Proton Exchange Membrane Fuel Cell
Electrocatalyst Losses

A Thesis Presented to

The Faculty of the Interdisciplinary Graduate Program

in Environmental Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Masters of Science in Environmental Engineering

By

Edward W. Miller

May 2002

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ACKNOWLEDGEMENTS

I express my deepest appreciation to Dr. Ted Cleveland for his encouragement and patience in both research and academic endeavor. I would also like to thank Dr. Supramaniam Srinivasan, and GlobeTech, Inc. for the extensive financial assistance, comments on my research, and professional guidance. Gratitude is also due to Dr. Roberts for her assistance in serving on my committee and expending the time to review my work.

The Environmental engineering laboratories at the University of Houston have provided a safe and professional atmosphere for these experiments. Louis Simms and Dr. Tony Tripp have been extremely supportive to the evolving experimental requirements that have levied upon them throughout the timeline of this thesis and I share my greatest admiration for their efforts.

I would like to thank my wife, Karena, for her support and patience. Thank you for the endless assurance and faith in me.

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ABSTRACT

Fuel Cells offer the energy conservation and environmental solutions in electric power generation. The utilization of Proton Exchange Membrane Fuel Cells (PEMFC) as power sources for automobiles is expected to introduce the widespread "commercialization" of fuel cells into the retail market. The introduction of fuel cells on a commercial level will amplify the existing environmental problems associated with platinum and Platinum Group Elements (PGE). Platinum serves as the Electrocatalyst in PEMFC. Platinum is the Electrocatalyst for the anodic reaction, of electro-oxidation of hydrogen and the cathodic reduction in PEMFC.

Traditional PEMFC construction and assembly results in a "start-up" condition, which causes platinum losses from the membrane and electrode assembly surface. The amount of platinum loss has been considered to be negligible during the lifetime of the fuel cell. This research investigates the validity of the "start-up" condition and provides experimental results supporting the performance criteria of the fuel cell. These investigations suggest that the "start-up" conditions are a result of fabrication methodology and that the performance of the fuel cell is not affected by the small amounts of the platinum electrocatalyst lost. There will, however be an economic advantage by recovery of the electrocatalyst lost during the short release time.

The economic advantages are associated with potential environmental hazard rather than monetary advantages. The environmental impact of anthropogenic platinum release is currently being reviewed in both Europe and the United States. The ecological and human impacts of platinum distribution are, to a great extent, still unknown.

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1.0 INTRODUCTION

The next decade will herald the introduction of the fuel cell vehicles into the commercial market. Automakers including, Dialmer Benz, General Motors, Honda, and Toyota have demonstrated fuel cell and hybrid vehicles in an attempt to usher the next generation of vehicles onto the road. Environmental impacts, due to automobile catalytic converter metals present in road sediment, will escalate with the adoption of a hydrogen economy based on fuel cells. Platinum Group Elements (PGE) such as platinum, palladium, and ruthenium are the primary electrocatalyst in low temperature Proton Exchange Membrane Fuel Cells (PEMFC). PEMFC are the best of the fuel cell candidates for electric vehicles, because of their high efficiency, power density, and release of only innocuous product water and waste heat.

The primary issue that will be faced by the automotive industry is one of simple environmental impact and economic gain. The environmental impacts of PGE on humans are expected to be carcinogenicity and sensitization. The toxicological impacts to the ecosystem have not been experimentally validated and are unknown. PEMFC are at a risk of inadvertently exacerbating the anthropogenic release of platinum.

1.1 Problem Statement

Platinum, palladium, and ruthenium are the primary electrocatalyst in low temperature fuel cells and automotive catalytic converters. PGE are currently present as biogeochemical contaminants as a direct result of the modern automobile 3-way catalytic converter. Anthropogenic emissions of PGE are currently being studied in Europe, and the United States, as a result of the dramatic increase in quantitative environmental impacts. The commercial introduction of PEMFC into the next generation of vehicles may result in a similar pattern of anthropogenic emissions being introduced into the environment due to electrocatalyst losses from these power sources.

