Synthesis and Characterization of Tin Oxide-Supported Platinum as a Cathode Catalyst in Direct Methanol Fuel Cells

A Major Qualifying Project Report

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By:
Manish Chawla
Tony Chou
Kevin McCarthy

Approved By:
Professor Ravindra Datta and Professor Jianyu Liang

Abstract

It is imperative to reduce society's reliance upon the limited supply of fossil fuels. Direct methanol fuel cells are an attractive solution but there are several problems encountered by contemporary carbon-supported catalysts including poor efficiency and short life cycles due in part to methanol crossover. The following research investigated the potential of SnO_2 as a replacement for carbon due to its reported high electrical conductivity, good corrosion resistance, and resistance to the effects of methanol crossover. In this paper, two synthesis methods to prepare Pt/SnO_2 are reported: the impregnation process and the colloidal process, both relying primarily on ethylene glycol as the reduction solvent. The synthesized Pt/SnO_2 material was characterized by TEM, SEM, EDX, and cyclic voltammetry.

Experiments demonstrated that tin oxide is a poor material for fuel cell electrocatalyst supports since it was unable to conduct a current in a fabricated catalyst layer. Despite this result, however, it was shown that synthesis conditions could be optimized in order to produce a Pt/SnO_2 product with very evenly distributed Pt particles (~5nm) embedded on SnO_2 by using the colloidal process with a relatively weak reducing agent and with longer reaction and stirring times.

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1.0 Introduction

Society is faced with major energy security and environmental challenges such as dependence on fossil fuels, deteriorating air quality, and greenhouse gas emissions. Increasing energy demand and the burning of fossil fuels to meet this demand has consequently led to staggering growth in carbon dioxide emissions, as shown in Figure 1.
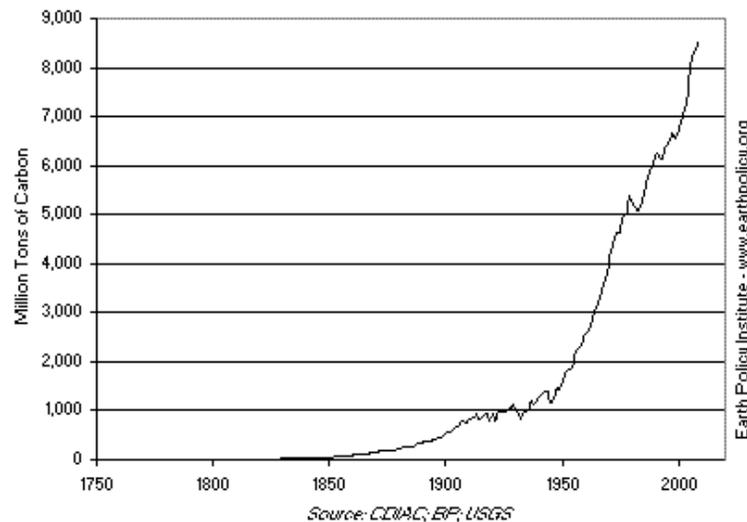
Figure 1. Global Carbon Dioxide Emissions from Fossil Fuel Burning, 1751-2009
(http://www.bgs.ac.uk/)

The demand for clean and sustainable energy sources has become a strong force in economic development. In particular, fuel cells have gained considerable attention as they can effectively provide power and be a part of a more competitive, secure, and sustainable clean energy economy. Unlike combustion processes, fuel cells do not operate in a high temperature environment and thus, no harmful chemical pollutants are formed from high temperature dissociative reactions such as nitride oxides, sulfide oxides, and carbon monoxide (Li, 2006). However, the widespread commercialization of fuel cells has been difficult so far because of prohibitive costs, and low durability, reliability, and performance. Ongoing research attempts to

address these short-comings in order to make fuel cells more economically attractive and commercially available.

While there are several different types of fuel cells, direct methanol fuel cells (DMFCs) have immense potential as an alternative energy generation method, especially for small electronic devices like mobile phones, personal data equipment, and camcorders. One of the main advantages of DMFCs is the stable nature of the liquid methanol fuel and its high energy density, which allows for longer usage time compared to standard batteries.

Currently, DMFCs have limitations in terms of performance, durability, and reactivity, which make them costly and less attractive. The electrocatalysts and corresponding catalyst layers play critical roles in fuel cell technology but platinum-based catalysts have several drawbacks including high cost, sensitivity to contamination, low tolerance for methanol oxidation, and platinum dissolution (Zhang, 2008). Current carbon-supported platinum catalysts degrade quickly and are susceptible to carbon corrosion. This study was undertaken in an attempt to rectify some of these problems.

In this study, tin oxide-supported platinum was synthesized and characterized in order to compare the Pt/SnO_2 electrochemical properties with contemporary XC-72 Vulcan carbon black. Evenly distributed and well-adhered platinum particles (2-5 nm) on tin oxide were desired in order to maximize surface area and increase the number of platinum active sites. This was done by varying parameters such as the synthesis method, the use of strong or weak reducing agents, and the reaction and stirring time in order to obtain optimal synthesis conditions. Unfortunately, cyclic voltammetry experiments on Pt/SnO_2 were unsuccessful because of its low conductivity.

2.0 Background

2.1 Brief History

The first fuel cell was developed in 1839 by Welsh scientist, William Grove (Larminie, 2003). His invention demonstrated water being electrolyzed into hydrogen and oxygen by passing an electric current through two externally connected platinum electrodes. When he replaced the power supply with an ammeter, a current began flowing. This was caused by the recombination of hydrogen and oxygen, generating an electric current. Grove called this device the *gas voltaic battery.* His experiment is shown in Figure 2.
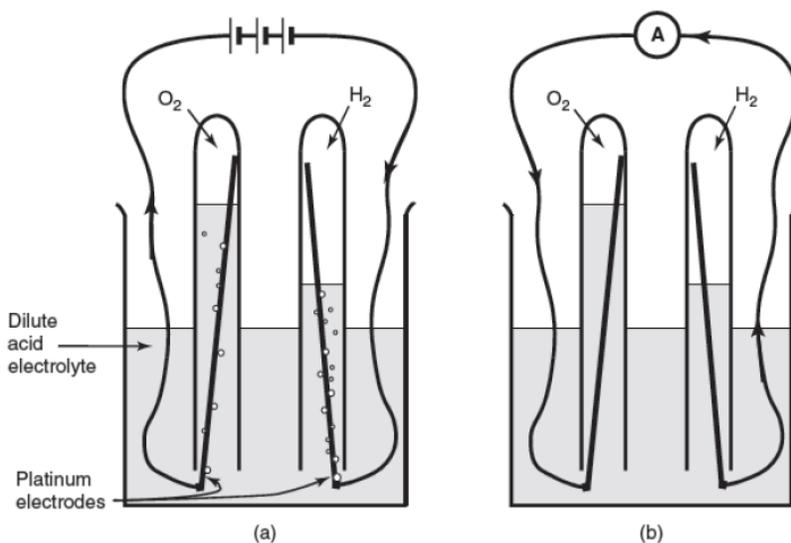
Figure 2. (a) A voltage is applied and water separates into hydrogen and oxygen. (b) A current flows. Oxygen and hydrogen are recombining.

The current produced by Grove's fuel cell was very small due to: the low contact area between the gas, the electrode, and the electrolyte; and the high electrolyte resistance amplified by the large distance between the electrodes. For the next 100 years, Grove's concept of a fuel cell was only used in isolated applications; nevertheless, it was an important discovery with great implications.

In 1932, Francis Thomas Bacon, an engineering professor at Cambridge University in England, began working on the *Bacon cell*, a primitive type of alkaline fuel cell, which he patented in 1960 (Bagotsky, 2009). In a public demonstration, the cell produced 5 – 6 kW and could power a welding machine, circular saw, and forklift (Zhang, 2008). Bacon's battery attracted significant attention and led to a greater interest in fuel cell technology.

In the early 1960s, Thomas Grubb and Leonard Niedrach of General Electric invented the first polymer exchange membrane fuel cell (PEMFC), which could be fueled by hydrogen or hydrocarbons at temperatures less than 150°C (Bagotsky, 2009; Zhang, 2008).

Starting in 1983, Ballard Power Systems began developing proof-of-concept PEMFC prototypes of all scales (Zhang, 2008). Early systems in 1991 produced 5 kW but by 2000 they managed to achieve systems with outputs of 80 kW.

Interest in fuel cells continues to intensify and evermore academic and industrial research is being dedicated to improving all aspects its performance, especially over the past decade. While there are still several limiting factors to the technology, fuel cells are efficient and environmentally friendly sources of energy with a promising future (Gasik, 2008).

2.2 Fuel Cell Principles

A fuel cell is a device that generates electricity by chemical reactions. The main advantages of fuel cells are their high energy conversion efficiency, low noise, low maintenance costs, and low emissions of harmful products (Zaidi, et al., 2009). Every fuel cell has two electrodes: the negative anode and the positive cathode. Sandwiched in-between the anode and cathode is an electrolyte that allows for the passage of ions and for the generated charge to move between the two electrodes. A schematic of a polymer exchange membrane fuel cell is shown in Figure 3 for a H_2-O_2 fuel cell.
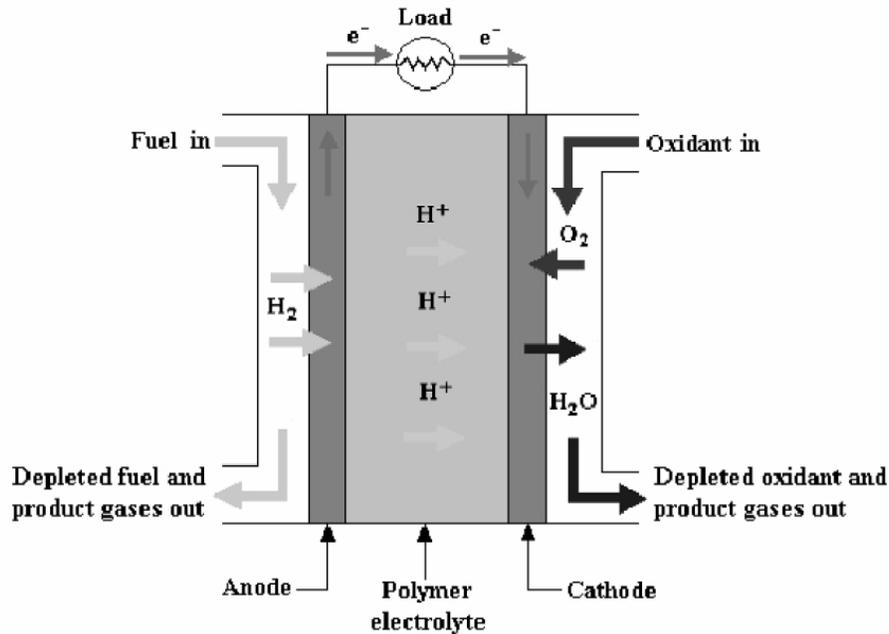
Figure 3. PEM Fuel Cell Principle
(http://electrochem.cwru.edu/encycl/)

Unlike a conventional battery, a fuel cell will theoretically never go dead and will continue to produce power as long as there is a constant supply of fuel.

2.3 Types of Fuel Cells

Fuel cells are differentiated by the type of electrolyte they use such as phosphoric acid, lithium, potassium carbonate salt, and polymer membranes (Larminie, 2003). Each has distinct advantages and disadvantages that make them more suitable for specific applications but the various types all play to their strengths in different ways. A summary of the different fuel cell types is presented in Table 1.

Table 1. Different Fuel Cell Types

Fuel Cell Type	Mobile Ion	Operating Temperature	Applications and Notes
Alkaline (AFC)	OH^-	50-200°C	Used in space vehicles
Proton Exchange Membrane (PEMFC)	H^+	30-100°C	Vehicles and mobile applications
Direct Methanol (DMFC)	H^+	20-90°C	Suitable for low power portable systems running for long times
Phosphoric Acid (PAFC)	H^+	~220°C	Large number of 200-kW systems in use
Molten Carbonate (MCFC)	CO_3^{2-}	~650°C	Suitable for medium to large-scale systems
Solid Oxide (SOFC)	O^{2-}	500-1000°C	Suitable for all sizes, 2-kW to several MW

2.3.1 Alkaline Fuel Cell (AFC)

Alkaline fuel cells were one of the first fuel cell systems developed. They had promising applications in spacecraft but problems with cost, reliability, ease of operation, ruggedness, and degradation of alkaline electrolyte because of reaction with carbon dioxide in air led to AFCs being overshadowed by other fuel cell technologies such as PEMFCs (Larminie, 2003). AFCs still has many advantages. Components are cheap. They rely on an alkaline solution as the electrolyte, most commonly a solution of potassium hydroxide (Bagotsky, 35). The KOH electrolyte is very low-cost and is the cheapest electrolyte material out of all the different types of fuel cells (Larminie, 2003). The electrodes are also very cheap since they can be made from a variety of non-precious metals. AFCs also have lower overvoltage at the cathode, which means they experience less voltage loss compared to low-temperature fuel cells.

2.3.2 Proton Exchange Membrane Fuel Cell (PEMFC)

Polymer exchange membrane fuel cells are one of the simplest types of fuel cells because they use a solid and stationary electrolyte, most commonly Nafion (Larminie, 2003). They operate at relatively low temperatures, which cause a slow reaction rate, but this is counteracted by using porous carbon electrodes containing platinum catalysts. PEMFCs, however, require very pure hydrogen as a fuel. Not only has finding a reliable source of pure hydrogen been problematic, but hydrogen must be stored in bulky, high-pressure tanks that make them impractical and unsafe for many applications.

2.3.3 Direct Methanol Fuel Cell (DMFC)

A solution to the hydrogen supply problem encountered in PEMFCs is to directly use methanol instead (Larminie, 2003). As a liquid fuel, methanol is considerably more practical than gaseous hydrogen; it is easily stored, transported, and refilled, and it also has higher energy density compared to hydrogen (Lu, et al., 2006). The power output, however, is very low because of self-poisoning of catalyst and methanol crossover. Even so, DMFCs are highly suitable for low-power portable electronics such as personal computers and cellular phones that require slow and steady consumption of electricity over long periods of time.

2.3.4 Phosphoric Acid Fuel Cell (PAFC)

Phosphoric acid fuel cells have seen widespread commercial applications where they are commonly used for stationary power generation; there are many 200-kW systems in use around the world (Larminie, 2003). PAFCs use liquid phosphoric acid contained in Teflon bonded silicon carbide matrix as the electrolyte and porous carbon electrodes that contain platinum catalysts (Larminie, 2003; U.S Department of Energy, 2012). Reaction rates are elevated by high operating temperatures of 170-200°C. PAFCs, however, rely on reforming natural gas to

hydrogen and carbon dioxide, which requires expensive and bulky external equipment that limits it to stationary use and relatively large scale.

2.3.5 Molten Carbonate Fuel Cell (MCFC)

Molten carbonate fuel cells are high temperature (~650°C) fuel cells that use a molten carbonate salt mixture suspended in a porous lithium aluminum oxide matrix as the electrolyte (U.S Department of Energy, 2012). They are currently being developed for natural gas and coal-based power plants, electrical utility, industrial, and military applications.

2.3.6 Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cells are another type of very high temperature fuel cells that use a non-porous ceramic compound as the electrolyte (Larminie, 2003). Operating at high temperatures allows for high reaction rates without expensive catalysts and it also allows for internal reforming without the need for a separate external unit. It is less developed than the other types of fuel cells, however, and the ceramic material is very expensive and difficult to handle. They also suffer from complex cooling systems, air and fuel pre-heaters, and difficult start-up procedures.

2.4 Direct Methanol Fuel Cells

2.4.1 Advantages

DMFCs are very similar to proton-exchange membrane fuel cells (PEMFCs). Instead of using hydrogen as the fuel source, methanol is used. Methanol is an energy dense liquid fuel with a higher power density than gaseous hydrogen. It is also easier and safer to store compared to compressed hydrogen gas. For portable and mobile applications, it is desirable to have a fuel that is liquid at atmospheric pressure and temperature for easy distribution and storage (Li, 2006).

DMFCs operate at low temperatures and are simple, compact, and lightweight. Similar to PEMFCs, DMFCs can use a solid polymer such as Nafion as the electrolyte (FC Tec, 2011).

2.4.2 Applications

DMFCs can be used to power small electronic devices like mobile phones, personal data equipment, and camcorders because of their light weight, easy portability, and onboard storage (Li, 2006). They can store high-energy content in a limited space and produce a small amount of power for a long period of time. There is a need for longer usage times for applications such as laptops and handheld devices, and DMFCs emerge as an interesting option due to high-energy density and the harmless nature of liquid methanol (Arico, et al., 2010).

2.4.3 DMFC Components and Operation

Direct methanol fuel cells generate electrical power through oxidation and reduction reactions that take place at the anode and cathode, respectively. At the anode, methanol is oxidized with water to form carbon dioxide and protons, which pass through a selective membrane to produce water at the cathode via the following anode and cathode reactions:

$$\text{Anode: } CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2$$

$$\text{Cathode: } 6H^+ + 6e^- + \frac{3}{2}O_2 \rightarrow 3H_2O$$
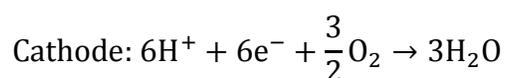
From the above reactions, it is important to notice that water is required for the oxidation of methanol and water is also formed at the cathode. Although it seems that the water from the cathode can be used at the anode, water is actually transported from the anode to the cathode from the methanol and water mixture feed, providing hydration for the polymer exchange membrane necessary for proton conduction (Li, 2006). Methanol and water are adsorbed on a catalyst that contains platinum nanoparticles attached on a surface with larger carbon particles

that act as a support. The platinum is usually highly dispersed on the support so that there is a higher surface area in contact with the methanol reactant.

The diluted liquid methanol first passes from the anode through a gas diffusion layer before coming into contact with the catalyst at the cathode. Similarly, at the cathode, oxygen passes through a gas diffusion layer before reaching the platinum supported catalyst. The main function of the gas diffusion layer is to diffuse reactant gas to the catalysts on the membrane electrode assembly via a carbon-based porous substrate that is generally wet-proofed with a PTFE (Teflon) coating to ensure that pores do not become congested with liquid water (Litster & Mclean, 2004). Protons that are formed from the reaction at the anode side are transported to the cathode side via a polymer electrolyte membrane medium. The standard material used as an electrolyte is Nafion[®] because of high resistance to chemical degradation, strong bonds that allow for the development of thin films, ability to absorb large amounts of water, and allowance of hydrogen ions to move freely through the membrane (Zhang, J, 2008). Electrons produced from the oxidation reactant are transported through an external circuit from the anode to the cathode which creates the electrical power. A schematic of direct methanol fuel cell operation is shown in Figure 4.
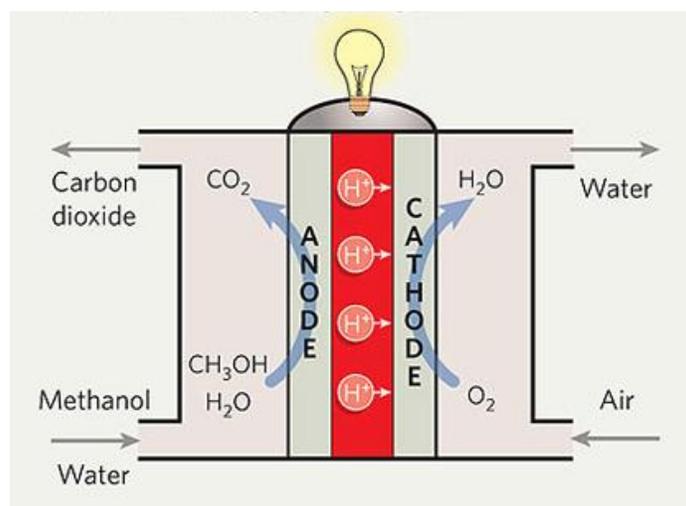
Figure 4. Direct Methanol Fuel Cell Schematic

2.4.4 Performance

The peripheral equipment needed for DMFCs include feeding of an aqueous methanol solution for the anode and the removal of carbon dioxide gas in addition to supplying air or oxygen. DMFCs have a lower working voltage because the oxidation of methanol is a slow reaction because of strong adsorption of CO on catalyst surface that leads to polarization of the negative electrode (Bagotsky, 2009). The achievable current and voltage depend on many factors including the thickness of the membrane, nature of the catalyst, and surface area of the electrode. Due to these aspects, it is very difficult to compare the performance parameters of DMFCs in different laboratories (Bagotsky, 2009). Optimum solutions and operating conditions, however, can be found for particular cells.

2.4.5 Limitations

One of the major limitations of DMFCs is caused by the phenomenon known as methanol crossover where methanol diffuses through the membrane without reacting and results in a waste of methanol fuel, polarization of the cathode, and a significant decrease in efficiency. In DMFCs, carbon monoxide is an intermediate species that poisons the platinum catalyst and thereby blocks sites and increase polarization reducing the electric potential of the fuel cell. The mechanism for methanol oxidation showing all intermediate species is shown in Figure 5 (note carbon monoxide).

$$CH3OH \xrightarrow{-H^+,-e^-} CH2OH \xrightarrow{-H^+,-e^-} CHOH \xrightarrow{-H^+,-e^-} COH$$

$$CH2O \xrightarrow{-H^+,-e^-} CHO \xrightarrow{-H^+,-e^-} CO$$

$$HCOOH \xrightarrow{-H^+,-e^-} COOH$$

$$CO2$$
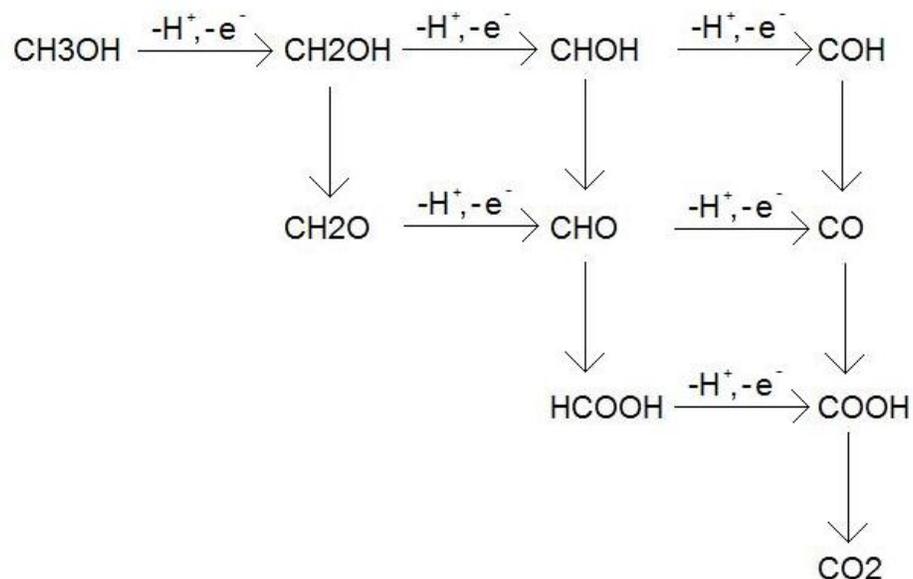
Figure 5. Methanol Oxidation Mechanism

To alleviate this problem, the platinum catalyst is often alloyed with ruthenium.

Furthermore, low-temperature oxidation of methanol to hydrogen ions and carbon dioxide

requires a more active catalyst, which typically means an order of magnitude larger quantity of

expensive catalyst is required than in conventional PEMFCs (Du, et al., 2007).

3.0 Literature Review

3.1 DMFC Catalysts

Platinum is the most critical single-component catalyst used in low temperature fuel cells because of its catalytic activity in room temperature electro-oxidization reactions. Catalytic activity of the metal depends strongly on nanoparticle shape, size, and size distribution. There are few electrode materials that are suitable for use in methanol oxidation electro-catalysis because of an acidic electrode and membrane interface (Sung, et al., 2011). It was concluded that platinum is the only metal that can withstand acidic conditions inside a fuel cell, but it is expensive and therefore has limited the large-scale application of fuel cells (Sung et al., 2011).

The primary steps in methanol oxidation at the anode include methanol absorption, methanol disassociation, water absorption, water activation, and carbon monoxide oxidation. The formation of OH by water activation on the platinum surface is a necessary step in the removal of CO that requires a high potential (Liu, et al., 2006). Such a high potential will limit the fuel cell application of a pure platinum catalyst. The reactions during methanol absorption are shown below:

$$Pt + CH_3OH \rightarrow Pt - (CH_3OH)_{ads}$$

$$Pt - (CH_3OH)_{ads} \rightarrow Pt - (CH_3OH)_{ads} + H^+ + e^-$$

$$Pt - (CH_2OH)_{ads} \rightarrow Pt - (CH_2OH)_{ads} + H^+ + e^-$$

$$Pt - (CHOH)_{ads} \rightarrow Pt - (CHOH)_{ads} + H^+ + e^-$$

$$Pt - (COH)_{ads} \rightarrow Pt - (CO)_{ads} + H^+ + e^-$$
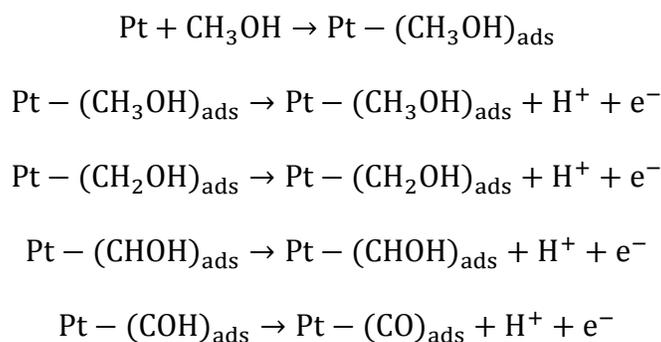
In addition, water dissociates primarily on Ru:

$$Ru + H_2O \rightarrow Ru - (H_2O)_{ads}$$

$$Ru - (H_2O)_{ads} \rightarrow Ru - (OH)_{ads} + H^+ + e^-$$

And finally:

$$Pt - (CO)_{ads} + Ru - (OH)_{ads} \rightarrow Pt + Ru + CO_2 + H^+ + e^-$$
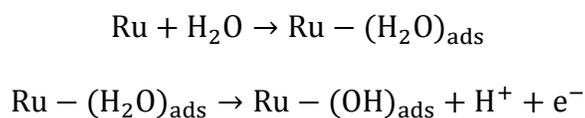
Even though platinum is the most active metal for dissociative adsorption of methanol, it can, thus, readily poisoned by carbon monoxide, an intermediate species in the methanol electro-oxidation reaction as shown in Figure 6.
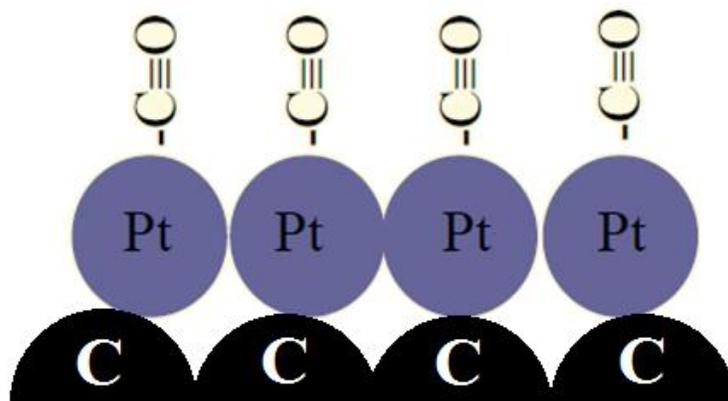
Figure 6. Carbon Monoxide Attaches to Platinum and "Poisons" the Catalyst

For a pure platinum catalyst, the adsorption of carbon monoxide can occupy active sites by bridge bonding and this results in slower kinetics. It also results in decreased fuel consumption efficiency and power density. In order to improve the oxidation kinetics of methanol, platinum is usually alloyed with another metal such as ruthenium which is more effective in dissociating water (Liu, et al., 2006). When compared with platinum, Ru atoms, thus, promote the oxidation of CO to CO_2. The catalytic activity of the Pt-Ru catalyst strongly depends on the composition, structure, and particle size. To obtain optimal fuel cell performance, a high catalyst loading is required because of CO poisoning, which hinders the commercialization of DMFCs due to higher costs (Liu, et al., 2006).

As an alcohol, methanol is miscible with water. Since the polymer exchange membrane is hydrated with water, unreacted methanol spreads into the water in the polymer exchange

membrane and reaches the water on the cathode side (Li, 2006). The methanol at the cathode is not utilized in producing a current and results in lower fuel efficiency. Methanol at the cathode is electro-oxidized while oxygen is reduced. This creates a mixed potential. Further, the heat of reaction due to methanol oxidation and oxygen reduction occurring simultaneously can degrade the cathode catalyst (Maillard, et al., 2002). Currently, the platinum catalysts on a support at the cathode are not sufficiently active but efforts are being made to increase this (Li, 2006).

In order to maximize the activity of platinum while minimizing the amount needed, it is important to adhere platinum nanoparticles in the range of 2-5 nm on surfaces of supporting nanomaterials that are low cost, have high surface area, and are good electrical conductors (Hyung-Wook, et al., 2011).

New catalysts for both the anode and cathode are currently being researched in order to enhance the methanol electro-oxidation kinetics. When analyzing new catalysts, there are two major challenges, namely performance and cost reduction. Performance of the catalyst depends on its activity, reliability, and durability (Sung, et al., 2011).

3.2 Carbon as a Support

Compared to unsupported Pt catalysts that were used a decade or more ago, supported catalysts have several advantages over unsupported catalysts. Supported catalysts have shown higher activity and stability due to good dispersion, high utilization of catalysts, and stable nanoparticles (Zhang, J, 2008). Some properties that make desirable catalyst supports include high surface area, porosity, electronic conductivity, and stability to corrosion in acidic media. Currently, carbon-supported metal catalysts are most commonly used and they enhance catalytic performance and efficiency thanks to their high surface area (Zhang, et al., 2010). The porous nature of carbon black assures gas diffusion to the active sites. Carbon supports also have good

electric conductivity which allows electron transfer from catalytic sites to conductive carbon electrodes and then to the external circuit in order to provide electricity (Zhang, 2008). The carbon support enables uniform dispersion of Pt nanoparticles, reduces sintering, and provides electronic continuity. The support with dispersed Pt nanoparticles also maximizes surface area of contact between the catalyst and the reagents. Carbon black materials are fairly inexpensive to synthesize, which makes it very attractive for use in fuel cells.

Carbon also offers other advantages over alternative materials. Carbon is a relatively light element so using it in fuel cells is not only catalytically and cost-effective but also very weight-efficient. This makes the cell more flexible for use in a wide assortment of applications. Carbon is also used because it is effective at low temperatures. This allows the cell to be mobile since it does not need a cooling system in order to keep temperatures within a certain range (Bagotsky, 2009).

3.2.1 Carbon Corrosion

A major disadvantage of carbon is that it is susceptible to corrosion at the cathode interface. Corrosion of carbon not only means the catalyst will have to be replaced, but it also results in many problems during the fuel cell's lifetime. When carbon is oxidized, it is no longer as effective and functionality decreases. The presence of Pt can accelerate the rate of carbon corrosion and can be more severe where Pt particles reside; this weakens the attachment of Pt nanoparticles (Tang, 2005). Furthermore, carbon oxidation decreases the electronic continuity of the catalyst layer and Pt nanoparticles become inactive in the electrochemical reactions (Tang, 2005). There is also a loss of interaction between the Pt particles and the carbon support itself when corrosion occurs.

Carbon dioxide is formed from the reaction at the anode and escapes as a gas from the fuel cell. This also causes the carbon substrate to wear away and cause gaps in the material. In addition, carbon corrosion is accelerated at high voltages, high temperature operating conditions, and at low humidity operating conditions (Tang, 2005).

The corrosion is stimulated by many operating conditions that are synonymous with fuel cells. One of these conditions is high water levels. Since water is a major product of the fuel cell reactions, it is certain to accumulate within the cell at some point. Therefore, using a substrate that is susceptible to these conditions offers problems and should be avoided. Another cause of corrosion is low pH. Since fuel cells have water as a product, the water inevitably becomes acidic.

High temperatures can also cause carbon corrosion. Since the reaction in fuel cells is exothermic, energy is released and causes temperatures to rise. This means that to effectively use carbon, one would have to keep the fuel cell at a lower temperature during the entirety of its lifespan.

Once corroded, carbon becomes highly hydrophobic. As stated, water is a product of the reaction, and if it is unable to pass through the carbon substrate, it will build up and cause severe problems in the fuel cell.

3.3 Metal Oxides as a Support

Recently, there have been efforts focusing on using metal-metal oxides for improving the durability as well as the electrochemical oxidation reaction and the carbon monoxide tolerance of the platinum-based catalysts. These supports can decrease the adsorption energy of carbon monoxide, convert poisonous carbon monoxide intermediates into carbon dioxide, and improve the durability of platinum catalysts by increasing mobility of the CO group on platinum

nanoparticles (Chun, et al., 2010). The transfer of protons to the surface of metal oxide supports can create clean active sites on the surface of platinum and prolong the effective dehydrogenation of the catalyst (Sung, et al., 2011). Metal oxides are also stable under operating conditions of fuel cells and are resistant to oxidation.

According to studies done by Sung et al. (2011), utilization of metal oxides such as TiO_2 and SnO2 have shown great potential. The Pt/TiO_2 electro-catalyst resulted in enhanced catalytic activity compared with that of pure platinum without an oxide matrix. Size-controlled platinum nano-particles were embedded in TiO_2 by sputtering. Through electronic microscopic images, the mean diameter of the platinum nanoparticles was varied from about 2 to 4 nanometers and the platinum nanoparticles were confirmed to be polycrystalline as the TiO_2 matrix was amorphous (Sung, et al., 2011). It was justified that the electronic structure of the platinum catalyst depends mainly on particle size and the TiO_2 support, which weakens the Pt-CO bonding due to changes in chemisorption properties (Sung, et al., 2011). The presence of the TiO_2 support played a major role in improving tolerance of CO oxidation because of a higher electronic density on platinum. The electronic interaction between Pt and TiO_2 increased the electronic density on Pt and therefore weakened the CO adsorption. Since the reaction between the absorbed CO and oxygen atoms or OH groups are rate-determining steps during CO oxidation, the presence of weakly bonded CO and oxygen on the Pt surface favored higher reaction rates. Therefore, the TiO_2 support has the ability to provide highly reactive oxygen species and thus show good tolerance toward CO oxidation (Sung, et al., 2011).

3.3.1 Tin Oxide Support Properties

The use of tin oxide as a substrate in fuel cells offers many advantages over the widely used carbon. One of the main advantages of tin oxide is it's resistance to oxidation when exposed

to high potentials. Electrochemical properties of SnO_2 and carbon supports were examined using cyclic voltammetry (CV) as potential was varied from 0 to 1.3 V (Zhang, et al., 2010). It was discovered that at potentials above 0.9 V, the current for carbon supports increased while the current observed for SnO_2 support was small, indicating that tin oxide is highly resistant to oxidation when subjected to high potentials. This property of tin oxide relieves the problem of the carbon substrate's susceptibility to corrosion. Tin oxide does not oxidize within the cell, which allows for improved efficiency and durability. The resistance to oxidation also means that none of the valuable platinum within the substrate will be wasted and the use will be maximized in order to lower costs with less platinum and increase efficiency.

The lattice structure of the tin oxide substrate allows for easy manipulation of pore size, making it a favorable material. This is important since the substrate is impregnated with nano-sized platinum particles. Being able to control the distribution can help make the process more effective by evenly distributing the platinum over the entire surface with a desired concentration (20-60 wt %).

Another characteristic about tin oxide substrate is that it helps with the reduction of oxygen in the cell reaction. It also displays many traits associated with semiconductors. These characteristics are a major factor as to why tin oxide has been used in gas sensors to detect hydrogen and other gases. In gas sensors, the specific surface area of the material being used is one of the main determinants of its effectiveness. The specific surface area is largely based on a material's ability to become porous. Tin oxide is able to be both mesoporous and macroporous, making it a widely used material in gas sensors.

