remove dissolved O₂. High-purity potassium hexachloroplatinate, K₂PtCl₆ (Aldrich), was used as the source of platinum for electrodeposition procedures and nanoparticle synthesis on multiwalled carbon nanotubes. Palladium chloride, PdCl₂ (Aldrich), was used as the precursor to palladium nanoparticles in electrodeposition procedures. Auric chloride, AuCl₃ (Alfa Aesar), was used as the source of gold for depositions. Ruthenium chloride, RuCl₃ (Acros), was used during Ru nanoparticle synthesis on MWCNTs. Copper sulfate, CuSO₄ (Acros), was used to make 0.1 M Cu²⁺ solutions for copper underpotential deposition procedures. Ceria (cerium oxide) nanoparticles were prepared by published procedures¹-⁴ and commercially available ceria nanoparticles (Aldrich) were also used for electrode fabrication during electrodeposition procedures. Cerium nitrate, Ce(NO₃)₃ (Acros) was used as precursor to ceria in the synthesis of ceria nanoparticles supported on carbon nanotubes. Microfyne graphite powder (Dixon) with 44 micron size was used as precursor to graphene oxide in modified Hummer’s method. Potassium permanganate (Acros) and hydrogen peroxide (Aldrich) were used as oxidizing agents in graphene oxide synthesis. NaCl (Aldrich)
was used to make 0.1 M electrolyte solutions in 0.5 M graphene electrodeposition suspensions. Multiwalled carbon nanotubes (MWCNTs) were purchased from Nanolab (Newton, MA) with a diameter of 10–20 nm and length about 5–20 μm. Polystyrene sulfonic acid (PSS) (Aldrich) was used as a dispersing agent for MWCNTs in aqueous suspensions. Sodium hydroxide (NaOH) (Acros) and sodium borohydride (NaBH₄) (Aldrich) were used as oxidizing and reducing agents respectively in nanoparticle synthesis on MWCNTs. Nafion® (Ion Power) was obtained as 5% solutions in ethanol which were used in MWCNT suspension to immobilize composite material on electrode surfaces. Graphite plates were used as working electrodes for MWCNT composites. Platinum foils were used as substrates for composite materials in spectroscopy and microscopy studies. All chemicals were used as received unless otherwise specified.

**General Procedures**

*Pt/Ceria, Pt/Au/Ceria and Pt/Pd/Ceria Electrode Fabrication via Electrodeposition.*

Bimetallic/ceria composite electrodes were prepared by electrodeposition, using a CH Instruments model CHI400A (CH Instruments, Inc.) potentiostat, without regard for the liquid junction. A custom-made 50 mL cell was used for the electrodeposition experiments. In each case, a 5 mM nanoceria suspension in a mixed solution of potassium hexachloroplatinate, auric chloride or palladium chloride totaling a 2 mM concentration of metal ions (in 0.5 M sulfuric acid) was prepared for the electrodeposition procedure. The concentration of individual metal ions (Pt⁴⁺, Pd²⁺, Au³⁺) was varied while keeping the total concentration 2mM. The working electrode was placed in the solution containing the metal ions. The reduction of metal ions on the working electrode surface was accomplished by holding the electrode potential at -0.200 V vs the Ag/AgCl reference, for a total of 600 s. Throughout the electrodeposition, the suspended
solution was stirred at rotations close to 200 rpm with use of a magnetic stir bar to keep the deposition current constant to a value of nearly $1.0 \times 10^{-4}$ A. The electrodeposition of metal ions in the presence of a higher concentration of nanoscale ceria particles causes the occlusion of ceria in the growing metallic film. Figure 9 demonstrates ceria nanoparticles being “trapped” on the surface of a Pt working electrode.

![Diagram of electrodeposition](image)

**Figure 9. Electrodeposition of Pt and Au with inclusion of nanoceria**

When the ceria particles are “trapped” on the Pt electrode surface, the procedure yields Pt:CeO$_2$, Pt:Au:CeO$_2$ and Pt:Pd:CeO$_2$ composite electrodes. Once the composite electrodes were fabricated, their catalytic ability was determined for the electrooxidation of formic acid, methanol and ethanol.

*Graphene/Pt/Ceria Electrode Fabrication via Electrodeposition.* Graphene oxide (GO) was prepared by modified Hummer’s method. Graphite was oxidized by concentrated H$_2$SO$_4$ and
KMnO$_4$ and during a process that lasted 3 hours. Graphene oxide was purified by washing with de-ionized water and subsequent centrifugation through 3 wash/centrifuge cycles, or until near neutral pH was obtained. The quality of GO obtained from different synthesis procedures is an interesting discussion. It has been shown that more highly oxidized GO forms more stable suspensions in water than poorly oxidized GO. The more stable suspensions are preferable to applications in the electrodeposition procedures used in this study. It was determined that during GO synthesis procedures that the resulting product was a mixture of poorly oxidized graphite, GO with small sheet size and well oxidized GO with large sheet size. In an effort isolate the preferable highly oxidized GO with larger sheet size, it was also found that the three products could be separated through adjusting centrifuge rotation speeds. The highly oxidized GO with large sheet size forms very good dispersions in water and during centrifugation fell out of solutions only at rotation speeds above 8000 rpm. The less oxidized and smaller GO sheets were therefore removed by centrifuging samples at lower rotation speeds and discarding the resulting pellet. The desirable GO was then removed from solutions by centrifuging at a rotation speed of 8500 rpm. The light brown/yellow product was in stark contrast to the dark brown pellet that was previously removed. The GO was then used in electroreduction procedures.

Suspensions of GO/water were prepared by tip sonication in 0.5 mg/mL concentrations. Graphene films were synthesized from the electrodeposition of graphene oxide (GO) from aqueous suspensions with 0.1 M NaCl as support electrolyte. Graphene electrodeposition was performed by holding a constant potential of -1.155 V v. Ag/AgCl for 420 s. As demonstrated in figure 10, during electroreduction procedures, a metallic/black looking film was formed on the working electrode substrate.
Figure 10. Electro-Reduction of Graphene Oxide to form Graphene Film

Following electoreduction, the working electrodes were then allowed to dry in order to insure the graphene films were well attached to the working electrode. Subsequently, Pt and ceria electrodeposition proceeded from a suspension of 2 mM Pt ions and 5 mM nanoceria. The electrodeposition was carried out at -0.2 V for 600 s while stirring the solution at rotation speed close to 200 rpm. Figure 11 displays the formation of the Pt/CeO$_2$ network on the surface of graphene films.
Graphene/Pt/CeO$_2$ composites were fabricated on Pt working electrodes for electrochemical analysis, and 1 cm$^2$ Pt foils for scanning electron microscopy (SEM), Raman spectroscopy and FTIR.

**MWCNT/Pt/Ru/Ceria Electrode Fabrication.** MWCNTs were dispersed in water using polystyrene sulfonate (PSS). As the dispersion was sonicated PSS stabilized the nanotubes in water through charge repulsion. The negatively charged PSS layer attracts metal ions and serves as a template for subsequent nano-structure formation. Interaction of growing nuclei with the large number of surface sites (-SO$_3^-$) facilitated the material to grow in nanoscale dimensions and retard interparticle agglomeration.$^5,6$ Once the MWCNTs were dispersed, Ce(NO$_3$)$_3$ was added to the dispersion. Ceria nanoparticles were formed by the oxidation of Ce$^{3+}$ ions onto the surface of MWCNTs through the drop-wise addition of NaOH which acts to oxidize the metal ions to CeO$_2$. Pt/Ru nanoparticles were formed by adding Pt and Ru ions (H$_2$PtCl$_6$ and RuCl$_3$) to the
dispersion and reducing the ions onto the MWCNT surface through the addition of NaBH$_4$.

Figure 12 shows a simplified image displaying the attraction of metal nanoparticles to the PSS/MWCNT surface followed by the oxidation of ceria and reduction of Pt/Ru nanoparticles.

**Figure 12. Synthesis of Pt/Ru/Ceria Nanoparticles on MWCNTs**

Composites of various Pt/Ru concentration were synthesized by adding ions in the following Pt:Ru ratios: 3:1, 2:1 and 1:1. The concentration of cerium nitrate was held constant during the synthesis of all MWCNT/CeO$_2$ composites. All composite material was washed with de-ionized water and then centrifuged through 3 wash/centrifuge cycles. Electrodes were fabricated by combining the as synthesized MWCNT/Pt/Ru/CeO$_2$ composites with Nafion® and water, then spray coating the dispersions onto glassy carbon electrodes using an airbrush. Flow-rate of spray coating procedures was held constant to insure uniform composite film thickness. Total composite mass deposited was calculated by weighing the working electrodes before and after
spray coating procedures. The catalytic ability of the as-fabricated composite electrodes was determined for the electrooxidation of methanol and ethanol.

**Techniques**

*Three Electrode Apparatus.* Voltammetry experiments investigate the half-cell reactions at an electrode where current is monitored vs. applied potential. In order to conduct such experiments, at least two electrodes must be used. The first electrode is referred to as the working electrode and is defined as the electrode where the desired potential is applied. The second electrode makes up the other half-cell and must maintain a known potential which is used as a reference for the working electrode. The second electrode must also act to balance the charge added or removed by the working electrode. The difficulty with this system is that it is extremely difficult to maintain a constant reference potential while passing current through the same electrode.\(^7\) Therefore, a third electrode is often employed to solve the problem of reference electrode polarization.\(^8\)\(^-\)\(^10\) In a three electrode setup the potential is applied between the working and reference electrodes, while the current passes between the working and counter electrode. A typical three electrode apparatus is shown in figure 13.
In this work a three-electrode apparatus was used for all CV and electrodeposition procedures. Working electrodes consisted of polycrystalline 2 mm diameter platinum electrodes, 2 mm diameter gold electrodes, 2 mm glassy carbon electrodes or graphite plates with an Ag/AgCl electrode used as the reference electrode, and a platinum wire electrode used as a counter electrode. All electrodes were obtained from CH Instruments, Inc. CH Instruments 400A and 660D potentiostats were used to obtain all electrochemical measurements.

Cyclic Voltammetry. Cyclic voltammetry (CV) is a voltammetry technique that involves the current response of a small stationary electrode that results from the application of a triangular voltage as seen in figure 14.
The voltage is first swept from low to high and then back to the initial voltage. The point at which the voltage stops increasing and begins decreasing has been termed the “switching” potential. The potential range chosen for CV procedures depends entirely upon the application. When testing composite electrodes for alcohol or formic acid oxidation the potential range used is -0.15 V to 1.25 V (vs. Ag/AgCl) on a Pt working electrode.\textsuperscript{11-14} A typical current response from the oxidation of methanol on Pt working electrodes can be seen in figure 15.
Figure 15. CV of Pt electrode towards the electrooxidation of methanol in 0.5 M H₂SO₄

There are many features in a CV that can give information about the oxidation of fuels. In the CV for methanol it can be seen that there is one peak in the forward (anodic) direction and one peak in the reverse (cathodic) direction. The peak in the forward direction (0.4 V to 0.9 V) corresponds to the oxidation of methanol. The onset potential is near 0.4 V. Onset potentials can vary depending on the material used for the working electrode and lower onset potentials generally indicate catalytic enhancement. Oxidation processes during CV are diffusion limited; therefore, species at the surface of the static electrode begin to deplete rapidly during sweeps of potential. The current in the forward scan, in theory, may increase to infinity; however, the slow diffusion of methanol from bulk solution causes the peak to round off near 0.75 V. The current proceeds to drop as the species at the surface of the electrode depletes. The highest point in the forward scan of CV is termed the peak anodic current ($i_{pa}$). When comparing CVs from different composite electrodes, the $i_{pa}$ is the single most important feature. When scan rate is held constant
(in this work 100 mV/s) the \(i_{pa}\) is directly proportional to the catalytic ability of the electrode surface.\(^{15-19}\) The voltage at which the \(i_{pa}\) is reached is related to the Gibbs free energy. Lower peak potentials indicate lower \(\Delta G\) and the presence of catalysis. When surface area effects are normalized, the current density (\(j\)) can be determined and higher peak current density (\(j_{pa}\)) is indicative of faster oxidation kinetics. It is; therefore, correct to say that an electrode which produces a higher \(j_{pa}\) has greater catalytic ability for the electrooxidation of methanol.\(^{20-22}\) In the reverse scan there is also a peak between 0.6 V to 0.3 V. It is generally agreed that this peak (peak cathodic current or \(i_{pc}\)) is associated with the removal of incompletely oxidized carbonaceous species (mostly CO) formed during the forward scan.\(^{23}\) Studies have shown that comparing the ratio of \(i_{pa}\) to \(i_{pc}\) can provide information about the tolerance of composite electrodes to carbonaceous poisons.\(^{23-25}\)

The morphology of CVs for the oxidation of ethanol differs from those for methanol. The forward scan of ethanol contains two peaks near 0.6 V to 0.9 V and 1.0 V to 1.2 V, corresponding to the complete and incomplete oxidation of ethanol respectively. The relative height of the peaks in the forward scan may give information about the preferred oxidation mechanism of the electrode catalyst; however, more studies are necessary to verify this observation. The \(i_{pc}\) for ethanol oxidation is relatively higher than that for methanol due to the production of more incompletely oxidized carbonaceous material.\(^{26-28}\)

Formic acid also presents a unique morphology in CV curves. Similar to ethanol, two peaks are seen in the forward CV scan when Pt electrodes are used as the catalyst surface. These two peaks at 0.2 V to 0.4 V and 0.7 V to 0.9 V have been ascribed to the complete and incomplete oxidation mechanisms of formic acid. Unlike ethanol, the oxidation of formic acid
has been well studied and it is generally agreed that the relative height of the two peaks can be used to determine the primary mechanism of formic acid oxidation on a particular composite surface.\textsuperscript{13,29-32} It has been well documented that the incomplete oxidation mechanism is favored when using Pt working electrodes while the complete oxidation mechanism is favored when using Pd working electrodes. Ongoing research is seeking to understand the difference between Pt and Pd promoted oxidation of formic acid.\textsuperscript{29,33,34}

*Electrochemical Quartz Crystal Microbalance (EQCM).* Techniques involving EQCM are widespread throughout electroanalytical research. An EQCM system was used in this research to study the deposition of various materials onto electrode surfaces during electroreduction procedures. An EQCM system monitors the mass per unit area by measuring the change in frequency of a quartz crystal resonator during electrochemical experiments. The resonance is directly affected by the addition or removal of small amounts of mass at the surface of the crystal. EQCM crystals are designed with electrodes on both sides of the crystal resonator. On the top of the crystal there is one broad electrode which is used as the working electrode in electrochemical experiments. The other side of the crystal has two corresponding electrodes which mirror one another and are separated by about 1 mm. When an alternating current is applied between the two electrodes a standing shear wave is generated as shown in figure 16.
The shear wave generated from the potential applied between two electrodes on a QCM crystal can be altered by adding or removing mass from the working electrode of the crystal. In general, EQCM systems allow for resolution down to 1 Hz on crystals with a resonant frequency between 4 – 6 MHz. The Sauerbrey equation relates the change in resonant frequency to the mass change at the surface of the working electrode.

\[ \Delta F = (-F_0^2) \frac{\Delta m}{N} \frac{1}{\rho_q A} \]  

\( \Delta F \) is the change in frequency of the quartz resonator, \( F_0 \) is the resonant frequency, \( \Delta m \) is the mass change, \( N \) is a constant, \( \rho_q \) is the density of the quartz and \( A \) is the electrode area. Due to their indirect relationship, mass gain from the surface of the working electrode would result in a decrease in resonant frequency.

In this study, EQCM experiments were carried out on polished EQCM crystals coated with a 100 Å Ti adhesion layer, followed by 1000 Å Au or 1000 Å Pt. Electrochemical and EQCM experiments were performed on a CH Instruments model 400A (CH Instruments, Inc.) potentiostat and Maxtek Research QCM system (Inficon). The Sauerbrey equation was used to calculate mass gained from the surface of working electrodes during electrodeposition procedures. The deposition of Pt, Pd, Au and graphene was studied in this work.
Scanning Electron Microscopy (SEM)/ Energy Dispersive X-Ray Spectroscopy (EDX). To gain a better understanding of the surface morphology of composite electrodes, SEM was performed. As-fabricated Pt/Au/Ceria, Pt/Pd/Ceria and Graphene/Pt/Ceria composites were analyzed. Graphene films were imaged after the deposition of a 200 Å layer of Pd from Pd sputter coating (EMITECH K550). EDX was used in tandem with SEM to estimate the concentration of metal and metal oxide composites fabricated from electrodeposition procedures. SEM and EDX experiments were performed on a Zeiss ULTRA-55 Field Emission Gun SEM equipped with a Noran System 7 EDX system.

Transmission Electron Microscopy (TEM). In studies that determine the metal loading on MWCNTs, TEM images are typically the best approach to monitor nanoparticle growth. \(35-37\) In this study TEM images were obtained for MWCNT composites to monitor the synthesis of Pt, Ru and ceria nanoparticles. MWCNT composites were loaded on 400 mesh copper grids (Electron Microscopy). TEM experiments were performed on a JEOL TEM-1011 at 100 kV.

High Resolution TEM (HRTEM)/ EDX. To gain a better understanding of nanoparticles grown on MWCNTs, HRTEM was performed. MWCNT composites were loaded on lacy carbon copper grids (Electron Microscopy) in order to provide better resolution between the carbon background and MWCNTs. EDX was performed in tandem in order to determine the composition of the as-synthesized nanoparticles. HRTEM and EDX experiments were performed using a FEI Tecnai F30 TEM equipped with an energy dispersive x-ray detector.

X-Ray Photoelectron Spectroscopy. Composite materials synthesized in this work were further investigated using X-ray photoelectron spectroscopy (Physical Electronics 5400 ESCA
XPS). XPS was used to determine the composition of composite material as well as estimate the atomic ratio metals/metal oxides.