PEMFC performance degradation is associated with electrocatalyst poisoning and polymer membrane degradation. It is theorized that PEMFC exhibit a "start-up trait", which is responsible for performance improvements in the fuel cell and small amounts of electrocatalyst loss. The "start-up" of a PEMFC is best defined as the removal of particulate matter from the electrode surface. The performance of a PEMFC generally increases after approximately 24 hours of operation. This research is intended to make a quantifiable determination of the PEMFC electrocatalyst losses and analysis of performance criteria.

1.2 Background

Similar to a battery, fuel cells involve electrochemical reactions to produce electricity. Fuel cells are best described as electrochemical engines, with no moving parts, which will operate as long as there is a continuous feed of fuel (hydrogen, hydrocarbon, or alcohol and oxidant). In comparison to a combustion engine, the fuel cell is quiet, more efficient, has no side reactions (i.e. emissions), and no vibrations. In a PEMFC, a proton conductive polymer membrane serves as the electrolyte where hydrogen combines with oxygen, generally from the air, to form a water molecule. Economic obstacles and a societal apprehension surrounding historical hydrogen usage, the Hindenburg is an example of this apprehension, are the basis of the technology transfer reluctance.

The cost of the fuel cell has been reduced through the development of a supported electrocatalyst in the PEMFC electrodes and an increased level of cell performance [1-3]. The cost, weight, and volume of the PEMFC will have to undergo further reduction in order for these power plants to compete with traditional combustion engines.

Dramatic improvements in power and weight have been made with the increased level of research and development activity through the 1980's and 1990's. The higher power density is a result of new membrane technology and ultra low platinum loadings [4]. The PEMFC has a technological advantage over competing fuel cell systems, due primarily to the ability to produce a high power density at relatively low temperature range (50-80°C).

1.2.1 History of the Fuel Cell

In 1839, Sir Walter Grove invented the fuel cell. At that time water electrolysis was a well-known process, and it occurred to Grove, that if electricity could force water to separate into hydrogen and oxygen, H_2 and O_2 fed individually into the two electrodes may lead to the recombination of the gases into water and also produce electricity [6]. Grove's water electrolysis cell contained (i) dilute sulfuric acid as the electrolyte (ii) two platinum strips in inverted closed tubes, and hydrogen and oxygen were formed by electrolysis of water. Initially about 5 of the Grove cells were connected in series and the hydrogen and oxygen gases evolved from these cells were then fed into the fuel cell. Grove noted the electrical power generation and formation of product water. Grove reported his work and produced a bank of 50 cells and invented the Grove Cell Stack. 1889 saw the address of Mond, and Langer reporting an extension of Grove's developmental work (air, not O_2; coal gas, not H_2).

In 1894 a renowned German physical chemist, Wihelm Ostwald, gave an address that stressed the thermodynamic advantages of direct electrochemical energy conversion from chemical to electrical energy and possible environmental advantages, as compared with the standard method of using a steam engine and dynamo. He envisioned two pathways for the future development of technology. On the one hand, combustion engines would work inefficiently, burdened by Carnot efficiency limitations on the conversion from heat to mechanical energy, and causing the pollution to rise to an unacceptable level. On the other hand, fuel cells would work efficiently, silently, and without pollution. "No Smoke, No soot, No fire" [7].

A more remarkable early fuel cell contribution was due to Jacques, who engineered a massive brick structure inside which there operated a cell containing an anode of carbon, while the cathode operated on air. Jacques cell functioned in molten NaOH at ~ 1V and ~100mA cm^{-2} for over six months [6]. The largest fuel cell built by Jacques in the 19th century was a 1.5 kW system. It had a 100 cells connected externally in series [8].

The "Modern Era of Fuel Cells" is generally attributed to Sir Francis T. Bacon. 1932 saw Bacon conducting fuel cell experiments as a hidden project while he worked at Parson, a well known British turbine manufacture, using high temperatures (~200°C) and high pressures (~40 atm) to reduce the polarization. The most important contribution that Bacon made was the introduction of electrodes having two layers of different pore size. The small-pore layer was in contact with the electrolyte and introduced this by capillary action to the boundary layer with the large-pored layer, filled with H_2 or O_2. Bacon was able to demonstrate a 5 kW system, which could power a

2-ton forklift. The Pratt and Whitney Aircraft bought the license to Bacon's U.S. Patents and led to the first application of alkaline fuel cells in the Apollo Space Missions.