3.3.2 Pt/SnO2 as an Electrocatalyst

Although ruthenium alloyed with supported platinum increases the CO tolerance of the catalyst, the tolerance level is still very inefficient and not economical for commercialization (Matsui, et al., 2005). They studied the use of SnO_2-supported platinum catalysts, which are well known catalysts for gas phase CO oxidation without CO poisoning the platinum. This electrochemical oxidation of CO was analyzed and compared with Pt/C and PtRu/C catalysts. Through CO stripping voltammetry, it was observed by Matsui et al. (2005) that the peak potential of pre-adsorbed CO was almost the same as the Pt/C catalyst, but greater than that of the PtRu/C catalyst, as shown in Figure 7.
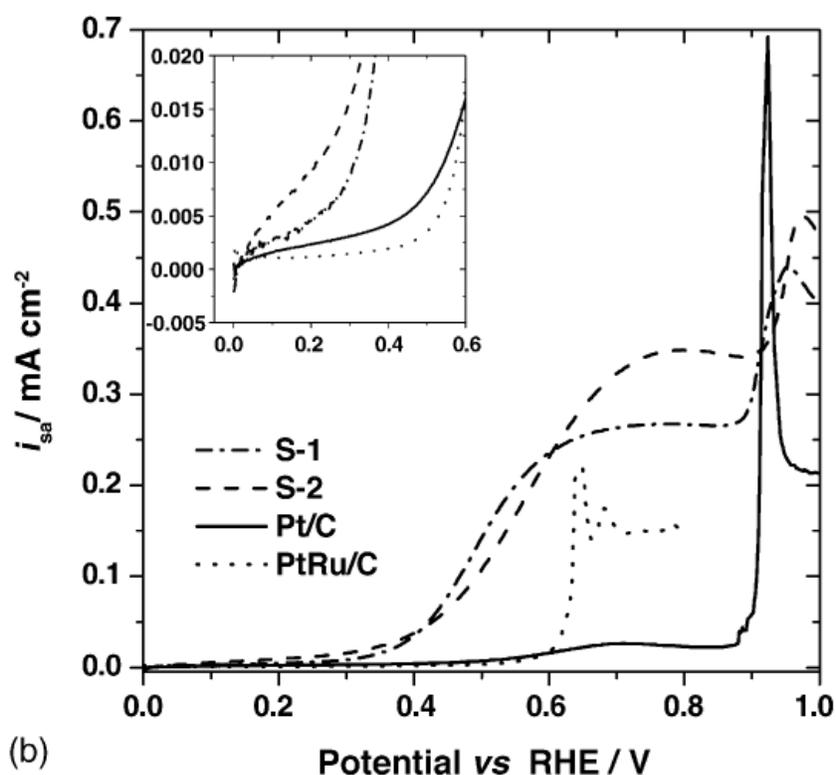
Figure 7. CO Oxidation Comparison

The S-1 and S-2 graphs represent Pt/SnO$_2$ catalysts synthesized by different procedures. At potentials lower than 0.9 V, which is approximately the peak potential for all the catalysts

besides PtRu/C, the Pt/SnO$_2$ catalysts showed great electrocatalytic activity for CO oxidation due to high oxidation peaks. It was concluded that Pt/SnO$_2$ catalysts promote oxidation of CO into CO$_2$ better than PtRu/C catalysts and therefore can increase CO tolerance.

Tin oxide-supported platinum is also a suitable catalyst for the oxygen reduction reaction that takes place on the cathode side of the fuel cell.

Figure 8 depicts the mass activities of the catalysts divided by the platinum mass at 0.85 V.
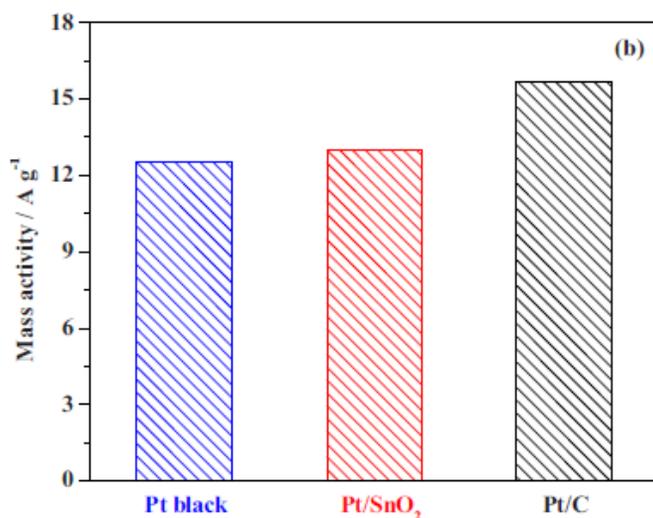
Figure 8. Mass Activities for Oxygen Reduction Reaction

It was shown that the Pt/SnO$_2$ catalyst displayed a slightly higher mass activity compared to Pt black. The improved activity is due to good dispersion of Pt nanoparticles on the SnO$_2$ support and also excellent interaction between the SnO$_2$ support and the Pt nanoparticles. This makes Pt/SnO$_2$ a suitable catalyst for the oxygen reduction reaction at the cathode (Zhang, et al., 2010).

It was also shown that Pt/SnO$_2$ catalysts are more stable and corrosion resistant than Pt/C catalysts. According to Zhang et al. (2010), both samples showed a gradual decline in surface area with potential cycling (1800 cycles) due to the loss of platinum active sites. However, the

Pt/C catalyst had a 60% loss in surface area while the Pt/SnO$_2$ catalyst had only a 40% loss in surface area under similar conditions, as shown in Figure 9.
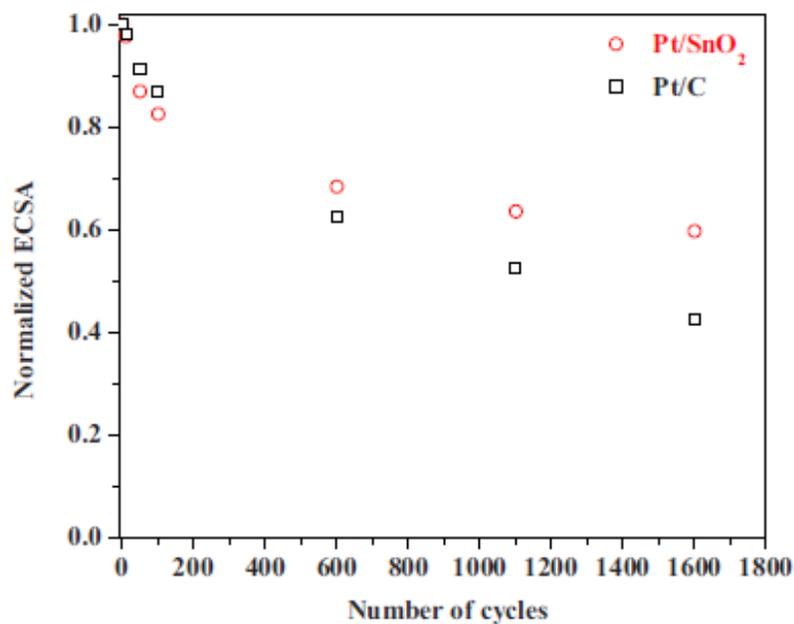
Figure 9. Electrochemical Surface Area (ECSA) Loss Comparison for Pt/SnO$_2$ and Pt/C

This indicated that the Pt/SnO$_2$ catalyst was more electrochemically stable. The smaller surface area loss can also be related to its corrosion resistant properties.

3.3.3 Increasing Tin Oxide Conductivity

Tin oxide can become more conductive by doping it with hypervalent donors; this leads to an increase in electronic conductivity and also improves the electrocatalytic activity associated with charge transfer processes.

According to Takasaki et al. (2011), carbon-free Pt electrocatalysts using tin oxide as the electrocatalyst support material were prepared and its electrocatalytic activity and durability were characterized against voltage cycling. The results of this test are shown in Figure 10. It was shown that electronic activity could be improved by doping SnO$_2$ with Nb^{5+} and Sb^{5+}, even though durability slightly decreased.
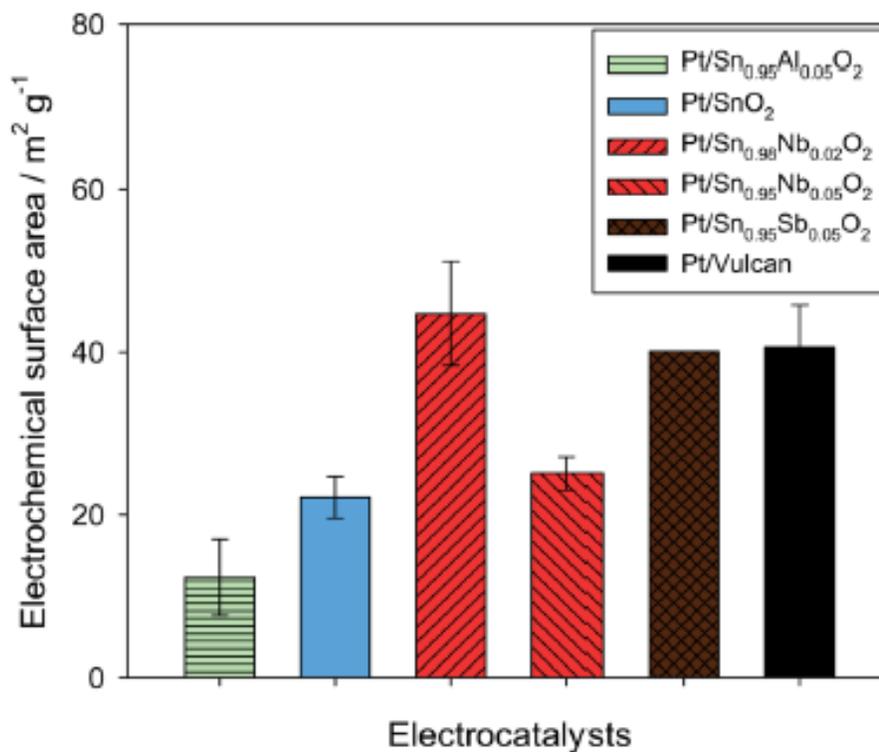
Figure 10. Electrochemical Surface Area of Various Electrocatalysts

3.3.4 Disadvantages of Tin Oxide

Despite many advantages, tin oxide also has many disadvantages as a platinum catalyst support. Cost is probably the biggest. Since carbon is much cheaper, it is much more widely used and studied. Compared to other metal oxides, tin oxide is actually one of the least expensive materials but it is still more expensive than carbon. Tin oxide is also more difficult to work with than carbon, making the synthesis process more cumbersome. Whereas carbon usually requires only a single step to have the platinum impregnated, tin oxide usually needs to be synthesized separately to meet required characteristics before it undergoes the impregnation process.

4.0 Methodology

The ability to manipulate the Pt/SnO_2 particle size within a small range (~<5 nm) is critical for maximum fuel cell performance and for the effective utilization of raw materials. Two synthesis procedures and their effect on the product size are herein reported: the colloidal method and the impregnation method. Other variables that were taken into consideration are the strength of the reducing agent, the reaction time, and the subsequent stirring time. The products were then isolated and characterized by a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy-dispersive x-ray microscopy (EDX) in order to determine particle size, distribution, and composition. Cyclic voltammetry was used to determine the electrochemical properties of the Pt/SnO_2 material. An overview of the experimental process is shown in Figure 11. Exact variables used are shown in Table 2.
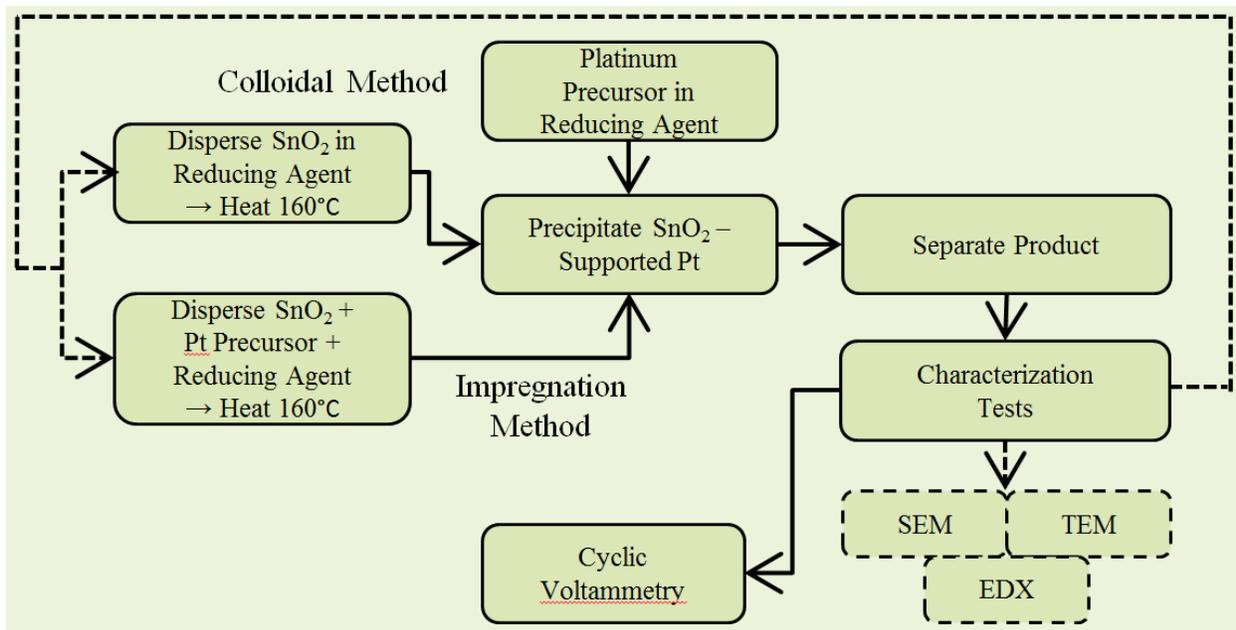
Figure 11. Experimental Overview

Table 2. Experimental Variable Data

Experiment	SnO$_2$ (g)	SnO$_2$ Solvent (mL)	Pt Precursor (10mg/mL) (mL)	Theoretical Loading	Process	Reducing Agent	Rxn Time (hrs)	Stir Time (days)
1	0.0201	DI (25)	1.33	20	Impreg	NaBH$_4$	N/A	1
2	0.0302	EG (13)	2.00	20	Colloidal	EG	3	2
3	0.0305	EG (10)	2.00	20	Colloidal	EG	4	1
5	0.0304	EG (10)	2.00	20	Impreg	EG	4	2
6	0.0306	EG (10)	6.00	42	Colloidal	EG	4	2
7	0.0306	DI (25)	N/A	40	Impreg	EG	4	2
8	0.0930	EG (30)	16.53	40	Colloidal	EG	4	2
9	0.0917	EG (30)	36.70	60	Colloidal	EG	4	2
10	0.0934	EG (30)	6.23	20	Colloidal	EG	4	2
12	0.0899*	EG (30)	16.53	40	Colloidal	EG	4	2
13	0.0900*	EG (30)	6.00	20	Colloidal	EG	4	2
14	0.0903**	EG (30)	36.70	60	Colloidal	EG	4	2

*NanoArc© tin oxide

**calcinated NanoArc© tin oxide

DI = distilled water, EG = ethylene glycol

4.1 Preparation of Platinum Precursor Solution

The necessary platinum nanoparticles were reduced from a precursor solution of chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot (H_2O)_6$, Sigma-Aldrich, >37.50% Pt basis). The reduction of chloroplatinic acid occurs by the following reactions:

$$H_2PtCl_6 \cdot 6H_2O \rightleftharpoons PtCl_4 + 2HCl + 6H_2O$$

$$PtCl_4 \rightleftharpoons PtCl_2 + Cl_2$$

$$PtCl_2 \rightleftharpoons Pt + Cl_2$$

For the impregnation method, chloroplatinic acid was dissolved in distilled water to produce a 10 mg/mL solution. For the colloidal method, where ethylene glycol was used as the solvent/reducing agent, it was necessary to dissolve the chloroplatinic acid directly in EG instead of water to produce a 10 mg/mL solution. This of course means that even prior to its introduction to tin oxide, some of the platinum particles begin to reduce into nanoparticulates – without the benefit of reacting with tin oxide at 160^0C. It was important to avoid the combination of water and EG because previous research has shown that even small amounts of water greatly increases

the size of the resulting particle (Li et al., 2003). The effects demonstrated by Li, et al's experiment are shown in Table 3.

Table 3. Effect of DI Water Content in EG Solution on the Preparation of Pt/MWNTs

DI water content (%, volume ratio)	Pt particle size (nm)
0	2.0
5	2.5
15	3.2
40	4.0
70	4.5

[a] Determined by the Scherrer formula from the Pt (220) peak.

The consequence of this procedure was shown to be negligible as the resulting particle sizes were found to be within the desirable range.

4.2 Notes on Tin Oxide

For these experiments, tin oxide that was already available in the lab from an unknown source was used. The tin oxide was used as-received except for Experiment #14 where the tin oxide was calcinated in a $400^{0}C$ oven for 6 hours. This process has many effects such as oxidation and decomposition of volatile compounds and is thought to be a general step necessary for the preparation of the tin oxide material for electrocatalytic applications. Many sources that used off-the-shelf tin oxide as well as sources that used lab synthesized tin oxide involved calcination before further processing (Kamiucu, N., et al, 2009; Zhang, P., et al, 2010).

Experiments 1-7 were pilot tests so relatively small amounts of tin oxide were used, as shown in Table 2. Ideal conditions were determined by these pilot tests and beginning with Experiment 8, efforts were scaled-up in anticipation of characterization tests that would require a larger sample.

4.3 Testing Optimum of Reducing Agent

It was necessary to determine the effect of the strength of reducing agents on Pt particle size. Two different chemicals were tested: $NaBH_4$ (Alfa Aesar, 98%) and ethylene glycol (Sigma-Aldrich, 99.99%). $NaBH_4$ is a relatively strong reducing agent compared to ethylene glycol. The impregnation procedure was used for both experiments since it is relatively simple to perform compared to the colloidal method.

4.3.1 Sodium Borohydride (Exp #1)

SnO_2 (20 mg) was dispersed in 25-mL distilled water by sonicating for 30 minutes, stirring for 30 minutes, followed by sonication for 1 hour. These steps ensured that the tin oxide particles were not congregated and were well-dispersed, thus allowing for more efficient and complete reaction. The mixture was secured in a clamp with stirring.

The appropriate amount of platinum precursor (1.33 mL) to produce a 20 wt% Pt-basis product was sonicated for 15 minutes, stirred for 15 minutes, and then introduced to the tin oxide drop-wise using a syringe. Then, freshly made 0.1M $NaBH_4$ solution (1.0 mL) was slowly added. The mixture was allowed to stir overnight. Procedure continues in Section 5.6.

4.3.2 Ethylene Glycol (Exp #5)

The procedure for using ethylene glycol as the reducing agent is only slightly different from the procedure for sodium borohydride. SnO_2 (30 mg) was dissolved in 10-mL ethylene glycol by sonicating for 30 minutes, stirring for 30 minutes, followed by sonication for 1 hour. These steps ensured that the tin oxide particles were not agglomerated and were well-dispersed, thus allowing for more efficient and complete reaction.

The mixture with stirring was secured in a heating mantle controlled by a temperature controller (Cole-Palmer EW-89000-10) and a J-type thermocouple (Cole-Palmer), as shown in Figure 13. A counter-current water reflux was implemented. The set-up was purged with nitrogen for ten minutes prior to heating in order to induce an inert atmosphere so that the ethylene glycol would remain stable.
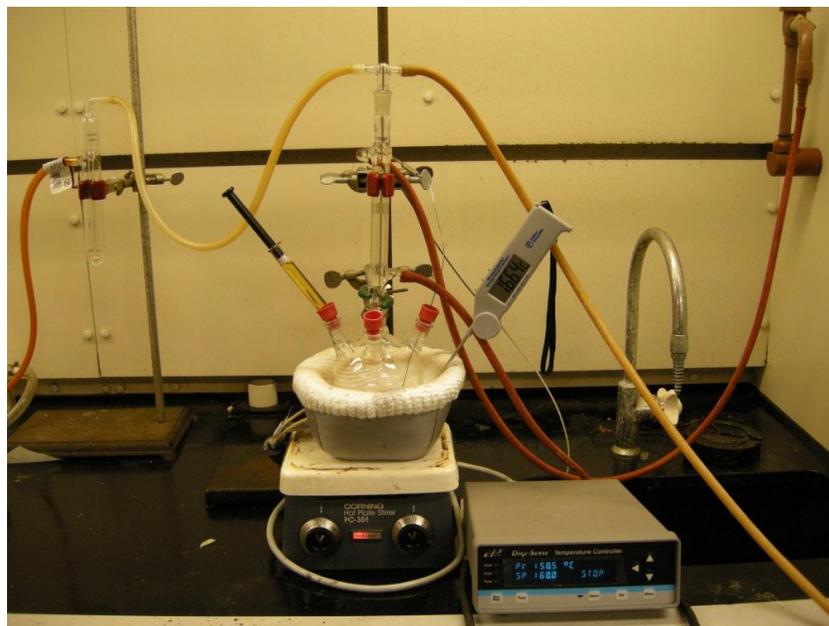
Figure 12. Colloidal Set-up with Ethylene Glycol

The appropriate amount of platinum precursor (2.00 mL) to produce a 20 wt% Pt-basis product was diluted with 5-mL EG, sonicated for 15 minutes, stirred for 15 minutes, and then introduced to the tin oxide drop-wise (1 drop/sec) using a syringe. The mixture was heated to 160°C and allowed to react for 3 hours, starting when the solution first reaches the reaction temperature. The heater was turned off. When the mixture cooled to 60°C, the water reflux and nitrogen were turned off and it was allowed to stir for 2 days. Procedure continues in Section 5.6.

4.4 Testing Impregnation vs. Colloidal Method

Having determined ethylene glycol as the preferred reducing agent, differences between the impregnation and colloidal method were next evaluated. The procedure for the colloidal process with EG is very similar to the impregnation process with EG – differing only in the point at which the platinum precursor is introduced.

4.4.1 Colloidal Method (Exp #6)

SnO_2 (30 mg) was dissolved in 10-mL ethylene glycol by sonicating for 30 minutes, stirring for 30 minutes, followed by sonication for 1 hour. These steps ensured that the tin oxide particles were not agglomerated and were well-dispersed, thus allowing for more efficient and complete reaction.

The set-up for the colloidal method with ethylene glycol is the same as for the impregnation method, as previously shown in Figure 13.

The appropriate amount of platinum precursor (2.00 mL) to produce a 20 wt% Pt-basis product was diluted with 5-mL EG, sonicated for 15 minutes, and stirred for at least 15 minutes until it was ready to be mixed with tin oxide. When the tin oxide was up to the temperature, the Pt precursor was injected drop-wise (1 drop/sec) using a syringe. It was necessary to remove the rubber stopper several times during the reaction in order to refill the syringe, so this was done quickly. Based on the results, the effects of disturbing the nitrogen atmosphere appear to be minimal if done swiftly. The mixture was allowed to react for 3 hours, starting from when the Pt precursor was first injected. The heater was turned off. When the mixture cooled to 60°C, the water reflux and nitrogen were turned off and it was allowed to stir overnight. Procedure continues in Section 5.6. The results of this experiment were compared with the results of Experiment #5.

4.5 Testing Variations in Reaction and Stirring Time (Exp #2, 3, and 6)

After settling on the colloidal process and ethylene glycol as the reducing agent, TEM images revealed there was incomplete adhesion between the platinum and tin oxide particles. The reaction and stirring time were varied in order to improve particle interaction and to reduce the waste of reactants. The same procedure as described in section 5.4.1 was used, except stirring and reaction time were varied as shown in Table 4.

Table 4. Reaction and Stirring Variables

Experiment	Process	Reducing Agent	Reaction Time (hrs)	Stirring Time (days)
2	Colloidal	EG	3	2
3	Colloidal	EG	4	1
6	Colloidal	EG	4	2

4.6 Separation of Pt/SnO2 from Reaction Mixture

At the end of stirring, the reaction mixture was transferred to a beaker. The mixture was transferred to six 2-mL plastic conical centrifuge tubes. They were centrifuged until a clear separation layer was noticeable, as shown in Figure 13, approximately 20-45 minutes.
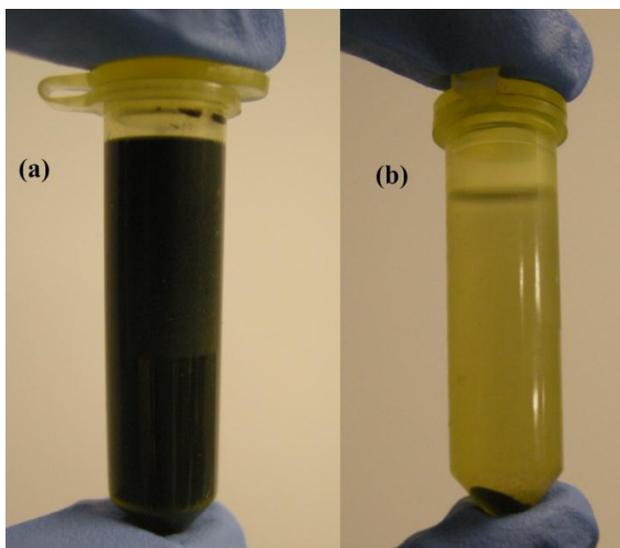

Figure 13. Reaction Mixture Before (a) and After (b) Centrifugation

The top "clear" layer was carefully removed via glass pipette. Then, more of the reaction mixture was transferred to the tubes. The collection of material on the bottom of the tubes was dispersed by a combination of shaking and sonication. They were centrifuged again and the steps were repeated until all the reaction mixture was separated. After the final top layer was removed, it was necessary to clean the product material several times with distilled water. The previous steps were repeated except that the tubes were filled with distilled water. This was done at least three times. Afterwards, the tubes were left open to dry on the counter. It was then suitable for observation under SEM and EDX.

4.7 Preparation of Sample for TEM

After the third separation described in Section 5.6, 0.5 mL of sample was transferred to an empty tube. It was diluted with distilled water until it appeared not too light and not too dark. The sample was sonicated for at least 45 minutes. About 2-5 drops of the mixture was deposited onto a 300 mesh copper grid and allowed to dry overnight on the counter. The sample was observed using TEM. An image of the 300 mesh copper grid is shown in Figure 14
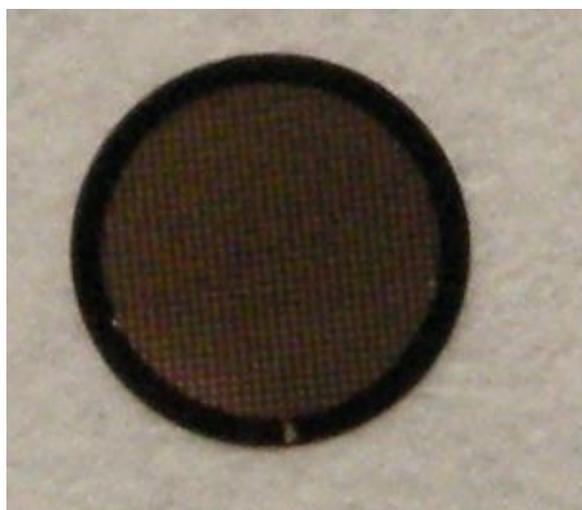
Figure 14. 300 Mesh Copper Grid for TEM

4.8 Cyclic Voltammetric Test

The measurable current that could be achieved by the prepared electrocatalyst was found by cyclic voltammetry using the standard three-electrode configuration consisting of a glassy carbon electrode, platinum mesh electrode, and Ag/AgCl as the working, counter, and reference electrode, respectively, as shown in Figure 15.
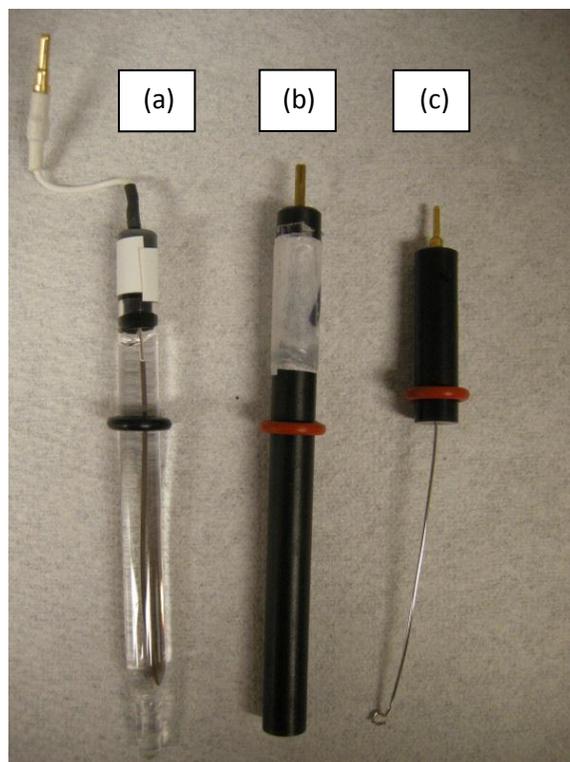
Figure 15. (a) Reference, (b) Working, (c) Counter Electrode

This test involved the dispersion of the chosen material (ie. tin oxide, XC-72 carbon, tin oxide-supported platinum, XC-72 carbon-supported platinum) in a solvent, coating of the slurry onto the working electrode, and then subjecting the sample to a sweeping voltage for hundreds of cycles. There were many intervening steps, which will be elaborated upon in the following sections.

4.8.1 Polishing Working Electrode

The surface of the working electrode required cleaning and polishing prior to every test. It was gently washed with distilled water and dried under pressurized air. A special leather pad was wetted with distilled water and then 1-2 drops of alumina polishing solution was dropped in the center. The working electrode was very gently rubbed against the pad and alumina in medium circular motions for about 30 seconds, using enough strength to maintain contact but not so aggressive to potentially damage the surface, as shown in Figure 16.
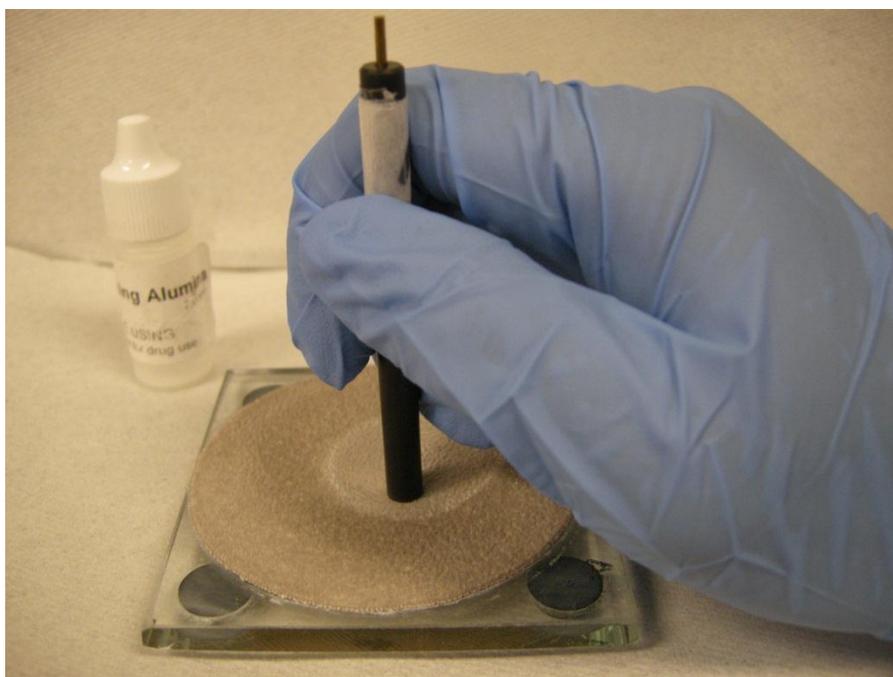
Figure 16. Polishing Working Electrode

It was important to polish the electrode in only one direction, either clockwise or counter-clockwise, without changing directions in the middle of the process. After 30 seconds, the electrode was gently rinsed with distilled water and dried with pressurized air. The electrode was tested using a 2mM potassium ferricyanide with 1M potassium nitrate in water solution. The result of this test determined if the polishing had been adequately performed or if further polishing was required.

4.8.2 Testing of Working Electrode

The reference, working, and counter electrode were immersed in a 2mM potassium ferricyanide with 1M potassium nitrate in water test solution, as shown in Figure 17.

Figure 17. Electrodes Set-up for Testing

The electroanalyzer was turned on and then the BAS100W program was opened. In methods, sweep techniques and cyclic voltammetry were selected, as shown in Figure 18.
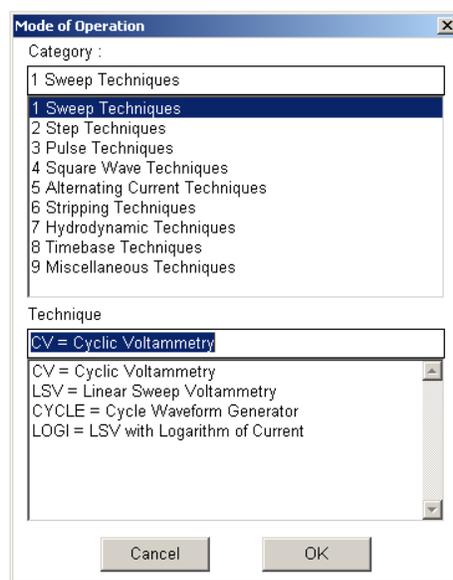
Figure 18. Selecting Mode of Operation in BAS100W

On the next screen, the values for low and high voltage, etc. are shown in Figure 19.

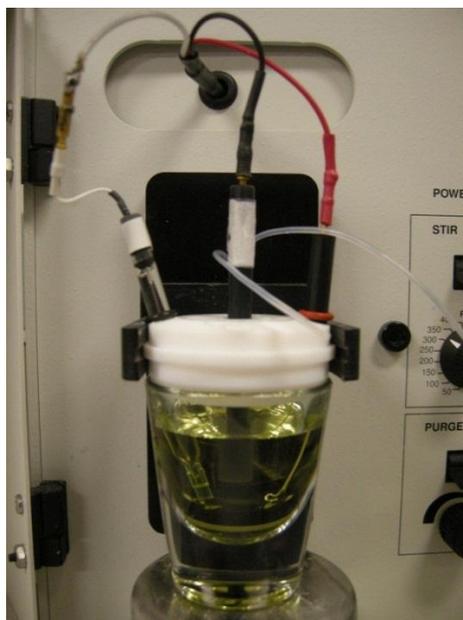**Figure 19. BAS100W Parameters for Testing Working Electrode**

Then, the run was started. If the difference in potential between the two peaks was less than 75 mV, then the working electrode was adequately polished and was ready for testing with a coated material. If the difference between the two peaks was greater than 76, then the electrode should be repolished; a 74-75 difference is borderline and should be repolished, if desired.

The electrodes were removed from the solution and thoroughly washed with distilled water and dried. The reference electrode was returned to its saline vessel.

4.8.3 Coating Sample onto Working Electrode

A slurry of the catalyst material was prepared by combining 20 mg of sample with 7-mL distilled water, 3 drops of 5 wt% Nafion in isopropanol, and then sonicated for 2 hours. The working electrode was secured level in a clamp with the polished surface facing upwards. Using a pipette, 7.0 microliters of the homogenous slurry (just enough to form a drop on the pipette tip

without falling) was transferred directly onto the center of polished surface. The result is shown

in Figure 20.
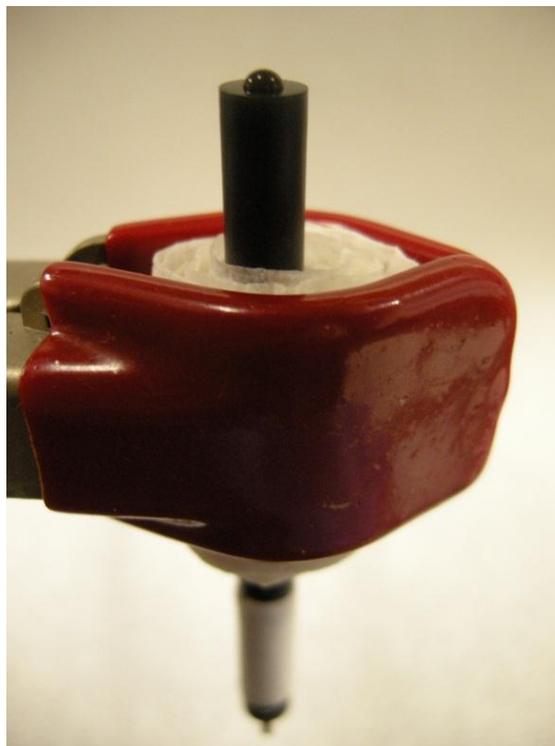
Figure 20. Sample Deposited onto Working Electrode

After the sample was completely dried, another drop was applied. In total 2-5

drops/layers were applied to the electrode surface depending on the observed coverage; the

sample should be covering all parts of the shiny area. Note that the homogenous slurry was

sonicating during the intervening time between layers, thus ensuring well-dispersed particles.