*Raman Spectroscopy*. GO and graphene composites have been widely studied using Raman spectroscopy. The Raman spectrum of graphene has been reported to show bands at 1330-1360 cm\(^{-1}\) and \(~1580\) cm\(^{-1}\) designated as the D and G bands respectively.\(^{38-41}\) The D band does not occur in bulk graphite and its presence indicates a decrease in symmetry due to the hexagonal network of carbons with defects. The relative height of the D and G bands has shown to provide information about the extent of reduction of GO to graphene.\(^{38,40}\) A higher ratio of D to G bands has been seen in graphene which is thought to be the result of increased defect concentration. In this study Raman spectroscopy (Renishaw RM 1000B Micro-Raman) was used to determine the presence of graphene in reduced GO samples. The Raman spectrometer was equipped with a 532nm line of solid Si laser, a single spectrograph fitted with holographic notch filters, and an optical microscope (Leica microscope with motorized XYZ stage) rigidly mounted and optically coupled to the spectrograph. The spectrometer was calibrated with a Si standard using a Si band positioned at 520.3 cm\(^{-1}\).

*X-Ray Diffraction (XRD)*. XRD was performed in order to gain a better understanding of the Pt/Au/Ceria composite synthesized through the electrodeposition of metal ions. A Rigaku D/Max Beta X-Ray diffractometer was employed. Analysis was performed over a 2\(\theta\) range of 30\(^{0}\)-90\(^{0}\). Powder samples were supported on a metal sample holder.

*Determination of Pt and Pd Electrochemically Active Surface Area (ECA) Using Adsorbed Hydrogen*. An important parameter in electrochemical heterogeneous surface catalysis is the surface area. The mechanism in electrochemical catalysis is determined by the electrode-
electroactive species charge transfer through the electrode surface. Therefore, reaction rates and
electrical currents are directly proportional to the surface area. Microscopy techniques are
able to assisting in geometric surface area estimates; however, the presence of porous and
rough surfaces cause large discrepancies between geometric and real electrochemically active
surface areas (ECA). One method of ECA determination that has been well documented for
Pt and Pd electrodes, is the adsorption of hydrogen atoms. When Pt or Pd electrodes are
immersed in acidic solutions and negative potentials are applied, the reduction of H\(^+\) and
adsorption of H atoms onto Pt or Pd occurs.

\[
\text{H}^+ (\text{aq}) + e^- + \text{site} \rightarrow \text{H}_{\text{ad}} \\
\]

At sufficiently negative potentials the formation of a H\(_{\text{ad}}\) monolayer is achieved. Figure 17 shows the adsorption of H atoms onto the Pt/Pd surface.
Figure 17. Adsorption of Hydrogen on Pt or Pd

Since this process is chemisorptive, the following equation can be used to calculate the ECA:

$$ECA = \frac{(n_a) (N_a)}{(d_m)}$$  \hspace{1cm} (2.3)

where $n_a$ is the moles of H atoms adsorbed, $N_a$ is Avagadros number and $d_m$ is the density of hydrogen. The adsorbed hydrogens can be removed by oxidizing the monolayer by applying higher potentials (reversing equation 2.2). From this process the following equation can be derived to determine the ECA:

$$ECA = \frac{(Q_m)}{(208 \, \mu C \, cm^{-2})}$$  \hspace{1cm} (2.4)

where $Q_m$ corresponds to the charge generated from the oxidation of the $H_{ad}$ monolayer. The charge (Qm) can be obtained from integrating the “hydrogen region” of a CV of Pt/Pd in 0.5 M H$_2$SO$_4$. Figure 18 shows a typical CV of a Pt electrode in 0.5 M sulfuric acid. The hydrogen region (-0.15 to 0.1 V) is labeled.
In this work the ECA of Pt and Pd electrodes was determined through the integration of the hydrogen region and calculation using equation 10.2. Since hydrogen atoms do not adsorb to Au or CeO$_2$ surfaces, the ECA calculated from this technique was assumed to have no contribution from Au or CeO$_2$ surface area. This technique was also used to preferentially determine the ECA of Pt and Pd in Pt/Au and Pd/Au composite electrodes.

_Determination of Total Surface Area Using Copper Underpotential Deposition._

Traditionally the ECA of Pt and Pd based electrodes is determined by the hydrogen adsorption method in acidic media. However, the introduction of bi- or tri- metallic catalysts can alter the activity of the Pt/Pd. In addition hydrogen adsorption cannot be used to determine the surface area of metals on which it does not adsorb, such as Au. In these cases a different method must be used to determine the total surface area. Underpotential deposition (UPD) is a technique that has been widely used in electro-analytical chemistry to determine the surface area of conductive electrodes. UPD is a phenomenon where the electrochemical reduction of a metal cation onto a
substrate occurs at a higher (more oxidative) potential than the calculated Nernst potential. This is attributed to the strong interaction between the electrodeposited metal with the electrode substrate on which it is depositing. In order for UPD to occur, the metal-substrate interaction must be more energetically favorable than the metal-metal interaction in the crystal lattice of that pure metal. The result of UPD is the formation of a single monolayer of metal deposited on the substrate. For the catalytic electrodes in PEMFC research, Cu has shown to be an excellent choice for UPD.\textsuperscript{43, 44, 46, 47} Based on the Nernst equation the potential for bulk Cu deposition is 0.05 V vs. Ag/AgCl reference in 0.5 M support electrolyte. UPD for Cu (Cu-UPD) has shown to occur between 0.04 to 0.65 V vs. Ag/AgCl on Pt substrates. Figure 19 shows the formation of a Cu monolayer on a composite electrode during a Cu-UPD procedure.

![Pt/Au/ceria Composite Electrode](image)

**Figure 19. Underpotential Deposition of Cu on Pt (Pd) and Au**
In this study Cu-UPD was used as a surface area calculation technique. Composite electrodes were first submerged in a 0.002 M CuSO$_4$ solution with 0.5 H$_2$SO$_4$ as support electrolyte. The potential was held at a constant 0.04 V vs. Ag/AgCl for 300s at the surface of the composite electrodes according to published procedures. Subsequently cyclic voltammetry was performed in the same solution. The resulting CV curves (example figure 20) show the potential region between 0.1 to 0.6 V in the forward scan where the Cu monolayer (formed during Cu-UPD) is stripped from the composite electrode.

![Figure 20. Cu-UPD on the surface of Pt/Au composite electrode](image)

Integration of this striping peak yields the charge generated from the oxidation of Cu according to the following equation:

$$\text{Cu}_{\text{upd}} \rightarrow \text{Cu}^{2+} + 2e^-$$

(2.5)

From this two electron process, the ECA can be calculated from

$$\text{ECA} = \frac{(Q_m)}{(420 \, \mu\text{C cm}^{-2})}$$

(2.6)
where $Q_m$ corresponds to the integrated peak from CV and 420 $\mu$C cm$^{-2}$ is calculated from the density of Cu, number of moles, and Avagadro’s number. The technique of Cu-UPD was used in this study to calculate the surface area of Pt/Au and Pt/Ru electrodes where the Au and Ru contribution could not be determined by hydrogen adsorption.

References


42. P. A. Research.


CHAPTER 3. STUDY OF NANOCERIA AGING EFFECTS ON PLATINUM/CERIA COMPOSITE ELECTRODS FOR THE OXIDATION OF ALCOHOLS

Introduction

Ceria has shown to be an excellent catalyst for the direct oxidation of alcohols in fuel cells; however, the exact redox chemistry of ceria towards electrooxidation of alcohols is not well understood.\(^1\)\(^-\)\(^7\) While much effort has been given to monitoring the effect of ceria on the oxidation of alcohols\(^7\)\(^-\)\(^9\), no study to date has explored the age dependence of nanoceria on its catalytic ability. We show here for the first time a study monitoring the effect of ceria age on the catalytic ability towards the electrooxidation of methanol and ethanol.

In order to better understand aging effects, ceria was aged in two different environments. The first method (method 1) involved the synthesis and aging of ceria in aqueous solutions. The solutions were kept under vacuum at 22°C and aged for 15 days. During this period electrodes were fabricated from electrodeposition suspensions described in the techniques section of this dissertation. The second method used to study ceria age (method 2) involved the deposition of Pt/ceria composites onto the surface of Pt working electrodes. The ceria was then allowed to age after having been immobilized on the electrode surface. The as fabricated electrodes were kept in sulfuric acid solution under vacuum. The results for this study are reported in the following sections.
Results and Discussion

_Electrode Aging via Method 1._ Electrodes were prepared daily from the hexachloroplatinate solutions from day 0 to 15 using HO or LO ceria. Figure 21a shows cyclic voltammetry scans performed in methanol using HO electrodes. The scans show a continuous decrease in current from day 0 to day 4. The current is at a maximum on day 0, the day it was synthesized. A drop in the oxidation current for methanol is observed as the electrode ages. The current drop is rather large initially, with the current dropping by a factor of 3 between day 0 and day 1. The current drop appears to reach a relatively stable value after 4 days. However, as the ceria solution keeps aging, an increase in the current is observed after day 7, extending a small increase until day 15. Figure 21b shows the HO electrodes showing a similar behavior in ethanol, reaching a stable minimum current at day 3. The current begins to rise after day 4 continuing to a small increase at day 15. The decrease in the current can be explained by two main possibilities.
First, as the particles age, agglomeration of the particles may be observed. The ceria nanoparticles synthesized are of nominally 3 to 5 nm in diameter.\cite{10-13} Agglomeration could increase this size substantially, affecting the dispersion of the Pt/CeO$_2$ composite catalyst as well as minimizing the available surface area of the ceria particles. However, such agglomeration cannot explain the regaining of the catalytic activity after several days of aging. A more plausible explanation is derived from the known phenomenon whereby ceria nanoparticles have exhibited...
reversible oxygen storage capacity and redox switching, in which the particles can reversibly cycle from Ce\(^{3+}\) to Ce\(^{4+}\) states.\(^{14-17}\) A cycling of this kind, over time, would affect the catalytic ability of the nanoceria toward the electrooxidation of alcohols such as methanol and ethanol. The CV scans for LO electrodes in methanol (Figure 21c) show that the current at day 0 is lower than the current on the following days. This result is in stark contrast to the results observed for the HO materials. It is also observed that the catalytic current is lower for the LO modified electrodes than the current of the HO modified electrodes on day 0. Unlike the HO modified electrodes, the current is observed to increase as the sample ages, by a factor of 2 and thus rises until it reaches a value comparable to that of the HO modified electrodes. Similarly, CV results (Figure 21d) for LO electrodes in ethanol are comparable to the results for methanol. These results suggest that the actual redox state of the cerium atom in the nanoceria particle plays a crucial role in the oxidation mechanism for the alcohol, citing the importance of ceria’s regenerative properties.\(^{15}\)
Figure 22. CVs of HO ceria and LO ceria electrodes coated daily on day 0 (a and b) and 15 (c and d). Shown are results from both methanol (a and c) and ethanol (b and d). Notice the alternating behavior between HO and LO.

Figure 22 shows comparison plots of HO and LO ceria electrodes towards the electrooxidation of methanol (Figure 22a and c) and ethanol (Figure 22b and d) on days 0 (Figure 22a and b) and 15 (Figure 22c and d). As can be seen, initially the HO ceria modified electrodes show higher catalytic ability towards the electrooxidation of both methanol and ethanol. Over time, however, the LO oxidizer modified electrodes increase in catalytic ability while the HO modified electrodes experience an overall decrease. Table 3 shows peak currents ($i_{pa}$) for both HO and LO modified electrodes towards the electrooxidation of methanol. Also
shown are ratios of the peak currents normalized using day 0 as a baseline to show the percent increase or decrease in current with the age of the electrode.

Table 3. Peak currents for HO and LO oxidizer ceria modified electrodes. Ceria was aged for 15 days in solution. On the indicated days electrodes were modified with the aged ceria and used for the electrooxidation of methanol. Peak currents were normalized using day 0 as a baseline to show the percentage increase/decrease in current at any particular day.

<table>
<thead>
<tr>
<th>Day</th>
<th>HO ceria</th>
<th>LO ceria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_p$ (mA)</td>
<td>Ratio ($i_p/Day X$)</td>
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<tr>
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<td>0.80</td>
</tr>
<tr>
<td>15</td>
<td>1.97</td>
<td>0.80</td>
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</table>

Electrode Aging via Method 2. In order to rule out any possibility of agglomeration, a different approach to the preparation of the electrode is employed. Electrodes were modified on day 0 with a suspension of potassium hexachloroplatinate and nanoceria made fresh on that day from both high and low oxidizer particles. This electrode was kept in sulfuric acid solution under vacuum, instead of cleaning and re-depositing from aged solution as described in method 1. The nanoceria modified electrode was allowed to age as the ceria catalyst was immobilized on the surface of the electrodes. This method did not allow the particles to agglomerate as they were immobilized in the Pt/CeO$_2$ composite. The same nanoceria modified electrodes were used for cyclic voltammetry in methanol on days 0, 1, 3, 4, 7, 11, and 15. Figure 23 shows the HO (a) and LO (b) ceria modified electrodes have a decreased catalytic ability toward the oxidation of methanol from day 0 to day 15. Table 4 shows peak anodic currents ($i_{pa}$) for both HO and LO modified electrodes towards the electrooxidation of methanol.
Table 4. Peak currents for HO and LO oxidizer ceria modified electrodes. Ceria was aged for 15 days on the surface of the electrode. On the indicated days the electrodes were used for electrooxidation of methanol. Peak currents were normalized using day 0 as a baseline to show the percentage increase/decrease in current at any particular day.

<table>
<thead>
<tr>
<th>Day</th>
<th>HO ceria</th>
<th>LO ceria</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i_p$ (mA)</td>
<td>Ratio ($i_p$/DayX)/(Ratio (Day0))</td>
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<tr>
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<tr>
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<td>0.64</td>
</tr>
</tbody>
</table>

Also shown are ratios of the peak currents normalized using day 0 as a baseline to show the percent increase/decrease in current. Since the nanoceria was immobilized for the duration of the aging, this drop in catalytic ability can be attributed to only a shift in the redox potential of nanoceria.
Figure 23. (a) CV of methanol on HO electrode coated once. The current decreases steadily from day 0 to 15. The decrease can be explained by a redox shift in ceria since the nanoparticles are immobilized, thus prevented from agglomeration. (b) CV of methanol on LO electrode coated once showing a similar behavior than the HO.

Therefore, agglomeration of nanoparticles is not a plausible explanation since the ceria was immobilized on the surface of the electrode. The fact that the electrode’s activity towards the oxidation of the alcohols is not recovered in this method (as opposed to method 1) is probably due to the “starvation” of oxygen for the prepared films, where particles are not able to efficiently re-generate once incorporated on the composite electrode. As agglomeration of the ceria particles can be ruled out, a clean platinum electrode was modified with nanoceria and then cyclic voltammetry was performed with this electrode in methanol. The modified electrode was
submerged in 30% hydrogen peroxide for 1 h allowing the redox state of the ceria to shift towards a higher ratio of Ce$^{4+}$. The CV of that electrode (Figure 24) shows a higher catalytic ability towards the oxidation of methanol.

![Figure 24. After immersing an electrode in 30% H$_2$O$_2$ for 1 h the current observed current for the oxidation of methanol increased. The H$_2$O$_2$ acts as an oxidizer, inducing a shift in the redox state of the nanoceria increasing its catalytic ability.](image)

These results show that once immobilized on the surface of the electrode, ceria can be oxidized (shifted from Ce$^{3+}$ to Ce$^{4+}$) and more effectively catalyze the oxidation of methanol. Since the more oxidized CeO$_2$ species (higher Ce$^{4+}$ ratio) has been observed to have higher catalytic ability towards the oxidation of alcohols,$^{18,19}$ the results can be explained by the oxidation of nanoceria by the peroxide which caused a redox shift and thus resulted in a higher catalytic ability. The increase in catalytic ability for the nanoceria modified electrode upon oxidation in peroxide suggests the redox shift to be a plausible explanation for the fluctuation of currents seen when the nanoceria was aged in solution as well as on the surface of the electrodes.
Conclusion

This study reports for the first time the effects of aging of nanoceria on the electrooxidation of methanol and ethanol. When ceria was aged in solution the HO ceria tended toward high initial catalytic ability in the alcohols with subsequent decrease over time and a slight final increase. This is contrary to the LO ceria, where an increase in catalytic ability is observed. When nanoceria was immobilized on the electrodes then aged, HO and LO electrodes showed similar trends in that the catalytic ability gradually decreased over time. It was determined that the aging effects arise due to a shift in the redox potential of nanoceria which are known to show reversible oxygen storage capacity, in which the particles can reversibly cycle from Ce\(^{3+}\) to Ce\(^{4+}\) states. Agglomeration of the nanoceria was dismissed as a major cause of electrocatalytic variation since ceria aged in solution as well as ceria aged on the surface of an electrode both experienced shifts in CV currents. Studies of modified electrode behavior in peroxide also lead to the conclusion that nanoceria aging effects are caused by redox shifts rather than agglomeration. This study suggests that although ceria is an excellent catalyst for direct alcohol oxidation, the redox chemistry of nanoceria must be carefully determined for making optimal use of nanoceria as a catalyst in direct alcohol fuel cells.

References


CHAPTER 4. PLATINUM/GOLD/CERIA COMPOSITE ELECTRODES
FOR THE OXIDATION OF ALCOHOLS

Introduction

Bimetallic electrode surfaces have been widely studied for applications in DAFCs. While Pt has shown to provide the highest catalytic ability toward the oxidation of alcohols, other transition metals have been used in Pt/metal composites to increase the oxidation kinetics. Our team has extensively investigated the utilization of nanoscale ceria particles incorporated on a Pt composite as a novel anode material for the direct oxidation of methanol and ethanol. Results from our experiments and from others have shown enhanced oxidation of methanol and, to a lower extent, ethanol by the preparation of ceria-modified electrodes that can assist in the oxidation of the alcohol. The main challenge with ethanol is that the complete electrochemical oxidation of ethanol into carbon dioxide is a complicated process involving 12 electrons and the energy-costly cleavage of a carbon–carbon (C–C) bond.\textsuperscript{1-3} The complete oxidation of the ethanol will require the utilization of other bifunctional or trifunctional catalysts that can facilitate the cleavage of a C–C bond at low temperature. With the purpose of improving the electrochemical oxidation of higher alcohols and of improving the poison tolerance of the anode in direct alcohol fuel cells (DAFCs), different bimetallic electrodes have been under study. Gold in particular presents as an intriguing catalyst. When present in macroscale particulate it shows little to no catalytic activity, but it exhibits enhanced catalytic activity in nanoscale.\textsuperscript{4-9} Due to this interesting behavior, recent efforts have been devoted to Pd–Au and Pt–Au intermetallics as alloy or nanoscale-clusters for the catalytic oxidation of alcohols.\textsuperscript{10-13} Motivated by the results
seen on bimetallic Pt–Au and with the ceria-modified electrodes for fuel cell applications, our group have explored the preparation of electrodeposited Pt–Au–CeO₂ composite electrodes by the simultaneous deposition of Pt and Au into the composite electrode. Such a method presents a facile and efficient alternative for the modification of the anode and the electrochemical enhancement of the oxidation current for both methanol and ethanol is presented. Ceria has also shown great promise for its ability to oxidize alcohols when composited with Pt and Pt/metal bimetallic electrodes.¹⁴⁻¹⁷ We report here the study of Pt/Au electrodes (with and without ceria) and their catalytic ability toward the oxidation of methanol and ethanol.