Nernst and his student, Schottky, constructed a pseudo-fuel cell using a thin rod or tube of a high temperature (i.e. glower or lamp) of ion conducting material ($ZrO_2 + 15\%Y_2O_3$). An electrolyte with practically the same composition is used in the state of the art solid oxide fuel cell (SOFC). Nernst also had the first ideas of redox fuel cells and for this purpose, he proposed multivalent ions of titanium, thallium, or cerium, which can be reduced or oxidized by hydrogen or oxygen [7].

1.2.2 Applications

The Gemini Space Program was the first critical application of fuel cells. Since then, every space vehicle has had a fuel cell on board as an auxiliary power source. The General Electric Company developed a solid polymer electrolyte fuel cell (PEMFC) for the Gemini Space Missions' from 1962 to 1966. The electrolyte was a thin membrane of polystyrene sulfonic acid. The use of a thin membrane led to the Membrane and Electrode Assembly (MEA), which is the basis for a fuel cell stack. The stack is essentially several MEA's connected in series with a bipolar plate. The General Electric stacks had problems associated with the membrane material; the polystyrene sulfonic acid became non-conductive after approximately 2 weeks of operation. Extremely high electrocatalyst loadings, 2-4 mg of platinum per square centimeter, were utilized in these cells. The membrane material was replaced, in the 1970s, by a perfluorinated sulfonic acid polymer (Nafion® from Dupont Chemical Company). The electron withdrawing nature of the CF_2 in the polymer and replacement of the C-H bonds by C-F bonds significantly enhanced the proton conductivity and the stability of the membrane. The Apollo Space Program continued the use of fuel cells and the Space Shuttle has three 96 cell fuel cell stacks on board as its power source. The National Aeronautics Space Administration (NASA) has funded the advent of fuel cells for closed systems, where the water is recycled and electrolyzed for fuel. The fuel cell is a key participant in any type of system where a high power density and a high energy density are vitally required.

1.2.3 Technological Advantages

The PEMFC has many advantages over other types of fuel cells. The lack of a liquid electrolyte eliminates the corrosion and contact problems. Using a polymer eliminates the mobility of an acid electrolyte in the stack, thus the stack design is also simplified. PEMFC also have the highest power densities attainable in comparison to all other fuel cells as a result of oxygen electrode kinetics and very low ohmic resistance in the linear region of the power density

The success of the internal combustion engine is greatly due to its rendering a range of travel in vehicle transportation of greater than 400 miles and utilization of cheap carbonaceous fuel (gasoline or diesel). The long-term impact of this short-term solution has manifested itself in the air pollution over most of the major cities in the United States and abroad. A new form of energy for transportation and energy production in general is desperately required. The fuel cell, specifically the PEMFC, is the most promising alternative power solution that is available. The auto industry is embracing the fuel cell as the answer to zero emission vehicles. Daimler Chrysler, Ford Motor Co., General Motors, Honda Motor Co., Nissan Motor Co., and Toyota are among the list of automobile manufactures that are researching the prospect of fuel cell powered vehicles [9]. The fuel cell has enlisted itself a clean and quiet energy source. Water is the fuel cell's only obvious emission, when pure hydrogen is used as the fuel.

1.2.4 Environmental Impacts

The main components present in fuel cell electrocatalysts include platinum, ruthenium, or palladium, which are all Platinum Group Elements (PGE). The gas electrodes in the PEMFCs are fabricated from high surface area carbon and a noble electrocatalyst, such as platinum. Electrocatalyst material losses from the surface of the electrode, by way of cell operation, are considered to be a "start-up" loss. The extent of anthropogenic release and the geographical distribution of these elements are unknown [10]. Studies, conducted in the 1970's prior to the introduction of the catalytic converter in California, attempting to establish a baseline platinum level have drawn heavy criticism as a result of the limitation in the analysis equipment and the techniques used. As a result of these limitations the baseline level required to demonstrate an alteration in the quantity and quality of the platinum in the environment currently doesn't exist. Data required to analyze atmospheric transport dynamics of aerosols contaminated by PGE is also not available [11-13].