After the appropriate number of layers was applied, a drop of 0.5wt% Nafion in methanol

solution was applied to the electrode surface. This acts as a binder and prevents the material from

peeling or falling off during the CV test. Figure 21 shows the desirable coverage of the electrode

surface.
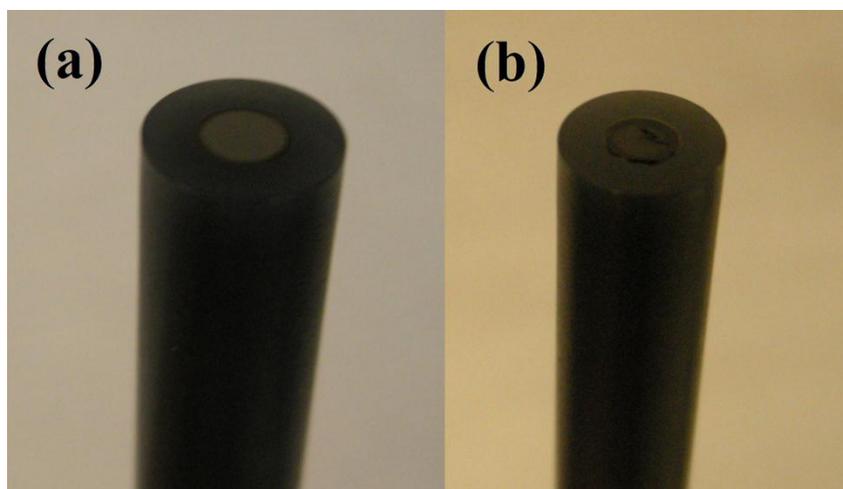
Figure 21. Working Electrode Without (a) and With (b) Sample Coated on Surface

4.8.4 Testing of Working Electrode with Sample

The procedure for measuring the current produced by the sample is similar to the procedure for testing the blank working electrode. The reference, working, and counter electrode were immersed in a 0.5 M methanol with 1 M sulfuric acid solution; this simulates the environment found in direct methanol fuel cells. The electroanalyzer was turned on and then the BAS100W program was opened. In methods, sweep techniques and cyclic voltammetry were selected, as before. On the next screen, the values for low and high voltage, etc. are shown in Figure 22; these values are different than before.
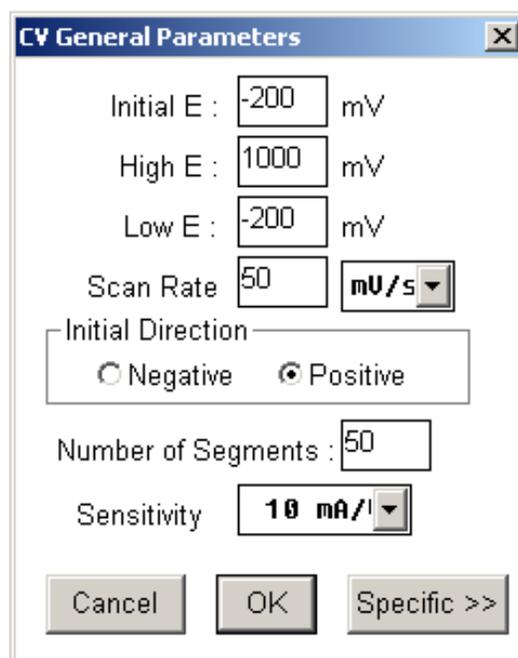
Figure 22. BAS100W Parameters for Testing Working Electrode with Sample

Then, the run was started. After one run was completed, it was saved and another run was started. Runs were continued until the measured current remained constant for a long period of time.

The electrodes were removed from the solution and thoroughly washed with distilled water. They were then dried with air. The reference electrode was returned to its saline vessel.

5.0 Results and Discussion

The results of the experiments provided valuable information regarding the optimal conditions for the synthesis of tin oxide-supported platinum as well as its feasibility as an electrocatalyst support for direct methanol fuel cells. Regarding the synthesis, several variables were changed in order to optimize conditions and achieve the target platinum particle size (<5 nm) with even distribution.

5.1 Strength of Reducing Agent

The strength of various reducing agents was investigated in order to determine their effect on the size of the synthesized platinum nanoparticles on tin oxide. The two reducing agents used were sodium borohydride, a relatively strong reducing agent, and ethylene glycol, a relatively weak reducing agent. Both experiments were performed using the impregnation method because it is a fast and simple process. Regardless, the purpose of this experiment was to determine the preferred reducing agent for future experiments.

As can be seen from Figures 23, the mean platinum particle size when using sodium borohydride as the reducing agent was 9.4 nm $\pm$ 1, while for ethylene glycol the mean platinum particle size was 8.2 nm $\pm$ 1, as shown in Figure 24. Ethylene glycol produced particles that were smaller on average. It can also be seen that the range in platinum particle sizes varies greatly. For both reducing agents, platinum particles were observed from 3 nm up to 22 nm. It would be advantageous to develop a more controllable synthesis method whereby the size of the platinum particles would not only be smaller on average but also kept within a smaller range.
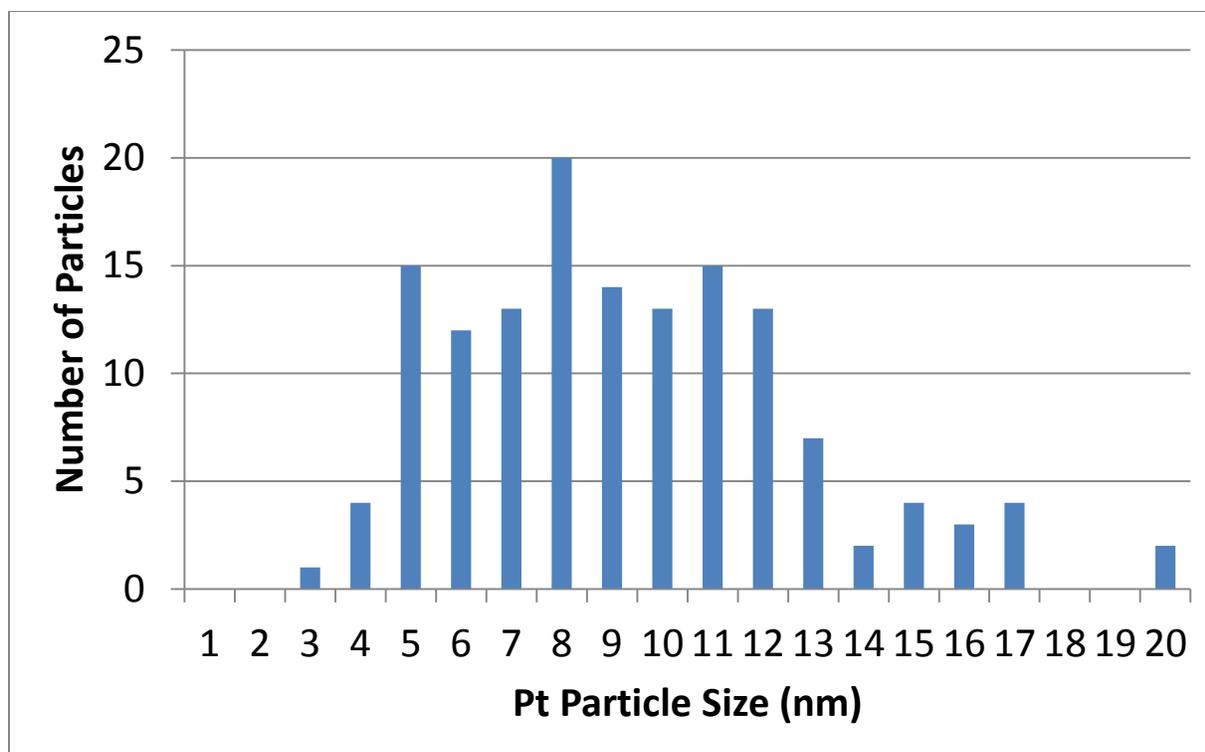
Figure 23. Pt Particle Size Distribution of Impregnation Method with NaBH₄
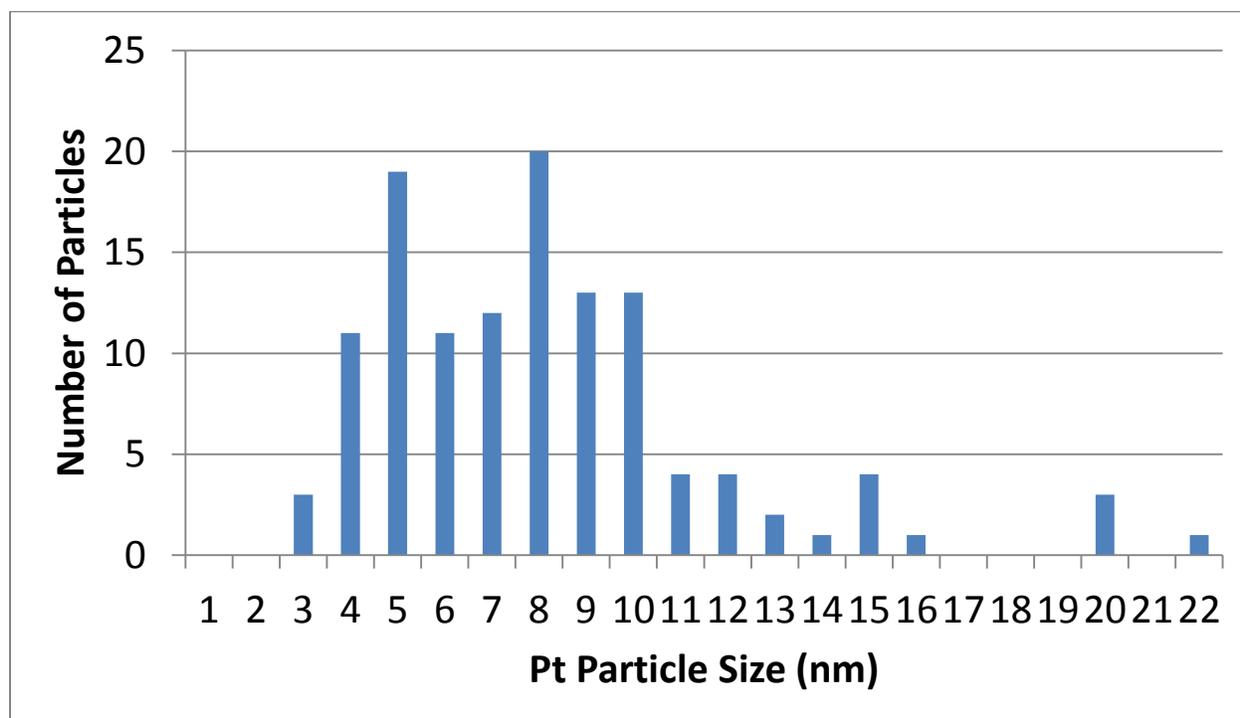
Figure 24. Pt Particle Size Distribution of Impregnation Method with Ethylene Glycol

It was concluded that using the weaker reducing agent, ethylene glycol, was the better choice since it resulted in a slower reaction rate, and therefore smaller particle sizes. Ethylene glycol produced smaller platinum nanoparticles than sodium borohydride.

5.2 Impregnation vs. Colloidal Method

Once the favorable reducing agent was determined to be ethylene glycol, a proper synthesis method that would result in smaller Pt particle size and range, and more even distribution on the tin oxide surface needed to be found. Two methods were compared, i.e., the impregnation method and the colloidal method. The main difference between the two methods is the point at which the platinum precursor is introduced to the reducing agent. In impregnation, all of the precursor is reduced at the same time since it is mixed with the tin oxide in the reducing agent before being heated to 160°C. With the colloidal method, the reducing agent and tin oxide are heated to 160°C first, and then the precursor is added drop-wise. This small difference ended up making a noticeable difference in particle size, as can be seen in the TEM images shown in Figures 25 and 26. Besides the size, it was evident that the platinum particles were very well-distributed on the tin oxide surface. It is also clear that there were no platinum particles floating in solution and that all the platinum particles adhered to the tin oxide.
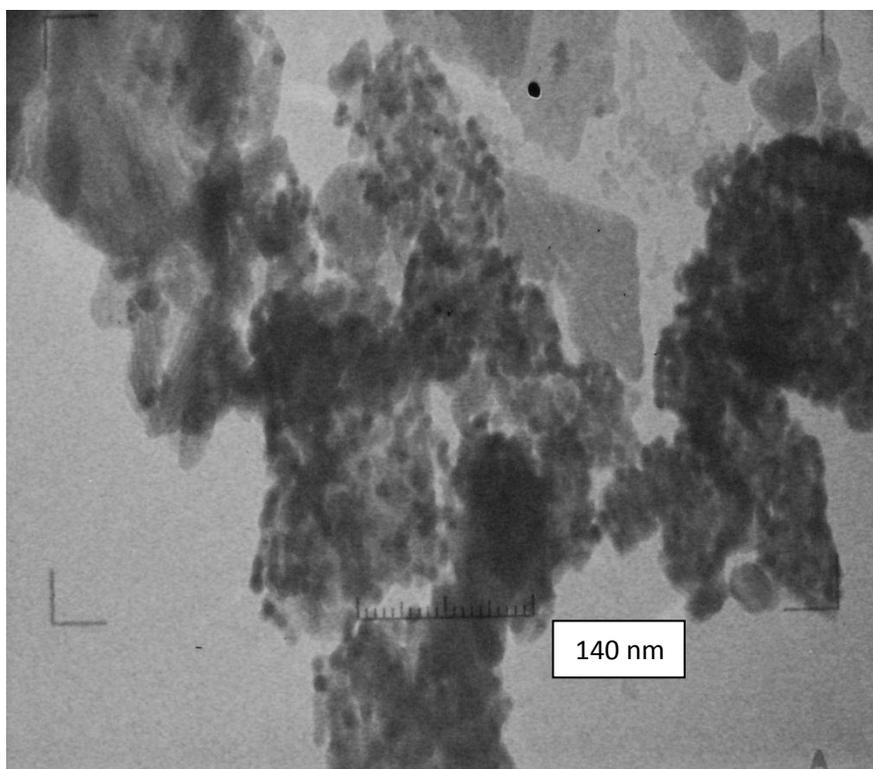
Figure 25. TEM of Pt-coated SnO$_2$; Impregnation Method with Ethylene Glycol
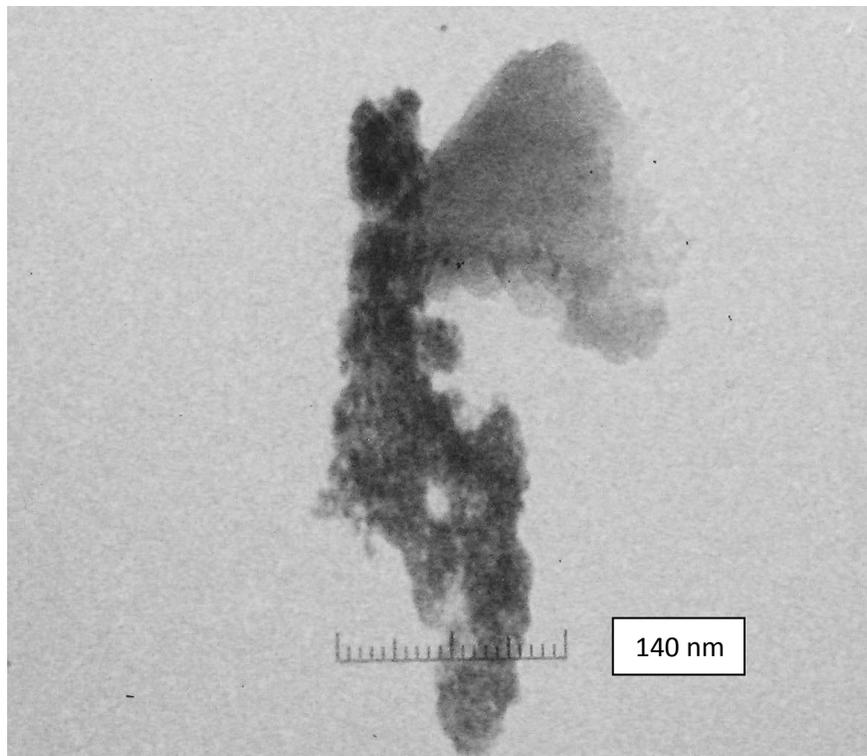
Figure 26. TEM of Pt-coated SnO$_2$; Colloidal Method with Ethylene Glycol

As previously shown in Figure 24, the mean platinum particle size produced by the impregnation method was 8.2 nm $\pm$ 1, while the mean platinum particle size produced by the colloidal method was 5.0 nm $\pm$ 1, shown in Figure 27.
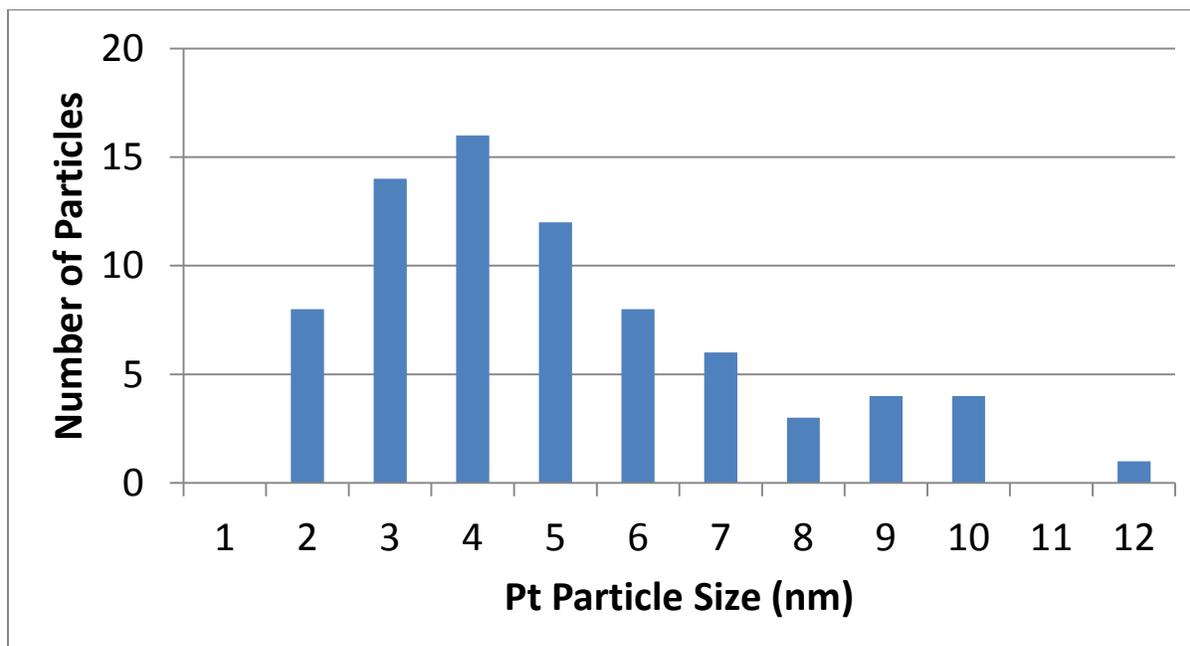
Figure 27. Pt Particle Size Distribution of Colloidal Method with Ethylene Glycol

It is clear that the colloidal method produced much smaller platinum particles than the impregnation method. Using the colloidal method, not only were the platinum particles smaller on average, but the range in sizes was also significantly reduced. The range in platinum particle size was reduced from 19 nm to 10 nm! This is extremely desirable as we are able to effectively control the synthesis of small platinum catalyst particles that will thereby make the fuel cell operate more efficiently.

It was found that the colloidal method was superior to the impregnation method, largely due to the way in which the platinum precursor was added. While using the colloidal method, platinum precursor was added drop-wise; this allowed for a complete reaction and kept the

concentration of the platinum very low since there was excess reducing agent. Since reaction rate is dependent upon concentration, adding the platinum and reducing agent drop-wise resulted in a lower reaction rate. During impregnation, since all the platinum is present, the concentration was much higher, meaning higher reaction rate, resulting in much larger particles.

5.3 Reaction and Stirring Time

Once the favorable reducing agent and synthesis method was found, reaction and stirring time were varied in order to optimize the utilization of reacting species. Reaction time referred to the time the solution was at reaction temperature (160°C), and stirring time referred to the total time starting when the mixture first reached 160°C. All other variable were kept constant throughout the experiments; all used the colloidal method with ethylene glycol as the reducing agent, and all were done with the same 20 weight percentage platinum.

As can be seen in Figures 26, 28, and 29 adjusting reaction and stirring time had a significant impact on the quality of the final Pt/SnO_2 product. In Experiment #2 using 3 hours reaction and 2 days stirring time, shown in Figure 28, a large number of platinum particles can be seen congregated on the left side near the tin oxide particles (right side) but did not actually adhere to them. Very few, if any, platinum particles can be seen attached to the tin oxide particles. We concluded that the particles did not have enough time to fully react and become free in the solution to adhere to the tin oxide.
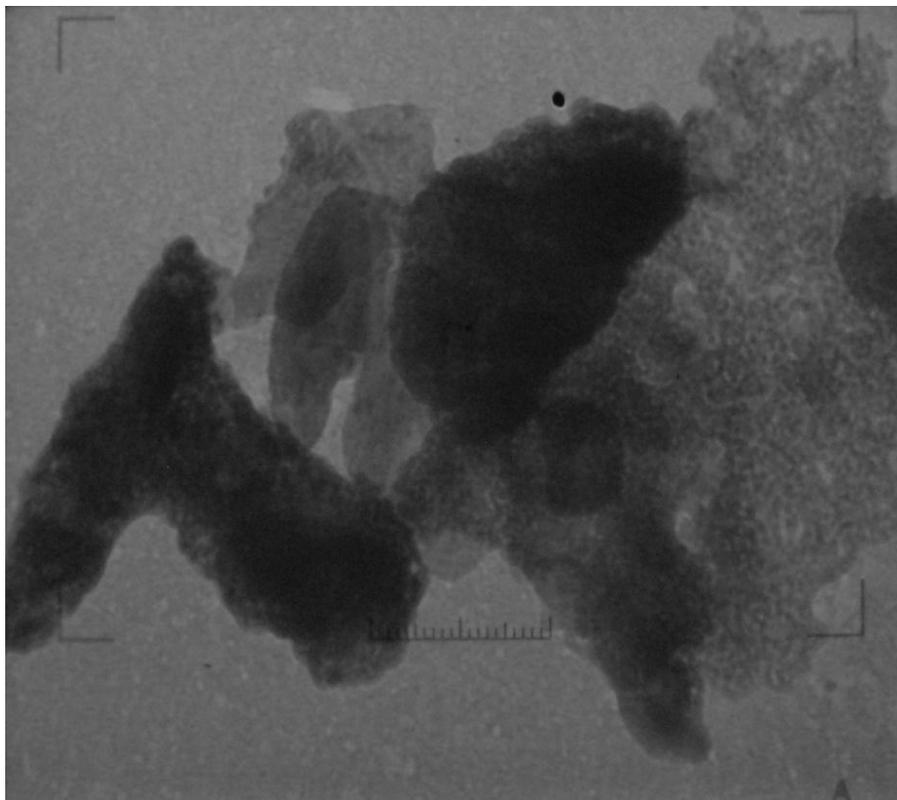
Figure 28. TEM of Pt/SnO$_2$; via Colloidal Method with 3 hour reaction and 2 days stirring
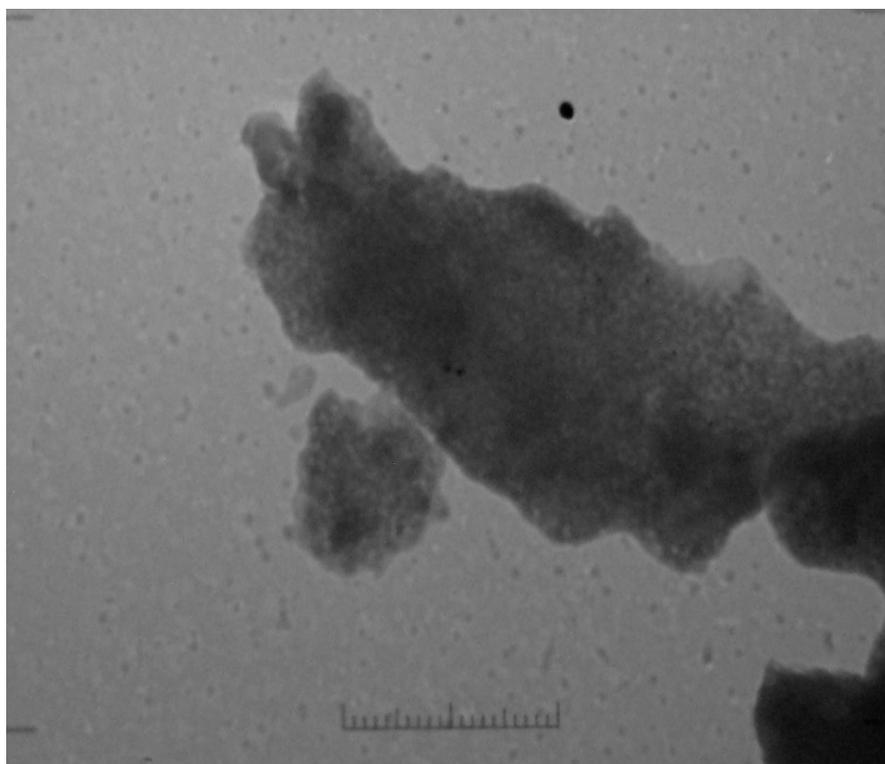
Figure 29. TEM of Pt/SnO$_2$; via Colloidal Method with 4 hour reaction and 1 day stirring

Experiment #3 using a 4 hour reaction and 1 day stirring time showed there was a good amount of bonding between the platinum and tin oxide but that there was also a large number of platinum particles floating freely in the solution, as shown in Figure 29. In the TEM image small platinum particles can be seen on the larger tin oxide particles. In the sea surrounding the tin oxide particles, however, many small platinum particles can be detected. These particles failed to adhere to the tin oxide and are essentially useless and would be lost if the material was further processed. It was concluded that while the platinum was fully reacted, it needed additional time to fully adhere to the tin oxide.

Experiment #6 combined the promising conditions previously tested by using 4 hour reaction and 2 days stirring time. The results are shown in Figure 26. Here, the platinum was evenly distributed and fully adhered to the tin oxide. No free particles can be found. It was concluded that longer reaction and stirring time resulted in better adhesion and distribution of platinum on the tin oxide.

5.4 Particle Morphology and Composition

The morphology and composition of the Pt/SnO_2 material was determined by SEM and EDX, respectively. The SEM image can be seen in Figure 30 and the EDX can be seen in Figure 31.
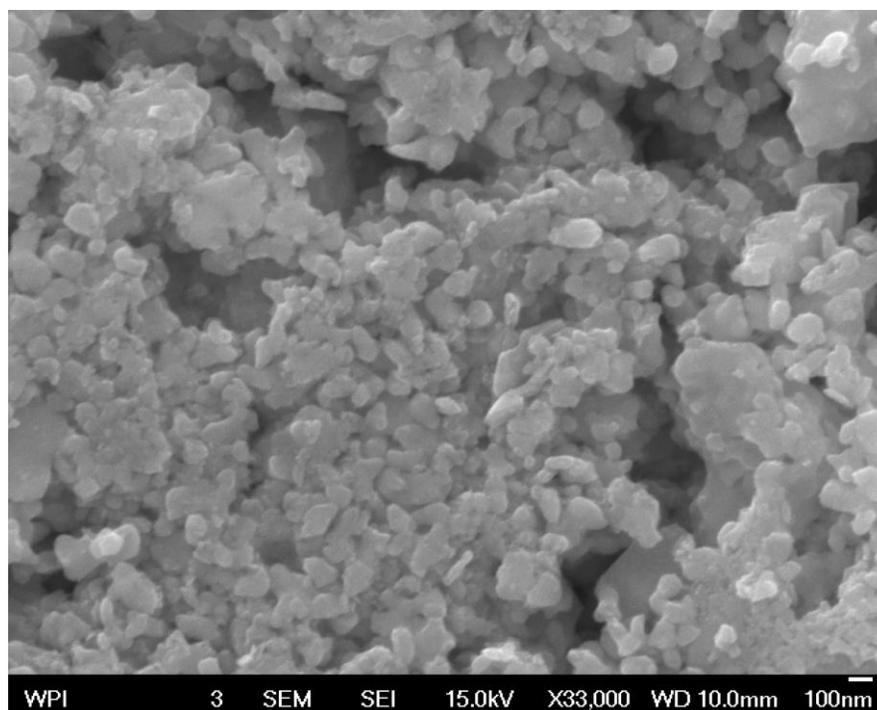
Figure 30. SEM of 20 wt% Pt-coated SnO$_2$
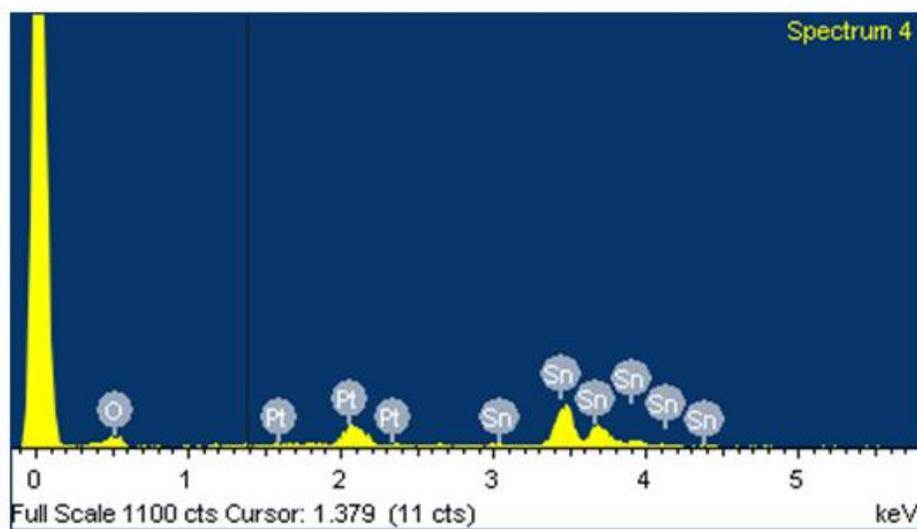
Element	Weight%	Atomic%
O K	23.49	71.13
Sn L	61.80	25.22
Pt M	14.71	3.65
Totals	100.00	

Figure 31. EDX of 20 wt% Pt-coated SnO$_2$

SEM partly helped to corroborate the conclusion regarding the achieved platinum particle size. Due to difficulties aligning the electron beam, the SEM was only able show particles up to 10 nm in size. EDX confirmed the presence of platinum. Since platinum particles were not observed on the tin oxide particles, it was concluded that the platinum particles were at least less than 10 nm in diameter.

SEM revealed the structure of the tin oxide material used in the experiments. The tin oxide particles were variously spherical, oblong, and square. The diameter of the particles ranged from 50-150 nm. They were evenly dispersed and were not clumped in any large areas.

EDX revealed the chemical composition of the sample and its relative ratios. It confirmed the purity of the samples, showing only platinum, tin, and oxygen, meaning foreign substances were not accidently added and that the sample was sufficiently washed during the separation process. It also confirmed the platinum weight loading percent on the tin oxide, meaning that precious platinum was not lost during the process and that it had all successfully adhered to the tin oxide. This was promising as waste of reacting species, especially expensive platinum, is undesirable.

5.5 Cyclic Voltammetry

Cyclic voltammetry measured the materials' electrochemical properties. Figures 32 and 33 show one run of the CV results for 20 wt% platinum supported on tin oxide and XC-72 carbon, respectively.
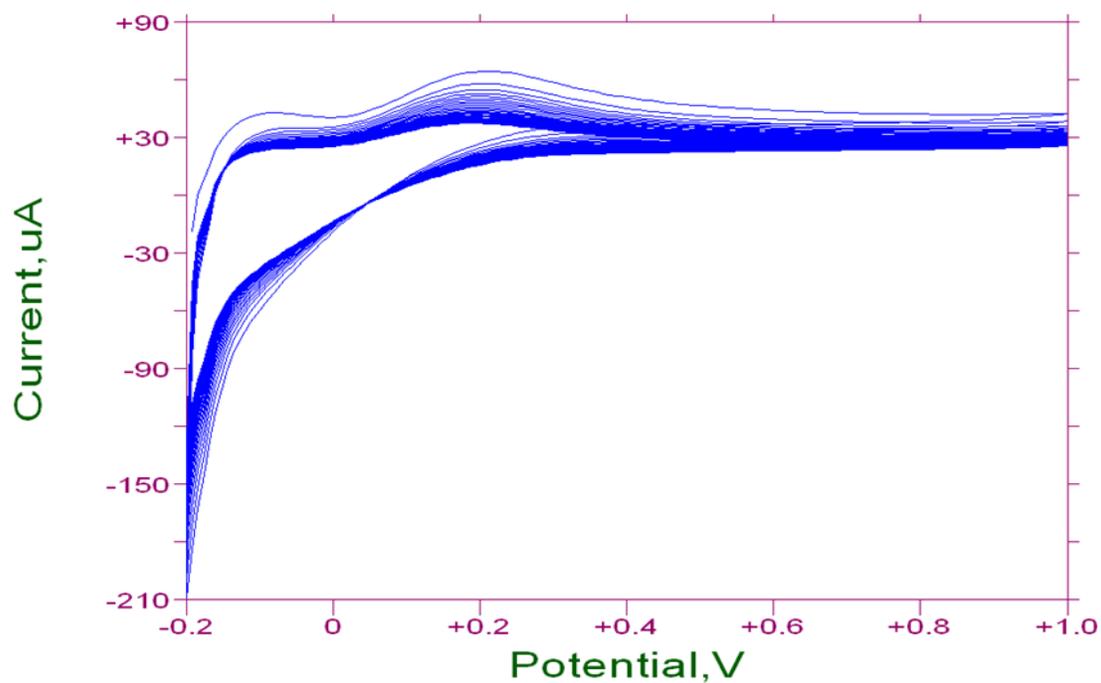
Figure 32. CV of Pt/SnO2 showing no methanol oxidation activity and virtually zero current
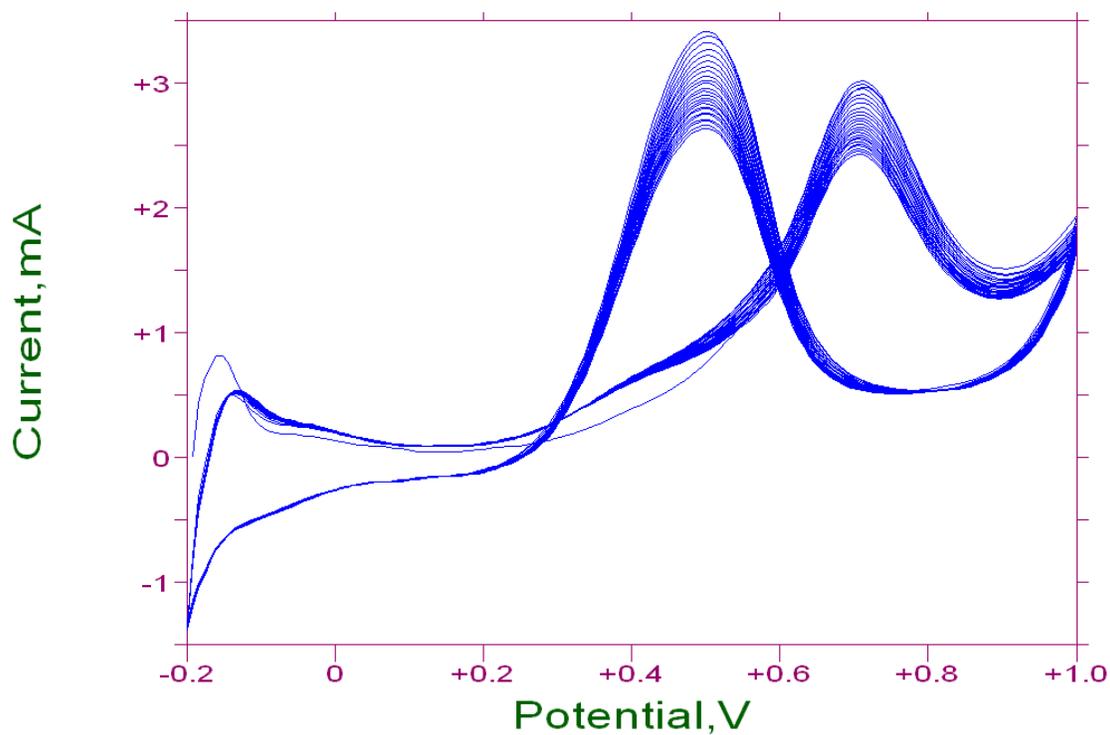
Figure 33. CV of Pt/C showing methanol oxidation activity over several cycles

As can be seen in Figure 33, carbon-supported platinum showed two distinct peaks, the left peak representing the oxidation of intermediates and the right peak representing the oxidation of methanol. However, with tin oxide we are unable to see any of these peaks. At the time, the reason for this was unknown. It might have been due to the platinum being unable to oxidize the methanol or that the tin oxide was unable to conduct a current. To pinpoint the problem, another test was performed using a fifty-fifty hybrid of 40 wt% Pt/SnO_2 and XC-72 carbon alone (resulting in a 20 wt% Pt/SnO_2 with XC-72). A mixture using unsupported carbon was used since carbon is a good electrical conductor. If the hybrid material developed oxidation peaks during the CV test, then it could be confirmed that the platinum catalyst was effective, that it was the tin oxide that was unable to conduct the current, and that tin oxide is the source of the problem. If methanol oxidation peaks were not observed, then the problem would have been with the platinum catalyst.