**Results and Discussion**

*Preparation of the Modified Pt:Au Electrode.* The cathodic electrodeposition of Pt and Au from a binary solution containing Pt⁴⁺ and Au³⁺ in the presence of ceria was used to prepare bimetallic composite electrodes. The total concentration of metal ions was kept constant in all cases equal to 2 mM (defined as the sum of the molarities for Pt and Au), while the concentration of ceria was kept at 5 mM. The electrodeposition was carried at -0.200 V for 600 s while stirring the solution. The voltammetry of the modified electrodes in sulfuric acid shows the characteristic features of both, the Pt and Au electrodes, respectively, depending on the ratios of Pt and Au used for the deposition. Figure 25 shows the CV of the modified electrodes in 0.5 M H₂SO₄ solution. Features from both metals in the cyclic voltammograms suggest the presence of crystalline domains from both metals on the composite electrode. For example, after the deposition of the Au, Pt, or Au/Pt composite, the electrode’s CV resembled that of the modified electrode, not showing any of the voltammetric characteristics of the underlying electrode. The CVs shown in Figure 25 report the values for the total amount of current, and not the current
density. Ideally, the reported values should be normalized for the surface area, and for a pure Pt electrode this can be easily carried out by looking at the hydrogen adsorption region.\textsuperscript{18, 19}

![Cyclic voltammograms of the modified electrodes in 0.5 M H\textsubscript{2}SO\textsubscript{4}: (a) Pt/ceria, (b) Pt:Au/ceria 50:50, and (c) Au/ceria showing the presence of Pt and Au crystalline domains (scan rate ) 100 mV/s).](image)

However, two big factors affect our interpretation of the electrochemically active surface area. First, most of these electrodes have a different ratio of Pt:Au making it difficult to determine the actual surface area. Second, due to the intermetallic nature of the materials, we cannot directly compare equivalent surface areas of Pt and Au which are presumed to have different catalytic properties. Finally, due to our lack of knowledge of any surface morphology effects on the modified electrodes, as well as an accurate picture of the mixed Pt and Au contents, such normalization will lack the required accuracy. It is interesting to observe that incorporation of Au into the Pt:Au film did not introduced major changes in the hydrogen adsorption region of the electrode, suggesting a change on the electrode’s morphology that effectively increased the Pt surface area at the lower Pt contents. The only electrode that is considerably different is the one modified with only Au. Although the true implications of the total surface area are not well
understood, we have not only looked at the total amount of current for the electrodes, but also compared the current density normalized to the Pt surface area. Our rationale was to consider the published works which asserts that gold in the micro- and microcrystalline form will have little or no catalytic enhancement for the oxidation of the alcohol. Normalization of the current to the amount of Pt surface area will allow us to correlate possible synergistic or morphology related phenomena. The potential used for the electrodeposition was chosen to be negative enough to ensure the reduction of both metals, but little is known about the rate of deposition of both metals.

The total amount of surface area was determined for each electrode by a combination of two steps. At first, the Pt covered surface area was determined by the total amount of charge associated with the hydrogen adsorption region. Since the Au sites on the electrode surface would not be included in the hydrogen adsorption region, copper underpotential deposition (Cu-UPD) was carried on the electrode, and the stripping of the total amount of copper from the electrode provided with the total amount of surface area (Pt and Au). Figure 26 shows both the monolayer formed from the adsorption of hydrogen and Cu in the two separate ECA determination procedures.
The Au covered area was obtained by the difference of the total amount of surface area and the Pt covered area. The values for the Pt and Au surface areas determined by the cyclic voltammetry are in excellent agreement with the molar ratios used for the electrodeposition.

Figure 27 shows the cyclic voltammetry for the Cu-UPD and the hydrogen adsorption region for an electrode prepared from a 1:1 molar ratio of Pt: Au. The values obtained from the electrochemically determined surface area were 50.4:49.6 for the electrode.
As a point for comparison, the Energy Dispersive X-ray (EDX) on the SEM microscope was also used as an approximate tool to estimate the atomic ratios of Pt/Au on the samples. Table 5 shows the EDX atomic compositions and measured Pt/Au ratios for the composite films.

Table 5. EDX Estimates of Atomic Concentration of Pt and Au for the Pt/Au/Ceria Electrodes Compared to the Molar Ratio Used in the Suspensions Used for the Deposition

<table>
<thead>
<tr>
<th>electrode no.</th>
<th>ratio of Pt: Au in suspension</th>
<th>EDX % Pt atom</th>
<th>EDX % Au atom</th>
<th>EDX ratio Pt: Au</th>
<th>predicted % Au</th>
<th>calc'd % Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:1</td>
<td>34.15</td>
<td>33.42</td>
<td>1:0.98</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>2*</td>
<td>0:2</td>
<td>5.31</td>
<td>62.79</td>
<td>1:11.82</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>2:0</td>
<td>60.79</td>
<td>0</td>
<td>1:0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1.5:0.5</td>
<td>23.28</td>
<td>11.45</td>
<td>2:1</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>5</td>
<td>0.5:1.5</td>
<td>34.37</td>
<td>48.65</td>
<td>1:1.41</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td>6</td>
<td>1:2</td>
<td>36.52</td>
<td>40.91</td>
<td>1:1.12</td>
<td>67</td>
<td>53</td>
</tr>
<tr>
<td>7</td>
<td>2:1</td>
<td>39.54</td>
<td>18.59</td>
<td>1:0.47</td>
<td>33</td>
<td>32</td>
</tr>
</tbody>
</table>

The values obtained by the EDX are in very close agreement with the molar ratios as well as the voltammetric determinations of the ECA, supporting that the obtained rate of deposition for both metals at -0.200 V appears similar. The EDX results show that in most cases, the atomic ratio of
Au appears slightly lower than that of Pt as predicted by their molar concentrations in the bath. The difference in the concentrations can be explained by the fact that the films are grown on a Pt electrode. As a porous morphology is created by the crystallites deposited, the SEM’s incident beam is also capable of probing the underlying Pt substrate, yielding an apparently higher amount of Pt. Another possibility is that the two different metal ions will deposit at a different rate. The deposition of Pt, Au, and Pt:Au on a 1:1 ratio was tested on the quartz crystal microbalance (QCM) in order to measure the deposition rates on the quartz crystal. After depositing the metal ion for a total of 600 s, the same amount of time used for the preparation of electrodes, a total mass load of 8.0, 7.0, and 8.8 µg was obtained for Pt, Au, and Pt:Au, giving deposition rates of 13.3, 11.7, and 14.7 ng/s, respectively. These values can be considered similar within the errors of the technique, especially when factors such as changes in viscoelasticity, solvation, and porosity of the deposited films are not well-known. Thus, we believe that the largest contribution to the difference between the deposited ratios and the actual ratios is mostly due to the contributions from the underlying Pt film.

In addition to EDX, X-ray photoelectron spectroscopy (XPS) was used to monitor the concentration of Pt and Au on the surface of the composite electrodes. Figure 28 shows the wide survey XPS spectra of the Pt/Au/ceria (Pt:Au 2:1) electrode. Similar results have been shown in other studies.4, 8, 10, 12, 24, 25
Figure 28. Wide survey XPS spectra of the as-prepared Pt/Au/ceria 2:1 electrode

The peaks at ~340 eV and ~90 eV correspond to Au 4d5 and Au 4f7 respectively. The peaks between 68 - 88 eV can be assigned to Pt 4f and correspond to metallic Pt. The previous peaks discussed, indicate that Pt and Au bimetallic catalysts were successfully co-deposited from ionic solutions. The calculated atomic concentration of Pt and Au is in good agreement with results from EDX data and further suggests that Pt and Au metallic concentrations on electrode surfaces can be predicted from the concentration of metal ions in deposition solutions. The peak at ~882 eV can be attributed to Ce 3d5. The concentration of cerium atom in the composite electrodes was calculated to be 0.7%.
X-ray diffraction (XRD) experiments were also carried out to study the crystalline nature of the Pt/Au bimetallic electrodes. Figure 29 shows the XRD spectrum of Pt/Au/CeO$_2$ (Pt:Au 2:1) electrode.

![XRD spectrum](image)

**Figure 29. XRD pattern for the Pt/Au/ceria 2:1 composite electrode**

The diffraction peaks of Pt, Au and ceria can be seen, indicating the coexistence in the sample. Peaks are apparent at around $2\Theta = 47^\circ$, $67^\circ$ and $87^\circ$ corresponding to the (200), (220) and (222) planes of the face-centered cubic (fcc) structure of Pt. The peaks at around $2\Theta = 43.7^\circ$, $64.1^\circ$ and $77.1^\circ$ are assigned to the (200), (220) and (311) planes of fcc Au respectively. Due to the similarity of the Pt and Au crystal structure two peaks are merged and cannot be distinguished. The large peak at $\sim 39^\circ$ corresponds to the merger of peaks at $37.5^\circ$ and $40^\circ$ which are attributed to the (111) plans of both Au and Pt. The peak at $\sim 82^\circ$ results from the merger of peaks at $81.2^\circ$ and $82^\circ$ which correspond to the (222) plane in Au and the (311) plane in Pt respectively.
Characteristic diffraction peaks were detected at 2Θ = 33.1°, 59.1° and 76.7° which correspond to the (200), (311) and (222) planes of the cubic fluorite structure of CeO₂. Similar data has been seen in other studies.⁹,²⁴

_Electrochemical Oxidation of Methanol on a Pt Electrode Modified with Pt/Au/Ceria Composite._ The cyclic voltammograms (CVs) were obtained with 1.0 M CH₃OH solutions in 0.5 M H₂SO₄ for each of the modified electrodes. As expected, the electrode modified with Au and ceria (no Pt) showed no noticeable activity toward the methanol oxidation, whereas the electrode modified solely with Pt and ceria showed enhanced catalytic activity over a bare Pt electrode as previously reported. However, when the electrodes were prepared with a combined Pt, Au, and ceria composite, different degrees of enhancement of the catalytic current were observed. When Au is present in the composite, the Pt electrodes showed a catalytic current similar to that of the Pt/CeO₂ electrode. Peculiarly, a larger enhancement is observed at a Pt/Au ratio of 2:1 combined with ceria. Such an electrode had a considerably higher current for the oxidation of methanol. Figure 30 shows the cyclic voltammetry for the oxidation of methanol on different Pt/Au/CeO₂ composite electrodes.
Figure 30. Cyclic voltammetry of the Pt/Au/ceria-modified Pt electrodes toward 0.1 M CH₃OH in 0.5 M H₂SO₄ for the different Pt/Au ratios of (a) 2:0, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 0:2. A noticeable increase in the oxidation current is observed for electrodes prepared from a deposition batch containing a 2:1 molar ratio of Pt:Au. Other ratios showed very similar catalytic enhancements.

The electrochemically active (ECA) area can be determined by the hydrogen adsorption region of Pt for the electrodes and the current density (current adjusted to the surface area) obtained. Figure 31 shows that for the current normalized Pt electrodes, the pure Pt/CeO₂ electrode outperforms the Pt/Au/CeO₂ results. Although the results appear to contradict an enhancement observed in Figure 30, they can be explained by the following considerations. First, the determination of the surface area does not take into consideration the surface area taken by the Au.
Figure 31. Cyclic voltammograms of the Pt/Au/ceria-modified Pt electrodes with (a) 2:0, (b) 2:1, (c) 1:2 toward 0.1 M CH$_3$OH in 0.5 M H$_2$SO$_4$ corrected for Pt-surface area using the hydrogen adsorption region. The bimetallic electrodes appear to have very similar electrochemical behavior per Pt surface area, even while having lower Pt overall loads due to mixing with Au. The Pt/ceria (no gold) electrode outperforms the bimetallic electrodes per amount of Pt.

It can be expected that the electrodes, being prepared from a constant total metal ion concentration, containing Pt/Au/CeO$_2$ will outperform the Pt/ceria electrodes in a Pt content basis. Second, the determination of the ECA will consider any possible synergistic effect of incorporating Au into the metal composite electrode or any changes in surface morphology besides the changes in surface area. Figure 32 shows the morphology of the Pt/Au/CeO$_2$ films as evaluated on the SEM.
Figure 32. Scanning electron microscopy images of the Pt/Au/ceria films electrodeposited on Pt-foil electrodes. A potential of -0.200 V vs Ag/AgCl was applied to a 2 mM metal ion solution in 0.5 M H₂SO₄ for a total of 600 s under constant, light stirring, keeping a constant deposition current of 1.0 × 10⁻⁴ A. The SEM images show films deposited from (a) Pt/ceria, to sharper, triangular crystallites for (e) Au/ceria. As the Au concentration increases, the composite morphology becomes rougher, increasing the active surface area. (f) Representative EDX spectra showing the presence of Pt and Au in the 2:1 Pt:Au grown film.
The SEM images of the film containing only Pt/ceria appear to be relatively smooth, with only a few crystallites on the surface (Figure 32a). In contrast, the SEM images from Au/CeO₂ films consisted of large, dendrite-like structures (Figure 32e). As the amount of Au is increased in the Pt/Au/CeO₂ film, the morphology evolves from small, round particles (higher Pt content), to smaller dendrite-like structures (higher Au content). The SEM results suggest that as the Au contents in the Pt/Au/ceria increases, there are significant changes in the morphology and in the surface area of the material. Further evidence of the increase on the surface area of the composite film is supported by the relatively large hydrogen adsorption area of the Pt, even in samples composed predominantly of Au. Thus far, we have only described the ratio of Pt/Au on the electrodes based on the molar ratios of the suspensions used on the electrodeposition bath. However, this assumes that by holding a potential of -0.200 V vs. Ag/AgCl we can deposit both Au³⁺ and Pt⁴⁺ at the same rate.

*Electrochemical Oxidation of Ethanol on a Pt Electrode Modified with Pt/Au/CeO₂ Composite.* The modified electrodes were also tested for the electrochemical characterization of ethanolic solutions in 0.5 M H₂SO₄. Ethanol’s use as a fuel has been hailed promising, but its application in fuel cells has been limited by the need to cleave a carbon-carbon (C-C) bond. When the composite electrodes modified with the same Pt/Au/Ceria composites as in the previous section were exposed to a 1.0 M ethanol solution, a similar behavior to that of methanol was observed. Figure 33 shows the electrochemical response of the modified Pt electrode toward the ethanol oxidation.
Figure 33. Cyclic voltammograms for the oxidation of 0.1 M CH₃CH₂OH in 0.5 M H₂SO₄ for the different Pt/Au/ceria-modified Pt electrodes with (a) 2:0, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 0:2 Pt:Au ratios. The electrode modified with a molar ratio of 2:1 Pt:Au shows a larger catalytic current for the oxidation of ethanol.

Once again, as expected, the Au/ceria electrode showed no catalytic activity toward the oxidation of ethanol. All of the Pt/Au/CeO₂-modified electrodes showed a catalytic enhancement over the nonceria Pt electrode for the oxidation of ethanol, just as was observed for the oxidation of methanol. As in the oxidation of methanol, the electrode modified from a bath solution with molar ratios of 2:1 Pt:Au showed the largest increase in the total amount of current before normalization for surface area. Overall, the electrochemical oxidation of ethanol appears to show a greater dependence on the Au contents in the composite electrode as the utilization of other Pt:Au ratios showed little or no enhancement for the oxidation of methanol. All Pt/Au/ceria containing electrodes showed enhanced catalytic activity over the electrode modified with Pt/CeO₂ only, suggesting the possibility of a synergistic catalytic effect between Pt and Au. The performance of the electrodes can be ranked in increasing order of Pt:Au ratio as 0:2, 2:0, 1:1, 1:2, and 2:1. The best performing electrode, as observed on all cases, was the Pt/Au ratio of 2:1,
providing a total amount of current more than twice the current of that for the Pt/ceria electrode. The electrochemical oxidation of ethanol also observed a higher relative increase in the current (when compared with the only Pt/ceria electrode) than the methanol-modified electrode. The increase in peak current for ethanol was 160%, while that of methanol was just 50%.

Considering the aforementioned difficulties associated with the electrochemical oxidation of methanol, such a preferred increase in the total current is a promising indicator that the Pt/Au intermetallic electrode provides added catalytic activity for the oxidation of ethanol.

To try to understand such a large increase in the total current, normalization over the Pt eca was performed. Figure 34 shows the normalized CV for the Pt/Au/ CeO₂ electrodes. From the normalized CV data it appears that for the case of the electrochemical oxidation of ethanol, the effect of the addition of Au to the electrode is even larger.

![Cyclic voltammograms of the Pt/Au/ceria-modified Pt electrodes with (a) 2:0, (b) 2:1, and (c) 1:2 toward 0.1 M CH₃CH₂OH in 0.5 M H₂SO₄ corrected for Pt-surface area using the hydrogen adsorption region. The Pt/Au/ceria catalyst exhibits greater activity for the electrochemical oxidation of ethanol than electrodes based on only Pt/ceria per Pt content. This observation is different from the case of methanol.](image-url)
The increased current for the 1:2 and 2:1 Pt/Au modified with ceria ratios is more than doubled over that of the Pt/ceria only electrode, suggesting some degree of catalytic enhancement.