The effect of PGE on an ecological system is primarily a function of bioaccumulation. The ability for a biological system to accumulate PGE is dependent on solubility and interactions with the soil, water, and air. Routes of PGE bioaccumulation include protein binding and biological methylation. The oxidation of PGE, by various methods, introduces an elevated level of PGE solubility and subsequently the bioavailability of these compounds. Once oxidized PGE can become a part of any number of soil complexes that would be conduits of exposure for ecological systems.

PGE catalyst losses from fuel cells would obviously increase the amount of anthropogenic refuse into the environment. Management of those losses may prove economically and ecologically advantageous. Determination of the amount of electrocatalyst being expelled from the fuel cell is a key element for any risk assessment activity.

1.3 Objectives

The objectives of this research are to examine the "start-up" conditions in a PEMFC, examine a probable cause of the "start-up" trait, provide performance analysis of the fuel cells, and examine the possible environmental and economical consequences. This research will provide quantitative amounts of platinum that are rejected from the fuel cell and calculate an economic impact associated with that quantitative amount.

1.4 Technical Approach

To justify the existence of a "startup" condition several experiments were conducted to quantify the immediate loss of electrocatalyst in the fuel cell. These experiments included a surface rinsing, mass flux, and electrical load-conditioning. The outcome of the Electrode Material Removal (EMR) and Mass Flux (MF) experiments were utilized to determine the duration of the constant electrical load conditions in the remaining experiments. The actual electrocatalyst losses, as measured by a Perkin-Elmer Inductively Coupled Plasma (ICP) Mass Spectrometer, are compared against a published average particle size of the gas diffusion electrode material in an attempt to derive a correlation between particle size and the extent of electrocatalyst loss.

Power production was used as the basis for evaluation of electrocatalyst losses as a function of the overall performance. The performance of the fuel cell is directly correlated to the amount of electrocatalyst present and the surface area of the electrocatalyst participating in the reactions. The power output of the fuel cell is dependent on the active surface area of the electrocatalyst and the physical limitations of the apparatus. Cyclic Voltammetry, a technique using a potentiostat and a function generator to yield a linearly varying voltage across a test cell establishes a correlation between the voltage and current in the test cell under transient conditions. Cyclic Voltammetry is used to determine the active surface area of the electrocatalyst. The physical limitations of the fuel cell depend on pressure, temperature, and flow rate of the fuel gases, as well as the fixture design itself. Fuel cell power output can be elucidated from a plot of the current density vs. potential. These measurements are made either galvanostatically or potentiostatically

2.0 EXPERIMENTAL DESIGN

The "start-up" condition is defined to be the virgin condition of a fuel cell Membrane and Electrode Assembly (MEA) prior to mechanical pressing. The fuel cell electrode composition and method of MEA fabrication may be responsible for electrocatalyst losses. The primary point of electrocatalyst loss is anticipated to be a result of the traditional fabrication method for MEA, where the assembly is heated to the polymer's glass transition point and mechanically pressed together under a pressure of 2 metric tons. This extreme mechanical pressure generally results in direct electrode material loss and may contribute to electrocatalyst losses through structural degradation of the electrode. Thus the electrode composition and MEA fabrication procedure are explained in subsequent sections.

These experiments are designed to examine the "start-up" conditions in a PEMFC, which result from MEA fabrication. The mass flux experiments are an exploratory tool that was utilized to observe any dependence on temperature or particle size. A quantitative analysis of the fuel cell product water was performed to collect an accurate concentration of electrocatalyst. Finally these experiments will provide an analytical explanation of the fuel cell performance based on Cyclic Voltammetry.

The initial experiment, the Electrode Material Removal (EMR) process, was used to establish a baseline for the concentration that was analyzed by the Perkin-Elmer Inductively Coupled Plasma (ICP) Mass Spectrometer. The EMR experiments included a preliminary and secondary weight record, which was used to calculate electrode material losses during MEA fabrication process. The next experiment, a Mass Flux examination, established a timescale for the electrocatalyst losses. Finally the constant load experiments provided fuel cell performance criteria and electrocatalyst utilization. The MF and constant load experiments were performed in tandem for analysis reasons.