As shown in Figure 34, we see that the methanol oxidation peaks are indeed present with the fifty-fifty hybrid mix, meaning the platinum was actively participating in the methanol oxidation reaction but that the tin oxide was unable to conduct the current.
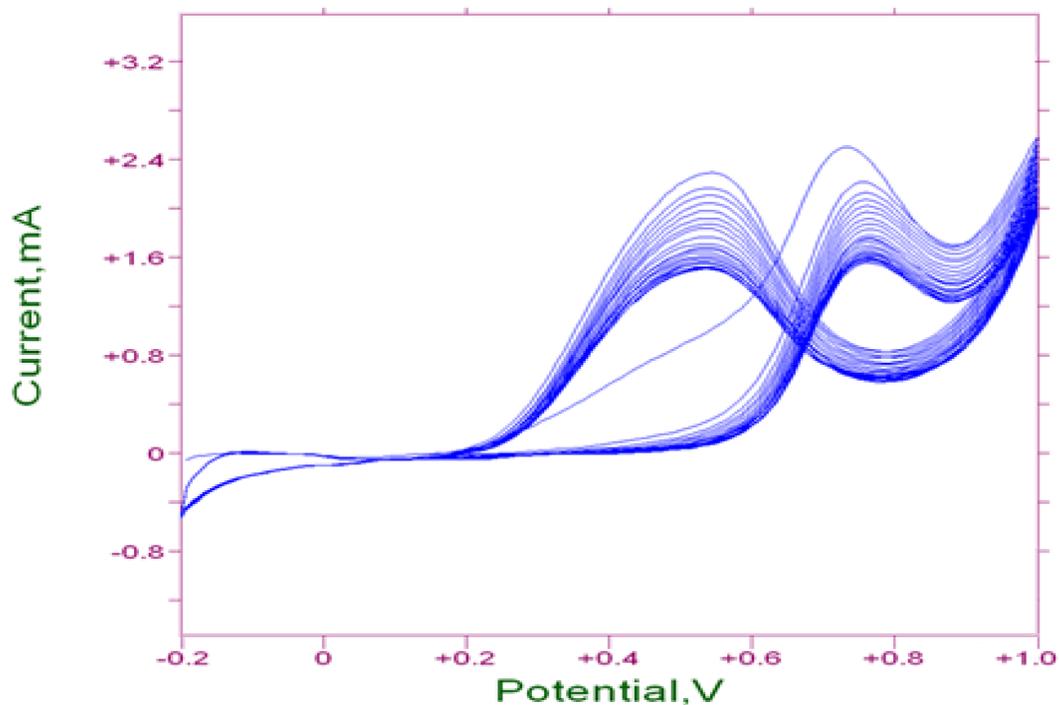
Figure 34. CV of 50:50 20 wt% Pt/SnO2 and XC-72 carbon showing methanol oxidation activity over several cycles

Despite this result, it does not appear that such a hybrid material can improve the performance of Pt/SnO$_2$ to economical level. As shown in Figure 35, the peak current density over time achieved by the hybrid mix is much less than that of platinum supported on conventional XC-72 carbon alone. Although a comprehensive cost analysis was not performed, it appears that mixing tin oxide and XC-72 Vulcan will not produce any cost-benefit.
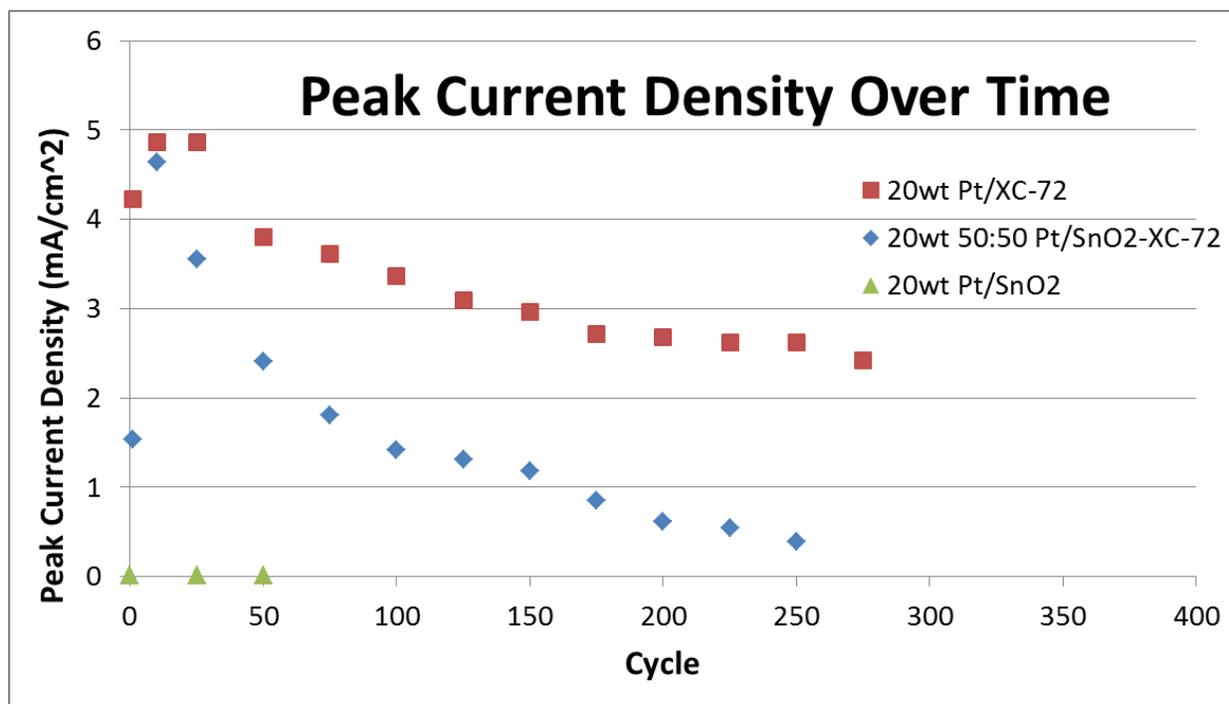
Figure 35. Peak Current Density Over Time for Various Pt-supported Catalysts

After concluding that the tin oxide was experiencing trouble conducting a current, CV tests were run on pure supports in order to observe differences in their electrical conductive properties and to see if perhaps the platinum support on the tin oxide was having some sort of adverse effect.

Shown in Figure 36 is a CV of the original tin oxide, showing it has virtually no conducting ability (the scale is significantly smaller than the others). Figure 37 shows results for a patented variety of tin oxide known as NanoArc designed specifically for cathode catalytic applications. At high potentials it is unable to hold any current. The XC-72 carbon is able to hold the current much more effectively at high voltages, as shown in Figure 38. Expected CV outputs for tin oxide and carbon black are given in literature, shown in Figure 39. These literature values are very similar to the results herein discussed. Compared to carbon, tin oxide is unable to match its conducting abilities at high voltages.

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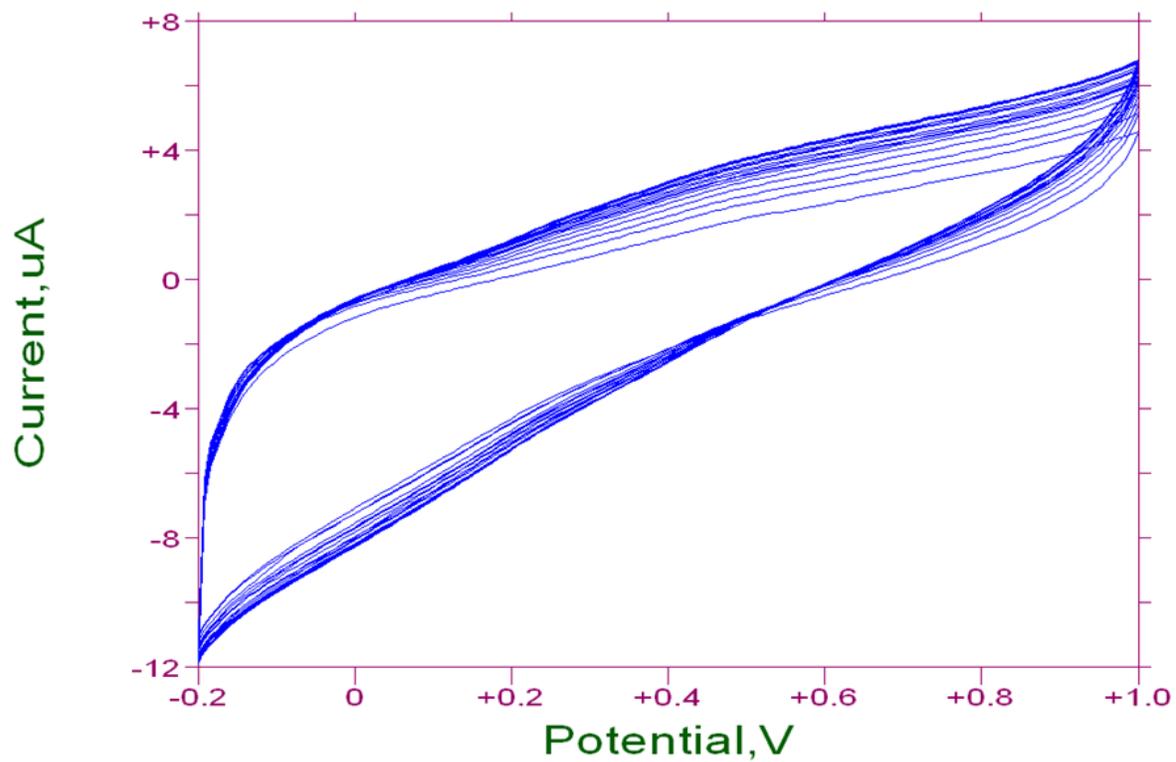
Figure 36. CV of SnO₂ Alone
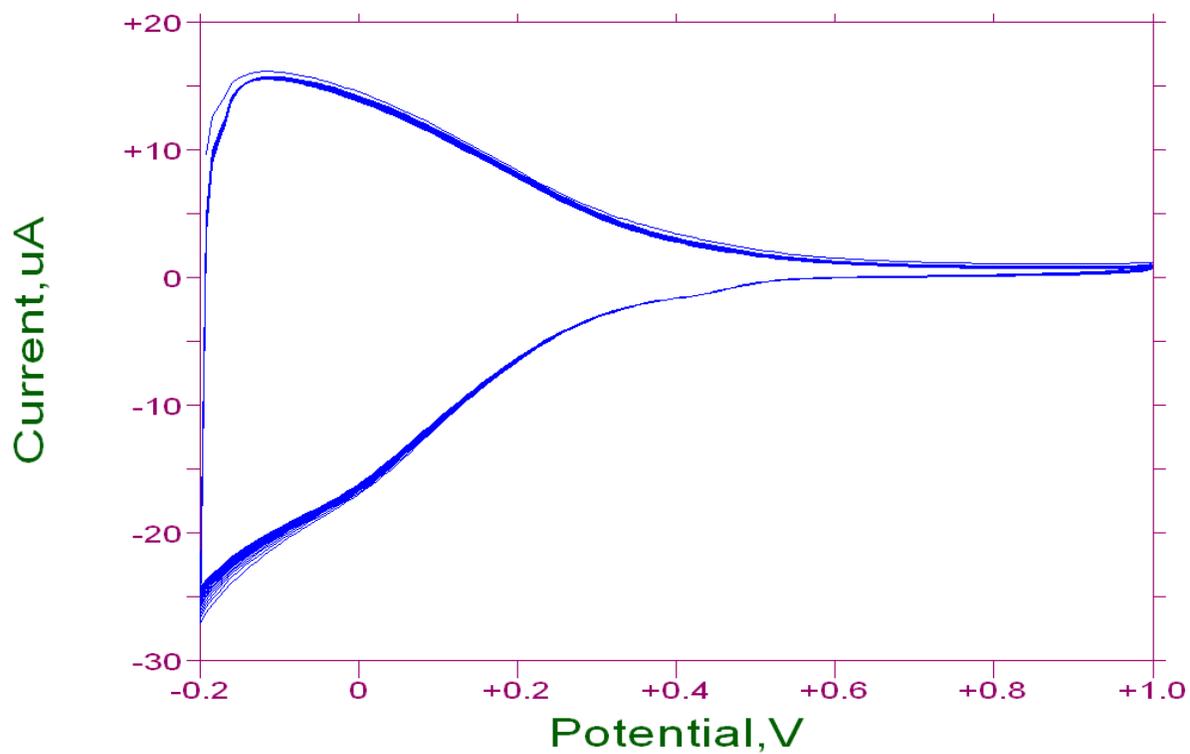
Figure 37. CV of NanoArc SnO₂ Alone
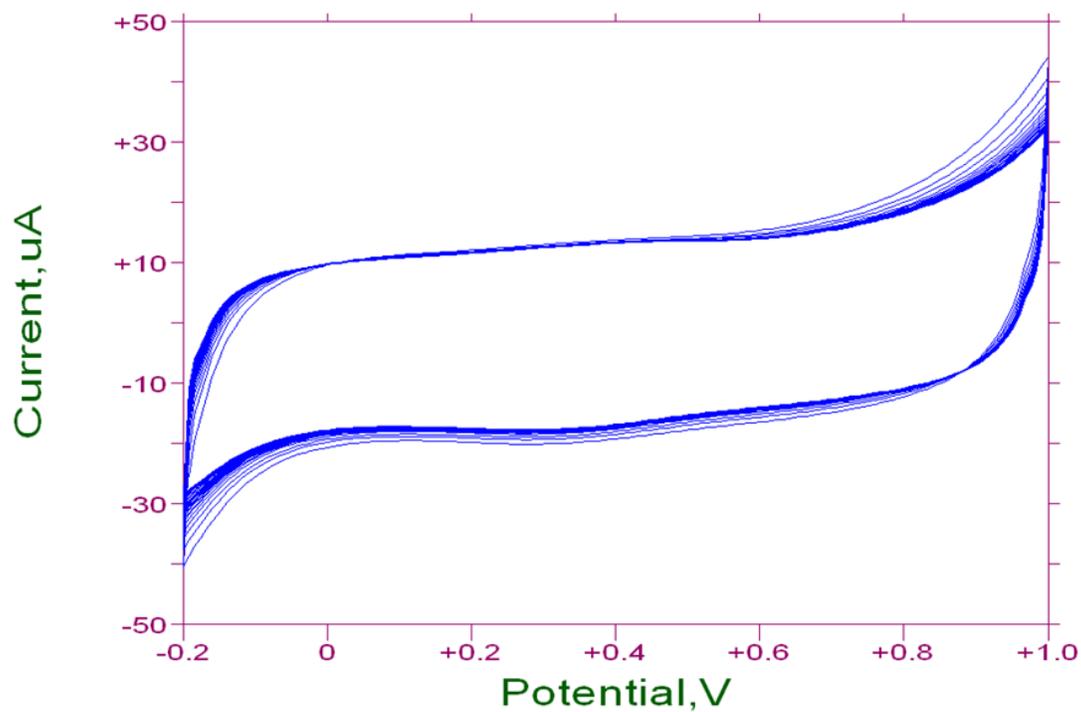
Figure 38. CV of XC-72 Carbon Alone
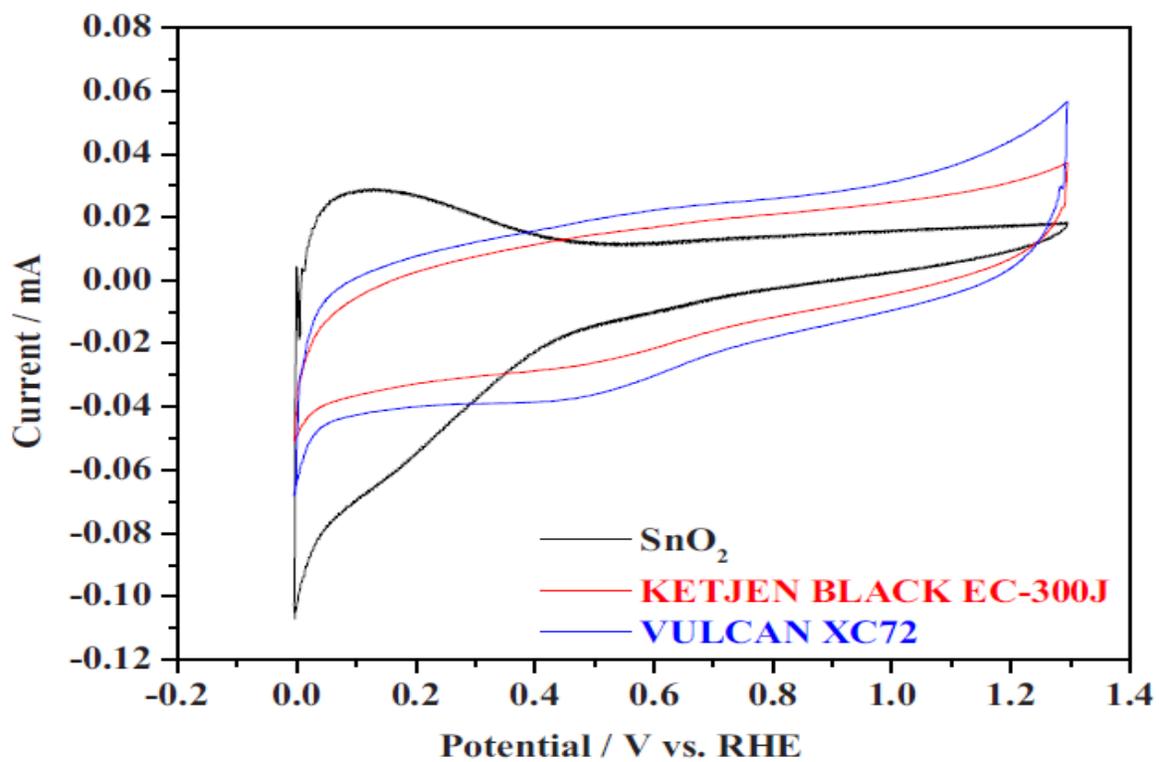
Figure 39. Literature Values for Expected CV Outputs
(Zhang, 2009)

6.0 Conclusions

Tin oxide was found to be an inferior support material for cathode catalysts in direct methanol fuel cells compared to XC-72 Vulcan carbon black. The Pt/SnO_2 material and tin oxide were unable to draw a current during the electrochemical tests. It was, however, able to conduct a current after mixing the Pt/SnO_2 material with XC-72 Vulcan. This proved that the platinum catalyst was still active but that the tin oxide was unable to transfer the electrons in any meaningful way. This asserts the conclusion that the tin oxide used in these experiments had high electrical resistance and poor electrical conductivity.

Despite these unexpected results, a suitable method for synthesizing platinum onto tin oxide was successfully optimized. It was found that certain synthesis variables could be controlled in order to improve the quality of the Pt/SnO_2 product. The use of a weaker reducing agent, ethylene glycol, was found to produce smaller platinum particles than a stronger reducing agent, sodium borohydride. Next, it was found that the colloidal method produced smaller particles than the impregnation method. And finally it was found that longer reaction time (4 hours) and longer stirring time (2 days) resulted in better bonding and distribution between the platinum nanoparticles and the tin oxide support. If an appropriate inorganic oxide support is found, then the results of this study would be useful in catalyst synthesis.

7.0 Future Work

For future work pertaining to this project, the following suggestions are made. First, tin oxide should have good electrical semiconducting properties, but the results of this project seem to indicate otherwise; testing to determine the tin oxide material's resistance as an electrode should be performed to see if it has any electron conducting ability. Also, it is common to dope catalyst supports with various metals in order to improve their conductivity and other properties, so experiments should be conducted to see if such changes can help make tin oxide a superior catalyst support compared to XC-72 carbon black. Finally, during the cyclic voltammetry test, the working electrode and sample were immersed in a 0.5 M methanol in 1M sulfuric acid with water solution; this simulates the environment expected in a direct methanol fuel cell. In practice, however, the performance of the material is noticeably different than in a real direct methanol fuel cell. It is suggested that future work be made to construct a membrane electrode assembly with the catalyst material and test it in a functioning direct methanol fuel cell. These tests would decisively determine the performance capabilities of the Pt/SnO_2 catalyst materials in fuel cells as opposed to simply cyclic voltammetry procedures.

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Appendix A: Detailed Laboratory Procedures

Experiment 1: NaBH4; Impregnation; 20 wt%; 1 day stirring
Conducted on October 10, 2011 – October 11, 2011 in WB337

Impregnation Process with NaBH$_4$
-> weighed 0.02010 g of SnO2 and transferred to 100-mL round-bottom flask
-> added 24.9 mL of DI water
-> stirred for 15 min (14:13-14:29)
-> sonicated for 10 minutes (14:29-14:39)
-> while stirring; (14:40 Oct 10,2011 – 15:54 Oct 11,2011)
    -> prepared platinum precursor
        -> weighed 0.3558 g Chloroplatinic acid hexahydrate
        -> added 35.6 mL DI water to produce 10mg/mL DI water solution
        -> stirred (14:25-14:39)
    -> used pipette and added 1.33 mL of Pt solution drop-wise
    -> prepared 0.1M NaBH4 solution
        -> weighed 0.0765 g NaBH4
        -> added 20.0 mL DI water
    -> added 1.00 mL of <u>freshly</u> made NaBH4 solution drop-wise
    -> stirred overnight until October 11 (15:54)
-> removed from stirring

Separation of Product for TEM and SEM (October 11, 2011)
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
->transferred sample to six 2-mL conical centrifuge tubes
    -> centrifuged for 3 minute (16:03-16:06)
    -> clear top layer of liquid in centrifuge was removed via glass pipette. Additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
    -> centrifuged for 20 minutes (15:16-15:36)
        -> removed top layer of clear liquid
        -> added more sample evenly into tubes. Filled tubes up to the 2mL line with DI water. Shook tubes. Sonicated for 5 minutes, shook tubes, sonicated for 5 minutes (15:50-16:00). Dried outside of tubes.
        -> centrifuged for 20 minutes (16:03-xx16:24)
            -> removed top layer of liquid as before
            ->diluted each tube up to the 1mL line with DI water. Shook tubes. Sonicated briefly to disperse any Pt that may be stuck to the bottom.
            ->combined contents of tubes; transferred contents of 3 tubes into the other 3 tubes. Filled each tube up to the 2mL mark with DI water, if necessary. Dried tubes. Shook tubes.
            ->centrifuged for 20 minutes (16:44-17:06)
                ->removed top layer of liquid

->diluted each tube up to ~0.66mL line with DI water. Shook tubes. Sonicated briefly to disperse any Pt that may be stuck to the bottom.

->combined contents of tubes; transferred contents of 2 tubes into the third remaining tube. Filled the tube up to the 2mL mark with DI water, if necessary. Dried tubes. Shook tubes

> ->transferred ~0.5mL of sample from tube to another centrifuge tube – for SEM. The sample was diluted with DI water until it appeared not too dark and not too pale.
>
> ->~7 drops of sample were transferred onto a 300 mesh TEM grid. It was allowed to dry overnight on the counter.

->filled a dummy tube up to the 2mL line with DI water in order to maintain symmetry in the centrifuge. Centrifuged for 25 minutes (17:23-17:46)

> ->removed top later of liquid
>
> ->tube was left open in a beaker to air dry overnight (due to occupation of the oven)

Experiment 2: Ethylene Glycol; Colloidal; 20 wt%; 3 hour reaction; 2 day stirring
Conducted on November 9, 2011 – November 11, 2011 in WB337

Preparation of Chloroplatinic Acid Hexahydrate Solution
-> weighed 0.1142 g chloroplatinic acid hexahydrate
-> added 11.0 mL EG to make 10 mg/mL EG solution
-> sonicated for 20 minutes (13:24-13:42)
-> stirred for 20 minutes (13:43-14:05)

Dispersion of SnO2 in EG
-> weighed 0.0302 g SnO2 and transferred to 50-mL four-neck round bottom flask
-> added 13.0 mL EG – too much will make separation difficult
-> sonicated 10 minutes; shook lightly every couple minutes to promote dispersion (13:41-13:53)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> measured 0.20 mL chloroplatinic acid solution
      -> diluted with 0.80 mL EG
      -> sonicated 10 minutes (14:15-14:22)
      -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and slowly heated tin oxide mixture to 160C,
-> added Pt solution dropwise, very, very slowly (14:25-14:40)
-> at ~16:00, realized not enough Pt solution was added for the desired wt percent so we:
      -> combined 1.8 mL Pt precursor with ~4 mL EG
      -> sonicated (16:02-16:04)
      -> added very slowly drop-wise to SnO2 (16:08-16:32)
      -> continued stirring
-> heater was turned off (18:30)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (19:22)
-> sampled was left to stir for two nights overnight until Nov 11 (13:09)

*Notes on set-up
- Temperature control
  o Tends to overshoot target temperature if left to increase to 160C on its own
    ▪ Turn on unit, turn off at temperature of 90C, 120C, 140C. After turning off, allow unit to continue heating up naturally until it stabilizes somewhat, then turn on again.
    ▪ Once temperature of 160C is reached, the unit can be left to maintain temperature. Once it reaches 160C, temperature spikes do not generally occur.
- Nitrogen/Water Feed
  o Turn on once heating starts
  o Ensure nitrogen feed bubbles at stable rate, not too high to waste nitrogen, not too low that nitrogen is no longer being fed.

- Replace syringe/stopper with stopper after Pt solution added
- Add Pt solution very very slowly – produces smaller particles

Separation of Product for TEM

-> transferred product from flask to 50mL beaker

-> transferred product from beaker to three 2.0mL plastic conical centrifuge tubes: enough to perform TEM. If results look good, then we can purify the rest for SEM, etc.

-> centrifuged (13:16-13:35)

-> removed top layer of liquid from each tube

-> diluted two tubes with a small amount of water, shaken, sonicated (4minutes) and combined into one tube, sonicated. Filled a dummy tube with water to maintain symmetry in centrifuge.

-> centrifuged (13:54-14:19) top layer rather dark, but that's ok.

-> rinsed, shaken, sonicated (14:21-14:24)

-> transferred ~0.5mL to another tube->diluted, shaken, sonicated (14:26-14:29)

    -> transferred 30 microliters (more like 5 drops) sample onto TEM grid

    -> performed TEM (14:30-whenever)

Separation/Drying for SEM November 14

-> sonicated sample briefly to loosen particles stuck on the walls of the flask

-> transferred sample to 6-2mL conical centrifuge tubes

-> centrifuged (12:32-12:52)

-> continued adding remaining sample to centrifuge tubes, shaken, sonicated 3 minutes those combined tubes.

-> cleared top layer of liquid of remaining 5 tubes, rinsed with water, shaken, and sonicated for 8 minutes. Centrifuged all 6 tubes (13:07-13:27)

-> cleared top layer, rinsed 3 tubes with water, shaken, sonicated (13:32-13:39)

    -> combined these 3 tubes with remaining tubes, filled up to 2mL line, shaken, sonicated (13:40-13:44). Centrifuged (13:44-14:04)

    -> cleared top layer, rinsed 2 tubes with DI water, shaken, sonicated (14:08-14:12)

    -> combined with remaining tube, filled up to 2 mL line, shaken, sonicated (14:15-13)

-> centrifuged (14:18-14:40)

-> cleared top layer, put open tubes in beaker in oven at 65C overnight to dry.

Experiment 3: Ethylene Glycol; Colloidal; 20 wt%; 4 hour reaction; 1 day stirring

Conducted on November 16, 2011 – November 18, 2011 in WB337

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on November 9, 2011.

Dispersion of SnO2 in EG
-> weighed 0.0305 g SnO2 and transferred to 50-mL four-neck round bottom flask
-> added 10.0 mL EG – too much will make separation difficult
-> sonicated ~45 minutes; shook lightly every 5 minutes to promote dispersion (13:47-14:37)
-> removed from sonication and stirred for 20 minutes (14:38-15:00)
-> removed from stirring and sonicated for ~45 min (15:00-15:48)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> sonicated beaker of Pt solution prepared on Nov 9th for ~10 minutes
      -> stirred sample (covered by box) for 15 minutes (15:30-15:48)
      -> measured 2.0 mL chloroplatinic acid solution
      -> diluted with 5.5 mL EG
      -> sonicated for 15 minutes (15:50-16:00)
      -> stirred for however long (covered by box) until ready to be injected
-> after EG set-up complete, stirred and heated tin oxide/EG to 160C
-> added Pt solution dropwise, very, very slowly drop-wise using syringe at a rate of 1 drop/sec (16:18-17:07)
-> continued heating and stirring for 3 hours, starting when Pt solution was first added
-> heater was turned off (19:20)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (20:10)
-> sampled was left to stir overnight until Nov 17 (12:32)

Separation of Product for TEM November 17
-> transferred product from flask to 50mL beaker
-> sonicated sample for 25 min (12:35-13:00)
-> filled one 2-mL plastic conical centrifuge tube with product
      -> centrifuged for 30 minutes (13:06-13:36)
      -> removed top layer of liquid
      -> diluted tube with acetone up to the 2mL mark
      -> shook tube and sonicated for one hour (13:41-14:40)
      ->transferred 2 drops onto TEM carbon grid 300 mesh.

Separation of Sample for SEM November 18
-> sonicated sample for 30 min (9:18-9:49)
-> transferred sample from beaker to six 2-mL conical centrifuge tubes.
-> centrifuged for 45 min (9:58-10:43)
      -> removed top layer of liquid from each tube.

-> transferred remaining sample from beaker equally into the six tubes. Rinsed beaker with small amount of DI water and transferred volume to tubes.
-> filled remaining volume of tubes with DI water
-> shook tubes and sonicated for 15 minutes (11:00 – 11:15)
-> centrifuged for 90 min (11:17-12:45)

>->removed top layer of liquid from each tube
-> diluted each tube with DI water to the 1mL mark. Shook tubes. Sonicated 10 minutes (12:49-12:57).
-> transferred contents of four tubes evenly into the remaining two tubes. Filled up to 2mL mark with DI water.
-> shook each tube and sonicated for ~10 minutes (12:59-13:07)
-> centrifuged for 45 min (13:08-13:53)

>-> removed top layer of liquid from each tube
-> diluted each tube with a small amount of DI water. Shook tubes and sonicated ~10 minutes (13:55-14:03)
-> transferred contents of two tubes into the remaining tube. Filled up to 2mL mark with DI water.
->shook each tube and sonicated for ~10 minutes (14:05-14:13)
-> filled dummy tube with DI water to maintain symmetry in centrifuge. Centrifuged for ~45 min (14:14-14:48)
-> cleared top layer. Put open tubes in beaker in oven at 65C overnight to dry.

Experiment 4: Ethylene Glycol; Impregnation; 20 wt%; 4 hour reaction; 2 days stirring - Incomplete

Conducted on November 30, 2011 – November 30, 2011 in WB337

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on November 9, 2011.

Dispersion of SnO2 in EG
-> weighed 0.0311 g SnO2 and transferred to 50-mL four-neck round bottom flask
-> added 10.0 mL EG – too much will make separation difficult
-> sonicated for 30 minutes; shook lightly every 5 minutes to promote dispersion (13:47-14:18)
-> removed from sonication and stirred for 20 minutes (14:20-14:40)
-> removed from stirring and sonicated for 30 minutes (14:41-15:11)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
    -> sonicated beaker of Pt solution prepared on Nov 9th for ~10 minutes
    -> stirred sample (covered by box) for 15 minutes (15:00-15:15)
    -> measured 2.0 mL chloroplatinic acid solution
    -> diluted with 5.5 mL EG
    -> sonicated 15 minutes (15:16-15:30)
    -> stirred for however long (covered by box) until ready to be injected
-> combined the choloroplatinic acid solution with the tin oxide slurry
-> stirred and heated mixture to 160C for 4 hours (starting when the solution first reaches 160C) (15:50-xx)
    -> another group used N2 during this 4 hour reaction step experiment. They used high N2 flow. Water back-flowed from bubbler into flask, contaminating the sample and causing the temperature to drop to ~141C (19:07)
-> heater was turned off
-> sample discarded the next day after it cooled down

Experiment 5: Ethylene Glycol; Impregnation; 20 wt%; 4 hour reaction; 2 days stirring

Conducted on December 2, 2011 – December 4, 2011 in WB337

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on November, 9, 2011.

Dispersion of SnO2 in EG
-> weighed 0.0304 g SnO2 and transferred to 50-mL four-neck round bottom flask
-> added 10.0 mL EG – too much will make separation difficult
-> sonicated for 30 minutes; shook lightly every 5 minutes to promote dispersion (12:24-12:54)
-> removed from sonication and stirred for 20 minutes (12:55-13:15)
-> removed from stirring and sonicated for ~45 minutes (13:16-14:00)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> sonicated beaker of Pt solution prepared on Nov 9th for ~10 minutes
      -> stirred sample (covered by box) for 15 minutes (13:27-13:42)
      -> measured 2.0 mL chloroplatinic acid solution
      -> diluted with 5.5 mL EG
      -> sonicated 15 minutes (13:45-14:00)
-> combined the choloroplatinic acid solution with the tin oxide slurry
-> stirred and heated mixture to 160C for 4 hours (starting when the solution first reaches 160C) (14:16-18:15)
-> heater was turned off (18:15)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (18:57)
-> sampled was left to stir 2 days until Dec 4 (12:40)

Separation of Product December 4
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred product to six 2mL centrifuge tube
-> centrifuged for 20 minutes (12:50-13:11)
-> removed top layer of liquid from each tube
-> diluted each tube up to the 2mL mark with DI water
-> sonicated one tube for 1 hour (13:26-14:25) for TEM analysis. Stored remaining tubes in beaker for possible study (SEM) later on if needed.
-> transferred 3 drops onto TEM carbon grid 300 mesh
-> allowed grid to dry overnight on counter

Experiment 6: Ethylene Glycol; Colloidal; 40 wt%; 4 hour reaction; 2 days stirring
Conducted on January 21, 2012 – January 23, 2012 in WB337

Used 2 mL of 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on November, 9, 2011 and new solution prepared on January 21, 2012.

Preparation of Chloroplatinic Acid Hexahydrate Solution
-> weighed 0.3454 g chloroplatinic acid hexahydrate
-> added 34.5 mL EG to make 10mg/mL EG solution
-> sonicated for 20 minutes (12:59-13:13)
-> stirred for 20 minutes (13:14-13:34)

Dispersion of SnO2 in EG
-> weighed 0.0306 g SnO2 and transferred to 50-mL four-neck round bottom flask
-> added 10.0 mL EG – too much will make separation difficult
-> sonicated for 30 minutes; shook lightly every 5 minutes to promote dispersion (12:12-12:32)
-> removed from sonication and stirred for 20 minutes (12:33-12:57)
-> removed from stirring and sonicated for ~45 min (12:58-13:43)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
       -> sonicated beaker of Pt solution prepared on Nov 9th for ~10 minutes
       -> stirred sample (covered by box) for 15 minutes (13:13-13:29)
       -> measured 2.0 mL chloroplatinic acid solution from Nov 9, 2011 and 4.0mL of chloroplatinic acid solution from January 21, 2011; total 6.0 mL of Pt precursor.
       -> diluted with 15.0 mL EG
       -> sonicated for 15 minutes (13:39-14:07)
       -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C.
-> added Pt solution dropwise, very, very slowly using syringe at rate of 1 drop/sec (14:27-15:48)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (18:30)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (19:28)
-> sampled was left to stir two days until Jan 23 (14:18)

Separation of Product for TEM and SEM January 23
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 20 minutes (14:29-14:51)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.

-> centrifuged for 20 minutes (15:16-15:36)

    -> removed top layer of clear liquid

    -> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes. Filled tubes up to the 2mL line with DI water. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.

    -> centrifuged for 20 minutes (16:03-16:24)

        -> removed top layer of clear liquid

        -> filled tubes up to the 2mL line with DI water. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.

        -> combined contents of tubes; transferred contents of 3 tubes into the other 3 tubes. Filled each tube up to the 2mL mark with DI water, if necessary. Dried tubes. Shook tubes.

        -> centrifuged for 20 minutes (16:44-17:06)

            ->removed top layer of clear liquid

            -> diluted each tube up to ~0.66mL line with DI water. Shook tubes. Sonicated briefly to disperse any Pt that may be stuck to the bottom.

            -> combined contents of tubes; transferred contents of 2 tubes into the third remaining tube. Filled the tube up to the 2mL mark with DI water, if necessary.

                ->transferred ~0.5mL of sample from tube to another centrifuge tube – for SEM. The sample was diluted with DI water until it appeared not too dark and not too pale.

                ->~7 drops of sample were transferred onto a 300 mesh TEM grid. It was allowed to dry overnight on the counter.