The results suggest that the ternary electrode of Pt/Au/CeO$_2$ does not particularly benefit the electrochemical oxidation of methanol. The increases observed in the electrochemical oxidation of methanol can be easily explained due to the changes in the morphology and Pt surface area of the film once Au is incorporated. However, the increase in the electrochemical oxidation current observed for ethanol is larger than what can be attributed to such changes in morphology and surface area. It was also observed that in all cases, an increase in the total oxidation current also incurred in a slight shift to higher potentials (increased overpotential). The increase in the over-potential is small, and we believe that it can be attributed to the changes in the film morphology affecting the electrochemical behavior of the composite film. Moreover, for the case of ethanol, a strong oxidation band is also observed at potentials of around 1.2 V vs Ag/AgCl, associated with the incomplete oxidation, or four-electron pathway of the ethanol leading into the two-carbon products of acetic acid and acetaldehyde.$^{2,28,29}$ Such a band is also increasing in the modified electrodes, although it is observed that the relative size of such peak becomes smaller when compared to the first oxidation peak for the alcohol as Au is incorporated. The change in the ratio of the two anodic peaks suggests that there may be an enhanced catalytic effect of the ternary Pt/Au/CeO$_2$ electrode, in which the Pt/Au concentrations may enhance the more complete oxidation (carbon cleavage) of the ethanol over the incomplete oxidation, generating smaller amounts of the 2-carbon products.

*Electrochemical Oxidation of Alcohols on the Au Electrode Modified with Pt/Au/CeO$_2$ Composite.* To further analyze possible synergistic effects of the ternary Pt/Au/CeO$_2$ electrode,
similar experiments were also carried out in which a gold electrode was modified with the different Pt/Au/\text{CeO}_2 as opposed to a Pt electrode. The modified Au electrodes were tested in a 0.5 M H\textsubscript{2}SO\textsubscript{4} solution and their cyclic voltammetry was reminiscent of the metals that it was modified with (Pt, Au, or Pt/Au), without any noticeable signs of the underlying Au surface. Moreover, the voltammetry of the modified electrodes in H\textsubscript{2}SO\textsubscript{4} appears indistinguishable from those of the modified Pt electrodes. This observation supports our previous idea that a relatively thick, crystalline film is grown on the electrode, isolating most of the underlying electrode from the electrode-solution interface, although small cracks or voids in the deposited film are presumed to exist. The Au electrodes modified with different ratios of Pt/Au/\text{CeO}_2 showed an enhancement in the total current for the electrochemical oxidation of methanol on the Pt/Au/\text{CeO}_2 electrode prepared from a 2:1 Pt:Au ratio, followed by the 1:2 Pt:Au ratio. Upon correcting for the Pt surface area, it becomes apparent in Figure 35 that the Pt/\text{CeO}_2 electrode outperforms (per Pt contents) the Au containing electrodes.
Figure 35. (a) Cyclic voltammetry of the Pt/Au/ceria-modified Au electrodes toward 0.1 M CH₃OH in 0.5 M H₂SO₄ for the different Pt/Au ratios of (a) 2:0, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 0:2. A noticeable increase in the oxidation current is observed for electrodes prepared from a deposition batch containing a 2:1 molar ratio of Pt:Au. Other ratios showed very similar catalytic enhancements. (b) Cyclic voltammograms of the Pt/Au/ceria-modified Au electrodes with (a) 2:0, (b) 2:1, and (c) 1:2 toward 0.1 M CH₃OH in 0.5 M H₂SO₄ corrected for Pt-surface area using the hydrogen adsorption region. As for the Pt based electrodes, the electrode modified with a Pt only appears to perform better for the oxidation of methanol (per Pt area).

Such behavior was nearly identical with the behavior toward the electrochemical oxidation of 1.0 M methanol solutions with modified Pt electrodes. It is important to note again that such normalization is not entirely accurate as it plays no regard to the amount of gold on the surface.
The same electrodes were also tested for the electrochemical oxidation of ethanol. When ethanol was electrochemically oxidized on the modified Au electrodes, an enhancement in the total amount of current was observed for all electrodes (Figure 36), very similar to the results obtained for a modified Pt electrode (Figure 33 and Figure 34).
Figure 36. (a) Cyclic voltammograms for the oxidation of 0.1 M CH$_3$CH$_2$OH in 0.5 M H$_2$SO$_4$ for the different Pt/Au/ceria-modified Au electrodes with (a) 2:0, (b) 2:1, (c) 1:1, (d) 1:2, and (e) 0:2 Pt:Au ratios. The electrode modified with a molar ratio of 2:1 Pt:Au shows a larger total current for the oxidation of ethanol. (b) Cyclic voltammograms of the Pt/Au/ceria-modified Au electrodes with (a) 2:0, (b) 2:1, and (c) 1:2 toward 0.1 M CH$_3$CH$_2$OH in 0.5 M H$_2$SO$_4$ corrected for Pt-surface area using the hydrogen adsorption region. The Pt/Au/ceria catalyst exhibits greater activity for the electrochemical oxidation of ethanol than electrodes based on only Pt/ceria, especially for electrodes prepared from a 1:2 Pt:Au ratio.

When normalized, as in the case of the Pt electrode, an enhancement on the current is observed for the oxidation of the alcohol. A noticeable difference is that for the modified Au electrode, the
highest amount of current obtained was for the Pt/Au/ceria electrode with a composition of 1:2 Pt: Au as opposed to 2:1 Pt: Au as in the case of the Pt electrode. The ratio of the currents from both anodic peaks appear to favor the first oxidation peak as it was observed for the modified Pt electrodes. From the results, it becomes apparent that there is a synergistic relation between Pt, Au, and ceria that enhances the electrochemical oxidation of ethanol.

**Conclusion**

It is found that although pure, crystalline Au has no noticeable catalytic activity toward either methanol or ethanol oxidation in acidic media, it does exhibit enhanced catalytic activity toward both alcohols when in the presence of Pt. In all cases studied, electrodes containing a mixture of Pt and Au in the metal-ceria composite (Pt/Au/CeO\(_2\) composite electrode) exhibited higher total oxidation currents for the oxidation of the alcohol than the electrodes containing only Pt-ceria in the absence of Au. Such results suggest that the Pt-Au intermetallic in the composite electrodes can behave as a good ternary catalyst for the oxidation of the alcohols. The results suggest that the electrode may either have an apparent higher poison tolerance or synergistic effect for the catalytic oxidation of the alcohols. Although the oxidation of both methanol and ethanol show enhancement, upon normalizing for the Pt ECA it becomes apparent that the mixed Pt/Au electrodes have an increasingly exposed surface area. However, the increase in the oxidation current for ethanol is considerably larger than what can be predicted by changes in surface area alone. The similarity of the cathodic sweeps for all the different ratios of Pt/Au suggests a similar degree of poison tolerance for the modified electrodes. When considering these results, the possibility of a synergistic effect is then supported by the CV data as a viable source for the preferential catalytic enhancement for the oxidation of the ethanol. Thus, the larger
increase in current for ethanol suggests the presence of some synergistic catalytic effect in the Pt/Au/CeO$_2$ catalyst, and that the increase in the catalytic current is not solely the case of a higher degree of poison tolerance or surface area. One possibility for this difference can be that the nature of the rate limiting step in the oxidation of methanol is different from that of the oxidation of ethanol, which involves the cleavage of a carbon-carbon bond. The nature of the underlying electrode to be modified (either a Au or Pt electrode) proved not to be significant, suggesting that the electrodeposition apparently forms a thick film of crystalline nature, and the underlying electrode surface is effectively separated from the electrode-solution interface. Although the Direct Methanol Fuel Cell has made it attractive to oxidize methanol as a fuel, ethanol is the greener alternative. The modified electrodes show not only enhanced catalytic activity for the electrochemical oxidation of the alcohols, but also a greater effect for the oxidation of ethanol. These results are promising for the development of novel direct alcohol fuel cells and warrant further research in order to identify and quantify the actual products from the oxidation of ethanol and to correlate the electrochemical behavior with theoretical predictions.

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CHAPTER 5. GRAPHENE/PLATINUM/CERIA COMPOSITE ELECTRODES FOR THE OXIDATION OF ALCOHOLS

Introduction

Due to its thinness, mechanical strength, transparency, conductivity and high surface area, graphene has recently become the focus of intense research efforts for many applications including DAFCs, supercapacitors, sensors, and transistors. One of the simplest methods for graphene synthesis is the reduction of nonconductive graphene oxide (GO). The polar organic groups in GO make it easily dispersible in water. Many methods exist for the reduction of aqueous GO suspensions including thermal reduction, flash reduction, enzymatic reduction, or chemical reduction using hydrazine. The direct electrochemical reduction of GO from suspensions allows for the production of highly controllable films. However, unmodified graphene films have limited application in the field of catalysis since in most applications graphene must be modified to provide useful catalytic properties. In order to increase the surface area and stability of electrode catalysts researchers have studied the effect of supporting metal nanoparticles on carbon materials including graphite, carbon nanotubes and graphene.

Traditionally, Pt catalysts have been the most popular and effective anode in DAFCs due to their ability to catalyze the complete electrochemical oxidation of alcohols. However, Pt catalysts suffer from a variety of drawbacks including high cost, electrode poisoning (mostly from CO), and mass transport limitations. Much effort has been devoted to the study of bifunctional catalysts that provide higher poison tolerance, reduce cost and increase resistance to corrosion. One catalytic material that has recently shown to provide excellent catalytic activity
towards the electrochemical oxidation of alcohols is nanoceria (nanoscale cerium oxide). In the nanoscale, ceria can store and release oxygen with little distortion to the lattice, as nanoceria can reversibly undergo redox processes from Ce\(^{3+}\) to Ce\(^{4+}\). Due to this oxygen capture and release capacity, nanoceria has been investigated for its use in the field of DAFCs.

Motivated by results seen for electrochemically reduced graphene and bifunctional Pt/Ceria electrodes, we report for the first time Graphene/Pt/CeO\(_2\) composite electrodes synthesized from the electrodeposition of both graphene and Pt/CeO\(_2\) suspensions. Also reported is the catalytic ability of these novel electrodes toward the electrochemical oxidation of methanol and ethanol for applications as DAFC anodes. In this study we compare the alcohol oxidation ability of Graphene/Pt (GP), Graphene/Pt/CeO\(_2\) (GPC) and Pt/CeO\(_2\) (PC) composites.

**Results and Discussion**

**Composite Surface Characterization.** Due to the polar functional groups GO is easily dispersed in water; however, upon electro-reduction most of these polar groups are removed and the resulting graphene precipitates onto the surface of the working electrode creating a conductive film. When Pt/ceria is subsequently electrodeposited, nanoceria is trapped onto the surface of the graphene film by the electro-reduced Pt, creating a bifunctional metal/metal oxide electrode surface. Pt and nanoceria bifunctional catalysts have shown to increase the peak current of alcohol oxidation in CV. Three different composite electrodes were fabricated in this study: Graphene/Pt/CeO\(_2\) (GPC), Graphene/Pt (GP), and Pt/CeO\(_2\) (PC). GPC was made through the electro-reduction of graphene oxide from an aqueous suspension followed by the electrodeposition of Pt/CeO\(_2\). Similar to the GPC electrode, GP was fabricated by
electrodeposition of Pt nanoparticles on graphene films. The PC electrodes were made by the electrodeposition of Pt/CeO$_2$ suspensions on a clean Pt surface.

Graphene films were fabricated by immersing Pt working electrodes in 0.5 mg/mL GO suspensions with 0.1M NaCl as support electrolyte. During GO deposition procedures a constant -1.15V vs. Ag/AgCl was applied for 7 minutes with constant stirring. Black deposits were observed to form on the surface of electrodes. Electrodes were removed from GO suspensions and allowed to dry resulting in the formation of dark opaque films on the surface of Pt electrodes. Films were also fabricated on Pt foil in order to perform Raman spectroscopy (Renishaw RM 1000B Micro-Raman). The Raman spectrum of graphene has been reported to show bands at 1330-1360 and around 1580 cm$^{-1}$ designated as the D and G bands respectively. Figure 37 shows the spectrum of electrochemically reduced graphene.

![Raman spectra](image)

**Figure 37.** Raman spectra of electrochemically reduced graphene (red) and graphene oxide (black) showing the D and G bands near 1350 and 1585 cm$^{-1}$ respectively
The spectrum shows peaks at 1350 and 1585 cm\(^{-1}\) corresponding to the D and G bands respectively. The D peak does not occur in bulk graphite and indicates a decrease in symmetry due to the hexagonal network of carbon atoms with defects.\(^{25,32}\) The intensity of the D band is also known to be higher than the G band in graphene and the opposite is true for graphene oxide. The relatively high ratio of D and G intensity is thought to be the result of increased defect concentration present in graphene.\(^{33}\)

The graphene film was further investigated to determine graphene deposition rate and thickness using an electrochemical quartz crystal microbalance (EQCM) system during electrodeposition procedures. Graphene was deposited from 0.5 mg/mL GO suspensions with 0.1M NaCl as support electrolyte onto QCM crystals with 100 Å Ti adhesion layer, followed by 1000 Å Pt. The plot of mass vs. time is shown in figure 38.

![EQCM data showing the deposition of graphene from dispersions of GO](image-url)
As can be seen the mass increases substantially for the first 7 minutes of deposition. During the last 9 minutes the mass seems to plateau around 0.9 \( \mu \text{g/cm}^2 \). It was observed during deposition procedures that a black film was first deposited across Pt surfaces, followed by agglomeration of larger graphene particles. Once these particles became sufficiently large it was observed that they detached from the surface of the QCM crystal leaving black agglomerations in the deposition solution. This phenomenon explains the plateau seen in figure 38. The fluctuation above and below the plateau is caused by the growth and subsequent detachment of graphene particles from the crystal. It can be determined from this data that there exists a maximum graphene film mass load that can be achieved using the previously indicated deposition parameters. It is apparent that that graphene mass load can be controlled by altering deposition time. In this study the deposition time was held at 7 minutes in order to achieve comparable films with the maximum graphene mass load.

Following the deposition of graphene films, Pt and Pt/CeO\(_2\) suspensions were electrodeposited onto the graphene modified Pt electrodes following published procedures\(^{15, 34} \). In order to determine the effect of graphene films on deposition of metal nanoparticles, Pt and Pt/CeO\(_2\) suspensions were also electrodeposited on unmodified Pt surfaces. Surface morphology of all electrodeposited composite materials was characterized using SEM (Zeiss ULTRA-55 FEG SEM). Figure 39 shows SEM images of the composite material fabricated in this study.
Figure 39. SEM images of (a) graphene film, (b) Pt/ceria nanoparticles deposited on a Pt substrate, (c,d) Pt/ceria nanoparticles deposited on a graphene film and (e,f) Pt nanoparticles deposited on a graphene film.

Figure 39a shows the SEM image of a typical graphene film formed in this study by electrodeposition from GO. The folds and ridges are characteristic of the mesostructure of graphene films and comparable results have been found in other studies.\textsuperscript{5,6,36} Figure 39b displays the metal Pt nanoparticles formed on Pt substrates through the electrodeposition of
Pt/ceria suspensions. The formation of a uniform surface can be seen with recurring particles with diameters close to 40 nm. The overall structure appears to be flat with points protruding from the surface. Pt or ceria nanoparticles cannot be distinguished which may indicate that ceria nanoparticles are completely encapsulated by Pt. Figure 39c is the SEM image of the GPC electrode which displays a more porous structure than PC. The GPC surface shows a uniform network of Pt nanoclusters. Figure 39d shows a higher resolution image of the GPC surface where smaller nanoparticles can be seen in the construction of the clusters. The dimensions of the smallest particles are between 20-30 nm. Underlying and incorporated into the composite there are also spherical structures with diameters close to 80 nm. These particles are thought to form due to the presence of ceria trapped on the surface of graphene films. The spherical particles are not seen in any other sample which indicates that their formation is dependent on the graphene substrate and ceria particles in deposition suspensions. Overall the GPC surface is much more porous than the PC surface which may result in more exposed ceria nanoparticles protruding from the composite material. The more exposed ceria nanoparticles may lead to higher catalytic performance of GPC electrodes. As can be seen in figure 39e the growth of both Pt nanoclusters and nanorods is evident on the GP surface. Figure 39f indicates that the nanoclusters are similar in features and dimensions to the clusters seen in the GPC electrodes. The nanorods; however, are found only in the GP sample. The formation of these rods is thought to be a characteristic of the graphene substrate and the absence of ceria. The lack of rods in the other samples indicates that the presence of nanoceria acts to suppress the growth of large Pt structures during electrodeposition procedures.
Composite electrodes were further investigated using energy dispersive X-ray spectroscopy (EDX). Figure 40 shows the EDX spectrum of the GPC and PC composites.

![EDX spectrum](image)

**Figure 40.** EDX spectrum of (a) Graphene/Pt/Ceria (GPC) composite and (b) Pt/ceria (PC) composite

The presence of Pt, C, and O is clearly indicated. The C and O peaks are characteristic of the graphene substrate and air respectively, and the Pt peaks indicate that Pt was successfully electrodeposited onto graphene films. The absence of further peaks is attributed to the purity of
the composite material. The occlusion of ceria in the Pt network makes detection of the Ce atom difficult in electrodeposited samples. The EDX of the PC sample (figure 40b) yielded no indication of Ce; however, the EDX of GPC (figure 40a) clearly shows the characteristic Ce peaks around 5 keV. The zoomed view of the Ce peaks in GPC is provided in figure 41.

![EDX spectrum of Graphene/Pt/Ceria (GPC) composite displaying cerium peaks centered at 5 keV.](image)

**Figure 41.** EDX spectrum of Graphene/Pt/Ceria (GPC) composite displaying cerium peaks centered at 5 keV. The EDX data allowed for estimates of atomic concentration in the composite material. In the GPC electrode the atomic concentration of Pt and Ce was determined to be 68% and 1.4% respectively. As mentioned previously the EDX spectrum for GP showed no Ce peaks so a % concentration could not be estimated. The lack of Ce peak does not prove the absence of Ce which may still be present but encapsulated by Pt. Small portions of exposed ceria may still be present, but below the detection limits of EDX. Results from SEM and EDX indicate that Pt and ceria surface composition and morphology are strongly dependent on the substrate. It seems that the graphene substrate provides a template for the formation of highly ordered Pt clusters which
during deposition procedures immobilize ceria nanoparticles onto electrode surfaces. It is also shown that the ceria surface concentration is noticeable greater in Pt/ceria composites deposited on graphene films. The following discussion will describe the electrochemical effect of graphene/Pt/CeO$_2$ composites towards the electrooxidation of methanol and ethanol.

*Electrochemical Study of Composite Electrodes toward the Oxidation of Alcohols.* Prior to alcohol oxidation, the cleanliness and electrochemically active area (ECA) of all the modified electrodes was determined.$^{37-39}$ Immediately following deposition procedures, CVs were obtained for all electrodes in a 0.5 M H$_2$SO$_4$ solution. Figure 42 shows the overlaid CV plots of the GPC, GP and unmodified Pt electrodes in 0.5M H$_2$SO$_4$.