The Perkin-Elmer ICP mass spectrometer utilized for these experiments was calibrated using a range of standards that extended from 12 ppb to 0.625 ppb. All measurements beyond this range were considered to be Non-Detectable (ND). The ICP mass spectrometer was operated in accordance with standard practices, as outlined in the users manual, and the standards were prepared by volumetric dilution of an instrument standard, which is provided by the manufacturer. The calibration of the mass spectrometer is based on default methodology, which allows for instrumental auto-calibration of the plasma and mass spectrometer settings.

2.1 Electrode Composition

The gas diffusion electrode manufactured by E-TEK Incorporated, a solid polymer electrolyte electrode (ELAT), will be utilized for this experimental process and throughout the thesis material. The electrode itself is constructed from three different layers.

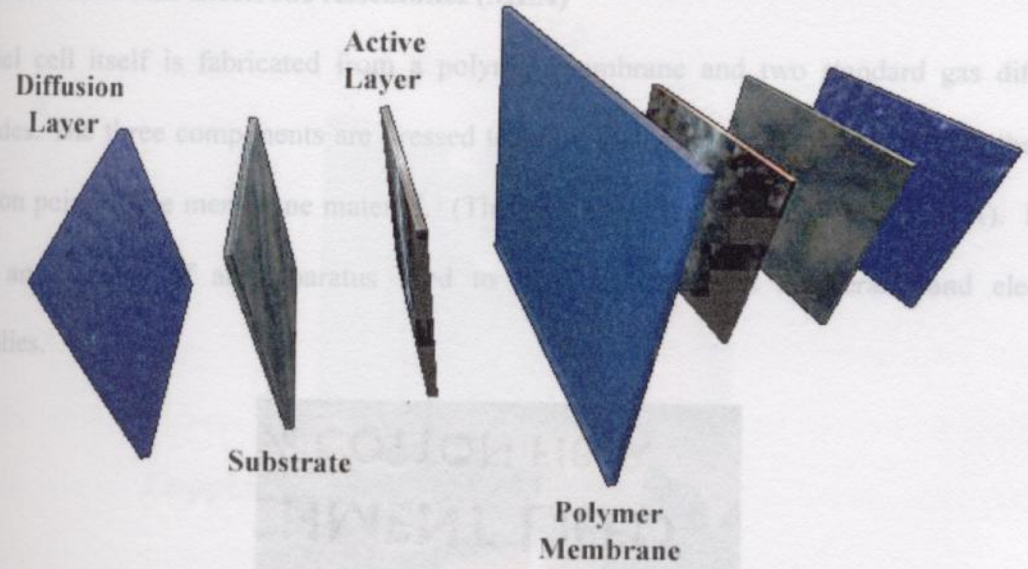

Figure 2-1 Internal components of a gas diffusion electrode

The three independent layers (diffusion, substrate, and active) of the electrode are the basis of the 3 dimensional reaction zone, inside of the electrode. The substrate material provides mechanical support for the electrode. ELAT electrodes have a plain carbon weave cloth of 3.4 oz/yd^2 with a thickness of 0.36 mm. The substrate material generally has gas-side wet proofing in the form of a hydrophobic fluorocarbon/carbon layer. The diffusion layer is applied to the gas interface layer of the electrode, thus acting as a gas dispersion layer of carbon. The active layer of the electrode contains the electrocatalyst, which has a loading determined by a specific weight of electrocatalyst dispersed over an area. The standard loading for ELAT electrodes is 20% Pt on Vulcan XC-72 at 0.35-0.50 mg/cm^2. The gas diffusion electrode is then treated with an electro-electrocatalyst, generally a tincture of the membrane material at a 5% weight, and heat treated in an oven to remove any organic compounds.

2.2 Membrane and Electrode Assemblies (MEA)

The fuel cell itself is fabricated from a polymer membrane and two standard gas diffusion electrodes. The three components are pressed together using 2 metric tons of force at the glass transition point of the membrane material. (This procedure is detailed in Appendix A). Figure 2.2 is an example of an apparatus used to fabricated PEMFC membrane and electrode assemblies.

Figure 2-2 Example of an apparatus used for fabrication of MEA's.