        ->filled a dummy tube up to the 2mL line with DI water in order to maintain symmetry in the centrifuge

        -> centrifuged for 25 minutes (17:23-17:46)

            ->removed top latey of liquid

            - >tube was left open in a beaker to air dry overnight

Experiment 7: Ethylene Glycol with Distilled Water; Impregnation; 40 wt%; 4 hour reaction; 2 days stirring

Conducted on January 22, 2012 – January 24, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on January 21, 2012.

Step 1. Disperse both the Pt precursor and SnO2 in a beaker containing DI water through stirring and sonication.
-> weighed 0.0306 g SnO2 and transferred to 50-mL four-neck round bottom flask
-> weighed 0.0532 g Chloroplatinic Acid Hexahydrate and combined with SnO2
-> added 25.0 mL of DI water
-> sonicated for 30 minutes; shook lightly every 5 minutes to promote dispersion (12:34-13:05)
-> removed from sonication and stirred for 20 minutes (13:06-13:26)
-> removed from stirring and sonicated for ~45 min (13:26-14:12)

Step 2. Heat up a flask containing pure EG solvent to 170C using the conventional refluxing system with nitrogen
-> measured 10.0 mL EG and transferred to 50-mL four-neck flask
-> secured in reflux set-up
-> heated up to 170C

Step 3. Slowly inject the homogeneous SnO2/H2PtCl6 dispersion into the hot EG solution.
-> injected Pt/SnO2 slurry dropwise, very, very slowly using syringe at rate of ~1 drop every 2 seconds using syringe (14:18-15:06)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
      -> *note* temperature of mixture boiled continuously at ~133F during 4 hour reaction
-> heater was turned off (18:20)
-> sample was allowed to cool slowly until it reached 60C, at which point the nitrogen and water were turned off (19:06)
-> sampled was left to stir two days until Jan 24 (12:03)

Separation of Product for TEM and SEM January 24
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 10 minutes (12:15-12:25)
-> removed top layer of clear liquid
-> diluted each tube up to the 2mL line with DI water. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> centrifuged for 10 minutes (12:35-12:45)
      -> removed top layer of clear liquid
      -> diluted each tube up to the 2mL line with DI water. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
      -> centrifuged for 10 minutes (12:55-13:06)
            -> removed top layer of clear liquid

-> diluted each tube up to the 1mL line with DI water. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> combined contents of tubes; transferred contents of 3 tubes into the other 3 tubes. -> filled each tube up to the 2mL mark with DI water, if necessary. Sonicated and shook tubes briefly
-> centrifuged for 10 minutes (13:20-13:30)

    ->removed top layer of clear liquid

    ->diluted two of the tubes up to 1mL line with DI water. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.

    -> combined contents of tubes; transferred contents of one tube into the other. -> filled the tube up to the 2mL mark with DI water, if necessary. Sonicated and shook tubes briefly

        ->With third tube (clear top layer removed), transferred ~0.5mL of sample from tube to another centrifuge tube – for SEM. The sample was diluted with acetone until it appeared not too dark and not too pale.

        -> ~5 drops of sample were transferred onto a 300 mesh TEM grid. It dried almost instantly because of the acetone solvent.

    -> filled a dummy tube up to the 2mL line with DI water in order to maintain symmetry in the centrifuge

    -> centrifuged for 10 minutes (13:40-13:50)

        -> removed top layer of clear liquid

        -> tube was left open in a beaker to air dry overnight

Experiment 8: Ethylene Glycol; Colloidal Scale-up; 40 wt%; 4 hour reaction; 2 days stirring

Conducted on January 28, 2012 – January 30, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on January 21, 2012.

Dispersion of SnO2 in EG
-> weighed 0.0930 g SnO2 and transferred to 500-mL four-neck round bottom flask
-> added 30.0 mL EG – too much will make separation difficult
-> sonicated for 20 minutes; shook lightly every 5 minutes to promote dispersion (9:40-10:02)
-> removed from sonication and stirred for 20 minutes (10:03-10:23)
-> removed from stirring and sonicated for ~45 min (10:23-11:10)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
    -> sonicated beaker of Pt solution prepared on Jan 21st for ~10 minutes
    -> stirred sample (covered by box) for 15 minutes (10:35-10:50)
    -> measured 16.53mL of Pt precursor into beaker using pipette
    -> diluted with 83.0 mL EG
    -> sonicated for 15 minutes (11:03-11:18)
    -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C.
-> added Pt solution dropwise, very, very slowly using syringe at a rate of 1 drop/sec (11:49-14:58)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (15:50)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (17:08)
-> sample was transferred to a 400 mL flask and left to stir two days until Jan 30 (12:37)

Separation of Product for TEM and SEM January 30
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 20 minutes (12:49-13:12)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all sample was separated
    ->centrifuged for 15 minutes (13:25-13:40)
    ->centrifuged for 20 minutes (13:52-14:12)
    ->centrifuged for 20 minutes (14:12-14:32)
    ->centrifuged for 20 minutes (14:43-15:04)
    ->centrifuged for 20 minutes (15:14-15:35)

->centrifuged for 20 minutes (15:45-16:05)

->centrifuged for 20 minutes (16:14-16:34)

    -> filled another centrifuge tube with sample. It was too light so we added three drops of sample from one of the tubes that has been centrifuging.

    -> sample was allowed to sonicate for ~45 min (16:45-17:47)

    -> transferred ~4 drops onto TEM 300 mesh copper grid

->centrifuged for 20 minutes (16:45-17:05)

->centrifuged for 20 minutes (17:17-17:37)

->centrifuged for 20 minutes (17:53-18:13)

->centrifuged for 20 minutes (18:25-18:45)

-> removed top layer

-> evenly added rest of remaining sample

-> added DI water to top off the tubes

-> sonicated briefly

-> centrifuged for 25 minutes (19:11-19:38)

    -> removed top clear layer

    -> combined tubes; added DI water to 1mL mark in three tubes and sonicated briefly. Transferred sample to other three tubes and sonicated briefly

    -> centrifuged for 25 minutes (19:53-20:18)

        -> removed top clear layer

        -> filled tubes up to 2-mL mark with DI and briefly sonicated

        -> centrifuged for 15 minutes (20:24-20:39)

            -> removed top clear layer

            -> filled tubes up to 2-mL mark with DI and briefly sonicated

            -> centrifuged for 15 minutes (20:46-21:01)

                -> removed top clear layer

                -> filled tubes up to 2-mL mark with DI and briefly sonicated

                -> centrifuged for 20 minutes (21:12-32)

                    -> removed top clear layer

                    -> left tubes open on counter to dry overnight

Experiment 9: Ethylene Glycol; Colloidal Scale-up; 60 wt%; 4 hour reaction; 2 days stirring

Conducted on January 28, 2012 – January 31, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on January 21, 2012 and 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on January 28, 2012.

Preparation of Chloroplatinic Acid Hexahydrate Solution
-> weighed 0.5074 g chloroplatinic acid hexahydrate
-> added 51.0 mL EG (10mg/mL EG)
-> sonicated for 20 minutes (16:07-16:28)
-> stirred for 20 minutes (16:30-16:50)
-> sonicated for 20 minutes (16:51-17:21)

Dispersion of SnO2 in EG
-> weighed 0.0917 g SnO2 and transferred to 500-mL four-neck round bottom flask
-> added 30.0 mL EG – too much will make separation difficult
-> sonicated for 20 minutes; shook lightly every 5 minutes to promote dispersion (14:37-14:58)
-> removed from sonication and stirred for 20 minutes (15:00-15:22)
-> removed from stirring and sonicated for ~45 min (15:23-17:21)
-> secured in reflux set-up

Precipitate Product
-> measured 12mL of Pt precursor prepared on January 21, and 24.7mL of Pt precursor prepared on January 28 (for a total of 36.7mL of Pt precursor), into beaker using pipette. Stirred beaker of Pt precursor before measuring to ensure well-disturbed solution
        -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C.
-> added Pt solution dropwise, very, very slowly using syringe (17:45-19:34)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (21:45)
-> sample was allowed to slowly cooly until it reached 60C, at which point the nitrogen and water were turned off (22:38)
-> sampled was left to stir two days until Jan 30 (12:31)

Separation of Product for TEM and SEM January 31
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 20 minutes (14:06-14:26)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all samples separated
        -> centrifuged for 20 minutes (14:38-14:58)

-> centrifuged for 20 minutes (15:07-15:27)
-> centrifuged for 20 minutes (15:36-15:57)
-> centrifuged for 20 minutes (16:06-16:26)
      -> filled another centrifuge tube with sample. Diluted with water so that it was not too light, not too dark – for TEM.
      -> sonicated for ~45 minutes (16:08-17:45)
      -> transferred ~4 drops onto TEM 300 mesh copper grid
-> centrifuged for 20 minutes (16:37-16:57)
      -> removed top clear layer
      -> combined tubes; added DI water to 1mL mark in three tubes and sonicated briefly. Transferred sample to other three tubes and sonicated briefly
      -> centrifuged for 20 minutes (17:23-17:43)
            -> removed top clear layer
            -> filled tubes up to 2-mL mark with DI and briefly sonicated
            -> centrifuged for 20 minutes (17:56-18:16)
                  -> removed top clear layer
                  -> filled tubes up to 2-mL mark with DI and briefly sonicated
                  -> centrifuged for 20 minutes (18:27-18:47)
                        -> removed top clear layer
                        -> filled tubes up to 2-mL mark with DI and briefly sonicated
                        -> centrifuged for 20 minutes (19:08-19:28)
                              -> removed top clear layer
                              -> left tubes open on counter to dry overnight

Experiment 10: Ethylene Glycol; Colloidal Scale-up; 20 wt%; 4 hour reaction; 2 days stirring

Conducted on February 21, 2012 – February 24, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on January 28, 2012.

Dispersion of SnO2 in EG
-> weighed 0.0903 g SnO2 and transferred to 500-mL four-neck round bottom flask
-> added 30.0 mL EG – too much will make separation difficult
-> sonicated for ~1 hour; shook lightly every 10 minutes to promote dispersion (15:00-16:03)
-> removed from sonication and stirred for 20 minutes (16:04-16:28)
-> removed from stirring and sonicated for ~40 min (16:28-17:11)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> sonicated beaker of Pt solution prepared on Jan 28th for ~10 minutes
      -> stirred sample (covered by box) for 15 minutes (16:50-17:09)
      -> measured 6.23mL of Pt precursor prepared on January 28 into beaker using pipette
      -> diluted with 15.0 mL EG
      -> sonicated at least 15 minutes (17:12-17:22)
      -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C using oil bath – took VERY LONG!!!
-> added Pt solution dropwise, very, very slowly using syringe (19:42-21:03)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (23:45)
-> sample was allowed to cool slowly until it reached 60C, at which point the nitrogen and water were turned off (00:30 February 22, 2012)
-> sampled was left to stir two days until Feb 24 (11:46)

Separation of Product for TEM February 24
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 20 minutes (12:05-12:26)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all samples separated
      -> centrifuged for 20 minutes (12:39-13:02)
      -> centrifuged for 20 minutes (13:15-13:59)
      -> centrifuged for 20 minutes (1413-1454)
      -> centrifuged for 20 minutes (1507-1547)(H2O)
      -> centrifuged for 20 minutes (1555-1615) water

-> centrifuged for 20 minutes (1622-16:43) last water
-> centrifuged for 20 minutes (17:00-17:30)
      -> filled another centrifuge tube with sample. Diluted with water so that it was not too light, not too dark – for TEM.
      -> sonicated for ~45 minutes (17:45-18:30)
      -> transferred ~4 drops onto TEM 300 mesh copper grid
-> remaining sample was not separated and saved in case sample was good

Experiment 11: Ethylene Glycol; Colloidal Scale-up; 40 wt%; 4 hour reaction; 2 days stirring

Conducted on March 27, 2012 – March 29, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on March 27, 2012

Preparation of Chloroplatinic Acid Hexahydrate Solution
-> weighed 0.7004 g chloroplatinic acid hexahydrate
-> added 70.0 mL EG (10mg/mL EG)
-> sonicated 20 minutes (14:16-14:36)
-> stirred 20 minutes (14:39-15:00)

Dispersion of SnO2 in EG
-> weighed 0.0997 g SnO2 and transferred to 500mL four-neck round bottom flask
-> added 31.0 mL EG – too much will make separation difficult
-> sonicated for 20 minutes; shook lightly every 5 minutes to promote dispersion (13:53-14:14)
-> removed from sonication and stirred for 20 minutes (14:15-14:37)
-> removed from stirring and sonicated for ~45 min (14:37-15:25)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> measured 16.53mL of Pt precursor into beaker using pipette. Stirred beaker of Pt precursor before measuring to ensure well-disturbed solution
      -> diluted with 40.0 mL EG
      -> sonicated at least 15 minutes (covered by box) (15:10-15:28)
      -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C
-> added Pt solution dropwise, very, very slowly using syringe (15:42-17:14)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (19:40)
-> sample was allowed to cool slowly until it reached 60C, at which point the nitrogen and water were turned off (21:03)
-> sample was left to stir two days until March 29 (13:04)

Separation of Product for TEM and SEM January 30
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 20 minutes (12:49-13:12)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all samples separated
      ->centrifuged for 15 minutes (13:25-13:40)

->centrifuged for 15 minutes (13:25-13:40)
->centrifuged for 20 minutes (13:52-14:12)
->centrifuged for 20 minutes (14:12-14:32)
->centrifuged for 20 minutes (14:43-15:04)
->centrifuged for 20 minutes (15:14-15:35)
->centrifuged for 20 minutes (15:45-16:05)
->centrifuged for 20 minutes (16:14-16:34)
    -> filled another centrifuge tube with sample. It was too light so we added three drops of sample from one of the tubes that has been centrifuging.
    -> sample was allowed to sonicate for ~45 min (16:45-17:47)
    -> transferred ~4 drops onto TEM 300 mesh copper grid
->centrifuged for 20 minutes (16:45-17:05)
->centrifuged for 20 minutes (17:17-17:37)
->centrifuged for 20 minutes (17:53-18:13)
->centrifuged for 20 minutes (18:25-18:45)
-> removed top layer
-> evenly added rest of remaining sample
-> added DI water to top off the tubes
-> sonicated briefly
-> centrifuged for 25 minutes (19:11-19:38)
    -> removed top clear layer
    -> combined tubes; added DI water to 1mL mark in three tubes and sonicated briefly. Transferred sample to other three tubes and sonicated briefly
    -> centrifuged for 25 minutes (19:53-20:18)
        -> removed top clear layer
        -> filled tubes up to 2-mL mark with DI and briefly sonicated
        -> centrifuged for 15 minutes (20:24-20:39)
            -> removed top clear layer
            -> filled tubes up to 2-mL mark with DI and briefly sonicated
            -> centrifuged for 15 minutes (20:46-21:01)
                -> removed top clear layer
                -> filled tubes up to 2-mL mark with DI and briefly sonicated
                -> centrifuged for 20 minutes (21:12-32)
                    -> removed top clear layer
                    -> left tubes open on counter to dry overnight

Experiment 12: Ethylene Glycol; Colloidal Scale-up; 40 wt%; 4 hour reaction, 2 days stirring

Conducted on March 28, 2012 – March 30, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on March 27, 2012

Dispersion of SnO2 in EG
-> weighed 0.0899 g SnO2 and transferred to 500-mL four-neck round bottom flask
-> added 31.0 mL EG – too much will make separation difficult
-> sonicated for 20 minutes; shook lightly every 5 minutes to promote dispersion (8:20-8:40)
-> removed from sonication and stirred for 20 minutes (8:40-9:07)
-> removed from stirring and sonicated for ~45 min (9:07-9:51)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> sonicated beaker of Pt solution prepared on Mar 27th for ~10 minutes
      -> stirred sample for 15 minutes (covered by box) (10:45-11:01)
      -> measured 16.53mL of Pt precursor into beaker using pipette
      -> diluted with 40.0 mL EG
      -> sonicated 15 minutes (11:05-11:25)
      -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C
-> added Pt solution dropwise, very, very slowly using syringe (11:27-12:47)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (15:30)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (16:20)
-> sample was left to stir two days until March 30 (13:45)

Separation of Product for TEM and SEM March 30
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 20 minutes (14:06-14:26)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all samples separated
      -> centrifuged for 20 minutes (14:38-14:58)
      -> centrifuged for 20 minutes (15:07-15:27)
      -> centrifuged for 20 minutes (15:36-15:57)
      -> centrifuged for 20 minutes (16:06-16:26)
            -> filled another centrifuge tube with sample. Diluted with water so that it was not too light, not too dark – for TEM.

-> sonicated for ~45 minutes (16:08-17:45)

-> transferred ~4 drops onto TEM 300 mesh copper grid

-> centrifuged for 20 minutes (16:37-16:57)

-> removed top clear layer

-> combined tubes; added DI water to 1mL mark in three tubes and sonicated briefly. Transferred sample to other three tubes and sonicated briefly

-> centrifuged for 20 minutes (17:23-17:43)

-> removed top clear layer

-> filled tubes up to 2-mL mark with DI and briefly sonicated

-> centrifuged for 20 minutes (17:56-18:16)

-> removed top clear layer

-> filled tubes up to 2-mL mark with DI and briefly sonicated

-> centrifuged for 20 minutes (18:27-18:47)

-> removed top clear layer

-> filled tubes up to 2-mL mark with DI and briefly sonicated

-> centrifuged for 20 minutes (19:08-19:28)

-> removed top clear layer

-> left tubes open on counter to dry overnight

Experiment 13: Ethylene Glycol; Colloidal Scale-up; 20 wt%; 4 hour reaction; 2 days stirring

Conducted on March 29, 2012 – April 1, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on March 27, 2012

Dispersion of SnO2 in EG
-> weighed 0.0899 g SnO2 and transferred to 500mL four-neck round bottom flask
-> added 30.0 mL EG – too much will make separation difficult
-> sonicated for 20 minutes; shook lightly every 5 minutes to promote dispersion (10:23-10:44)
-> removed from sonication and stirred for 20 minutes (10:45-11:05)
->removed from stirring and sonicated for ~45 min (11:05-11:52)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
       -> sonicated beaker of Pt solution prepared on March 27th for ~10 minutes (11:07-11:17)
       -> stirred for 15 minutes (covered by box) (11:17-11:32)
       -> measured 6.00mL of Pt precursor into beaker using pipette
       -> diluted with 15.0 mL EG
       -> sonicated for at least 15 minutes (11:38-11:53)
       -> stirred for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C
-> added Pt solution dropwise, very, very slowly using syringe (12:28-12:24)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (16:28)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (17:25)
-> sample was left to stir two days until April 1 (10:38)

Separation of Product for TEM and SEM (April 1 – April 3)
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 30 minutes (11:00-11:30)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all samples separated
       -> centrifuged for 20 minutes (11:45-12:28)
       -> centrifuged for 20 minutes (12:29-13:48)
       -> centrifuged for 20 minutes (13:50-14:28)
       -> centrifuged for 20 minutes (14:25-14:49)
       -> centrifuged for 20 minutes (14:56-15:28)
       -> centrifuged for 20 minutes (15:35-16:05)

-> centrifuged for 20 minutes (16:05-16:35)

    -> filled another centrifuge tube with sample. It was too light so we added three drops of sample from one of the tubes that has been centrifuging.

    -> sample was allowed to sonicate for ~45 min (16:45-17:47)

    -> transferred ~4 drops onto TEM 300 mesh copper grid

-> centrifuged for 20 minutes (17:00-two days). Sample was incredibly difficult to deparate effectively with a mere twenty minutes, so the sample was allowed to centrifuge for two days.

    -> removed top clear layer

    -> combined tubes; added DI water to 1mL mark in three tubes and sonicated briefly. Transferred sample to other three tubes and sonicated briefly

    -> centrifuged for 15 minutes (20:24-20:39)

        -> removed top clear layer

        -> filled tubes up to 2-mL mark with DI and briefly sonicated

        -> centrifuged for 15 minutes (20:46-21:01)

            -> removed top clear layer

            -> filled tubes up to 2-mL mark with DI and briefly sonicated

            -> centrifuged for 20 minutes (21:12-32)

                ->removed top clear layer

                -> left tubes open on counter to dry overnight

Experiment 14: Ethylene Glycol; Colloidal Scale-up; 60 wt%; 4 hour reaction; 2 days stirring; calcinated SnO$_2$

Conducted on April 10, 2012 – April 13, 2012

Used 10mg/mL EG Chloroplatinic Acid Hexahydrate Solution prepared on March 27, 2012

Preparation of SnO2
-> ceramic vessel was washed with acetone and sonicated for 30 minutes (13:35-14:05)
-> SnO2 was transferred to the ceramic vessel and heated in a 400C oven for 6 hours (14:11-20:23)
-> vessel was removed from oven and allowed to cool

Dispersion of SnO2 in EG
-> weighed 0.0903 g SnO2 and transferred to 500mL four-neck round bottom flask
-> added 30.0 mL EG – too much will make separation difficult
-> sonicated for 20 minutes; shook lightly every 5 minutes to promote dispersion (20:48-21:13)
-> removed from sonication and stirred for 20 minutes (21:16-21:37)
-> removed from stirring and sonicated for ~45 min (21:37-22:30)
-> secured in reflux set-up

Precipitate Product
-> prepared platinum precursor
      -> sonicated beaker of Pt solution prepared on March 27th for ~10 minutes (21:38-21:48)
      -> stirred for 15 minutes (covered by box) (21:48-22:03)
      -> measured 36.70 mL of Pt precursor into beaker using pipette
      -> diluted with 13.0 mL EG
      -> sonicated for at least 15 minutes (22:15-22:30)
      -> stir for however long (covered by box) until ready to be injected
-> after set-up complete, stirred and heated tin oxide/EG to 160C
-> added Pt solution dropwise, very, very slowly using syringe (23:05-23:55)
-> continued heating and stirring for 4 hours, starting when Pt solution was first added
-> heater was turned off (03:00)
-> sample was allowed to slowly cool until it reached 60C, at which point the nitrogen and water were turned off (0345)
-> sample was left to stir at least two days until April 13 (13:32)

Separation of Product for TEM and SEM April 13
-> sonicated sample briefly to loosen particles stuck on the walls of the flask
-> transferred sample to six 2-mL conical centrifuge tubes
-> centrifuged for 30 minutes (11:00-11:30)
-> removed top layer of clear liquid
-> additional Pt/SnO2 solution was evenly transferred to the same centrifuge tubes up to 2mL line. Product collected on the bottom of the tube was loosened by combination of shaking and sonication.
-> repeat until all samples separated

-> centrifuged for 20 minutes (11:45-12:28)
-> centrifuged for 20 minutes (12:29-13:48)
-> centrifuged for 20 minutes (13:50-14:28)
-> centrifuged for 20 minutes (14:25-14:49)
-> centrifuged for 20 minutes (14:56-15:28)
-> centrifuged for 20 minutes (15:35-16:05)
-> centrifuged for 20 minutes (16:05-16:35)

> -> filled another centrifuge tube with sample. It was too light so we added three drops of sample from one of the tubes that has been centrifuging.
> -> sample was allowed to sonicate for ~45 min (16:45-17:47)
> -> transferred ~4 drops onto TEM 300 mesh copper grid

-> centrifuged for 20 minutes (17:00-two days). Sample was incredibly difficult to deparate effectively with a mere twenty minutes, so the sample was allowed to centrifuge for two days.

> -> removed top clear layer
> -> combined tubes; added DI water to 1mL mark in three tubes and sonicated briefly. Transferred sample to other three tubes and sonicated briefly
> -> centrifuged for 15 minutes (20:24-20:39)
>
>> -> removed top clear layer
>> -> filled tubes up to 2-mL mark with DI and briefly sonicated
>> -> centrifuged for 15 minutes (20:46-21:01)
>>
>>> -> removed top clear layer
>>> -> filled tubes up to 2-mL mark with DI and briefly sonicated
>>> -> centrifuged for 20 minutes (21:12-32)
>>>
>>>> ->removed top clear layer
>>>> -> left tubes open on counter to dry overnight

Cyclic Voltammetry of 20 wt% Pt on Tin Oxide

Conducted on February 28, 2012.

Preparation of Homogenous Slurry
-> weighed 0.004g 20 wt% Pt/SnO2
-> combined with 2 drops 5wt% Nafion in isopropanol
-> added 1.0 mL of water
-> sonicated for at least 2 hours (13:01-15:32)
    - *note* Changed sonication water every hour because it gets hot.
-> continued sonicating until the sample was ready to be tested

Polishing of Electrode
-> gently rinsed working electrode with DI water
-> dried electrode with KimWipe, making sure not to touch tip.
-> dropped 1-2 drops of polishing aluminum (shake bottle prior) onto leather pad. Gently rinsed alumina with DI water to evenly spread it out
-> rubbed end of electrode on alumina in medium circular motion for ~1minute
      - *note* Be gentle, but aggressive enough to just maintain contact between surfaces, otherwise, the surface may be damaged/scratched. Only go in one direction – either counter clockwise or clockwise, do not change directions.
-> rinsed end of electrode with DI water
-> dried electrode with compressed air
-> cleaned leather pad with water making sure it's clean; otherwise, it may become rough and damage the electrode

Testing of Electrodes to Ensure It Is Well Polished (blank – no sample)
-> poured K3Fe(CN)6 solution into "shot-glass" and placed into voltameter.
-> working/polished electrode connected to black line. Inserted into center hole into potassium solution.
-> auxillary electrode (basically a platinum wire) connected to red line, inserted into right-side hole into potassium solution
-> reference electrode (use the one labeled X since it's newest) connected to clear line (Be EXTREMELY gentle since the wire may break, as it has before). Make sure there are no bubbles on the tip. If there are, then tap it so that bubbles rise. Inserted into left side hole into potassium solution.
-> turned on EC analyzer and allow to warm up for 1-2 minutes BEFORE opening program
-> opened BAS100W
    -select method
        -sweep techniques and cyclic voltemetry
        -Use default values:
            -Initial E:700V
            -High E: 750V
            -Low E: 0V
            -Scan Rate: 50mV/s
            -Positive Direction
            -Number of Segments: 3

-Sensitivity: 10microamps/V
-ok
-file -> setup options -> choose "Plus+"
-control -> start run
-f6 to see results
-high peak is oxidation, low peak is reduction. Check to see if distance between them (Ep) is ~75. If gap is over 80 then the electrode is not properly polished -> Redo
-close BAS100W program, then turn off EC analyzer
-disconnect electrodes, remove, and clean with DI water. Return reference electrode to its storage container.
- repeat cleaning and testing immediately before each coating since it can lose it's smoothness over time
-Return K3Fe(CN)6 solution back into beaker. Cover with box (it's light sensivtive)

Preparation of Electrode for Testing of Homogenous Slurry (Methanol Oxidation)
-secured polished electrode in clamp, level with table surface.
-make sure the slurry is sonicating up until the point it is ready to be deposited
-transfer 7 microliters of slurry onto electrode. Take sample from middle layer of solution – not top, not bottom. Return slurry solution to sonicator. When electrode has dried, transfer another 7 microliters of slurry onto electrode. Repeat for a total of 3-4 layers until the electrode is fully coated.
-transferred 7 microliters of 0.5wt% Nafion in ethanol onto electrode. It acts as a binder that prevents the sample from peeling off the surface. However, it acts as a source of protons and can block electron transfer if the layer is too big. Let dry on counter.

Testing of Homogenous Slurry/Catalyst (Methanol Oxidation) performed on February 14, 2012
-placed 0.5M sulfuric acid in 1M methanol shot glass into voltammeter
-connected auxiliary and reference electrodes as before. Make sure there are no bubbles in reference electrode. Connect working (catalyst) electrode. Make sure there are no bubbles on the electrode surface. Shake if necessary.
-plug in voltameter, turn on and allow to warm up for 1-2 minutes
-open BAS100W
-select method
-sweep techniques and cyclic voltemetry
-Use following values:
-initial E, -200mV, High E, 1000mV, Low E, -200mV, Scan rate, 50mU/s, sensitivity, 1mA, segments, 20 (=10 cycles).
-First few cycles can be neglected because Nafio needs time to be protonated and solution needs time to penetrate the sample/activate the catalyst.
-file->set up options
Check off "+Plus"
-control->start run
-Save Data for each run in "MQP SnO2" folder

-removed electrodes and 0.5M sulfuric acid vial. Washed electrodes with DI water and dry. Return reference electrode to storage container.
-close program, then shut off EC analyzer

Appendix B: Cyclic Voltammetry Data

20 wt% Pt on XC-72 Carbon
Cycle 1-25
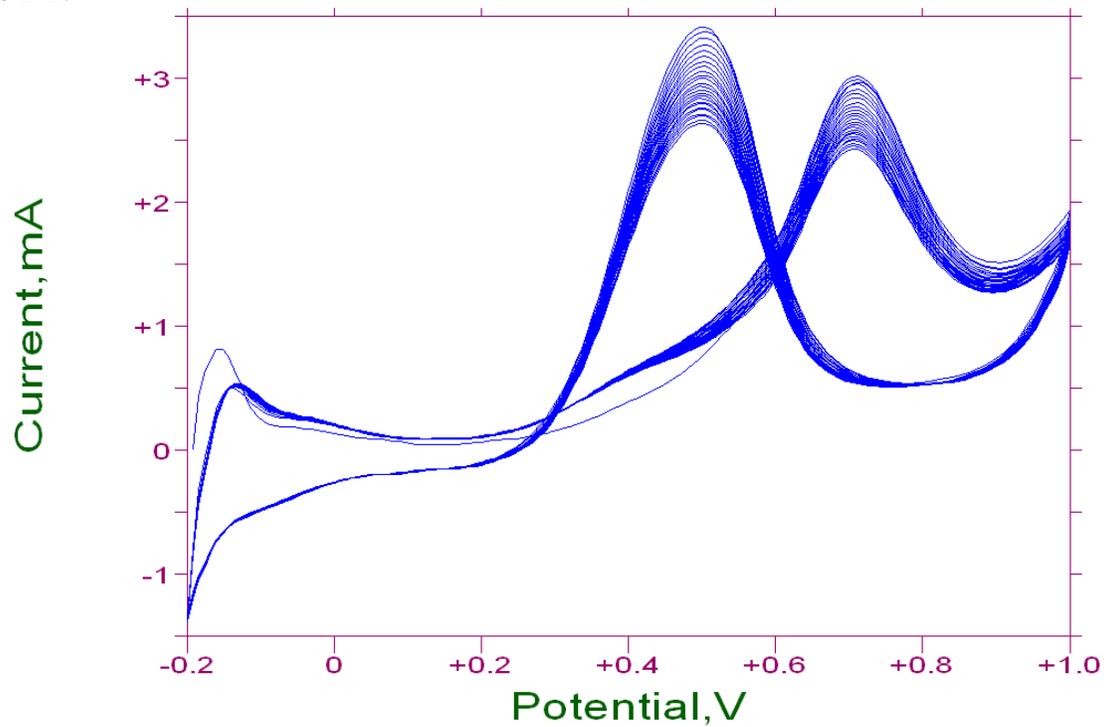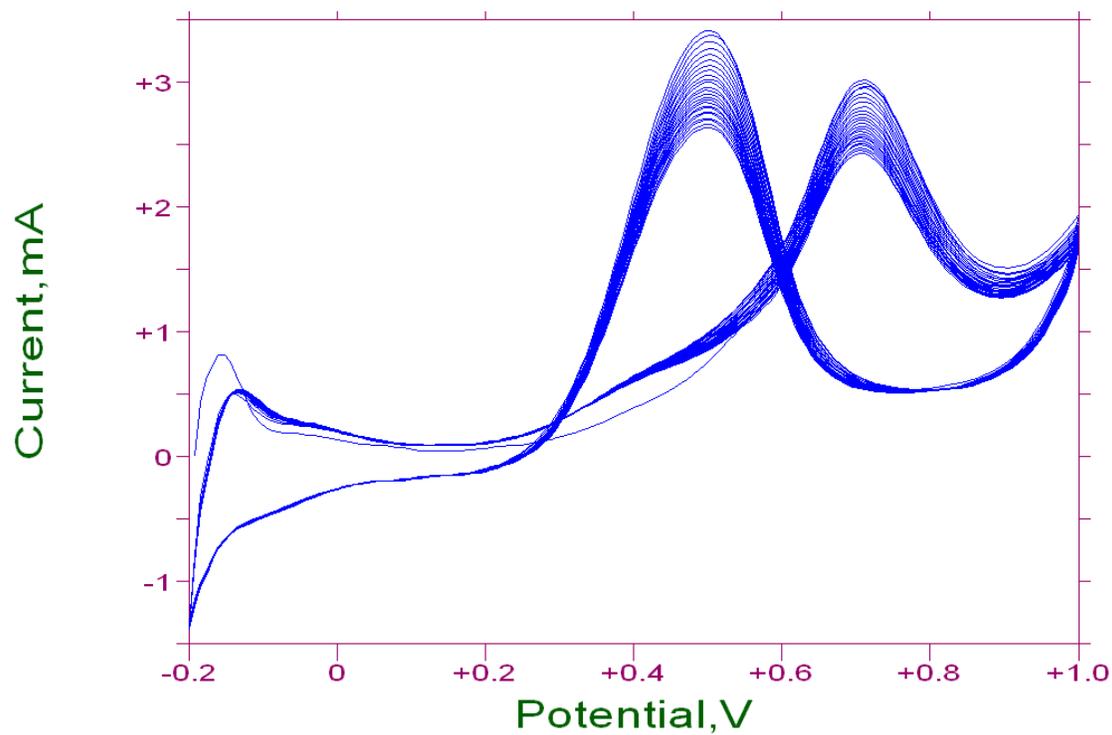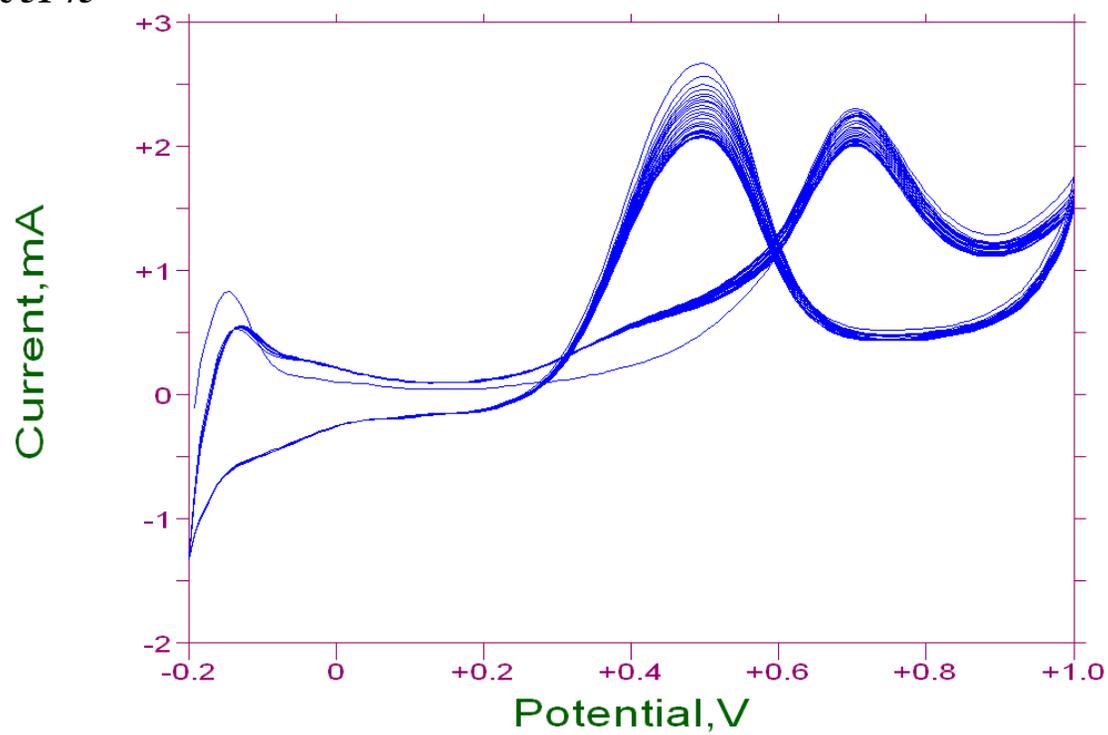
Cycle 26-50