![Figure 42. CVs of GPC, GP, and unmodified Pt electrodes towards a 0.5M H$_2$SO$_4$ solution](Image)

The characteristic hydrogen region (-0.15V to 0.1V), double layer region (0.1V to 0.7V) and oxygen region (0.7V to 1.2V) can be seen in the anodic scan of each electrode. These features
indicate the high concentration of Pt in each composite electrode. Since the hydrogen region results from the adsorption and oxidation of hydrogen on Pt surfaces, it has been well documented to provide information about the electroactive surface area (ECA) of Pt working electrodes. The ECA was determined for each electrode by the currents observed in the hydrogen adsorption region of Pt, and was used to calculate current densities for respective electrodes in methanol and ethanol.

The electrooxidation of methanol and ethanol was monitored for each electrode using CV. Prior to CV, all alcohol solutions were bubbled with N₂ for 15 minutes in order to remove all dissolved O₂. Figure 43 shows CVs of the three fabricated electrodes as well as a clean Pt electrode towards the electrooxidation of 1 M methanol in 0.5 M H₂SO₄ support electrolyte. The ordinate is given as current density which was calculated from the current and the ECA determined from hydrogen adsorption in acidic media.
Figure 43. CVs of composite electrodes towards the electrooxidation of 1M methanol in 0.5 M H₂SO₄.

The peak current in the anodic scan of CVs has traditionally been used to determine the catalytic ability of composite electrodes for alcohol oxidation. For comparison purposes, all CV scans were performed at a scan rate of 100 mV/s. A higher relative peak current density ($j_{pa}$) at constant scan rate, indicates greater catalytic ability toward alcohol oxidation. In this study all modified electrodes show highly increased catalytic ability for methanol oxidation compared to the unmodified Pt electrode. Results clearly show the highest $j_{pa}$ is given by the GPC modified electrode indicating a synergistic activity between graphene/Pt/CeO₂ composites towards methanol oxidation. The $j_{pa}$ of the GPC electrode is nearly 40% higher than the next best performing electrode. The catalytic ability of GPC is followed by the GP and PC electrodes which display very similar $j_{pa}$. The unique morphology seen in the GP electrode is the best explanation for the increase in catalytic ability. However, the presence of Pt nanorods is thought
to decrease the overall surface area limiting the catalytic ability of this composite material. While no ceria was detected in the PC sample, the increased catalytic ability may be the result of minimally exposed ceria surface sites which are beneath the detection limits of EDX. The rough surface morphology may also provide higher catalytic than the unmodified Pt electrode. From the electrochemical studies it seems that graphene substrates provide increased catalytic ability in Pt composite electrodes. This increase is particularly apparent in samples fabricated from the simultaneous electrodeposition of Pt and ceria. A possible explanation of this enhancement is the more exposed ceria surface concentration resulting from graphene films used as deposition substrates.

The catalytic ability of each electrode was also tested for the oxidation of ethanol. Ethanol presents as a promising candidate for DAFCs due to its availability from agricultural or biomass products. It also has the possibility of being a more efficient and safer alternative to methanol. The electrooxidation of ethanol; however, presents many challenges due to the C-C bond which causes the formation of many byproducts during oxidation procedures. More advanced catalytic materials are required prior to widespread application of ethanol in fuel cells. In order to address the drawbacks limiting the oxidation of ethanol, the electrodes fabricated in this study were also tested for their catalytic ability for ethanol electrooxidation. Similar electrochemical results to those seen for methanol oxidation are displayed for the oxidation of ethanol. Figure 44 presents the overlaid CV plots of composite electrode towards the electrooxidation of ethanol in 0.5M H₂SO₄. The ordinate is presented as current density which was calculated using the ECA for each composite electrode.
The GPC electrode again provides the highest catalytic ability, with peak currents close to double that of the next best electrode. The GP and PC electrodes are very similar in catalytic oxidation of ethanol. Similar effects as discussed for methanol are believed to promote the oxidation of ethanol on composite surfaces. The combined effect of surface morphology and ceria exposure contribute to the enhanced oxidation kinetics.

Electrochemical Effect of Graphene, Pt and Ceria for Alcohol Oxidation. The electrooxidation of methanol and ethanol have shown to proceed via mechanistic routes that produce incomplete oxidation species such as carbon monoxide.\textsuperscript{40-45} CO is a particular nuisance to alcohol oxidation since it binds strongly to Pt catalysts and requires a slow, rate limiting, oxidation reaction in order to be removed. This reaction is displayed in the following:

\begin{equation}
\text{Pt-CO}_{\text{ad}} + \text{H}_2\text{O} \rightarrow \text{Pt} + \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-
\end{equation}  \hspace{1cm} (5.1)
By the incorporation of graphene supported Pt nanoparticles, we believe the oxidation kinetics are improved by morphological and surface area effects which act to limit CO adsorption. The addition of ceria into Pt lattices is also believed to decreases CO adsorption due to the following mechanism:

\[
\text{CeO}_2 + \text{H}_2\text{O} \rightarrow \text{CeO}_2—\text{OH}_{\text{ads}} + \text{H}^+ + e^- \quad (5.2)
\]

\[
\text{Pt—CO}_{\text{ads}} + \text{CeO}_2—\text{OH}_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}^+ + e^- + \text{Pt} + \text{CeO}_2 \quad (5.3)
\]

Catalytic enhancement of PC electrodes is believed to be caused by ceria surface sites in much lower concentrations. GP electrodes display very porous morphology which is thought to limit CO adsorption. For both methanol and ethanol the GPC electrode displays the highest catalytic ability which is thought to be the result of both highly porous surfaces and more exposed ceria nanoparticles on composite surfaces. It appears that graphene substrates act to promote the growth of porous Pt networks during electrodeposition procedures which, when ceria is added, allow for more ceria surface sites to catalyze the removal of adsorbed CO.

**Conclusion**

Results from this study indicate that electrodes fabricated from the electrodeposition of graphene, Pt, and ceria, demonstrate high catalytic ability for the oxidation of methanol and ethanol. The data suggests that Pt nanoparticle morphology is strongly dependent on the graphene film used as a substrate. When ceria is incorporated into deposition suspensions it also acts to control the morphology of Pt networks. The catalytic ability of electrodes modified with graphene, Pt and ceria show 40% greater peak currents for methanol oxidation and 50% greater peak currents for ethanol oxidation compared to the next best electrode. It is believed that higher catalytic ability of these electrodes is based on both surface morphology of deposited Pt and
increased ceria surface sites which promote the removal of adsorbed CO. Further studies are being performed to determine the exact relationship between graphene/Pt/ceria nanoparticle formation during electrodeposition procedures, and the effect on alcohol oxidation.

References


CHAPTER 6. MWCNT/PLATINUM/RUTHENIUM/CERIA COMPOSITE ELECTRODES FOR THE OXIDATION OF ALCOHOLS

Introduction

Multiwalled carbon nanotubes (MWCNTs) have shown much promise as metal catalyst supports for electrodes in DAFCs.\textsuperscript{1-5} The size, size distribution, stability and morphology of metal nanoparticles are greatly affected by MWCNT/composite preparation method.\textsuperscript{6-10} The conventional impregnation method for metal loading involves the reduction of metal ions on the MWCNT surface in solution based techniques. Surface modification of MWCNTs has been used to greatly improve metal loading. Since the MWCNT surface is inherently inert, it is difficult to attach metal nanoparticles to the surface. Typical processes to induce nucleation sites on MWCNTs involve refluxing MWCNT in nitric acid.\textsuperscript{11-14} This process creates acidic sites on the MWCNT surface which promote the growth of metal nanoparticles.\textsuperscript{15, 16} Long reflux times and difficulties with using strong acids are major drawbacks to processing large quantities of modified MWCNTs. In this study, polystyrene sulfonic acid (PSS) was used as a dispersing agent for MWCNTs in aqueous metal nanoparticle synthesis. Along with creating uniform dispersions of MWCNTs, the sulfonate functional groups of PSS provide nucleation sites for the growth of ceria, Pt and Ru nanoparticles which removes the need to reflux in strong acid. The following discussion focuses on the synthesis of MWCNT/CeO\textsubscript{2}/Pt/Ru composite catalysts with different Pt/Ru metal loading. Also described is the electrochemical activity of these composites for the oxidation of methanol and ethanol.
Results and Discussion

Characterization of MWCNT Composite Material. Composites of various Pt/Ru concentrations were synthesized by adding metal ions to synthesis solutions in the following Pt:Ru ratios: 3:1, 2:1 and 1:1. Concentrations of cerium nitrate as well as the combined concentration of Pt and Ru were held constant throughout the synthesis procedure in order to provide comparable nanoparticle loading in the MWCNT composites. Electrodes were fabricated by combining the as synthesized MWCNT/CeO$_2$/Pt/Ru composites with aqueous Nafion® suspensions and spray coating the dispersions on glassy carbon working electrodes.

The composite material was investigated using X-ray photoelectron spectroscopy (Physical Electronics 5400 ESCA XPS) to identify the composition of composite material. Results show that after thorough washing of the sprayed electrode to remove residual ions, the major components remained. The wide survey XPS spectrum of MWCNT/Ceria Pt:Ru 3:1 composite is shown in figure 45, which displays pronounced Pt 4f7, Ce 4d + 3d5 and O 1s peaks in addition to the overlapped C 1s and Ru 3d region. Comparable results are seen in similar studies.$^{11-13, 17}$
The C 1s signal originates from the MWCNT background. The N 1s peak provides the possibility that unreacted CeNO$_3$ was present in the composite. The S 2p3 peak is characteristic of the SO$_3^-$ functional groups in PSS. It appears that Pt, Ru and ceria ions were successfully deposited onto the MWCNT/PSS surface through subsequent reduction and oxidation reactions.

In order to characterize the surface structure of metal nanoparticles grown on MWCNTs, TEM was performed. Figure 46 shows a typical TEM micrograph (JEOL TEM-1011) of MWCNT/CeO$_2$/Pt/Ru composite catalysts prepared in aqueous solutions.
Figure 46. Typical TEM image of metal nanoparticles supported on MWCNTs.

The TEM study shows that all MWCNT were coated similarly with metal nanoparticles indicating good uniformity within samples. The results obtained in this study show similarities to other studies where metal nanoparticles were grown on the surface of MWCNTs.\textsuperscript{6, 8, 9, 12} Figure 47 shows images of the MWCNTs coated with ceria (A,D), Pt/Ru (B,E) and Pt/Ru/CeO\textsubscript{2} (Pt:Ru 3:1 ratio) (C,F).
Figure 47. TEM images showing composites of (A,D) MWCNT/Ceria, (B,E) MWCNT/Pt/Ru, and (C,F) MWCNT/Ceria/Pt/Ru

Ceria nanoparticles can easily be seen on the surface of figure 47D. Size and shape of the nanoparticles varies. On average it seems that ceria nanoparticles have dimensions between 5-10 nm. Pt/Ru nanoparticles can be seen with much more uniform spherical dimensions in figure 47E. The size of these particles is between 4-5 nm and they are equally dispersed across the surface of the MWCNT. Pt/Ru and ceria nanoparticles are shown in figure 47F. The irregularly shaped ceria particles can be seen alongside the smaller, more uniform Pt/Ru particles. The image displays the possibility that Pt/Ru nanoparticles grow on the surface of ceria nanoparticles during the subsequent oxidation and reduction reactions.

To gain a better understanding of nanoparticles grown on MWCNTs, High resolution TEM (HRTEM) was performed in tandem with EDX. HRTEM and EDX experiments were
performed using a FEI Tecnai F30 TEM equipped with an energy dispersive x-ray detector.

Figure 48 shows the HRTEM of Pt/Ru/CeO$_2$ (Pt:Ru 3:1 ratio) composite on a MWCNT.

![HRTEM image of Pt/Ru/CeO$_2$ composite on MWCNT](image)

**Figure 48.** HRTEM image of MWCNT/Pt/Ru/ceria (Pt:Ru 3:1 ratio) composite showing metal nanoparticles supported on a MWCNT. Outside and inside diameter of the MWCNT are indicated.

The inside diameter of MWCNTs appears to be ~5nm and the outside diameter is close to 20nm. The layers of the MWCNT can also be distinguished and show to be ~0.3 nm apart. As can be seen, metal nanoparticles have dimensions of 4-5 nm. The distance between nanoparticles varies, but stays within 1-5 nm. The proximity of metal/metal oxide nanoparticles to one another has shown to impact the mechanism of alcohol oxidation. Smaller distances are preferred in order to allow the reaction of adsorbed (-OH) species on ceria and Ru with the CO adsorbed on Pt sites.

EDX was performed in tandem with HRTEM in order to determine the composition of the as-synthesized nanoparticles.

Figure 49 shows the dark field image of Pt/Ru/ceria nanoparticles grown on MWCNTs along with the EDX spectrum. The dark field TEM image shows the metal/metal oxide
nanoparticles well dispersed along the surface of the MWCNT. EDX results confirm the identity of Pt, Ru and ceria nanoparticles with clearly defined peaks for each. The C peak is the result of the MWCNT surface and the Cu peak is from the TEM grid used to mount the composite sample.

Figure 49. (A) Dark field TEM image of MWCNT/Ceria Pt:Ru 3:1 composite showing region scanned for EDX and (B) EDX spectrum of MWCNT composite.

Concentrations of Pt, Ru and ceria were estimated from EDX data. It was determined that the Pt and Ru content of the Pt:Ru 3:1 composite material was 6.4% and 1.1% respectively (Pt:Ru 5.8:1). In addition the Pt:Ru 2:1 composite was found to have 5.2% and 2.6% Pt to Ru
concentration (Pt:Ru 2:1), and the atomic concentration of the Pt:Ru 1:1 electrode was found to be 4.4% and 2.9% Pt to Ru respectively (Pt:Ru 1.5:1). Results are also listed in table 6. For the 3:1 Pt:Ru ratio and the 1:1 Pt:Ru ratio there appears to be a discrepancy between ratio of metal ions in solution and metal nanoparticle concentration on MWCNT surfaces. The difference in atomic ratio between the solution and resulting composite material is most likely due to the relative attraction of Pt and Ru either to the PSS anionic functional groups, the ceria surface, or both. Because of the complexity of the adsorbing surface and the added complication of the reduction step of the Pt and Ru, further studies are necessary to provide a clear mechanistic explanation of this trend. As will be seen, this discrepancy is accounted for in the determination of the electrochemical activity. The concentrations of ceria was found to be ~2% in each sample suggesting good reproducibility in Ce(NO$_3$)$_3$ oxidation procedures.

*Electrochemical Determination of Composite Electrode Surface Area.* In order to make composite electrodes for alcohol oxidation, MWCNT composite material was combined with Nafion® in aqueous suspensions and spray coated with an airbrush onto glassy carbon electrodes. An unmodified Pt electrode was used to compare the catalytic activity of composite electrodes. Before use in the catalytic oxidation of alcohols, the morphology of CV curves in 0.5M H$_2$SO$_4$ for MWCNT/Pt composite electrodes was used to determine Pt characteristics. The CVs of two electrodes showing the electrochemical measurement results of the MWCNT/CeO$_2$/Pt composite electrode alongside that of an unmodified Pt electrode are given in figure 50.
Figure 50. Cyclic voltammetry of MWCNT/Ceria/Pt modified electrode (black) and unmodified Pt electrode (red) in a 0.5M H2SO4 electrolyte solution. The hydrogen adsorption region for each electrode can clearly be seen in the potential region of -0.15 to 0.1 V vs. an Ag/AgCl reference electrode.

The cyclic voltammetry plot is presented with the ordinate in milliamps. The CV of the composite shows the characteristic hydrogen region (-0.15 to 0.1 V) which indicates Pt in on the surface of the electrode. It can be seen that the MWCNT/CeO2/Pt electrode has a much higher peak current in the hydrogen region which indicates higher electroactive surface area (ECA) in MWCNT/Pt composite samples. The ECA is a hugely important parameter as, for a given electrode size, higher ECA allows for an increased reaction rate. The hydrogen adsorption region is well known to provide information about the active Pt surface area in composite electrodes; however, the overlap of hydrogen and Ru oxidation currents makes the potential window from -0.15 to 1.00 V difficult to interpret in samples containing both Pt and Ru.18, 19 In order to better understand the active surface area of Pt/Ru composites, a variety of electrochemical techniques are in use.20, 21 Copper underpotential deposition (Cu-UPD) is one method that has shown good
results for Pt/Ru composite surface area determination. Copper is an ideal metal for UPD on both Pt and Ru because of the similarity of the atomic radii of the three metals. In this study the ECA was determined for all Pt/Ru composite electrodes by calculating the charge transfer from Cu monolayer oxidation in CuSO₄ solution according to published procedures. Figure 51 shows the Cu stripping region in CV of the MWCNT/CeO₂/Pt composite electrode between 0 to 0.5 V in the anodic scan.

![Figure 51. Cyclic voltammetry showing the stripping of Cu monolayer deposited during underpotential deposition.](image)

The specific charge transfer (Qₜₜ) can be obtained from integrating the Cu stripping region while assuming an adsorption ratio of a single Cu atom to each surface metal atom and an electrosorption valency of +2. The average charge value associated with Cu monolayer formation is 420 μC cm⁻². Therefore the ECA is calculated from the following:

\[ ECA = \frac{Q_{H}}{420 \, \mu C \, cm^{-2}} \]
Calculations of surface area for all electrodes were carried out by integrating the current voltage curve, correcting for background current and using the conversion factor of 420 µC cm\(^{-2}\). Since ECA is directly related to Pt/Ru metal concentration on the surface of electrodes, a higher or lower ECA indicates that metal loading is higher or lower respectively. The ECA calculated for all composite electrodes is shown in table 6 alongside the EDX estimates for Pt:Ru atomic concentration. From the EDX and ECA data, the Pt surface area was calculated for Pt:Ru composite electrodes.