The gas diffusion electrodes are held in place by gasket material and thin metal plates, insulated by a sheet of Tefzel® to prevent electrode material from adhering to the metal plate surface. The pressing procedure typically displaces some of the electrode material, thus altering the weight of the MEA. Therefore the weight of the MEA components prior to pressing and after pressing will be measured. The gasket material is in place to prevent to complete structural degradation of the MEA. The gaskets mechanically prevent the pressing of the electrodes through the membrane material.

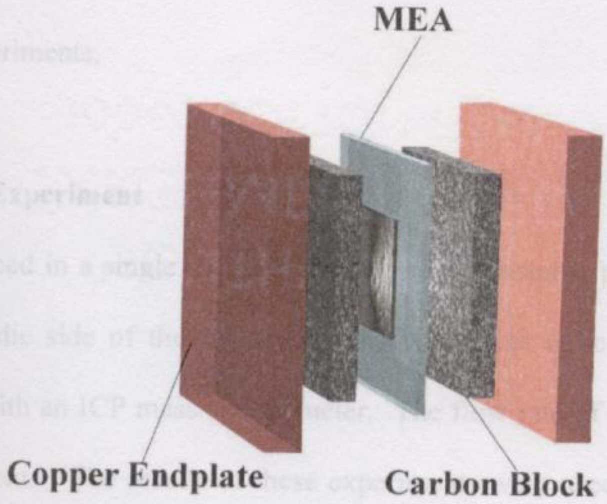

Figure 2-3 Construction of a typical single cell test fixture.

Figure 2.3 is a diagram of a typical single cell test fixture. All of the experiments were conducted in a similar test fixture (GlobeTech, Inc., model SSTF-5). The composition of a PEMFC single cell test fixture is comprised of two endplates, two carbon blocks, and a MEA. The endplates are used for current collection and the carbon blocks are primarily for conductivity and gas distribution.

2.3 Electrode Material Removal

In order to quantify structurally unsound electrode material the MEA was placed in an evaporation dish with 500ml of Millipore pure water (measuring 18Mohm) at an operating temperature of 60°C for a period of one hour. The wash water was collected and the concentration of Pt was analyzed with a Perkin-Elmer ICP mass spectrometer. The total amount of platinum collected was determined from the concentration and the volume of the collection bath. The results of this experiment were utilized to determine an appropriate flow-rate during the mass flux experiments.

2.4 Mass Flux Experiment

An MEA was placed in a single cell test fixture and a peristaltic pump was used to pass water through the cathodic side of the fuel cell. The water was collected and analyzed in a time relevant fashion with an ICP mass spectrometer. The flow rate of the water was determined by the EMR experiments. The results of these experiments were used to determine the amount of time necessary for the constant electrical load experiments.

2.5 Constant Power and Performance Experiments

Utilizing the results of the EMR and MF experiments, a timed electrical load experiment was conducted. The electrical load consisted of a carbon block variable resistance load, coupled with a multi-meter measuring the fuel cell current and potential over time. An automatic sampling machine, controlled by a PC, was used to collect samples over a 48 hour period in 9.6 hour sample intervals. Figure 2.4 is a picture of the automatic sampling apparatus used during the timed experiments.