Cycle 51-75

Cycle 76-100
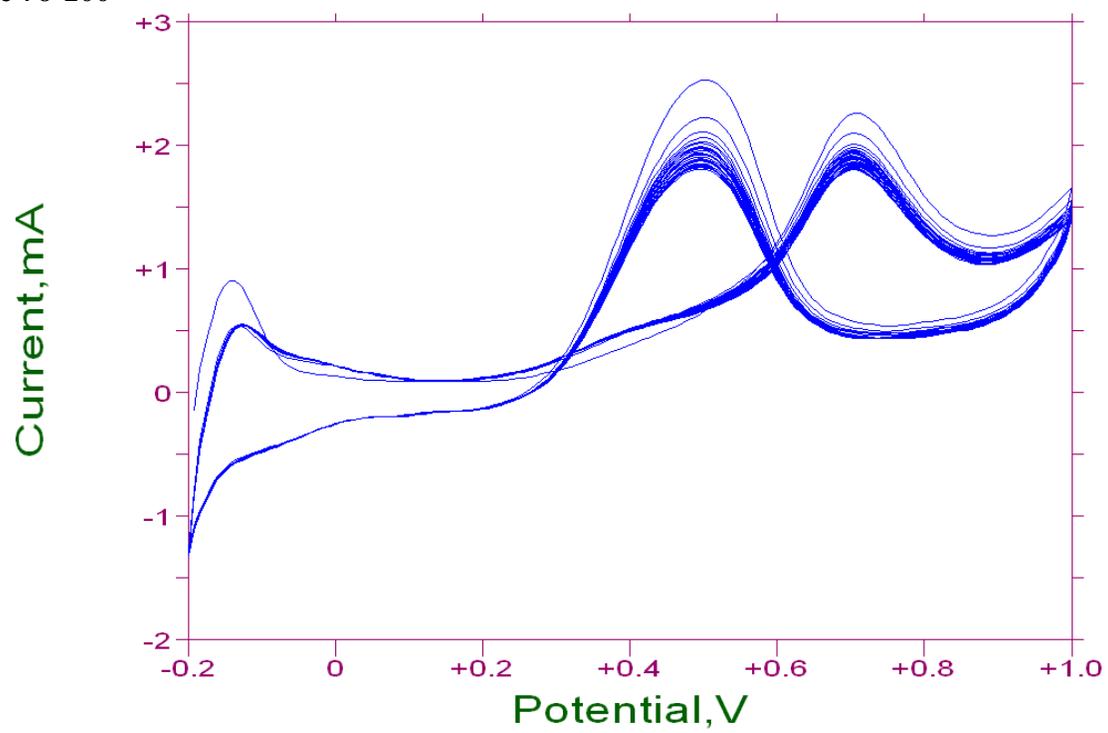
Cycle 101-125
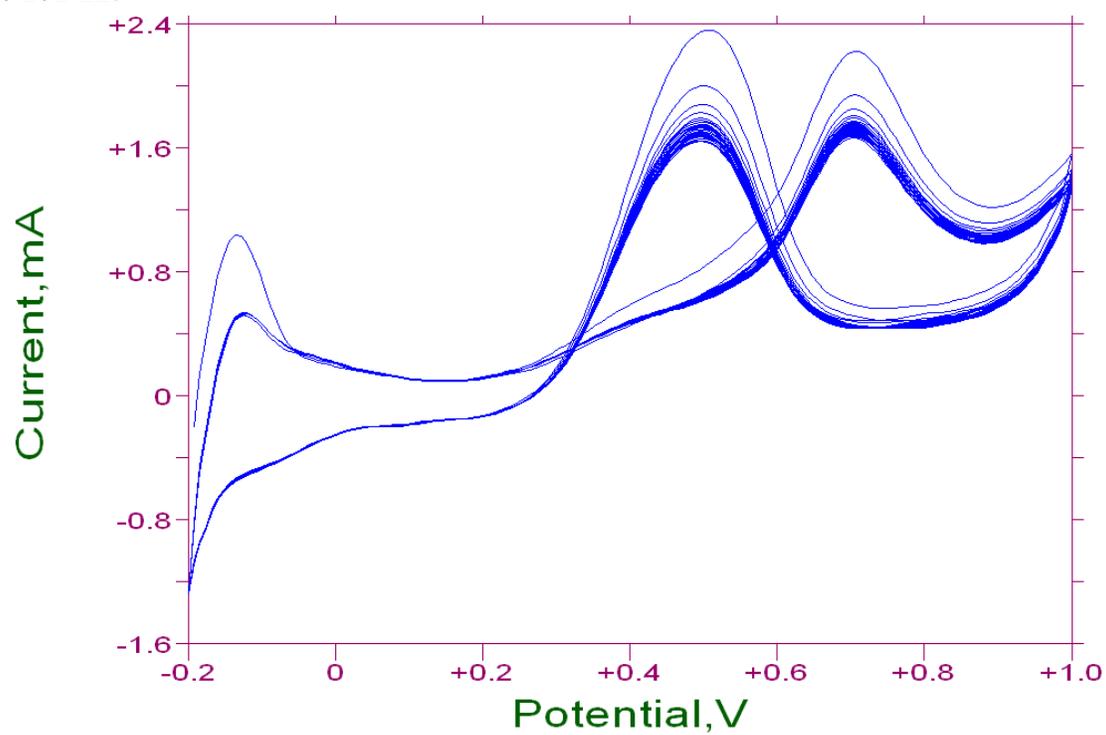
Cycle 126-150
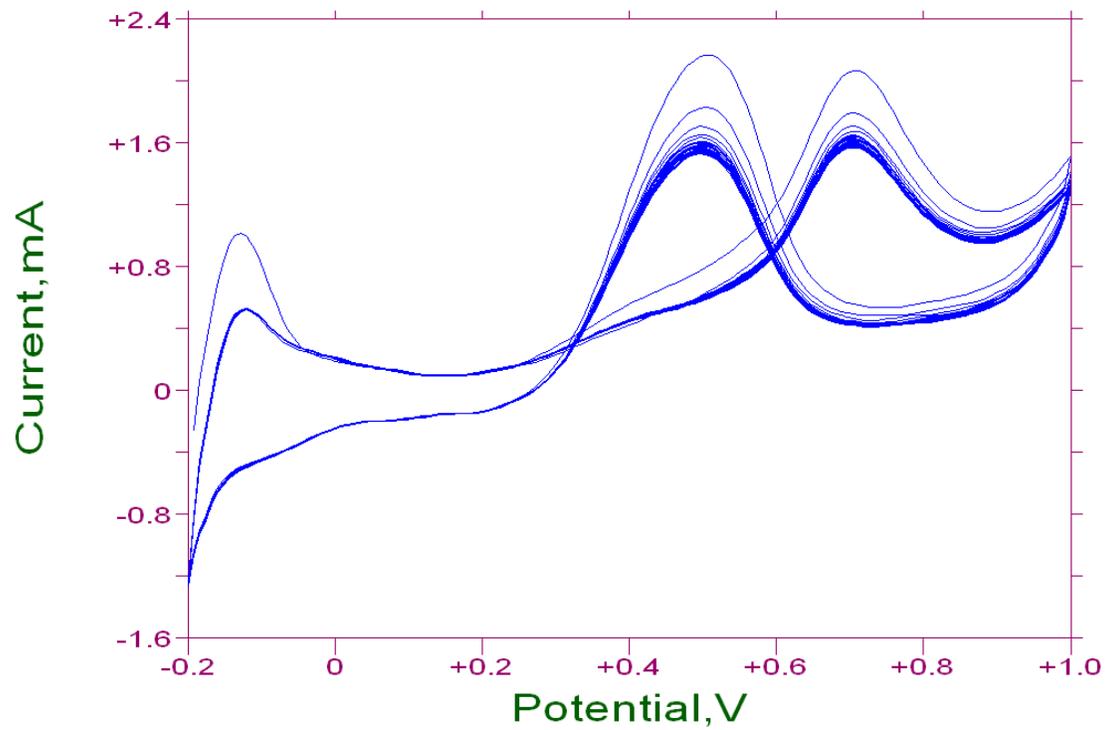
Cycle 151-175
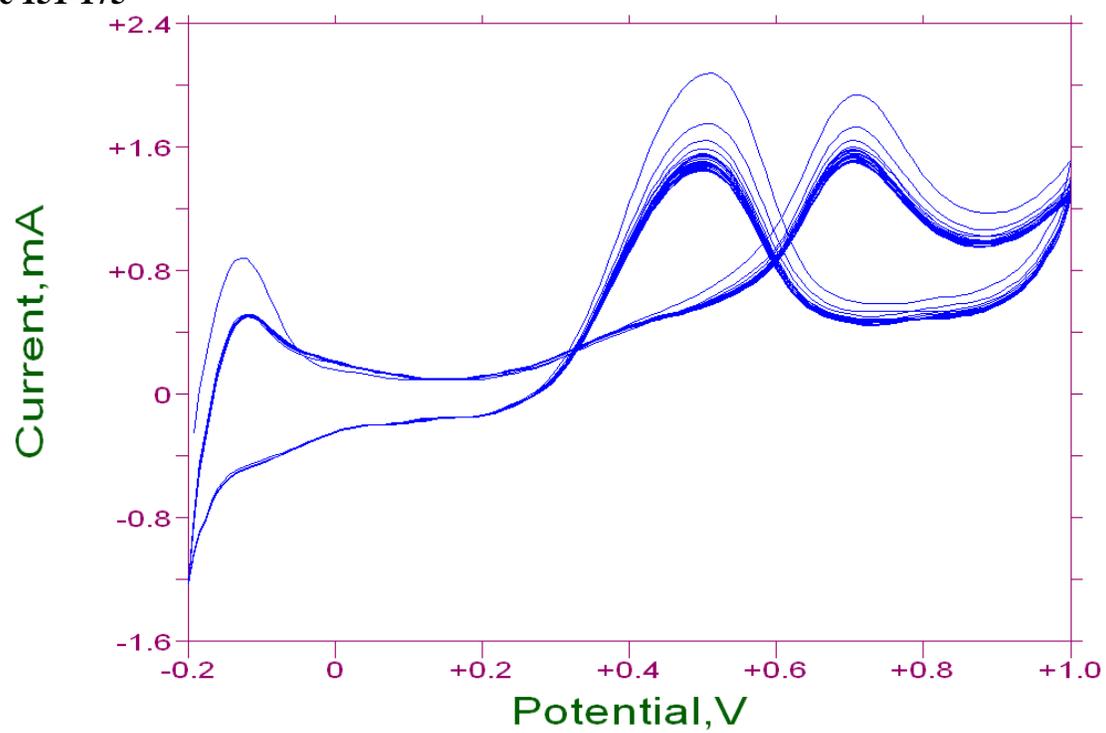
Cycle 176-200
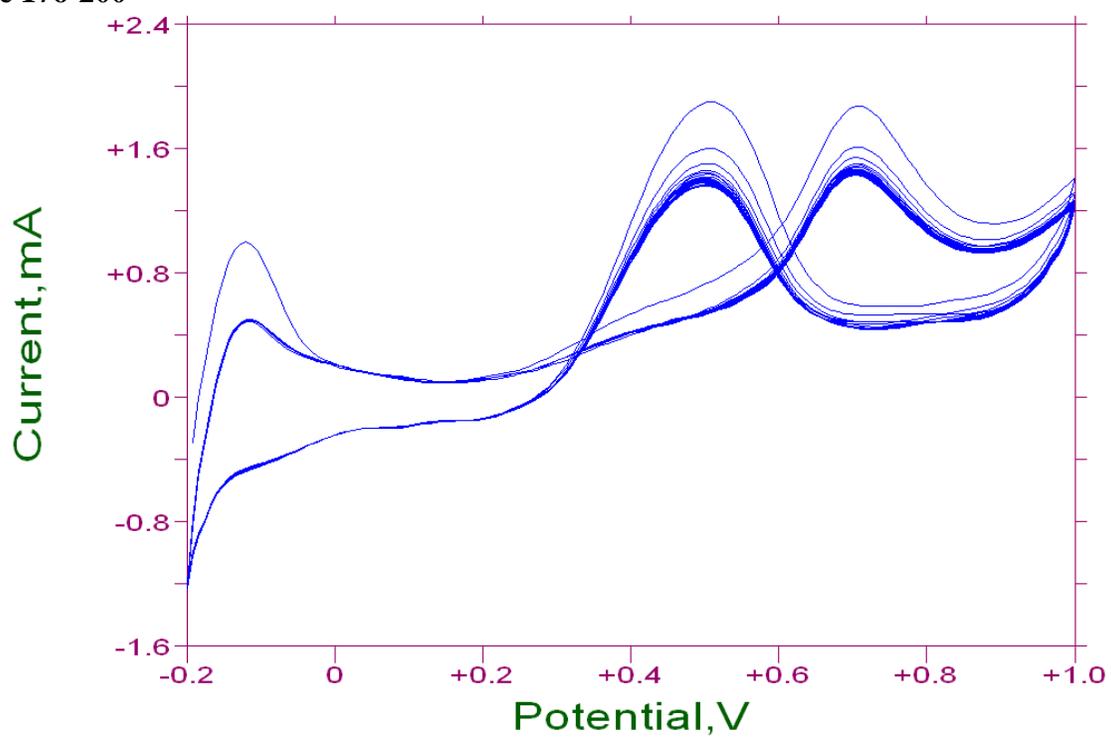
Cycle 201-225
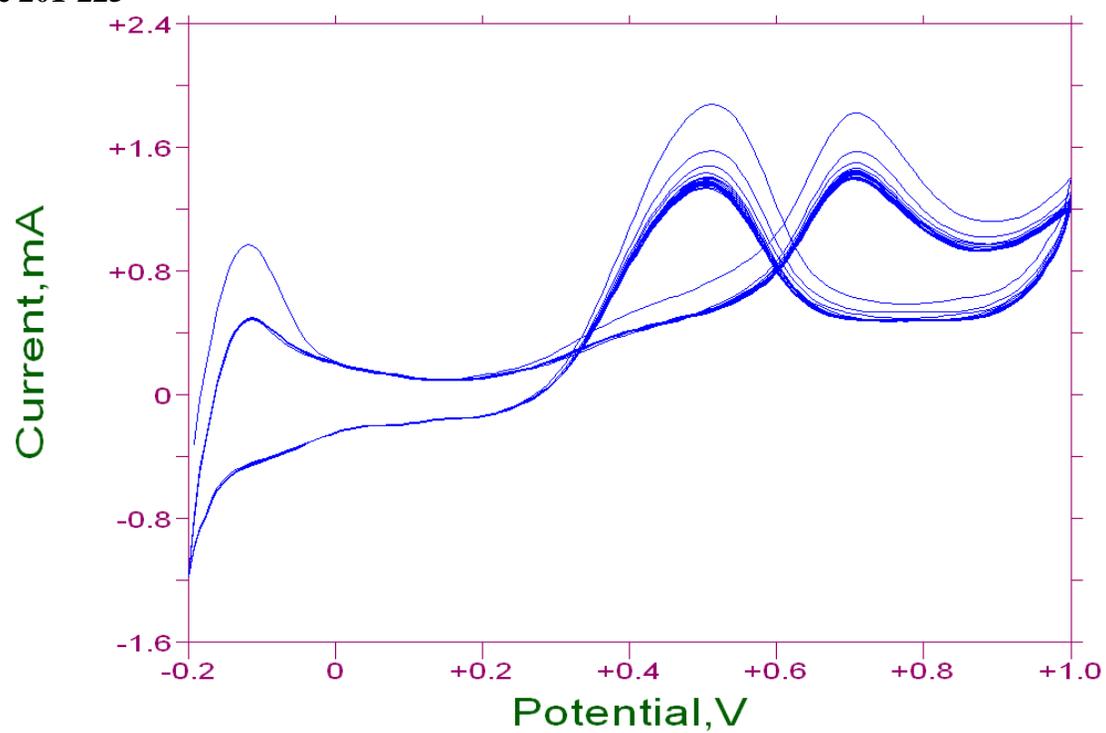
Cycle 226-250
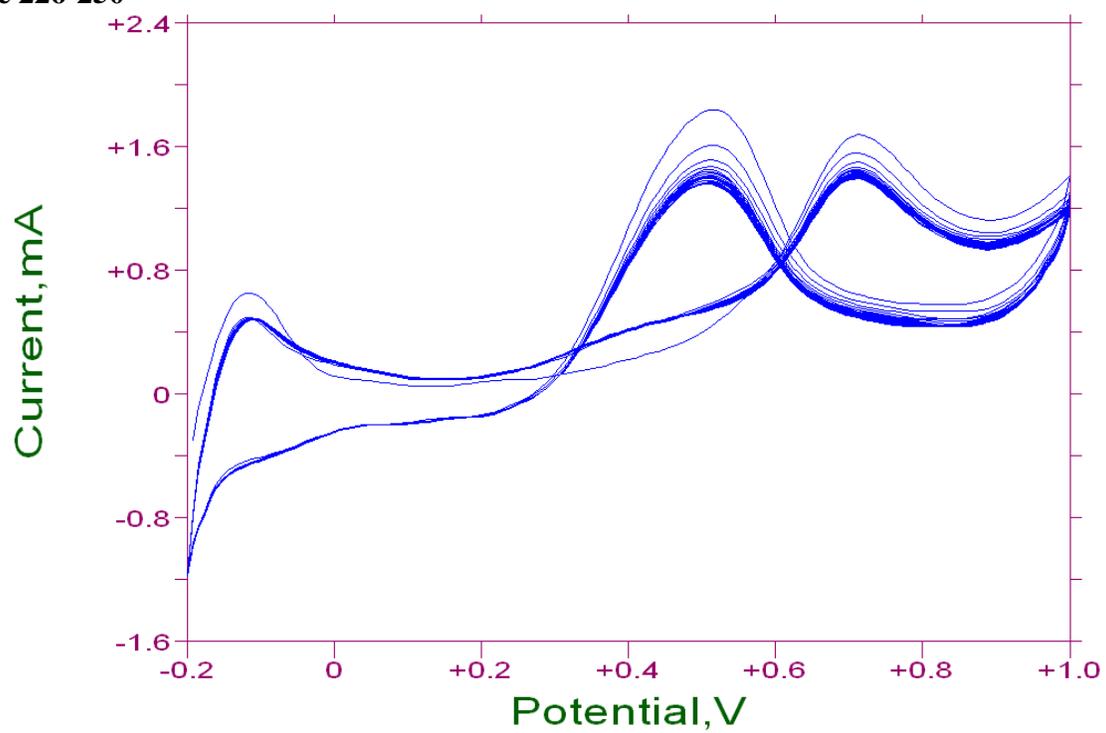
Cycle 251-275
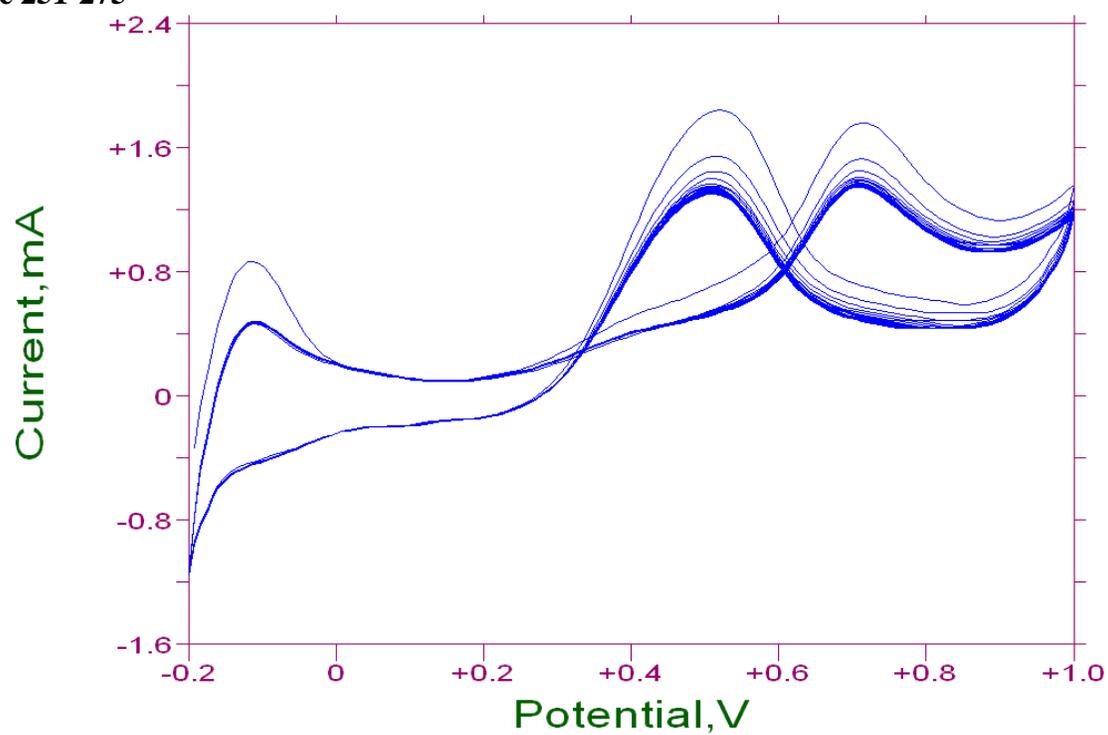
Cycle 276-300
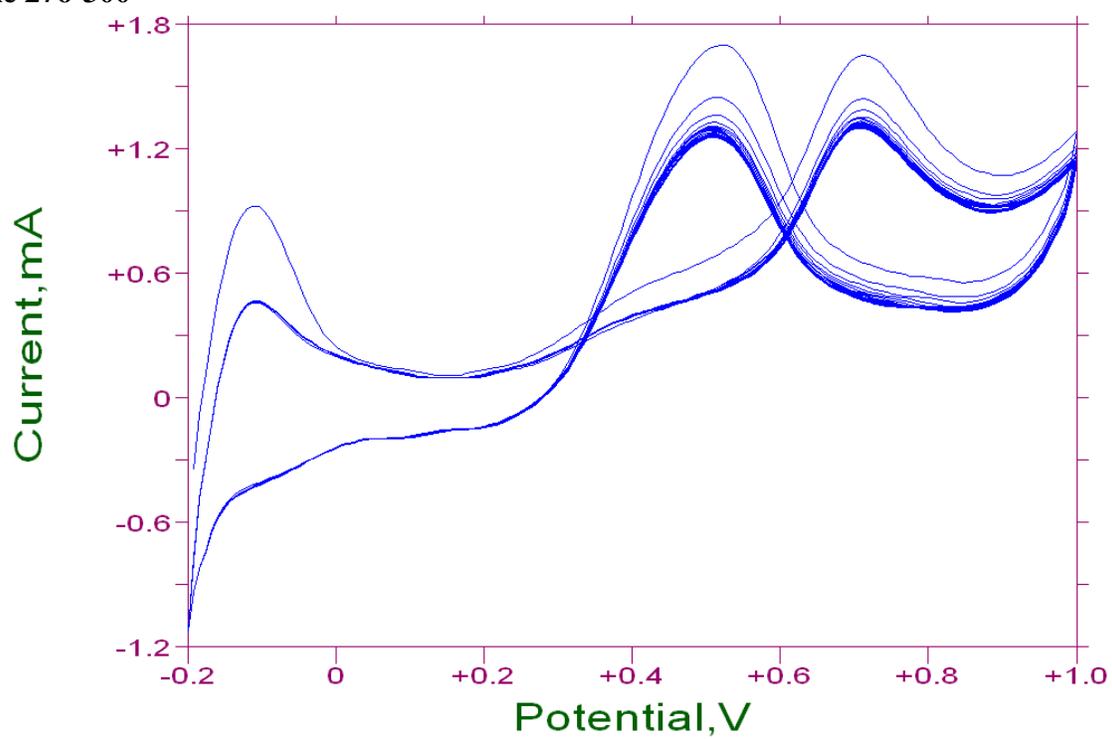
20 wt% Pt on SnO$_2$

Blank Electrode
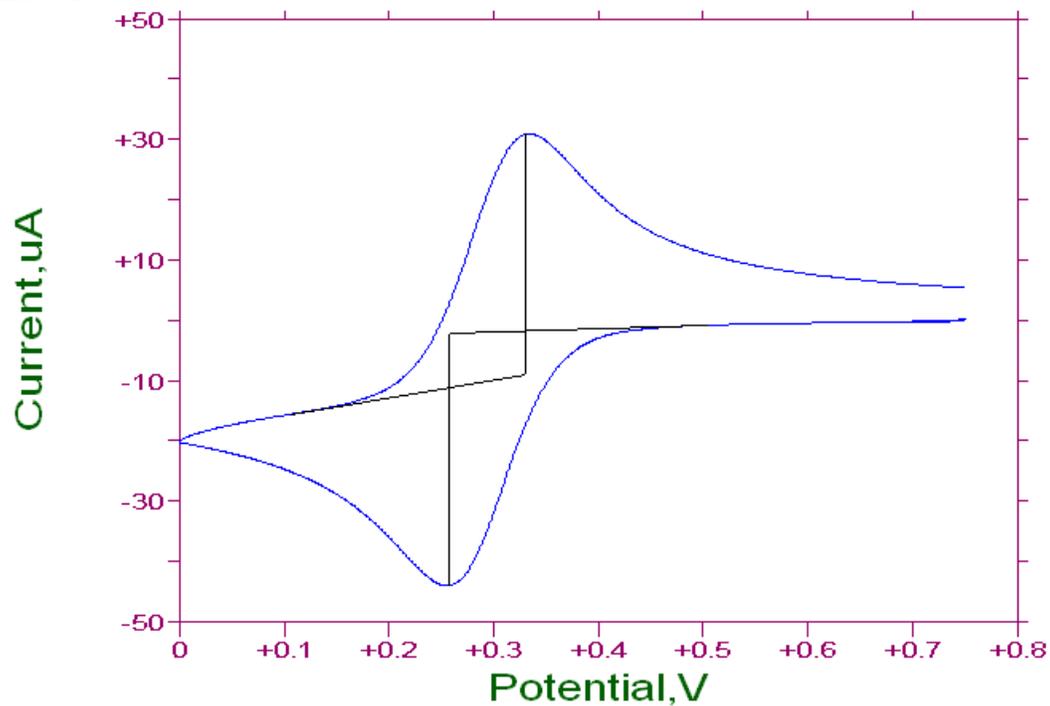
Segment 1:
Segment 2:
Ep = +257 mV
ip = -4.176e-005 A
Ah = -2.814e-006 A*V

Segment 3:
Ep = +331 mV
ip = +3.978e-005 A
Ah = +2.568e-006 A*V
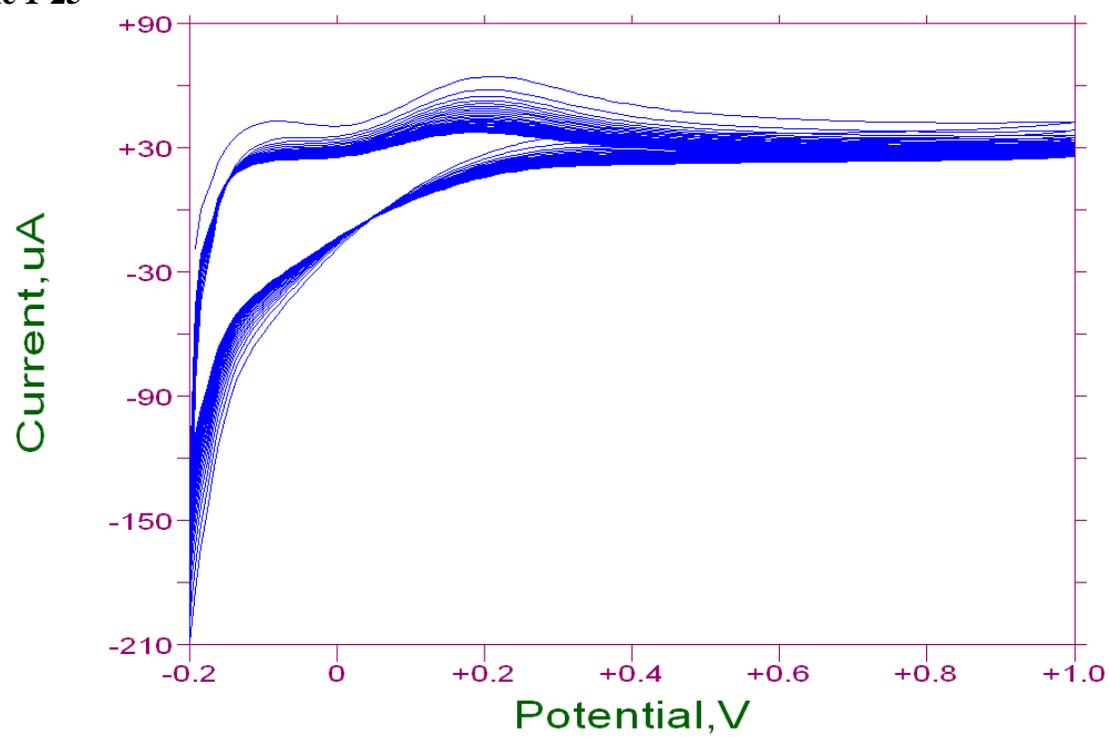
Cycle 1-25