Table 6. Calculated ECA for all modified electrodes with estimated Pt:Ru atomic ratios from EDX

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Pt:Ru From EDX</th>
<th>ECA</th>
<th>Pt Surface Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/Ceria Pt:Ru 3:1</td>
<td>5.8:1</td>
<td>1.42 cm(^2)</td>
<td>1.21 cm(^2)</td>
</tr>
<tr>
<td>MWCNT/Ceria Pt:Ru 2:1</td>
<td>2:1</td>
<td>0.93 cm(^2)</td>
<td>0.62 cm(^2)</td>
</tr>
<tr>
<td>MWCNT/Ceria Pt:Ru 1:1</td>
<td>1.5:1</td>
<td>0.72 cm(^2)</td>
<td>0.43 cm(^2)</td>
</tr>
<tr>
<td>MWCNT/Ceria/Pt</td>
<td>-</td>
<td>2.40 cm(^2)</td>
<td>2.40 cm(^2)</td>
</tr>
<tr>
<td>MWCNT/Pt</td>
<td>-</td>
<td>0.91 cm(^2)</td>
<td>0.91 cm(^2)</td>
</tr>
<tr>
<td>Unmodified Pt</td>
<td>-</td>
<td>0.07 cm(^2)</td>
<td>0.07 cm(^2)</td>
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</table>

All composite electrodes have at least one order of magnitude greater surface area than the unmodified Pt electrode. The data indicates that ECA is dependent on Pt, Ru and ceria content. The ECAs of MWCNT/CeO\(_2\) Pt and MWCNT/Pt electrodes demonstrate that the addition of ceria acts to increase the metal surface area. This may be the result of Pt/Ru nanoparticle formation on previously deposited ceria on the MWCNT surface. The rough MWCNT/ceria surface could act as nucleation sites for the formation of Pt and Ru nanoparticles. The highest ECA is given by the MWCNT/CeO\(_2\)/Pt electrode and the ECA dramatically decreases with the
addition of Ru. While Ru is well known to increase the catalytic ability of Pt electrodes towards the oxidation of alcohols, it seems that an increase in Ru$^{3+}$ ions during synthesis causes a decrease in ECA. The ratio of Pt to Ru determined from EDX may help explain this phenomenon. Since all synthesis solutions were prepared with a total of 2mM concentration of Pt$^{4+}$ and Ru$^{3+}$ ions, increasing Ru$^{3+}$ ion count necessarily causes a decrease in Pt$^{4+}$ ion concentration. Furthermore it seems that the Ru$^{3+}$ ions have a lower affinity to the MWCNT/PSS surface, therefore increasing the Ru$^{3+}$ ion concentration would act to decrease the overall Pt/Ru nanoparticle loading on MWCNTs. The ECA would then be adversely affected by higher Ru$^{3+}$ and lower Pt$^{4+}$ ion concentrations during nanoparticle synthesis. It is therefore important to determine the Pt$^{4+}$ and Ru$^{3+}$ ionic concentrations that result in composite material with both high surface area and catalytic ability.

The Pt surface area is an important aspect of the electrode fabrication. From the ECA and the Pt:Ru ratios estimated from EDX, the Pt surface area was calculated and shown in table 6. Not surprisingly, the MWCNT/Ceria/Pt electrode maintains the highest Pt surface area followed by the MWCNT/Ceria Pt:Ru 3:1 electrode which have the highest concentration of Pt ions during synthesis. After determination of ECA, and an estimation of Pt surface area, the electrodes were used for the oxidation of alcohols. The current density of methanol and ethanol oxidation with respect to the Pt surface area (j Pt) was calculated and compared to the current density calculated from ECA (j ECA).

Response of MWCNT Composite Electrodes towards the Oxidation of Methanol. The electrocatalytic activity of the MWCNT composite electrodes for the oxidation of methanol was characterized by CV in 1M methanol solutions with 0.5M $\text{H}_2\text{SO}_4$ as support electrolyte. Prior to
CV, all methanol solutions were bubbled with N\textsubscript{2} for 15 minutes to remove all O\textsubscript{2} dissolved in solution. Overlaid CV scans for methanol are presented in figure 52.

![Cyclic voltammetry of the MWCNT composite electrodes towards the oxidation of 1M methanol in 0.5 M H\textsubscript{2}SO\textsubscript{4}. The MWCNT/Ceria Pt:Ru 3:1 electrode shows the highest catalytic ability towards methanol oxidation.](image)

The potential was swept between -0.15 and 1.2 V vs. an Ag/AgCl reference electrode. The peak current in the anodic scan (i\textsubscript{pa}) of CVs is a typical metric for catalytic ability because it is a direct measure of the amount of alcohol oxidized. The electrode with the highest i\textsubscript{pa} is generally accepted as the electrode with the best overall catalytic performance. High i\textsubscript{pa} in composite electrodes can result from high surface area, synergistic catalytic effects or a combination of the two. As expected, the i\textsubscript{pa} of composite electrodes was higher than that for the unmodified Pt electrode indicating that MWCNT/Pt composites have significantly greater catalytic ability than unmodified Pt for the oxidation of methanol. This increased surface area imparted by the
nanodimensioned Pt combined with that of the support MWCNTs may account for the increased $i_{pa}$; however, the possibility of synergistic catalytic effects still remains. Next we attempt to deconvolute the effects of surface area from that of possible synergistic effects.

**Synergistic Effects of Ceria and Ru for Oxidation of Methanol.** Because the inclusion of co-catalyst species drastically changed the ECA of each electrode depending on the composition, some metric must be applied that can separate the effects of surface area and the activity of the composite surfaces. In order to deconvolute the combined contribution of surface area and co-catalyst species, calculations were performed to normalize the $i_{pa}$ to eliminate the contribution of surface area. In addition to providing information about Pt/Ru nanoparticle loading on MWCNTs, the calculated ECA was used to determine the current density ($j_{ECA}$) for the oxidation of methanol and ethanol for all composite electrodes. Although ECA estimates show that Pt:Ru composites with higher Ru concentration have lower surface areas, figure 52 shows that the composite with a Pt:Ru 3:1 ratio has the highest $i_{pa}$ for the oxidation of methanol. This indicates that the catalytic enhancement provided by Ru in a 3:1 Pt:Ru ratio is greater than the adverse effect of lowering the overall Pt/Ru loading in the sample suggesting a synergistic catalytic effect between Pt, Ru and ceria for methanol oxidation. The MWCNT/CeO$_2$/Pt electrode displays the next highest catalytic ability which is most likely the result of the high surface area. From Pt:Ru 3:1 to 1:1 the catalytic ability decreases as the Ru concentration increases. This supports the argument that there is an optimal concentration of metal ions during synthesis which results in composite material with higher catalytic ability for methanol oxidation. As expected the MWCNT/Pt electrode provides the lowest catalytic ability due to the absence of ceria.
In order to better understand the effect of surface area on the catalytic ability, the current density (j ECA) was determined for each electrode by dividing the current by the calculated ECA. Peak current density in the anodic scan (j_{pa} ECA) is a good indication of relative catalytic ability while excluding surface area effects. Figure 53 shows the overlaid plots of composite electrodes towards the electrooxidation of methanol. The ordinate is presented in current density (mA/cm²).

![Image of cyclic voltammetry](image.png)

Figure 53. Cyclic voltammetry of MWCNT composite electrodes towards the oxidation of 1M methanol in 0.5M H2SO4 with correction for surface area using Cu-UPD. The MWCNT/Ceria Pt:Ru 3:1 maintains the highest catalytic ability while the MWCNT/Ceria/Pt displays the greatest drop in peak current due to its high surface area.

The j_{pa} ECA is relatively lower than i_{pa} for the MWCNT/CeO₂/Pt electrode compared to the other electrodes. This indicates that the primary mode for the high current generated when oxidizing methanol was due to higher surface area effects. The MWCNT/CeO₂ Pt:Ru 3:1 has both the highest i_{pa} and j_{pa} ECA supporting previous studies which demonstrate the catalytic
advantage of Ru in Pt composites is provided by both high surface area and synergistic effects. The MWCNT/CeO\textsubscript{2} Pt:Ru 2:1 electrode shows a higher \( j_{pa} \) ECA than the MWCNT/CeO\textsubscript{2}/Pt electrode confirming that Ru acts as an important catalyst for methanol oxidation. Since Pt is the primary catalytic material for methanol oxidation, lowering Pt surface concentration by increasing secondary Ru catalyst concentration would eventually lead to a ratio of Pt:Ru that shows lower overall catalytic ability. The MWCNT/Ceria Pt:Ru 1:1 electrode displays a lower \( j_{pa} \) ECA than the MWCNT/CeO\textsubscript{2}/Pt electrode. This indicates that at certain concentrations the Ru acts to decrease the methanol oxidation ability of Pt/Ru composite catalysts. The peak current density calculated from the estimated Pt surface area (\( j_{pa} \) Pt) can help show the presence of secondary and tertiary catalytic effects. A study of the \( j_{pa} \) Pt gives clear indication of the catalytic ability of working electrodes based on Pt concentration. In this study it allows for the determination of the catalytic effects of Ru on Pt composite electrodes. When the current density is calculated from the Pt surface area, all Ru containing electrodes display greater catalytic ability towards methanol oxidation. This indicates that the presence of Ru nanoparticles has a strong effect on methanol oxidation. Table 7 summarizes the results for \( i_{pa} \), \( j_{pa} \) ECA and \( j_{pa} \) Pt for methanol oxidation.
Table 7. The peak current and current density towards methanol oxidation

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$i_{pa}$ (Methanol)</th>
<th>$j_{pa}$ ECA (Methanol)</th>
<th>$j_{pa}$ Pt (Methanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/Ceria Pt:Ru 3:1</td>
<td>9.5 mA</td>
<td>6.7 mA/cm$^2$</td>
<td>7.9 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Ceria Pt:Ru 2:1</td>
<td>2.9 mA</td>
<td>3.1 mA/cm$^2$</td>
<td>4.6 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Ceria Pt:Ru 1:1</td>
<td>1.6 mA</td>
<td>2.2 mA/cm$^2$</td>
<td>3.7 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Ceria/Pt</td>
<td>6.2 mA</td>
<td>2.6 mA/cm$^2$</td>
<td>2.6 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Pt</td>
<td>1.2 mA</td>
<td>1.3 mA/cm$^2$</td>
<td>1.3 mA/cm$^2$</td>
</tr>
<tr>
<td>Unmodified Pt</td>
<td>0.03 mA</td>
<td>0.4 mA/cm$^2$</td>
<td>0.4 mA/cm$^2$</td>
</tr>
</tbody>
</table>

It is also notable to discuss the peak current in the cathodic scan ($i_{pc}$). This large peak in the reverse scan is most often attributed to the stripping of CO and other carbonaceous species from the surface of electrodes during methanol oxidation. Such species form during the incomplete oxidation of methanol and the ratio of $i_{pa}/i_{pc}$ can indicate a preferential increase in catalytic ability vs. formation unreacted byproducts. A lower $i_{pc}$ may also indicate a preferential increase in the direct oxidation mechanism of methanol. The MWCNT composite with the highest $i_{pa}/i_{pc}$ ratio is the MWCNT/Ceria Pt:Ru 1:1 (that ratio being 4.4). This indicates that, as suspected, the Ru and ceria content acts to limit the formation of CO and other byproducts of the incomplete oxidation of methanol. It is believed that the proximity of Ru and ceria nanoparticles to Pt nanoparticles supported on MWCNTs as indicated by TEM allows for the reaction of CO adsorbed species on Pt with OH adsorbed species on Ru and ceria.

Response of MWCNT Composite Electrodes towards the Oxidation of Ethanol. In addition to methanol, the modified electrodes were also tested for electrochemical oxidation of ethanol. Ethanol’s use as a fuel has been hailed promising, but its application in DAFCs has been
limited due to the need to break the carbon-carbon (C-C) bond.\textsuperscript{23-26} Many composite catalysts have been proposed for ethanol oxidation in order to promote the direct oxidation mechanism (12e\textsuperscript{−}), or increase the amount of acetic acid (4e\textsuperscript{−}) produced in the incomplete mechanism compared to acetaldehyde or ethane-1,1-diol (2e\textsuperscript{−}). Similar to the methanol procedure, electrodes were exposed to 1M ethanol solutions in 0.5M H\textsubscript{2}SO\textsubscript{4} electrolyte and characterized using CV. Prior to CV, all ethanol solutions were bubbled with N\textsubscript{2} for 15 minutes to remove all O\textsubscript{2} dissolved in solution. Results for ethanol oxidation were very similar to methanol oxidation and the overlaid CVs can be seen in figure 54.

![Figure 54. Cyclic voltammetry of the MWCNT composite electrodes towards the oxidation of 1M ethanol in 0.5M H2SO4. Similar to methanol, the MWCNT/Ceria Pt:Ru 3:1 electrode shows the highest catalytic ability towards ethanol oxidation. All modified electrodes show a higher catalytic ability for ethanol oxidation compared to the unmodified Pt electrode. As can be seen, the MWCNT/CeO\textsubscript{2} Pt:Ru 3:1 electrode displays the](image-url)
highest $i_{pa}$ for ethanol oxidation followed closely by both the MWCNT/Ceria Pt:Ru 2:1 and MWCNT/CeO$_2$/Pt electrode. The lowest catalytic ability for ethanol oxidation is given by the MWCNT/Pt electrode due to the lack of ceria and Ru catalysts. The trends seen for ethanol oxidation are similar to those for methanol oxidation indicating similar catalytic enhancement most likely from CO removal on Pt sites. The results of the CVs are summarized in table 8 next to the corresponding electrodes and their respective surface areas. Table 8 clearly shows that higher ECA yields higher $i_{pa}$, but the effect of ceria and Ru in some notable variations of this trend. For example, the MWCNT/CeO$_2$ Pt:Ru 2:1 and the MWCNT/PT electrodes have very similar ECAs, but the $i_{pa}$ of the former is more than twice that of the later. This must be due to the aforementioned synergistic effects of the ceria and Ru in the catalytic oxidation of alcohols. 

*Synergistic Effects of Ceria and Ru for the Oxidation of Ethanol.* In order to assess the catalytic ability of the electrodes toward ethanol oxidation in the absence of surface area effects, the current density was calculated from the ECA of each electrode. Overlaid CV plots showing current density vs. E are given in figure 55.
Figure 55. Cyclic voltammetry of MWCNT composite electrodes towards the oxidation of 1M ethanol in 0.5M H2SO4 with correction for surface area using Cu-UPD. Similar to methanol, the MWCNT/Ceria Pt:Ru 3:1 maintains the highest catalytic ability while the MWCNT/Ceria/Pt displays the greatest drop in peak current due to its high surface area.

Similar to methanol, all the ceria containing electrodes promoted higher oxidation kinetics than electrodes without ceria. It can also clearly be seen in figure 55 that once the surface effects are normalized, all composite electrodes with Ru show significantly greater catalytic ability than those without Ru. This may indicate that Ru has a greater impact on ethanol oxidation than methanol oxidation. The \(i_{pa}\), \(j_{pa}\) ECA and \(j_{pa}\) Pt for ethanol oxidation are provided in table 8.
The complex nature of ethanol oxidation leads to a variety of unreacted byproducts which lower the overall current expected during electrooxidation reactions. Ru may, in addition to CO removal, promote the direct oxidation mechanism of ethanol leading to higher currents and less formation of unreacted carbacious species. It is also possible that Ru promotes the formation of AA yielding $4e^-$ per every ethanol as compared to $2e^-$ during the formation of ED or AAL.

Further studies are needed to determine the exact role of Ru in the catalytic oxidation of ethanol.

**Proposed Explanation of Catalytic Enhancement.** The mechanism of Ru and ceria for alcohol oxidation in Pt composites is not well understood. As mentioned previously the primary mode of catalytic enhancement is thought to precede from the reaction of $-\text{OH}_{\text{ads}}$ species on ceria and Ru sites with $-\text{CO}_{\text{ads}}$ species on Pt sites. A possible reaction for CO removal in Pt/Ru composites is displayed below:

$$\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru} - \text{OH}_{\text{ads}} + \text{H}^+ + e^- \quad (6.1)$$

$$\text{Pt} - \text{CO}_{\text{ads}} + \text{Ru} - \text{OH}_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}^+ + e^- + \text{Pt} + \text{Ru} \quad (6.2)$$

### Table 8. The peak current and current density toward ethanol oxidation

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$i_{pa}$ (Ethanol)</th>
<th>$j_{pa}$ (Ethanol)</th>
<th>$j_{pa}$ Pt (Ethanol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/Ceria Pt:Ru 3:1</td>
<td>15 mA</td>
<td>11 mA/cm$^2$</td>
<td>12.4 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Ceria Pt:Ru 2:1</td>
<td>7.9 mA</td>
<td>8.4 mA/cm$^2$</td>
<td>12.7 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Ceria Pt:Ru 1:1</td>
<td>5.2 mA</td>
<td>7.2 mA/cm$^2$</td>
<td>12.0 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Ceria/Pt</td>
<td>9.1 mA</td>
<td>3.8 mA/cm$^2$</td>
<td>3.8 mA/cm$^2$</td>
</tr>
<tr>
<td>MWCNT/Pt</td>
<td>1.8 mA</td>
<td>1.9 mA/cm$^2$</td>
<td>1.9 mA/cm$^2$</td>
</tr>
<tr>
<td>Unmodified Pt</td>
<td>0.09 mA</td>
<td>1.2 mA/cm$^2$</td>
<td>1.2 mA/cm$^2$</td>
</tr>
</tbody>
</table>
Ceria is thought to limit CO adsorption through a similar mechanism in Pt/ceria composites as shown in the following reactions:

\[
\text{CeO}_2 + \text{H}_2\text{O} \rightarrow \text{CeO}_2-\text{OH}_{\text{ads}} + \text{H}^+ + e^- \quad (6.3)
\]

\[
\text{Pt}--\text{CO}_{\text{ads}} + \text{CeO}_2-\text{OH}_{\text{ads}} \rightarrow \text{CO}_2 + \text{H}^+ + e^- + \text{Pt} + \text{CeO}_2 \quad (6.4)
\]

The synergistic catalytic enhancement of Ru and ceria in Pt/Ru/Ceria composites towards methanol oxidation can be expressed in the following:

\[
2\text{Pt}--\text{CO}_{\text{ads}} + \text{CeO}_2-\text{OH}_{\text{ads}} + \text{Ru}--\text{OH}_{\text{ads}} \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2\text{Pt} + \text{CeO}_2 + \text{Ru} + 2e^- \quad (6.5)
\]

More studies are needed to determine the exact mechanism of methanol and ethanol oxidation and determine the optimal concentration of Pt, Ru and ceria loading on catalytic surfaces. Subsequent studies will seek to address these issues.