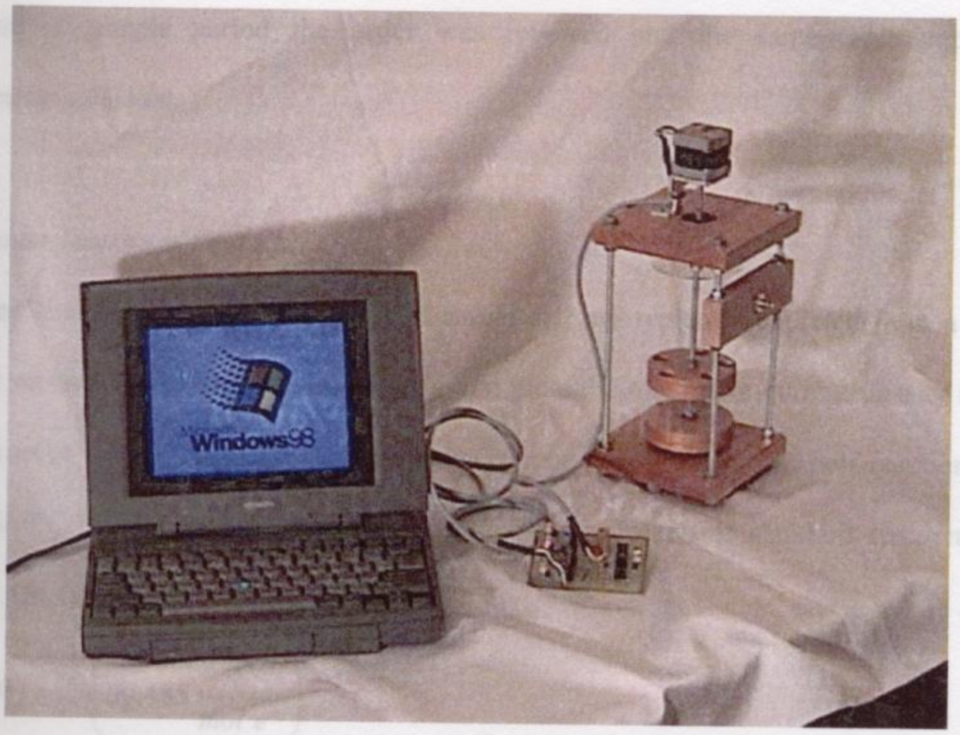

Figure 2-4 Personal Computer controlled auto-sampling mechanism.

Experimental variables that were manipulated for the purpose of electrocatalyst loss baseline establishment include platinum loadings of 20% platinum at 0.4 mg/cm^2 at 25°C and 75°C, 80% platinum at 5 mg/cm^2 at 50°C, and platinum black at 50°C. The 0.4 mg/cm^2 loading was not tested at 50°C since the EMR experiments and mass flux experiments are conducted at this operating temperature.

The experimental process was based on a sequence of measurements, which include constant load, current density, and cyclic voltammograms. An MEA was inserted into a clean fuel cell test fixture and attached to the fuel cell test station. Once the system reached experimental parameters a cyclic sweep was performed, followed by a current density sweep, and finally the cell was left under a constant resistance for the duration of the sample collection period. Upon completion of sample period the order was reversed and the same three experimental measurements collected.

2.5.1 *Power Density of the PEMFC*

The power density output characteristics of a fuel cell are typically depicted from a Potential (Voltage) versus Current density plot. This graph plots the maximum current density attainable at a given set of thermal and mass flow variables. From stoichiometry and half-reaction theory a single PEMFC should produce 1 ampere per 7cc of hydrogen at standard temperature and pressure. The calculation incorporates the following:

$$1 - mole\ H_2 = (2)\left(96{,}485\ \frac{C}{mol\ e^-}\right),$$

$$1 Amp = 1C/\sec,$$

$$\left(\frac{1\, C/_s}{(2)(96{,}485)}\right)\left(\frac{22.4L}{mole}\right)\left(\frac{1000cc}{L}\right)\left(\frac{60\ s}{\min}\right) = 6.964cc\ at\ 25^\circ C. \qquad [2.1]$$

In practice, the equipment used for the experimentation must operate at approximately 100cc per minute to insure proper functionality of the fuel cell test system. The overall efficiency of the fuel cell is dependent on the half-reaction chemistry described above and unfortunately the experiment is limited in scope, by the test equipment, to an electrocatalyst utilization interpretation.

The regions of power loss occur due to activation, ohmic, and mass transport limitations [14]. Analytical observation of the initial mass and active surface area will provide the basis for evaluation of the PEMFC.