60 wt% Pt on SnO$_2$

Cycle 1-25
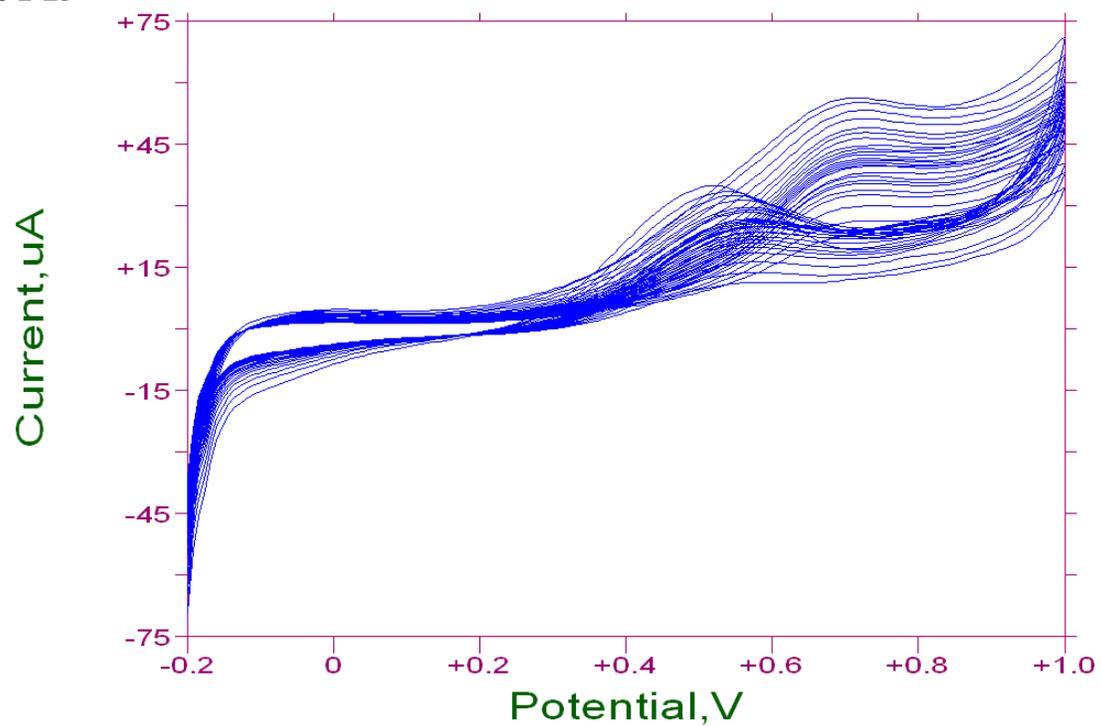
Cycle 26-50
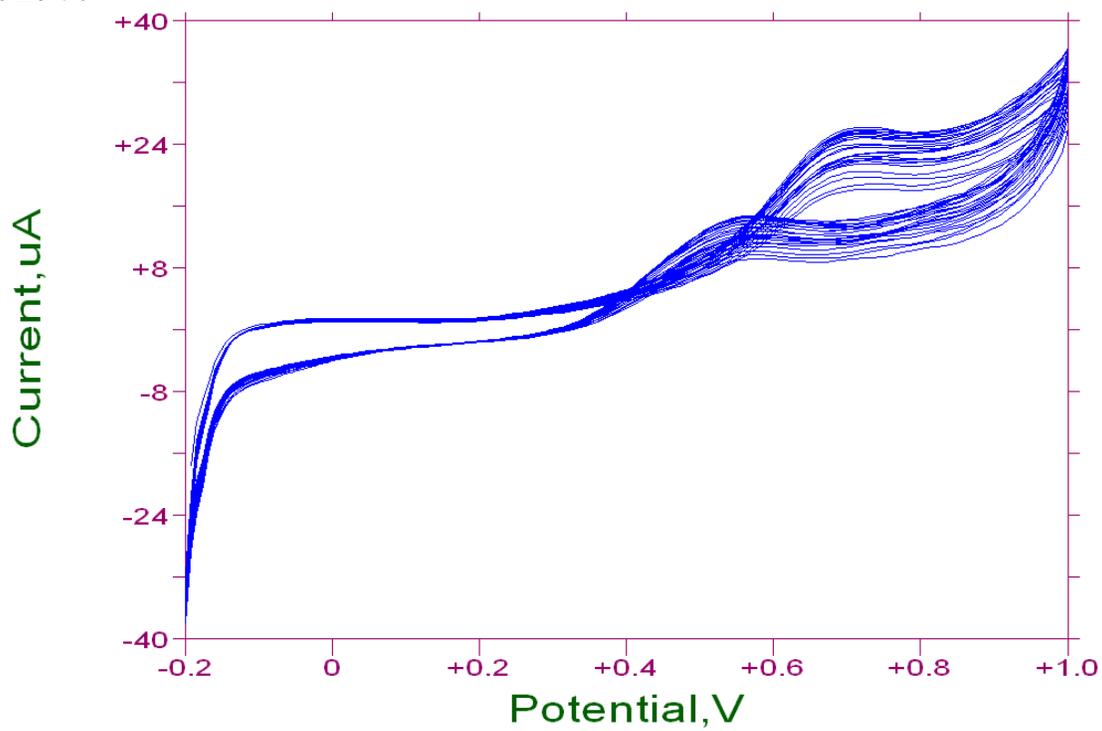
Cycle 51-75
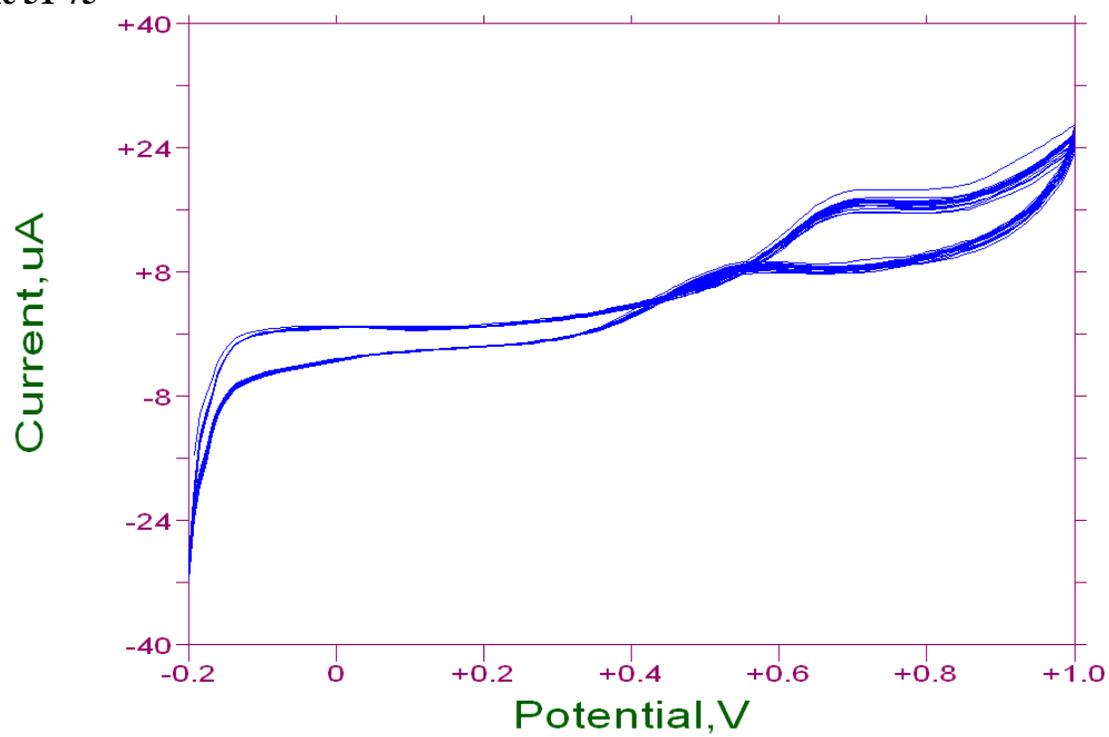
Cycle 76-100
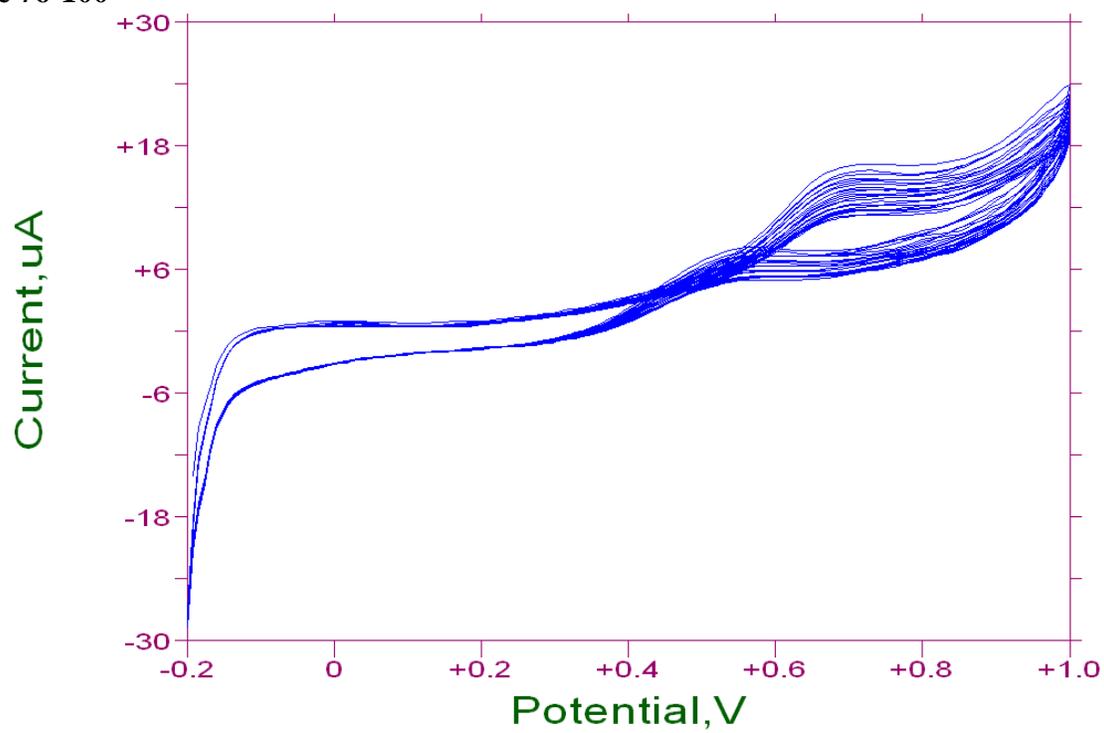
Cycle 101-125
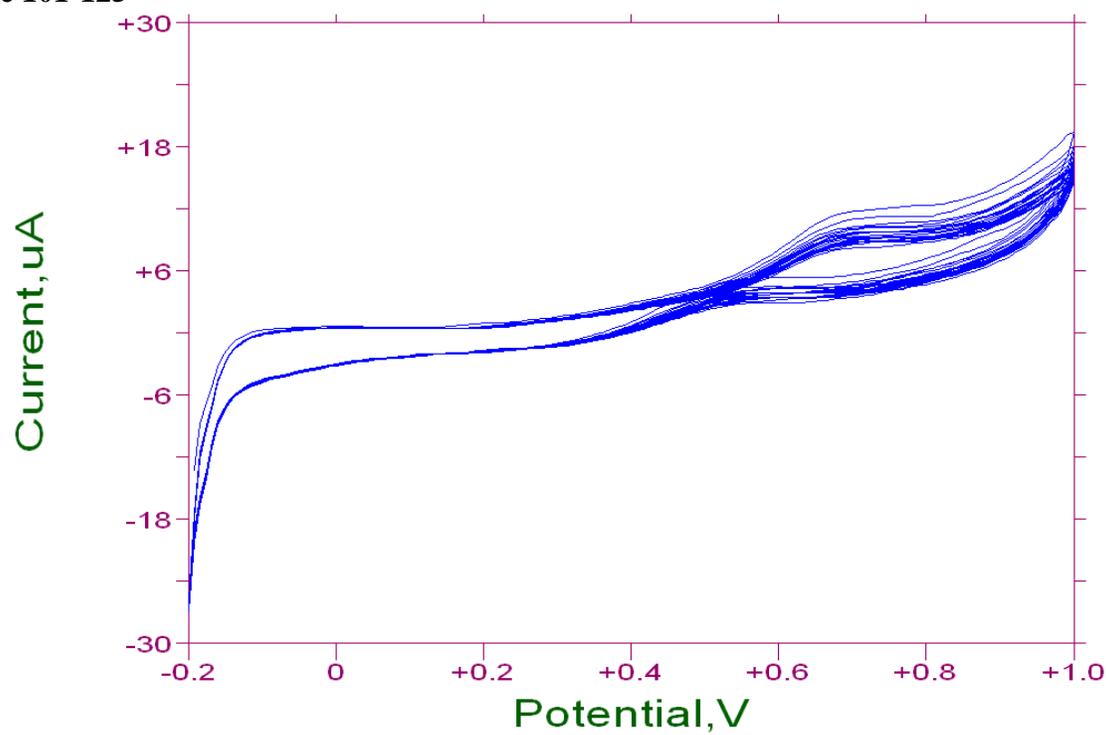
Cycle 126-150
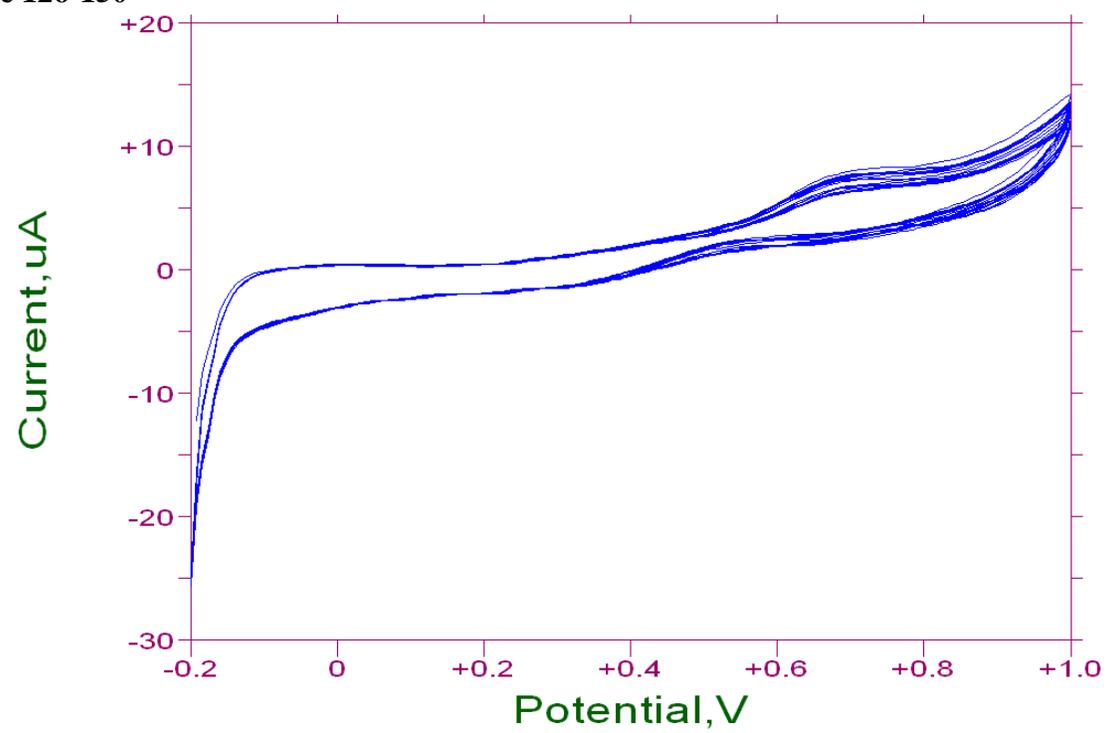
Cycle 151-175
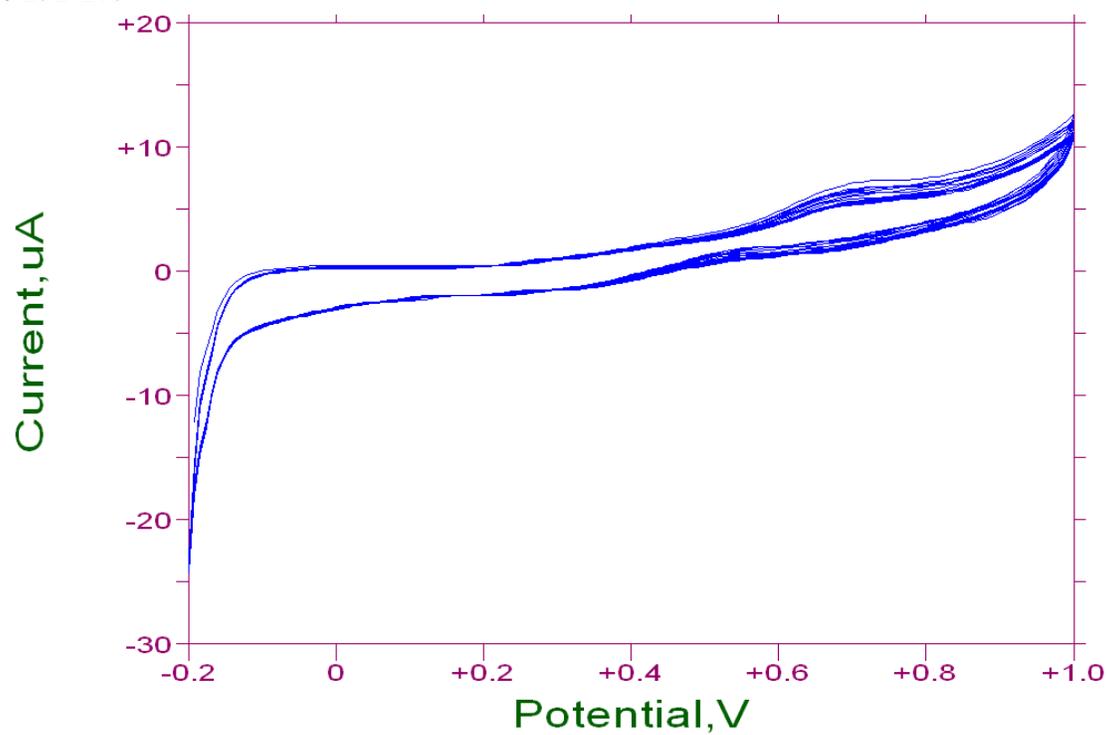
Cycle 176-200
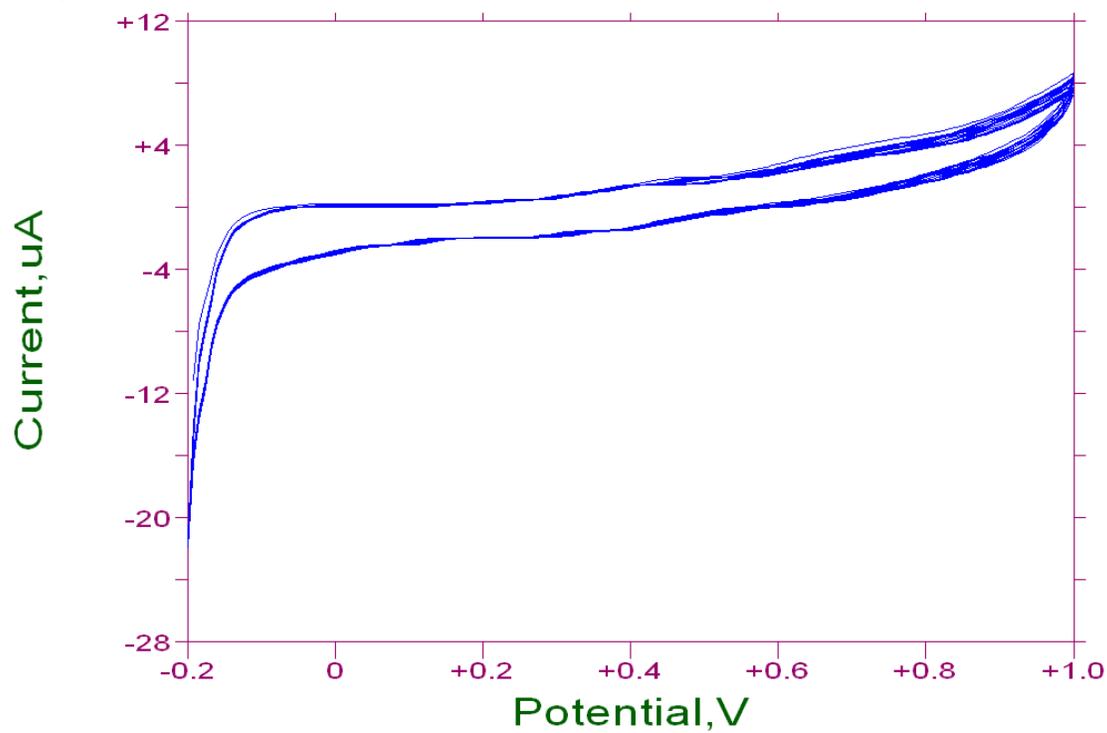
Cycle 201-225
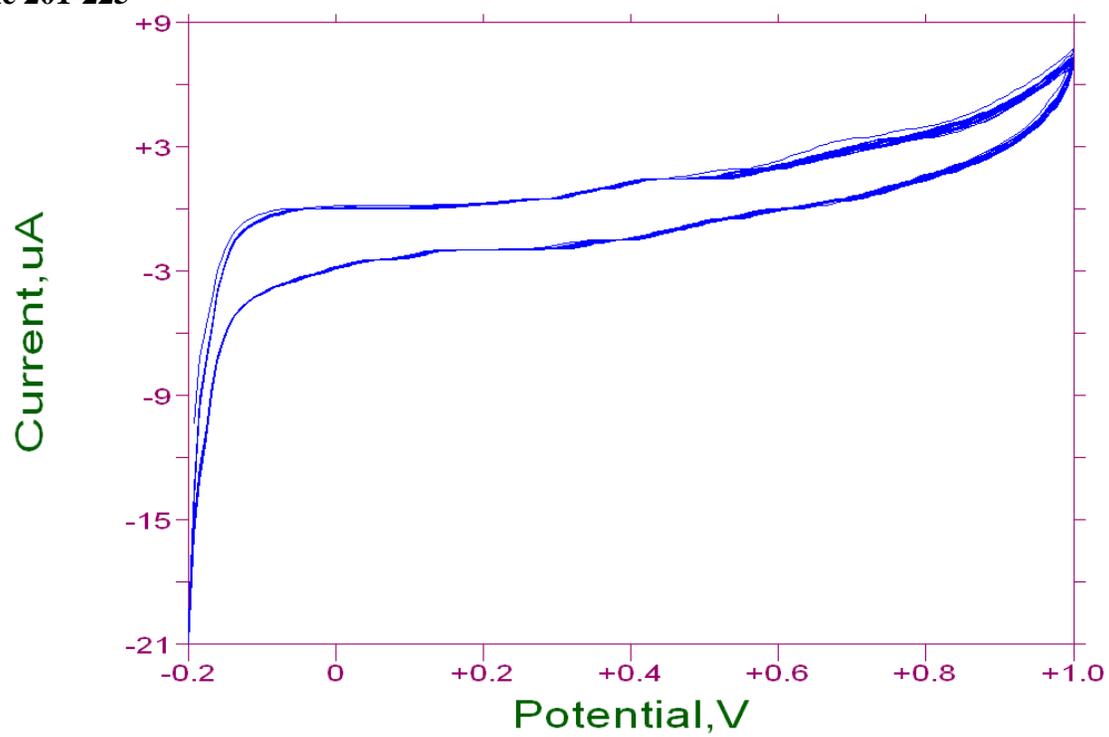
20 wt% Pt on NanoArc SnO$_2$
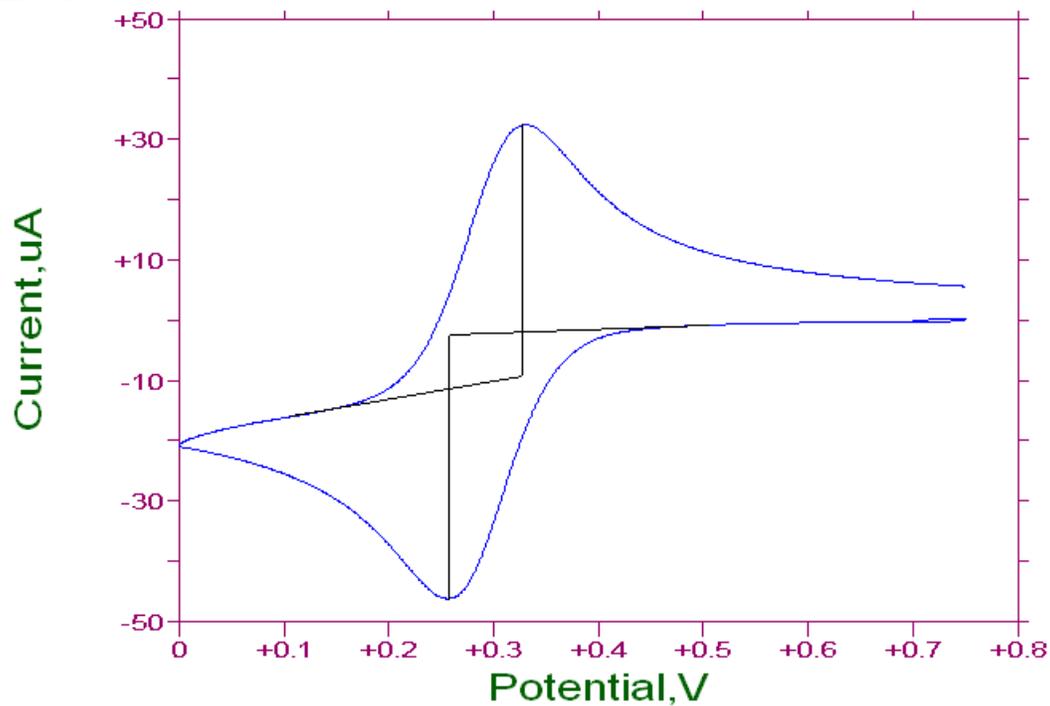
Blank Electrode


```
Segment 1:
Segment 2:
Ep = +258 mV
ip = -4.383e-005 A
Ah = -2.907e-006 A*V

Segment 3:
Ep = +328 mV
ip = +4.174e-005 A
Ah = +2.683e-006 A*V
```

Cycle 1-25
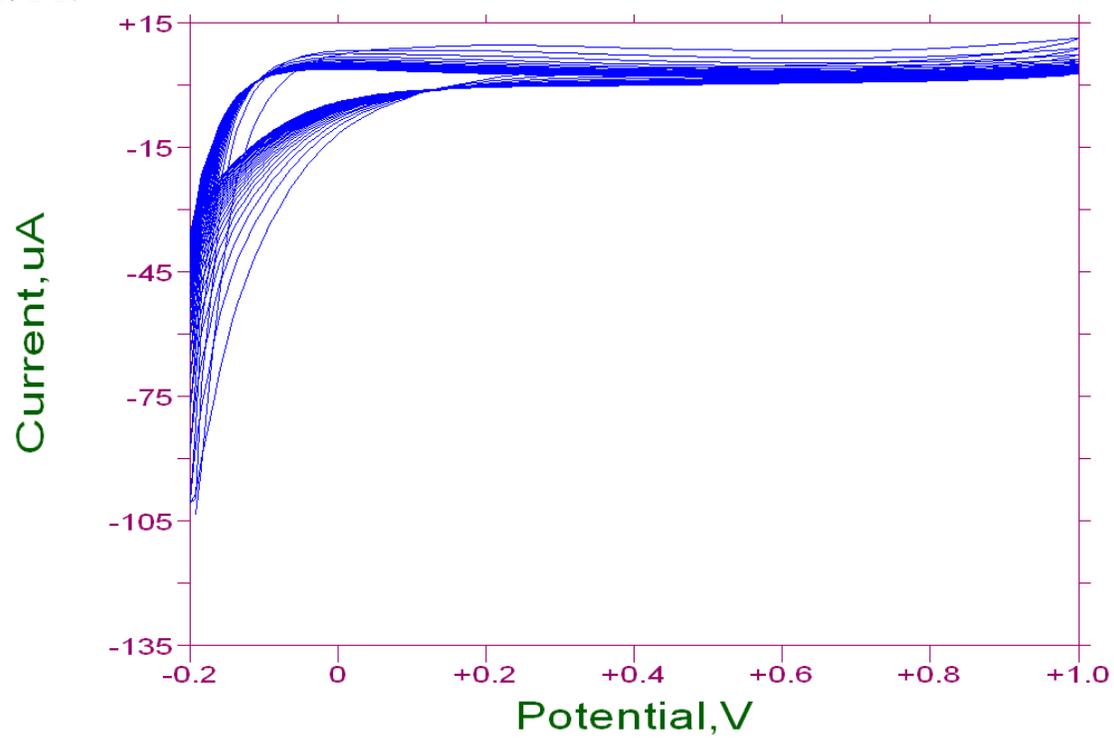
20 wt% Pt on Calcinated NanoArc SnO$_2$
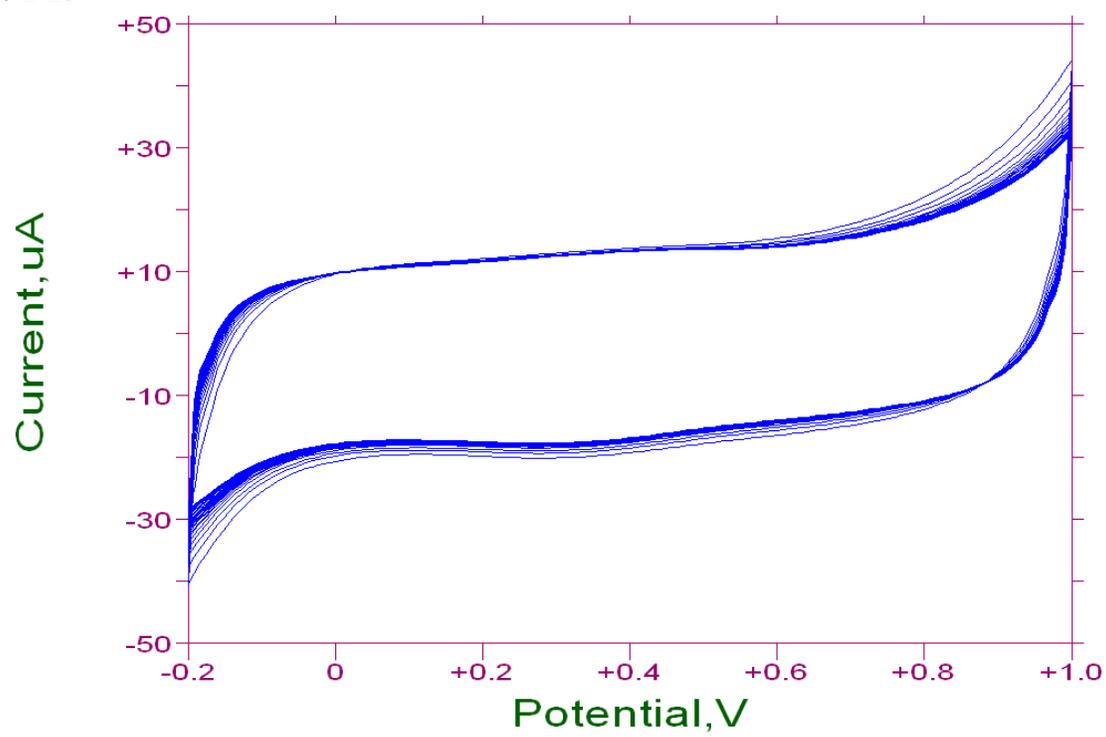
Blank Electrode
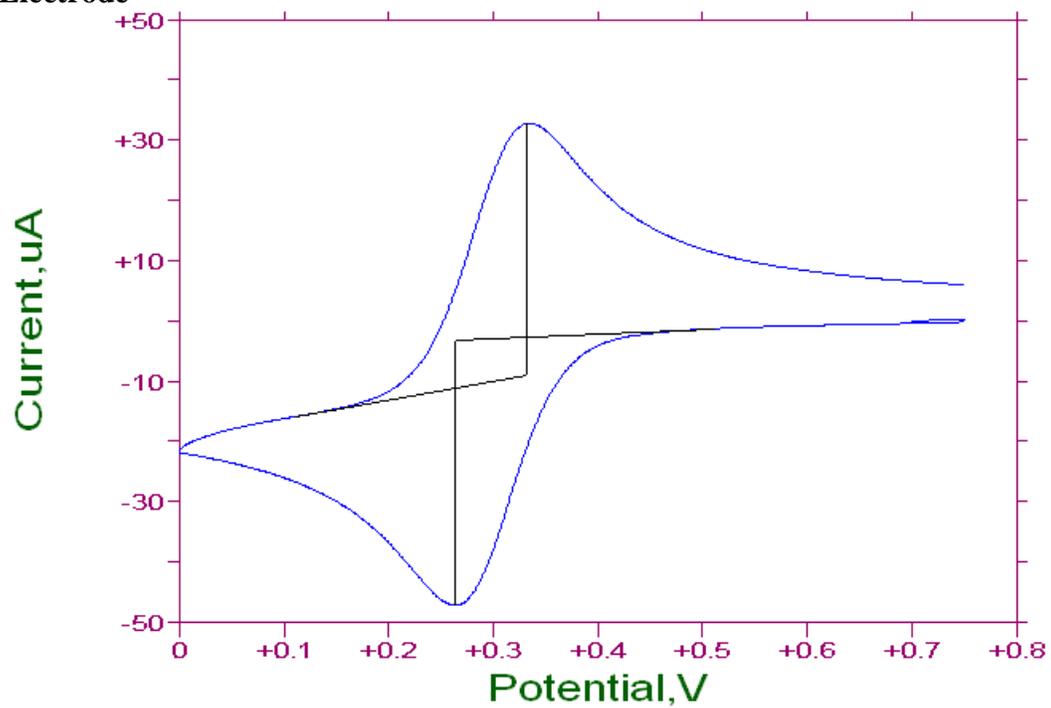
Segment 1:
Segment 2:
Ep = +264 mV
ip = -4.391e-005 A
Ah = -2.928e-006 A*V

Segment 3:
Ep = +332 mV
ip = +4.177e-005 A
Ah = +2.641e-006 A*V
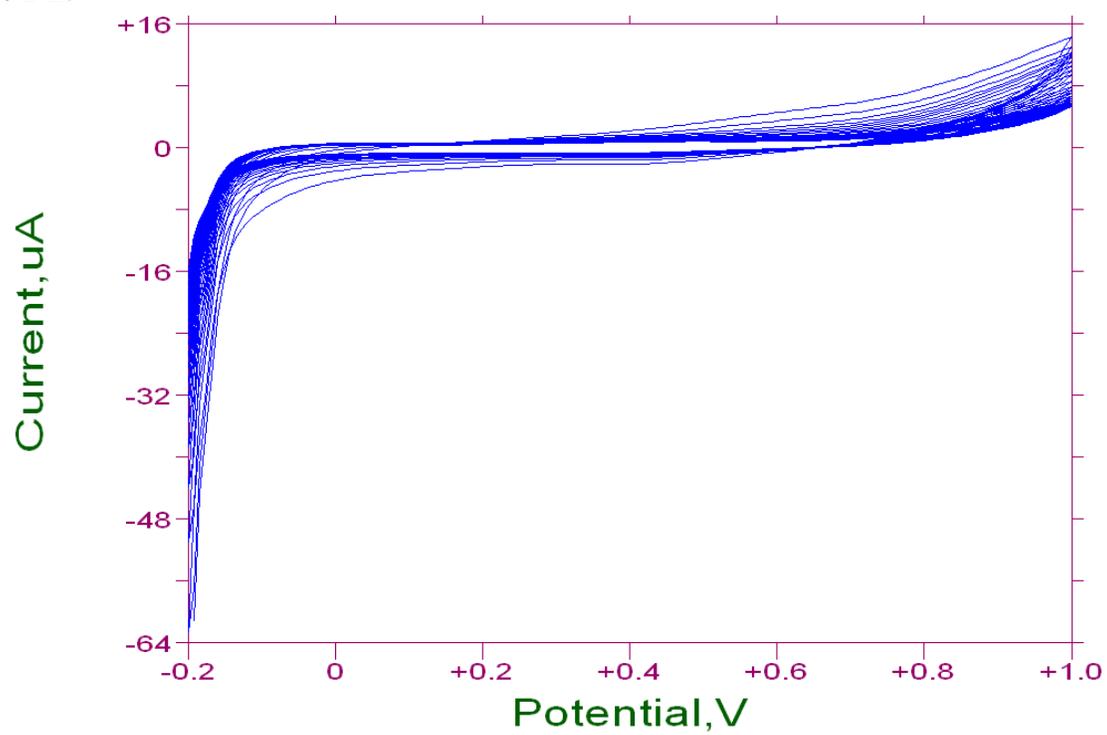
Cycle 1-25

40 wt% Pt on NanoArc SnO$_2$

Blank Electrode
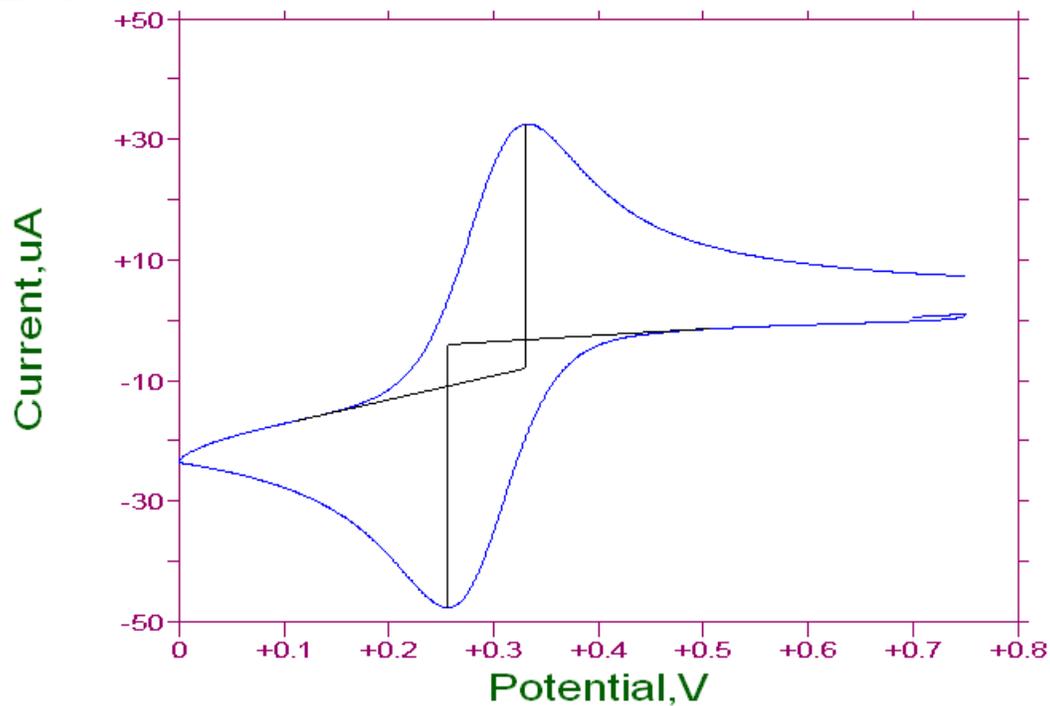
Segment 1:
Segment 2:
Ep = +256 mV
ip = -4.367e-005 A
Ah = -3.003e-006 A*V

Segment 3:
Ep = +330 mV
ip = +4.055e-005 A
Ah = +2.640e-006 A*V

Cycle 1-25
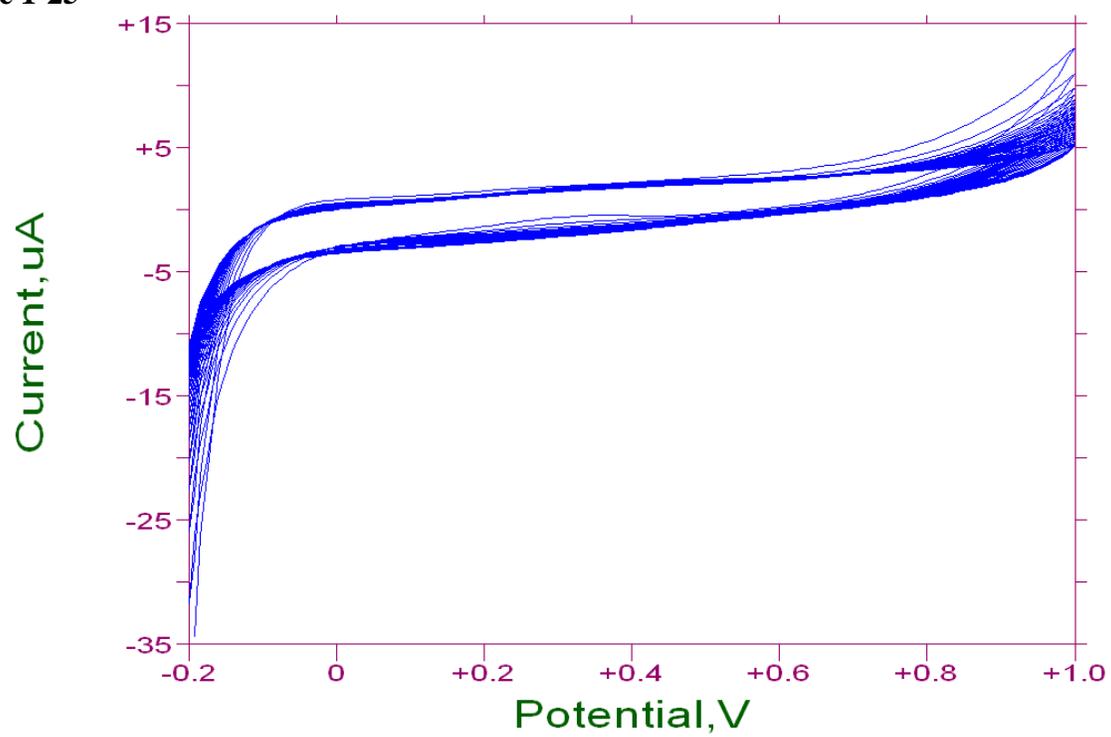
20 wt% Pt on NanoArc SnO₂ Mixed with XC-72 Carbon