**Conclusion**

We have demonstrated a completely aqueous process for synthesizing novel PSS/MWCNT supported Pt/Ru/CeO\(_2\) nanoparticles. These composites were characterized and used to fabricate composite electrodes for direct alcohol fuel cells. The electrochemical oxidation of methanol and ethanol was studied on all composite electrodes using cyclic voltammetry and compared to unmodified Pt electrodes. It is seen that the MWCNT/CeO\(_2\) Pt:Ru 3:1 electrode shows the highest catalytic ability towards the oxidation of methanol and ethanol. When surface area effects were eliminated, electrodes made with Pt:Ru ratios of 3:1 and 2:1 showed higher catalytic ability than electrodes without Ru. Every electrode modified with ceria shows greater catalytic activity than electrodes without ceria. Overall it was determined that there exists an optimal concentration of Pt, Ru and ceria that provides the greatest catalytic ability for the oxidation of methanol and ethanol. Furthermore, it is believed that the synthetic approaches in
this study can be applied to the fabrication of composite electrodes with various transition metal/metal oxide composition including Pt/Au/CeO\textsubscript{2}, Pt/Pd/CeO\textsubscript{2} and others. These results are promising for the development of novel direct alcohol fuel cells and warrant further research in order to identify and quantify the actual products from the oxidation of methanol and ethanol and correlate the electrochemical behavior with theoretical predictions.

References


CHAPTER 7. PLATINUM/PALLADIUM/CERIA AND PLATINUM/GOLD/CERIA COMPOSITE ELECTRODES FOR THE OXIDATION OF FORMIC ACID

Introduction

In addition to alcohols, formic acid has also shown promise for application in PEMFCs. Since electro-oxidation of small organic molecules is very sensitive to the properties of the electrode surface, reactions are influenced by the properties of the electrode material. Catalyst metals can thus be used to decrease poisoning effects and increase electrooxidation of fuels. Formic acid oxidation has been studied, for example, on polycrystalline and single crystal Pt, rhodium, palladium, and gold. Gold in particular presents as an intriguing catalyst. When present in macroscale particulate it shows little to no catalytic activity, but it exhibits enhanced catalytic activity in nanoscale. Due to this interesting behavior, recent efforts have been devoted to using Pt-Au intermetallics as alloy or nanoscale-clusters for the catalytic oxidation of formic acid. In addition to metal catalysts, many rare earth oxides have been used to modify electrode surfaces. CeO$_2$ has shown a great ability to store and release oxygen (oxygen carrying capacity) with little distortion of the lattice, as the cerium atom reversibly undergoes oxidation/reduction processes from Ce$^{4+}$ to Ce$^{3+}$. Considering the electrocatalytic effects of Pt-Au alloys and nanoceria, our group has explored the fabrication of Pt/Au/ceria composite electrodes through simultaneous electrodeposition of Pt and Au. In this study we measured electrocatalytic oxidation activity of formic acid on a various composited Pt/Au/ceria catalysts containing different concentrations of Pt and Au. While Pt composite electrodes have shown the
best kinetics for alcohol oxidation, Pd composites have shown to provide the highest catalytic ability towards the oxidation of formic acid.\textsuperscript{1,5} Ceria has also been used in DFAFC anodes and has given promising results. In this study we compare the formic acid oxidation ability of Pt/Au and Pt/Pd composites. We also show the impact of nanoceria on the catalytic oxidation ability of both Pt/Au and Pt/Pd bimetallic electrodes.

Results and Discussion

*Preparation of Pt Composite Electrodes.* The composite electrodes were prepared from a binary solution of Pt\textsuperscript{4+} and Au\textsuperscript{3+} or Pt\textsuperscript{4+} and Pd\textsuperscript{2+} in the presence of ceria. The total concentration of metal ions in the bimetallic solution was kept constant while the ratio of Pt to Au and Pt to Pd was fluctuated from 3:0 to 0:3. The concentration of ceria was maintained at 5 mM for every electrode. Electrodeposition was performed by insertion of the electrode into the solution and keeping the potential constant at -0.200 V (v.s. Ag/AgCl reference) for 600 s with constant stirring following published procedures.\textsuperscript{19-21}

Cyclic voltammograms of the Pt/Au modified electrodes in 0.5M sulfuric acid show characteristic features of both the Pt and Au electrodes. In Figure 56a the CV of the Pt:Au 1:1 modified electrode is shown alongside the CVs of clean Pt and Au electrodes.
The CV of the modified electrode contains features similar to both the Pt and Au electrodes suggesting the presence of both Pt and Au crystals at the surface of the electrode.\textsuperscript{22-24} In Figure 56b the CVs of the Pt and Pd modified electrodes are shown alongside the CV of a clean Pt electrode. The CV of the modified electrodes show a current that is several orders of magnitude greater than that of a clean Pt electrode, mostly due to an increase in the surface area of the electrode that arises from the electrodeposition of either metal. The CV of the Pt:Pd 1:1 modified electrode is also shown and displays similar features to the Pt and Pd modified electrodes. As shown in Figure 56a and b, CVs of the Pt/Au and Pt/Pd modified electrodes in 0.5M sulfuric acid both show a significant increase in current when compared to a clean Pt electrode.

CV’s shown in Figure 56 a and b report values for the peak current observed for each electrode in sulfuric acid electrolyte. This current response is in the absence of additional electrochemically active species and normally utilized to ascertain both the cleanliness of the electrode surface and the electrochemically active surface area (ECA).\textsuperscript{25-27} The determination of
the surface area of the electrode is carried out by normalizing the current over the hydrogen adsorption region. This allows for obtaining the current density, which is independent of surface area. Pt and Pd behave similarly toward the adsorption of hydrogen and results from other studies have shown that the hydrogen adsorption region is also a viable method for determining the eca of Pt/Au and Pt/Pd composite electrodes.\textsuperscript{19, 28, 29} The ECA was therefore determined for all Pt/Au and Pt/Pd composite electrodes through integration of the hydrogen adsorption region. Normalization of the composite electrodes was performed by comparing the various modified electrodes to electrooxidation of formic acid.

EDX was performed on each sample using the SEM microscope in order to determine atomic ratios of Pt, Au and Pd on the composite electrodes. Table 9 shows the EDX atomic compositions for the Pt:Au composite electrodes.

<table>
<thead>
<tr>
<th>Ratio of Pt:Au in Suspension</th>
<th>EDX % Pt atom</th>
<th>EDX % Au atom</th>
<th>EDX ratio Pt: Au</th>
<th>Predict % Au</th>
<th>Calculate % Au</th>
</tr>
</thead>
<tbody>
<tr>
<td>0:2</td>
<td>5.31</td>
<td>62.76</td>
<td>1:11.8</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>1:3</td>
<td>34.37</td>
<td>48.65</td>
<td>1:1.41</td>
<td>75</td>
<td>59</td>
</tr>
<tr>
<td>1:2</td>
<td>36.52</td>
<td>40.91</td>
<td>1:1.12</td>
<td>67</td>
<td>53</td>
</tr>
<tr>
<td>1:1</td>
<td>34.15</td>
<td>33.42</td>
<td>1:0.98</td>
<td>50</td>
<td>49</td>
</tr>
<tr>
<td>2:1</td>
<td>39.54</td>
<td>18.59</td>
<td>2.13:1</td>
<td>33</td>
<td>32</td>
</tr>
<tr>
<td>3:1</td>
<td>23.28</td>
<td>11.45</td>
<td>2:1</td>
<td>25</td>
<td>33</td>
</tr>
<tr>
<td>2:0</td>
<td>60.79</td>
<td>0</td>
<td>1:0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The values obtained by the EDX are in close agreement with molar ratios of Pt and Au in the deposition suspension. The difference in the ratios is most likely due to the fact that all samples were grown on Pt substrates. We determined that the ratio of concentration of Pt and Au in the
deposition solution is proportional to the concentration of the metals on the surface of the electrode. Results shown in Table 10 include EDX data from the Pt:Pd composite electrodes.

**Table 10. EDX Estimates of Pt and Pd Atomic Concentrations in Pt:Pd Composite Electrodes**

<table>
<thead>
<tr>
<th>Ratio of Pt:Pd in Suspension</th>
<th>EDX % Pt atom</th>
<th>EDX % Pd atom</th>
<th>EDX ratio Pt:Pd</th>
<th>Predict % Pd</th>
<th>Calculate % Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:0</td>
<td>0.97</td>
<td>45.75</td>
<td>1:47.2</td>
<td>100</td>
<td>98</td>
</tr>
<tr>
<td>1:3</td>
<td>11.00</td>
<td>24.88</td>
<td>1:2.26</td>
<td>75</td>
<td>69</td>
</tr>
<tr>
<td>1:2</td>
<td>24.33</td>
<td>43.45</td>
<td>1:1.79</td>
<td>67</td>
<td>64</td>
</tr>
<tr>
<td>1:1</td>
<td>30.20</td>
<td>32.25</td>
<td>1:1.07</td>
<td>50</td>
<td>53</td>
</tr>
<tr>
<td>2:1</td>
<td>39.35</td>
<td>25.32</td>
<td>1.55:1</td>
<td>33</td>
<td>39</td>
</tr>
<tr>
<td>3:1</td>
<td>27.11</td>
<td>10.23</td>
<td>2.65:1</td>
<td>25</td>
<td>27</td>
</tr>
<tr>
<td>2:0</td>
<td>60.79</td>
<td>0</td>
<td>1:0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The ratios of Pt:Pd calculated from EDX measurements are very similar to the ratios predicted from the concentration of Pt and Pd in the deposition suspension.

In order to better understand how the composition of the deposition suspension relates to the actual atomic composition of the modified electrodes, deposition rates were determined for the three metal ions of interest in this study. The deposition of Pt, Au, and Pd was tested on the QCM in order to measure the deposition rates on the quartz crystal. After depositing the metal ion for a total of 600 s, the same amount of time used for the preparation of electrodes, a total mass load of 8.0, 7.0, and 7.5 μg was obtained for Pt, Au, and Pd, giving deposition rates of 13.3, 11.7, and 12.5 ng/s, respectively. These values can be considered similar within the errors of the technique, especially when factors such as changes in viscoelasticity, solvation, and porosity of the deposited films are not well-known. Since the QCM data supports the EDX estimates for...
modified electrode atomic composition, we believe that the ratio of metal ions in deposition suspensions (for both Pt/Au and Pt/Pd) lead to electrodes with comparable atomic composition.

*Electrooxidation of Formic Acid on Pt/Au/Ceria Composite Electrodes.* Cyclic voltammograms (CVs) were obtained with 0.75M formic acid solutions in 0.5 M H₂SO₄ for all modified electrodes. It can be seen in Figure 57 that the electrode modified with Au and ceria (no Pt) showed no noticeable activity toward the formic acid oxidation.

![Cyclic voltammery of the modified electrodes in 0.75 M formic acid: (a) Pt/ceria, (b) Pt:Au/ceria 1:1, and (c) Au/ceria. Scans from the Au/ceria electrode show little to no catalytic ability for the electrooxidation of formic acid. The Pt/Au/ceria electrode shows increased catalytic ability compared to Pt/ceria electrodes. (scan rate = 100 mV/s).](image)

The electrode modified with Pt and ceria showed greater catalytic activity; however, the Pt/Au/ceria composite electrode shows the highest peak current suggesting that a synergistic effect is occurring between Pt and Au as a catalyst for electrooxidation of formic acid. The enhancement may be the result of Au providing cites along the surface of the electrode which do not allow strong interaction between CO and Pt. If the Pt-CO interaction is weakened CO is
more easily removed from the electrode surface freeing more cites for formic acid oxidation. In addition to the bimetallic enhancement, it can be seen in Figure 58 that ceria also improves the catalytic ability of the electrodes in agreement with previous studies.\textsuperscript{12, 16, 21, 30}

![Figure 58](image)

Figure 58. a) Pt/Au (1:1) composite electrode and (b) Pt/Au (1:1) electrode with ceria. As expected, electrodes modified with ceria show much higher catalytic ability.

Figure 58 shows two Pt: Au 1:1 electrodes; one having been modified with ceria and the other containing no ceria. As indicated the electrode modified with ceria has a higher current and therefore a greater catalytic ability toward the oxidation of formic acid. This catalytic effect can be explained by the formation of OH\textsubscript{ads} species on the surface of CeO\textsubscript{2}. It is hypothesized that these adsorbed species transform CO-species on the surface of the Pt/Au electrode to CO\textsubscript{2} releasing the Pt/Au sites for further electrochemical oxidation (see equations 5.2-5.3).
Figure 59 shows the electrochemical response of the modified Pt electrode toward oxidation of formic acid. All of the Pt/Au/ceria-modified electrodes showed a catalytic enhancement over the non-ceria Pt electrode for the oxidation of formic acid.
Figure 59. (a) Cyclic voltammetry of the Pt/Au/ceria-modified electrodes toward 0.75 M formic acid in 0.5 M H₂SO₄ for the different Pt:Au ratios of 1:3, 1:2, 1:1, 3:1, 2:1, and 2:0. A noticeable increase in the oxidation current is observed for electrodes prepared from a deposition batch containing a 3:1 molar ratio of Pt:Au. Other ratios showed very similar catalytic enhancements. (b) Cyclic voltammograms of the Pt/Au/ceria-modified electrodes with 1:3, 1:2, 1:1, 3:1, 2:1, and 2:0 toward 0.75M formic acid in 0.5 M H2SO4 corrected for Pt-surface area using the hydrogen adsorption region. The electrode with a 2:1 Pt:Au ratio shows the highest current density for the electrooxidation of formic acid.
The electrode modified from a bath solution with molar ratios of 3:1 Pt:Au showed the highest peak current before normalization for surface area. Overall, the electrochemical oxidation of formic acid appears to show a dependence on the Au contents in the composite electrode. All Pt/Au/ceria containing electrodes showed enhanced catalytic activity over the electrode modified with Pt/ceria only, suggesting the possibility of a synergistic catalytic effect between Pt and Au. The performance of the electrodes can be ranked in increasing order of Pt:Au ratio as 0:2, 2:0, 1:2, 1:3, 1:1, 2:1 and 3:1. In general it seems that increasing the Pt concentration provides higher catalytic ability toward formic acid oxidation. This is in agreement with previous work which demonstrates that Pt is primarily responsible for the catalysis of formic acid through the indirect oxidation mechanism (see equation 1.18). Au, therefore, acts only to promote this reaction by limiting CO adsorption. As expected larger ratios of Pt provide higher catalytic ability while small portions of Au increase this ability. It is apparent that careful attention must be made in determining the best ratio of Pt:Au to provide high catalytic ability for the electrooxidation of formic acid.

Current density of the electrodes was calculated using the hydrogen absorption region of Pt for all modified electrodes in order to eliminate surface area effects. As can be seen in Figure 59b, when normalized for surface area the Pt:Au 2:1 electrode shows the highest catalytic ability towards the oxidation of formic acid. This is in contrast to un-normalized results which clearly show Pt:Au 3:1 as the best ratio. Such surface area effects can be explained by the more aggregate surfaces of electrodes with higher Au concentration. Figure 60 shows the morphology of the Pt/Au/ceria films as evaluated on the SEM.
Figure 60. Scanning electron microscopy images of the Pt/Au/ceria films electrodeposited on Pt-foil electrodes. A potential of -0.200 V vs Ag/AgCl was applied to a 2 mM metal ion solution in 0.5 M H$_2$SO$_4$ for a total of 600 s under constant, light stirring, keeping a constant deposition current of 1.0 × 10$^{-4}$ A. The SEM images show films deposited from (a) 2:0, (b) 3:1, (c) 2:1, (d) 1:1, (e) 1:2, and (f) 1:3 Pt:Au, respectively. It is observed how the morphology changes from relatively smooth films and smaller round crystallites for (a) Pt/ceria, to sharper, triangular crystallites (e) Au/ceria. As the Au concentration increases, the composite morphology becomes rougher, increasing the active surface area. The SEM images of the film containing only Pt/ceria appear to be relatively smooth, with only a few crystallites on the surface (Figure 60a). In contrast, the SEM images from Au/ceria films consisted of large, dendrite-like structures (Figure 60e). As the amount of Au is increased in the Pt/Au/ceria film, the morphology evolves from small, round particles (higher Pt content), to smaller dendrite-like structures (higher Au content). The SEM results suggest that as the Au contents in the Pt/Au/ceria increases, there are significant changes in the morphology and in the surface area of the material. Further evidence of the increase on the surface area of the composite film is supported by the relatively large hydrogen adsorption area of the Pt, even in samples composed predominantly of Au. It seems from the SEM images that the 2:1 Pt:Au electrode has a rougher surface than the 3:1 Pt:Au electrode leading to a higher surface area. However, the
ECA calculated from adsorbed hydrogen was much larger for the Pt:Au 3:1 electrode indicating that although the Pt:Au electrodes seem to have a more rough morphology, it has fewer Pt cites available on the surface for catalysis. Despite the lower ECA, the Pt:Au 2:1 electrode displays the highest peak current indicating that there is a synergistic catalytic effect between Pt and Au that cannot be explained by surface area. This catalytic effect is further demonstrated by all the Pt:Au composite electrode which, when normalized for surface area, outperformed the Pt/ceria electrode. This indicates that the increase in the peak current observed for formic acid is larger than what can be attributed to such changes in morphology and surface area and suggests that there is a synergistic catalytic effect between Pt and Au for the oxidation of formic acid. A plausible explanation is that the presence of Au in the nanoparticle Pt/Au surface could help limit CO poisoning by weakening adsorption of CO through the ligand or electronic effect. The preferred increase in the total current density is a promising indicator that the Pt/Au intermetallic electrode provides added catalytic activity for the oxidation of formic acid.

*Electrooxidation of Formic Acid on Pt/Pd/Ceria Composite Electrodes.* Pt/Pd and Pt/Pd/ceria composite electrodes were fabricated by the electrodeposition of Pt, Pd and ceria from deposition suspensions. The ratio of Pt to Pd was altered to generate electrode with Pt:Pd ratios with the following concentrations: (2:0, 3:1, 2:1, 1:1, 1:2, 1:3, 0:2). Cyclic voltammograms (CVs) were obtained with 0.75M formic acid solutions in 0.5 M H₂SO₄ for all modified electrodes. It can be seen in 61 that the electrode modified with Pt shows an increase in catalytic ability toward the oxidation of formic acid compared to the clean Pt electrode.
Figure 61. Cyclic voltammetry of the modified electrodes in 0.75 M formic acid: (a) Pt modified, (b) Pd modified, and (c) Clean Pt unmodified electrode. Scans from the Pd modified electrode show great catalytic ability for the electrooxidation of formic acid. The Pt modified electrode shows increased catalytic ability compared to clean Pt. (scan rate = 100 mV/s).

The electrode modified only Pd also shows a noticeable increase in activity as compared to the clean Pt electrode, and also has a higher peak current than the Pt modified electrode. This supports previously reported work which shows that, in general, Pd performs as a better catalyst for the oxidation of formic acid. The catalytic effect of Pd is thought to be the result of Pd promoting formic acid through the direct oxidation mechanism (shown in equation 1.15) where no byproducts are formed.

It has been previously demonstrated that ceria improves the catalytic ability of the electrodes as stated in previous studies.\textsuperscript{15, 31, 32} In this study, Pt/Pd composite electrodes modified with ceria were tested and compared to the non ceria modified electrodes. Figure 62 shows the cyclic voltammograms of the Pt/Pd 1:1 and Pt/Pd/ceria 1:1 modified electrodes toward 0.75M CHOOH in 0.5 M H\textsubscript{2}SO\textsubscript{4}.
Figure 62. Cyclic voltammograms of the Pt:Pd 1:1 and Pt:Pd 1:1 with ceria modified electrodes toward electrooxidation of 0.75M CHO OH in 0.5 M H₂SO₄ corrected for Pt-surface area using the hydrogen adsorption region. The electrode containing ceria showed no increased catalytic activity towards the oxidation of formic acid.

No significant increase in catalytic activity can be observed in the electrode containing ceria.

Though not reported here, it was further demonstrated ceria did not improve the catalytic ability of any electrode containing Pd. These results are in contrast with previously published work on the oxidation mechanisms of other organic molecules such as methanol or ethanol. Ceria is notorious at improving the catalytic activity of the oxidation of formic acid when mixed with platinum, gold and ruthenium, but apparently it has no effect when combined with palladium.

This can be explained by understanding ceria’s primary mode of catalytic enhancement. Ceria is able to promote the oxidation of formic acid and alcohols through the minimization of adsorbed CO which reacts with CeO₂-OH. However, palladium is thought to promote the oxidation of formic acid through the direct pathway, thus little to no CO is formed. In this case, there is no
advantage in using ceria to minimize CO adsorption. On the other hand, ceria can then adversely affect the electrode by reducing the noble metal concentration on the electrode surface.

To better understand the relationship between Pt and Pd in the catalytic oxidation of formic acid, we studied the bimetallic characteristics of electrodes modified with different ratios of both metals. In Figure 63a, we show CVs of electrodes modified with varying ratios of Pt/Pd. All of the Pt/Pd-modified electrodes show a catalytic enhancement over the non-modified Pt electrode for the oxidation of formic acid.
Figure 63. (a) Cyclic voltammetry of the Pt/Pd modified electrodes (without ceria) toward the electrooxidation of 0.75 M formic acid in 0.5 M H$_2$SO$_4$ for the different Pt:Pd ratios of 0:2, 1:3, 1:2, 1:1, 2:1, and 3:1. A noticeable increase in the oxidation current is observed for electrodes prepared from a deposition bath containing a 1:3 molar ratio of Pt:Pd. Other ratios showed very similar catalytic enhancements but not as good. (b) Cyclic voltammograms of the Pt/Pd modified electrodes with 0:2, 1:3, 1:2, 1:1, 3:1, and 2:1 toward 0.75M CHO OH in 0.5 M H$_2$SO$_4$ corrected for Pt-surface area using the hydrogen adsorption region. The electrode with a 0:2 Pt:Pd ratio shows the highest current density for the electrochemical oxidation of formic acid, while Pt:Pd 2:1 follows it as a distant second.
The electrode modified from a bath solution with molar ratios of 1:3 Pt:Pd shows the largest increase in peak current prior to correcting for the ECA. It seems that electrodes containing higher concentrations of Pd display higher peak currents. This supports the prediction that Pd promotes the direct oxidation mechanism of formic acid, while Pt promotes the indirect oxidation mechanism. In order to eliminate surface area effects, the current density of the electrodes was calculated using the hydrogen absorption region of Pt and Pd for all modified electrodes. Hydrogen adsorbs on Pt and Pt in the same potential window so this technique is a viable method for determining the ECA for Pt:Pd composites as the surface area should include regions of both Pt and Pd. As can be seen in Figure 63b when normalized for surface area the Pt:Pd 0:2 electrode shows the greatest catalytic ability towards the oxidation of formic acid. Such surface area effects can be explained by the more surface aggregates in electrodes with higher Pt concentration. Further evidence of the increase on the surface area of the composite film is supported by the relatively large hydrogen adsorption area of the Pt, even in samples composed predominantly of Pd. Therefore, the 1:3 Pt/Pd electrode has a rougher surface than the 0:2 Pt/Pd electrode leading to a higher surface area. These conclusions are supported by the SEM images seen in Figure 64.
Figure 64. Scanning electron microscopy images of the Pt/Pd/ceria films electrodeposited on Pt-foil electrodes. A potential of -0.200 V vs Ag/AgCl was applied to a 2 mM metal ion solution in 0.5 M H2SO4 sulfuric acid for a total of 600 s under constant, light stirring, keeping a constant deposition current of 1.0 × 10⁻⁴ A. The SEM images show films deposited from (a) 3:1, (b) 2:1, (c) 1:1, (d) 1:2, (e) 1:3, and (f) 0:2 Pt:Pd, respectively.

Overall it seems that the particle size on the surface of the electrode increases with increasing concentration of Pd. Figure 64e shows the surface of the Pt:Pd 1:3 electrode has particles with much smaller size while the Pt:Pd 0:2 electrode shown in Figure 64f contains many larger particles. The increase in particle size explains the apparent decrease in electrode surface area.

Once normalized for surface area, every Pt/Pd modified electrode containing both metals showed lower peak currents than the Pd 0:2 electrode. The probable explanation is that Pd is involved with the direct oxidation of formic acid where little to no byproducts are formed and higher overall peak currents are achieved. When higher concentrations of Pt are included in the composite electrodes, the surface area increases; however, current density decreases indicating a change in the oxidation mechanism between Pt and Pd. This indicates that Pd is the superior
catalysts for formic acid oxidation and addition of Pt improves the oxidation of formic acid only through surface area effects.

Figure 65 displays overlays of CV plots from the best performing electrodes before and after surface area normalization. Overall it can be seen in Figure 65a that before surface area normalization, the Pt:Au 3:1 electrode with ceria and the Pt:Pd electrode without ceria have the highest catalytic ability for the oxidation of formic acid. Results indicate that the Pt/Au/ceria composite has a higher peak current, and is therefore a better performing electrode than the Pt/Pd composite. It is apparent that addition of Au and ceria to Pt catalysts greatly improves the oxidation of formic acid.
Figure 65. (a) Cyclic voltammograms of the Pt:Au 3:1 (with ceria) and Pt:Pd 1:3 (without ceria) modified electrodes toward electrooxidation of 0.75M CHOOH in 0.5 M H2SO4. (b) Cyclic voltammograms of the Pt:Au 2:1 (with ceria) and Pt:Pd 0:2 (without ceria) modified electrodes toward electrooxidation of 0.75M CHOOH in 0.5 M H2SO4 corrected for Pt-surface area using the hydrogen adsorption region.
When surface area effects are normalized it can be seen in Figure 65b that the Pt:Pd without ceria has a higher peak current than the Pt:Au 2:1 with ceria. While the catalytic activity of Pt is greatly enhanced by the addition of Au and ceria, this catalytic system is limited by the indirect oxidation mechanism. Pd, however, displays enhanced oxidation kinetics without the addition of Pt or ceria. In fact, the addition of any secondary or tertiary catalysts acts to decrease the catalytic ability of Pd electrodes. While results suggest that both Pt/Au/ceria and Pt/Pd electrodes show enhanced catalytic activity for the electrochemical oxidation of formic acid, when surface area effects are eliminated, Pd electrodes prove to be the superior catalysts.

**Conclusion**

In this study it was found that all modified electrodes outperformed the clean Pt electrode for the electrochemical oxidation of formic acid. Results for the Pt/Au composite electrodes showed that all ceria modified electrodes outperformed electrodes without ceria. Also, Au electrodes showed no catalytic ability for the electrooxidation of formic acid in acidic media. However, electrodes with Au in the presence of Pt show greater catalytic ability than Pt electrodes. These results indicate that the Pt:Au nanocrystals can perform as good ternary catalysts for the electrooxidation of formic acid. This catalytic effect may be caused by the combination of a higher poison tolerance (from CO) and a synergistic effect for the catalytic oxidation of formic acid. Although the oxidation of formic acid shows enhancement, upon normalizing for the Pt ECA it becomes apparent that the mixed Pt/Au electrodes have an increasingly exposed surface area. However, the increase in the oxidation current is considerably larger than what can be predicted by changes in surface area alone. Thus, the larger increase in
current suggests the presence of some synergistic catalytic effect in the Pt/Au/ ceria catalyst, and that the increase in the catalytic current is not solely the case of a higher surface area. For the Pt/Pd composite electrodes, results indicate that addition of ceria has no effect on the catalytic ability toward the oxidation of formic acid. Palladium therefore appears to be a more poison tolerant electrode when compared to platinum, which is the result of Pd promoting the direct oxidation of formic acid where little to no byproducts (such as CO) are formed. In addition, when the electrodes were normalized for surface area the electrode modified with Pd alone showed the highest catalytic ability. Although the oxidation of formic acid shows enhancement, upon normalization for Pt ECA it becomes apparent that the mixed Pt/Pd electrodes have an increasingly exposed surface area. The increase in current is lower than what can be predicted by changes in surface area. Thus the small increase in current suggests that there is no synergistic catalytic effect in the Pt/Pd/ceria catalyst, and the increase in current is solely the case of higher surface area. Furthermore, it seems that addition of secondary or tertiary catalysts act to limit the catalytic ability of Pd towards formic acid oxidation. While results suggest that both Pt/Au/ceria and Pt/Pd electrodes show enhanced catalytic activity for the electrochemical oxidation of formic acid, when surface area effects are eliminated, Pd electrodes prove to be the superior catalysts.

Formic acid in fuel cells has many advantages over methanol and other alcohols. It is a safe non-toxic alternative that can be used in high concentrations. The modified electrodes show enhanced catalytic activity for the electrochemical oxidation of formic acid. These results are promising for the development of novel direct formic acid fuel cells and warrant further research.
in order to identify and quantify the actual products from the oxidation of formic acid and to correlate the electrochemical behavior with theoretical predictions.

References


SUMMARY AND OUTLOOK

Motivated by the need for more efficient power conversion technologies, in this work, we have devoted much time and effort to understanding PEMFC catalysts. This dissertation is focused on the fabrication and characterization of composite materials as catalysts for alcohol and formic acid oxidation. Composite materials were synthesized through a variety of approaches including metal and graphene electrodeposition, and metal nanoparticle impregnation on MWCNTs. All composite materials were characterized for surface morphology and composition. Electrochemical characterization was carried out to determine the catalytic ability of each composite electrode towards the oxidation of alcohols and formic acid.

A variety of novel techniques were developed in this study to better fabricate and characterize composite materials. To date the determination of ECA in Pt-composite working electrodes has been an area of intense study. By designing the combined approach of Cu-UPD with H-adsorption, we have provided a straightforward and simple method to calculate the ECA of Pt/Au working electrodes. This technique can be adapted and applied to multiple areas of heterogeneous catalysis. We have also developed a method for GO purification using centrifugation. By making aqueous suspensions of GO and electro-reducing GO to graphene on working electrodes, we have created graphene films which have applications in catalysis as well as device fabrication. We have also successfully adapted previous techniques to design novel catalysts. Electrodeposition procedures were extensively studied to create bimetallic electrodes with interesting and useful catalytic properties. Metal nanoparticle impregnation on MWCNTs was also optimized to synthesize novel catalytic materials.
By understanding the present limitations of DAFCs and DFAFCs we have designed and fabricated many novel composite catalysts. Electrochemical and material characterization of these materials was also extensively carried out. This study presents for the first time the following composite materials: Pt/Au/Ceria, Pt/Pd/Ceria, Graphene/Pt/Ceria and MWCNT/Pt/Ru/Ceria. Electrodes were made from each of these composites, and the Pt/Au/Ceria, Graphene/Pt/Ceria and MWCNT/Pt/Ru/Ceria composites have all shown significant increases in the catalytic oxidation of methanol and ethanol. In addition, Pt/Au/Ceria and Pt/Pd/Ceria catalysts have proven to be useful for the oxidation of formic acid. The role of carbon substrates on catalytic ability was explored by designing composites of MWCNTs and graphene. We have also provided meaningful explanations as to the reason for advanced catalytic activity. Ceria in particular has been well examined as a component in PEMFC anode catalysts. The role of Pd, Ru and Au in Pt bimetallic electrodes is also well discussed. Table 11 provides a list of the most notable electrodes fabricated in this study along with their catalytic ability towards the oxidation of methanol, ethanol and formic acid.

**Table 11. Notable electrodes fabricated in this study**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$j_{pa}$ Methanol</th>
<th>$j_{pa}$ Ethanol</th>
<th>$j_{pa}$ Formic Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceria/Pt:Au 2:0</td>
<td>3.6 mA/cm$^2$</td>
<td>3.3 mA/cm$^2$</td>
<td>1.9 mA/cm$^2$</td>
</tr>
<tr>
<td>Ceria/Pt:Au 2:1</td>
<td>1.6 mA/cm$^2$</td>
<td>5.5 mA/cm$^2$</td>
<td>7.0 mA/cm$^2$</td>
</tr>
<tr>
<td>Graphene/Ceria/Pt</td>
<td>5.5 mA/cm$^2$</td>
<td>5.0 mA/cm$^2$</td>
<td>-</td>
</tr>
<tr>
<td>MWCNT/Ceria/Pt:Ru 3:1</td>
<td>6.7 mA/cm$^2$</td>
<td>11 mA/cm$^2$</td>
<td>-</td>
</tr>
<tr>
<td>Pt:Pd 2:0</td>
<td>-</td>
<td>-</td>
<td>10 mA/cm$^2$</td>
</tr>
<tr>
<td>Unmodified Pt</td>
<td>0.4 mA/cm$^2$</td>
<td>1.2 mA/cm$^2$</td>
<td>0.8 mA/cm$^2$</td>
</tr>
</tbody>
</table>
In an attempt to provide meaningful research in the area of alcohol and formic acid catalysis, we have continually compared our composite electrodes to those reported by other groups in scientific literature. The most straightforward method to compare fuel cell electrodes is by constructing fuel cell stacks and monitoring the device efficiency. This technique; however, exceeds the scope of most studies focusing on electrode composite synthesis and fabrication. The most accepted method for reporting electrode catalytic activity is through the $j_{pa}$ determined during oxidation sweeps of CVs. The $j_{pa}$ is calculated from the current divided by the surface area, or mass load of Pt. There is no agreement in literature as to a standard method for determining surface area or mass load, or how to report $j_{pa}$. This makes comparisons between studies very difficult. In this work we focused on electrochemical techniques to determine the electroactive surface area and used these values for $j_{pa}$ calculation. In order to monitor our success in alcohol oxidation catalysis, we compared our results to those of other studies which used similar techniques for ECA determination and $j_{pa}$ calculation. Table 12 shows the $j_{pa}$ during methanol oxidation for a variety of catalysts reported in literature.

**Table 12. Comparable composite electrodes reported recently in literature**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Substrate</th>
<th>Surface Area Calculation</th>
<th>$j_{pa}$ Methanol</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Au</td>
<td>Fluorine Doped Tin Oxide</td>
<td>Cu-UPD</td>
<td>1.4 mA/cm$^2$</td>
<td>1</td>
</tr>
<tr>
<td>Pt/ceria</td>
<td>MWCNTs</td>
<td>Hydrogen Adsorption</td>
<td>5.0 mA/cm$^2$</td>
<td>2</td>
</tr>
<tr>
<td>Pt/Ru</td>
<td>Carbon Nanofibers</td>
<td>Hydrogen Adsorption</td>
<td>6.0 mA/cm$^2$</td>
<td>3</td>
</tr>
<tr>
<td>Pt/Ru</td>
<td>MWCNTs</td>
<td>Hydrogen Adsorption</td>
<td>1.0 mA/cm$^2$</td>
<td>4</td>
</tr>
</tbody>
</table>
Our study compares well to these values for methanol oxidation. The Pt/Au/ceria electrodes from our work show faster oxidation kinetics than those previously reported elsewhere with similar systems. The primary explanation for this is the addition of ceria in our system. As no studies have previously reported graphene films as substrates for Pt or ceria nanoparticles, results can only be compared to similar systems such as Pt/ceria grown on MWCNTs. It appears that graphene supported metal particles display greater catalytic ability than similar particles supported on MWCNTs. Lastly, Pt and Ru systems have been greatly studied; however, to date no research has shown the catalytic ability of Pt/Ru/ceria nanoparticles supported on MWCNTs. The results shown in this dissertation indicate that ceria in combination with Ru has great impact on methanol oxidation, showing much higher $j_{pa}$ than previously reported in similar systems without ceria.

While in this study we have fabricated many electrodes which show greatly enhanced oxidation kinetics, more research is required to fully understand the catalytic mechanisms of each component and their effect on the oxidation of alcohols and formic acid. Future work may include the construction of fuel cell stacks using the catalysts developed in this research. A study of this kind would allow for more advanced calculation of fuel cell efficiencies. The waste water from fuel cell operation could also be useful in determining byproducts from the incomplete oxidation of alcohols and formic acid. This may lead to a better understanding of the catalytic oxidation mechanism of the materials described in this dissertation. Kinetic studies could also be performed using rotating disc electrodes to gain a better understanding of the direct and indirect oxidation mechanisms on composite catalysts. In situ studies of byproduct formation could be studied using direct electrochemical mass spectroscopy. A study such as this would provide
detailed analysis of the catalytic enhancement of composite materials. Great progress has been made in this dissertation toward developing fabrication methods, novel catalysts and electrochemical characterization techniques; however, there are many possibilities for future work. Understanding of this research can lead to multiple opportunities for the study of composite catalysts as electrodes in PEMFCs.

References


APPENDIX A: LIST OF RELEVANT PUBLICATIONS AND PRESENTATIONS