Cycle 1-25
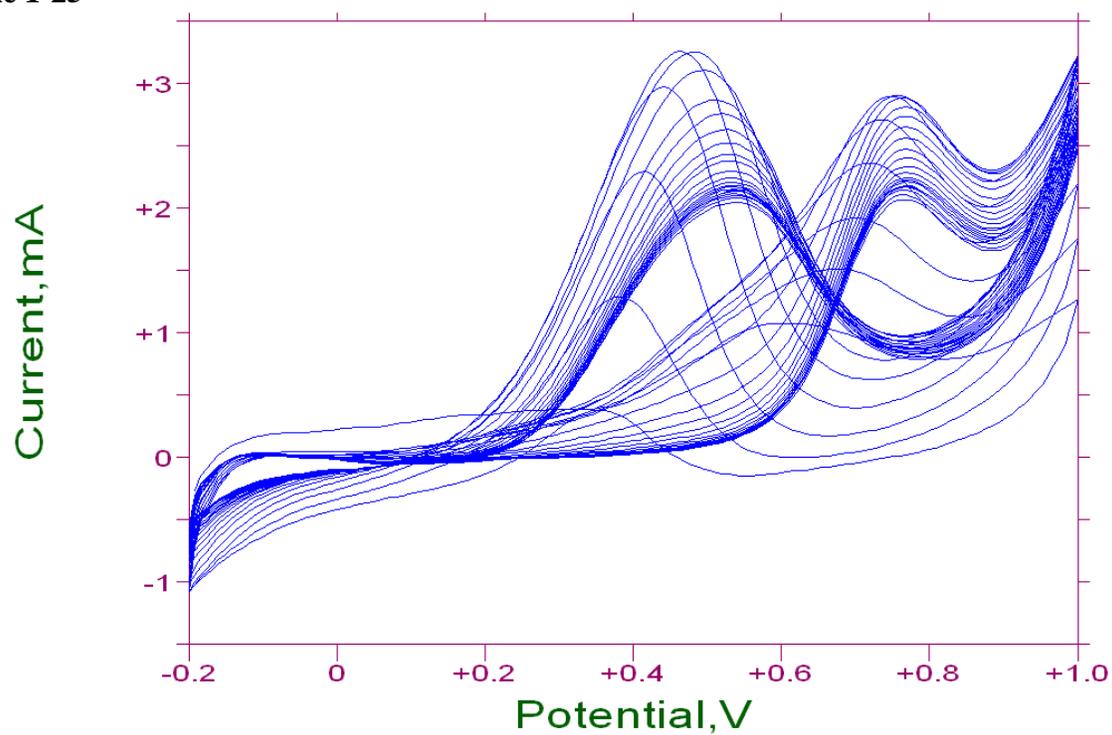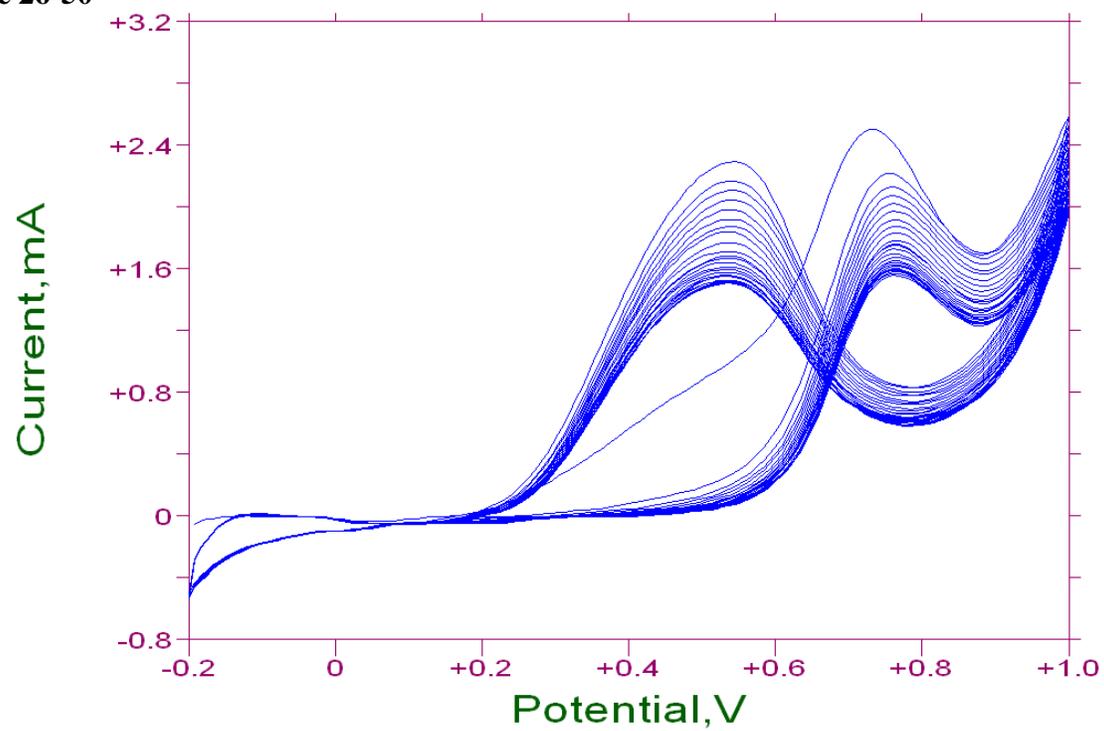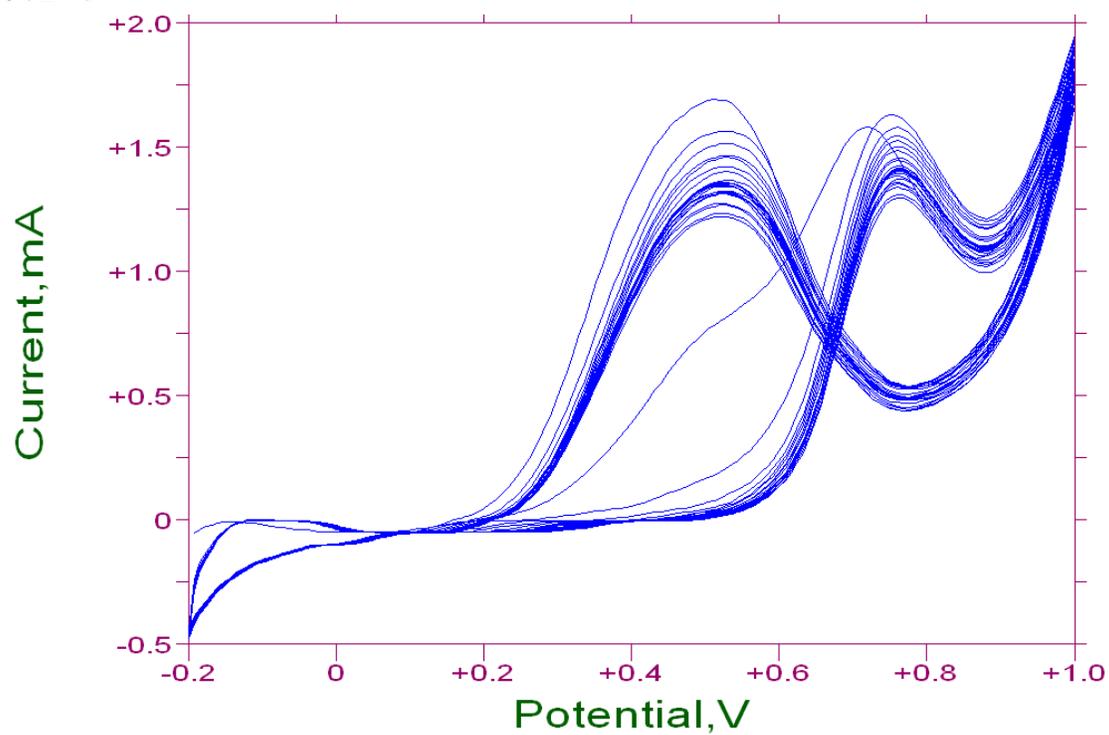
Cycle 26-50

Cycle 51-75

Cycle 76-100
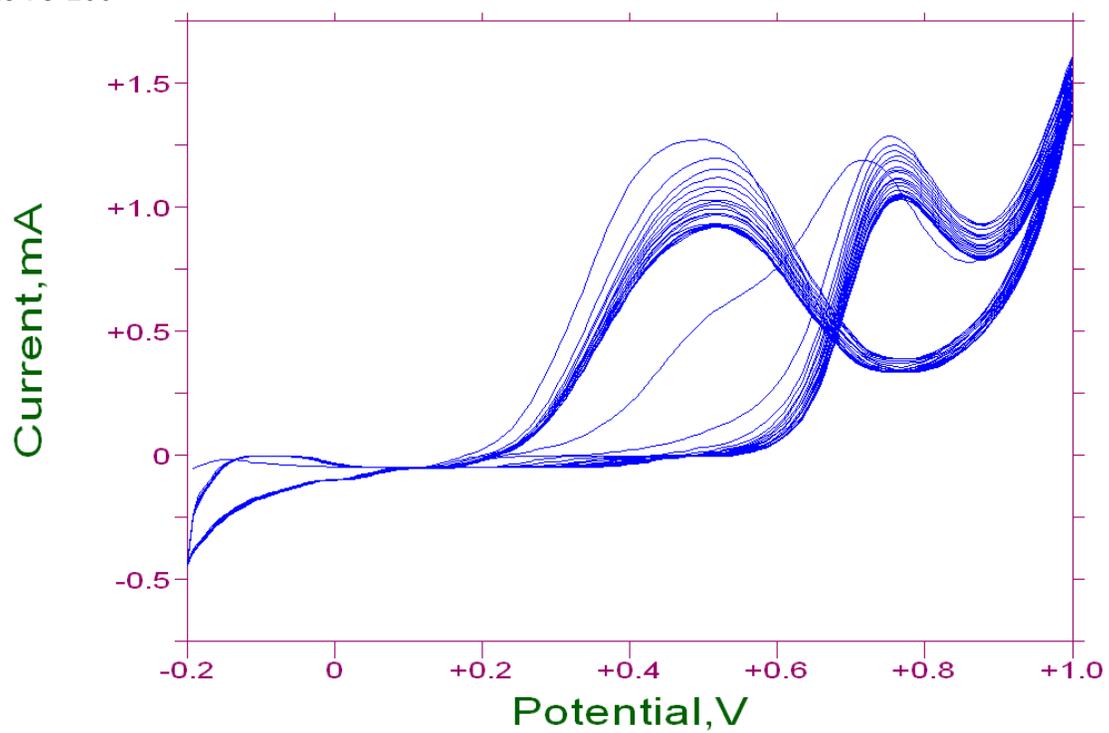
Cycle 101-125
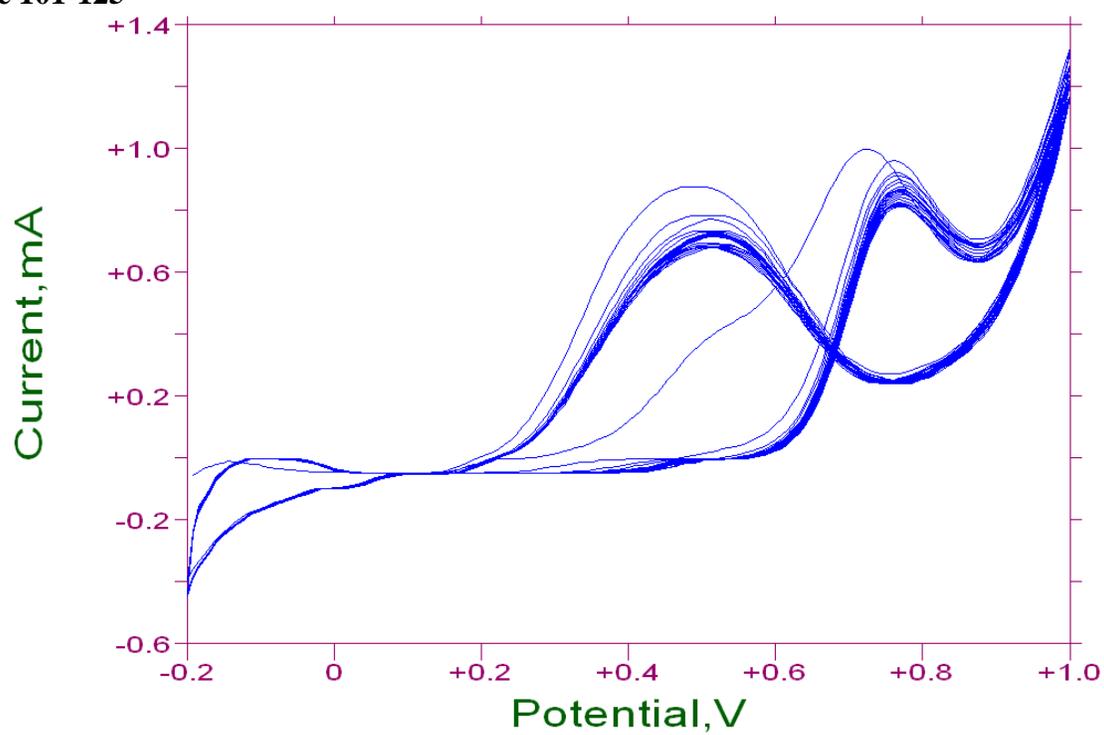
Cycle 126-150
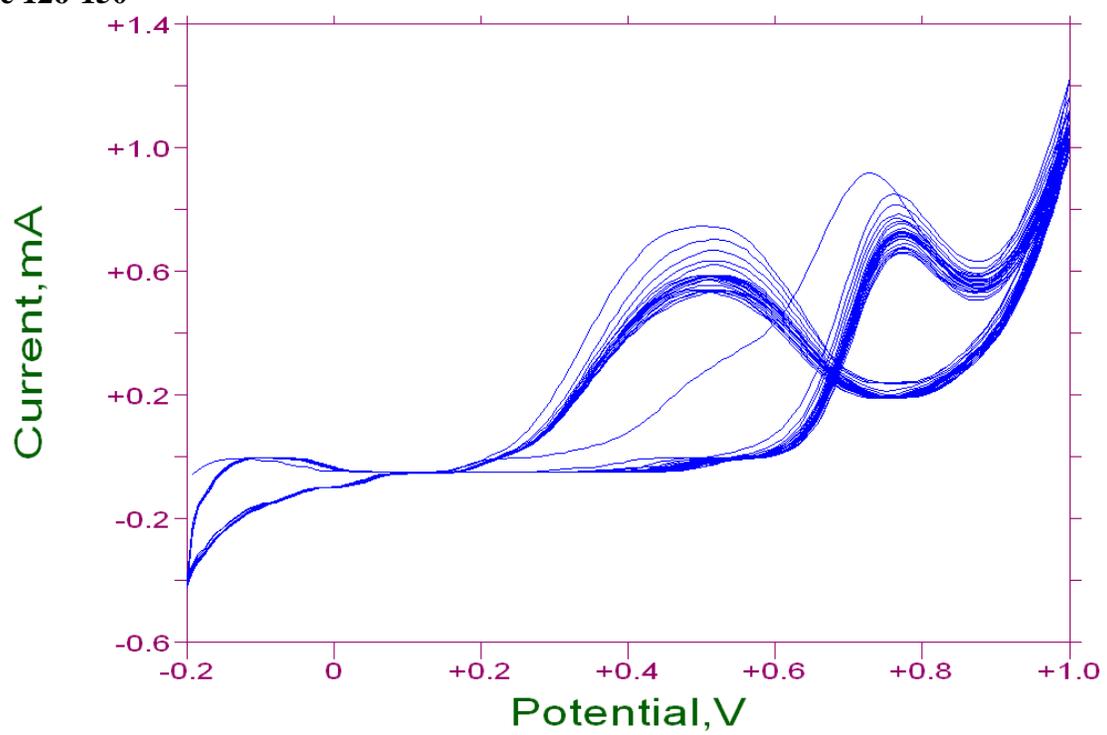
Cycle 151-175
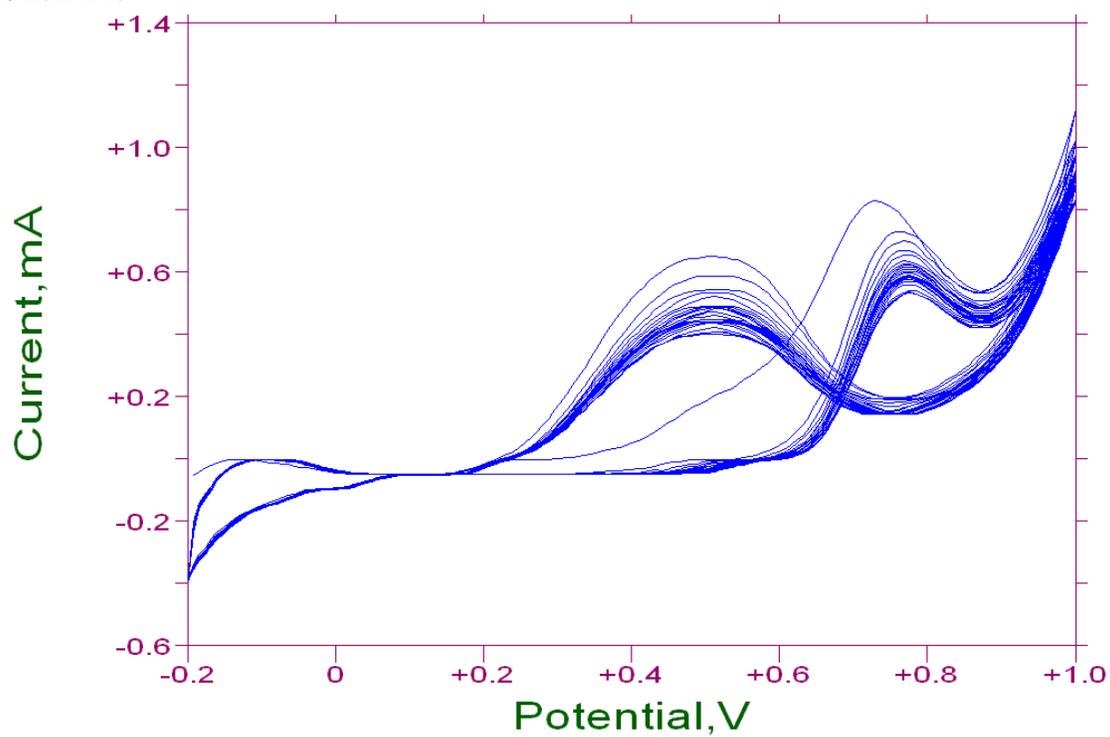
Cycle 176-200
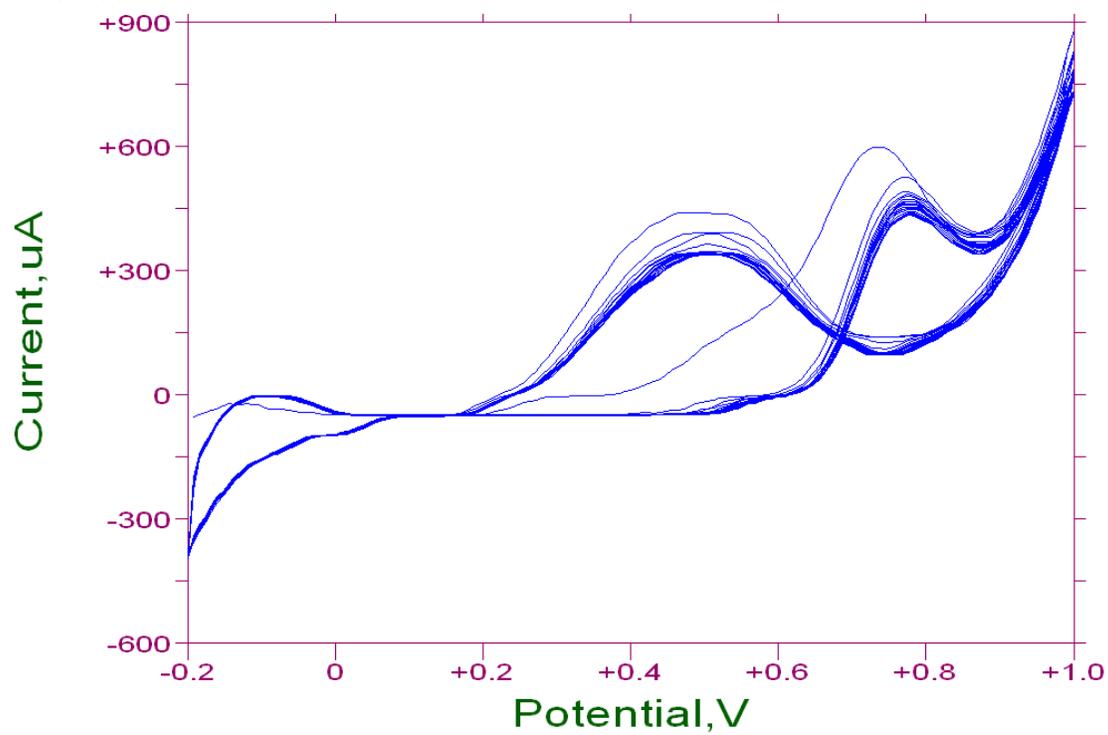
Cycle 201-225
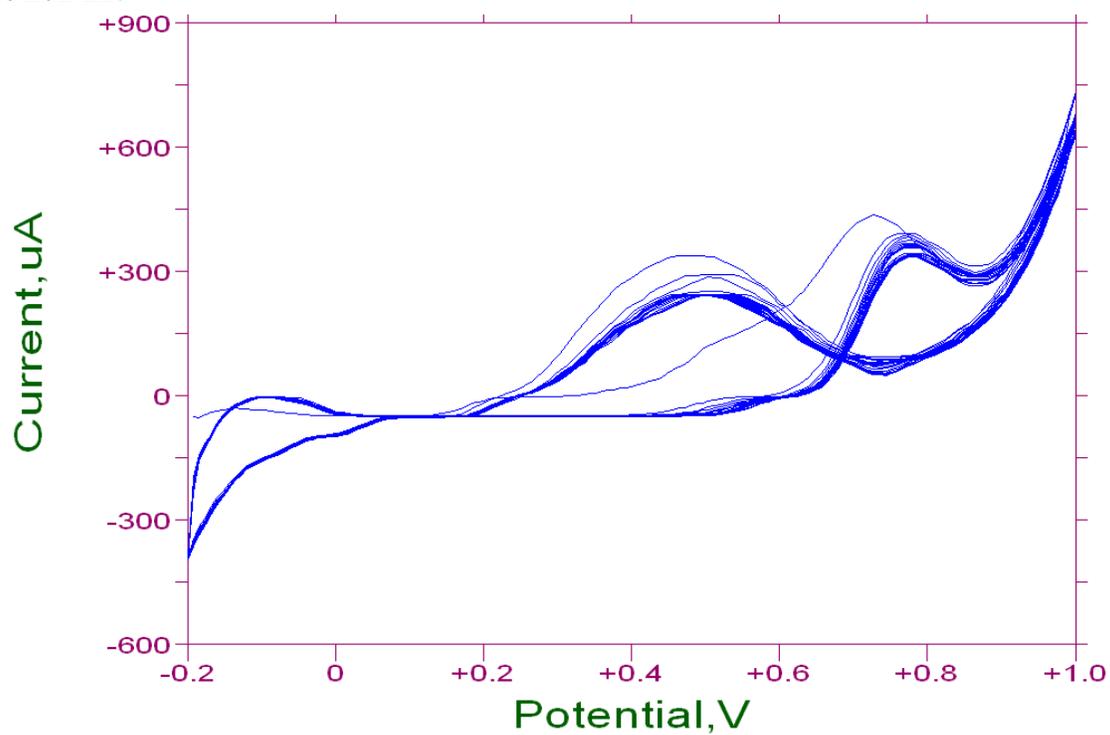
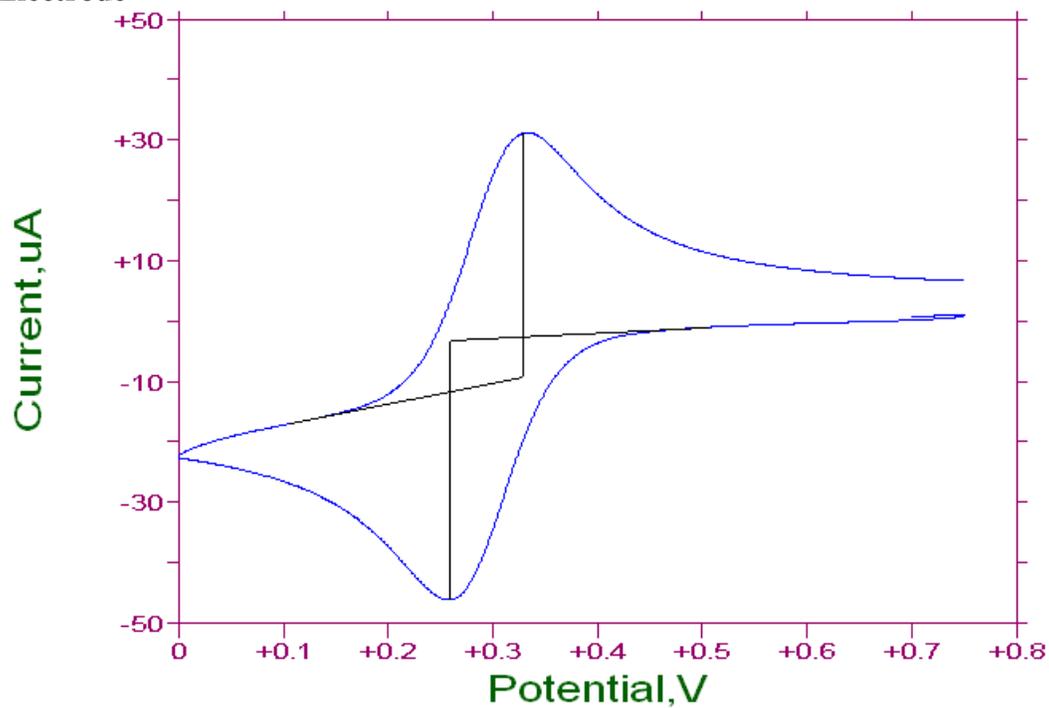**Cycle 226-250**
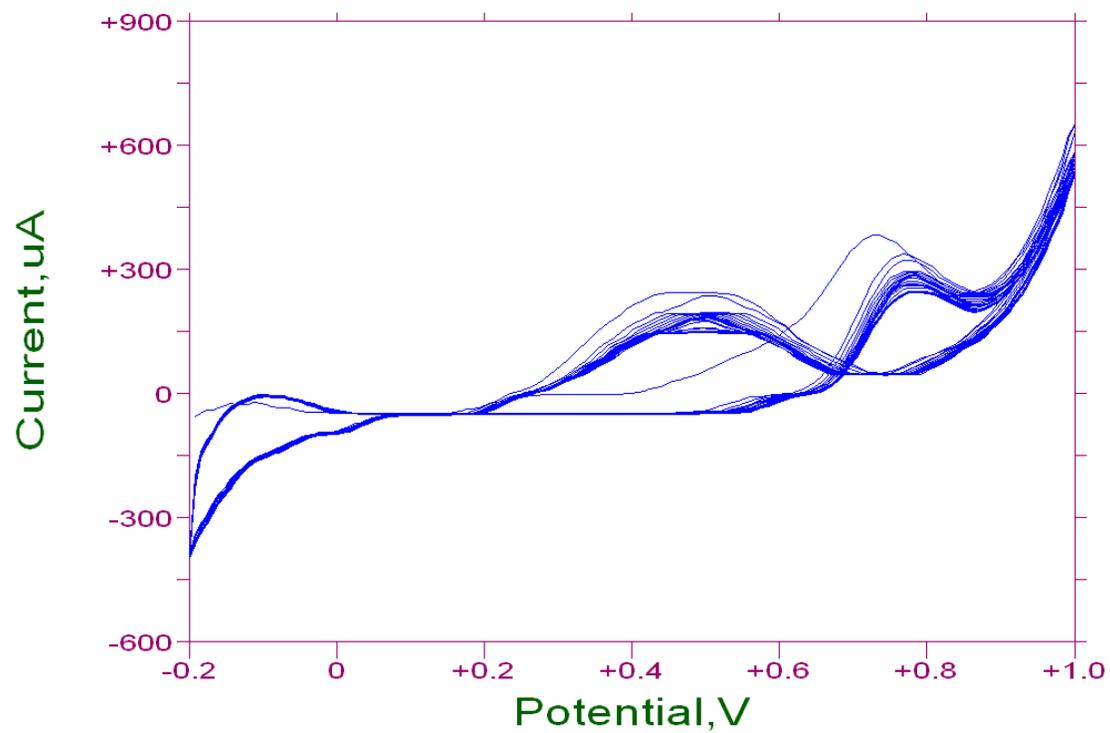
XC-72 Carbon Alone

Blank Electrode
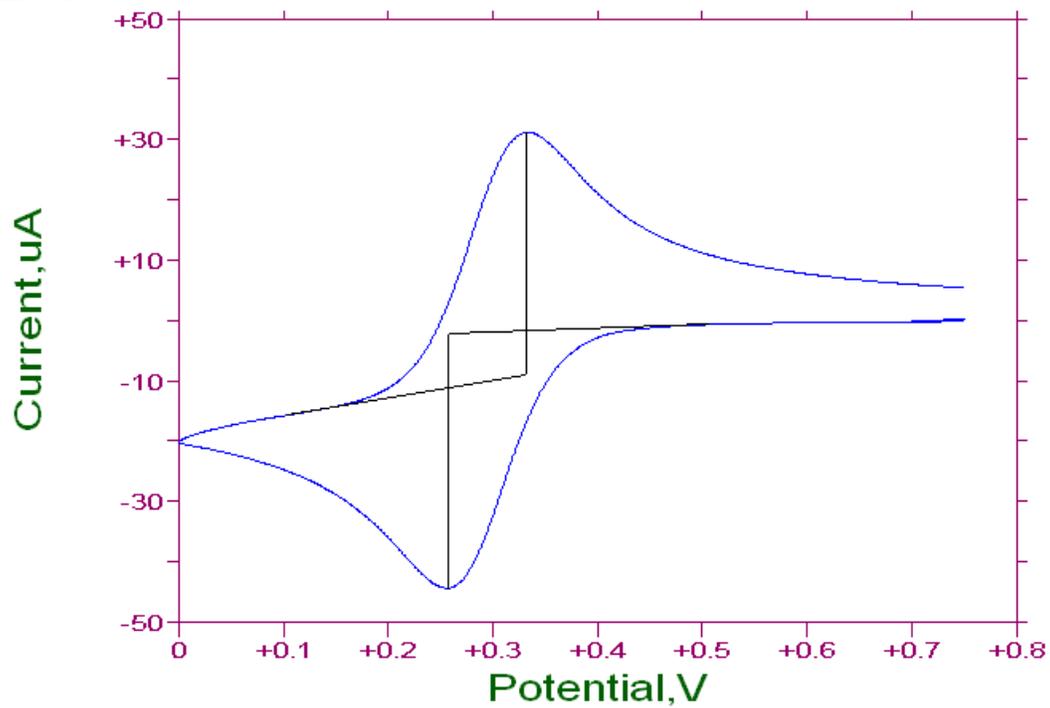

```
Segment 1:
Segment 2:
Ep = +257 mV
ip = -4.228e-005 A
Ah = -2.869e-006 A*V

Segment 3:
Ep = +332 mV
ip = +4.019e-005 A
Ah = +2.646e-006 A*V
```
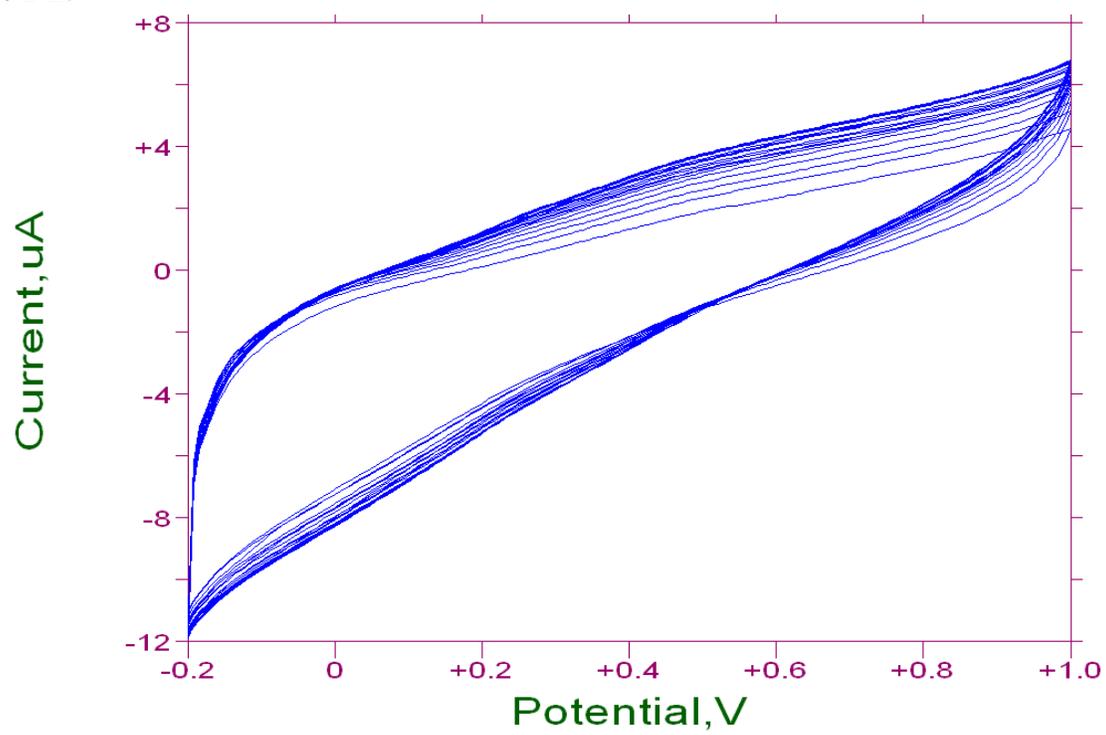
Cycle 1-25

SnO₂ Alone
Blank Electrode


```
Segment 1:
Segment 2:
Ep = +259 mV
ip = -4.288e-005 A
Ah = -2.869e-006 A*V

Segment 3:
Ep = +329 mV
ip = +4.030e-005 A
Ah = +2.538e-006 A*V
```
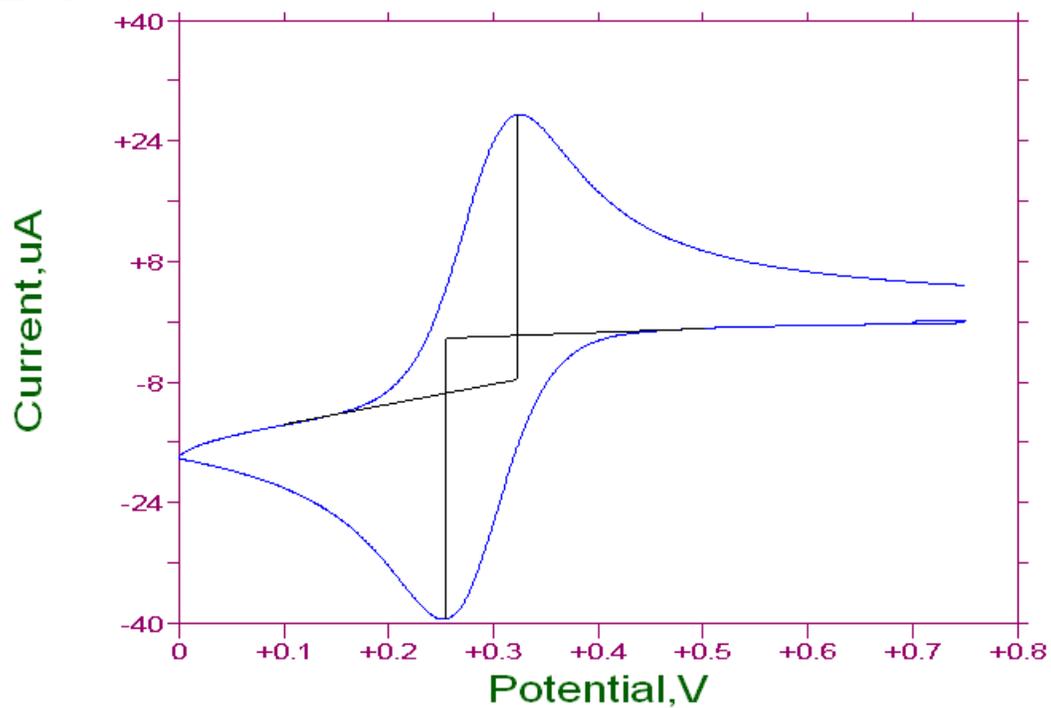
Cycle 1-25
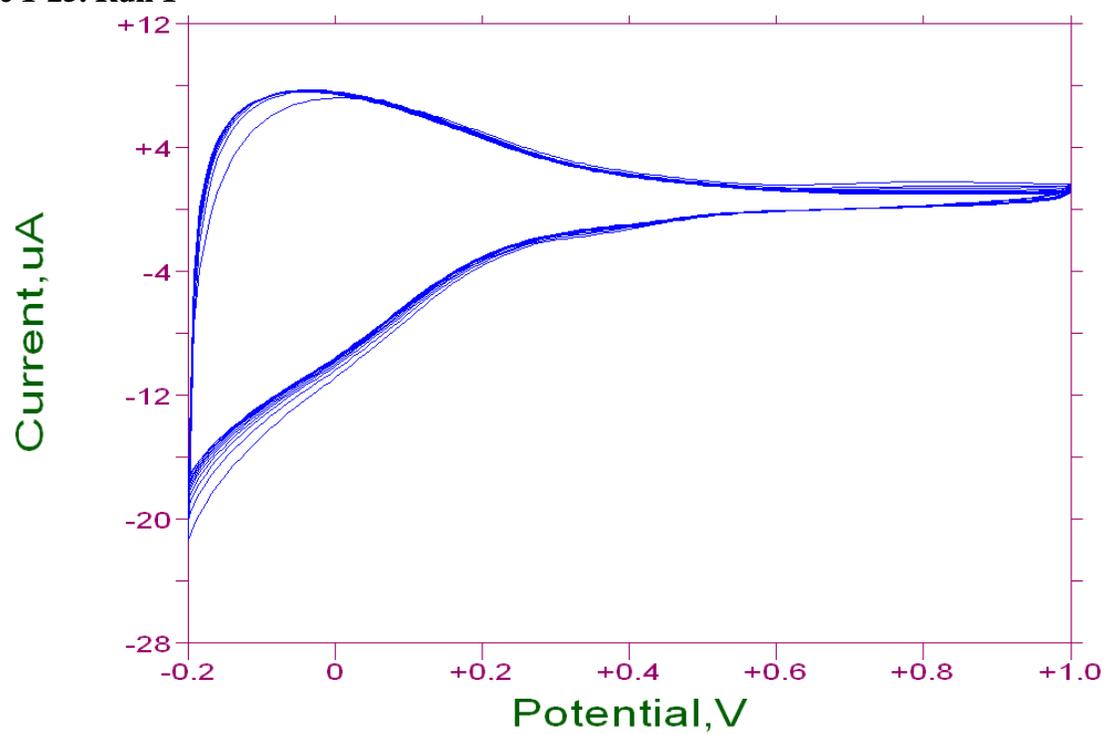
NanoArc SnO$_2$ Alone
Blank Electrode

Segment 1:
Segment 2:
Ep = +254 mV
ip = -3.723e-005 A
Ah = -2.446e-006 A*V

Segment 3:
Ep = +323 mV
ip = +3.515e-005 A
Ah = +2.250e-006 A*V

Cycle 1-25. Run 1

Cycle 1-25. Run 2