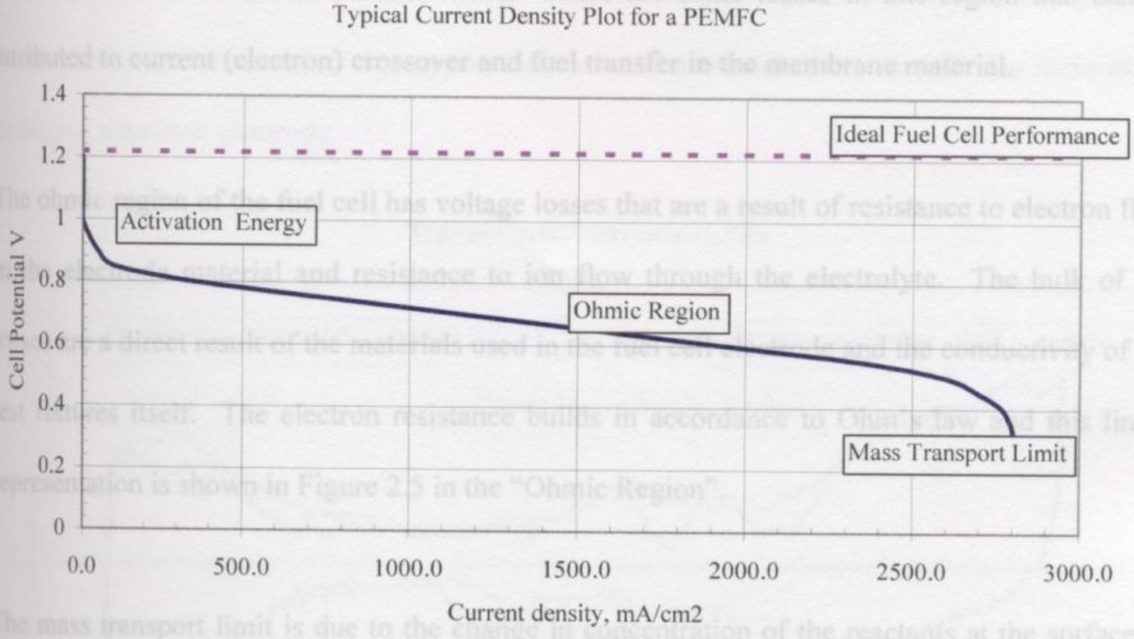

Figure 2-5 Typical current density plot for a PEMFC

Figure 2.5 identifies the three regions of a typical current density plot for a PEMFC. The ideal fuel cell will produce an infinite amount of current at the theoretical reduction potential.

A proportion of the voltage generated is lost in driving the chemical reaction that transfers electrons. In low temperature fuel cells the activation overvoltage is the most important irreversibility and cause of voltage drop. This is shown in Figure 2.5 in the "Activation Energy" region of the graph. There is an equilibrium in the fuel cell where the overall reaction,

$$O_2 + 4H^+ + 4e^- \leftrightarrow H_2O \qquad [2.2]$$

is taking place. There is a continuous flow of electrons from and to the electrolyte, thus the increased current is simply a shift in one direction for the fuel cell (Equation 2.2). In order to increase the current density of the fuel cell the reaction must be driven, however this driving force is in the form of an activation loss. There are some losses in this region that can be attributed to current (electron) crossover and fuel transfer in the membrane material.

The ohmic region of the fuel cell has voltage losses that are a result of resistance to electron flow in the electrode material and resistance to ion flow through the electrolyte. The bulk of the losses are a direct result of the materials used in the fuel cell electrode and the conductivity of the test fixtures itself. The electron resistance builds in accordance to Ohm's law and this linear representation is shown in Figure 2.5 in the "Ohmic Region".

The mass transport limit is due to the change in concentration of the reactants at the surface of the electrodes. The mass transport limitation is the point at which the electrocatalyst has become saturated and cannot support any further chemical reactions. This region, shown in Figure 2.5 "Mass Transport Limit", is a point where the electrocatalyst surface area is fully occupied and therefore limits the rate at which the reaction can occur.

2.5.2 *Cyclic Voltammograms and Roughness Factors*

Cyclic Voltammetry is a procedure to quantify the active amount of electrocatalyst. This quantity is based on the concentration of adsorbed hydrogen (1 atom per atom of platinum) as measured by the charge passing through the electrode in question. The amount of charge is a direct reflection of the electrocatalyst activity, thus a proportional graphical area correlates to an active electrocatalyst area. In order to determine the electrochemically active surface area of the electrodes, the cyclic voltammetric technique [15] will be applied with a Pine Instrument (bipotentiostat Model AFCBP1). High purity nitrogen, humidified at the operating temperature, will be passed on the test electrode chamber. High purity Hydrogen, humidified at the operating temperature, will be passed on the counter electrode. The counter electrode will also serve as the hydrogen reference electrode.

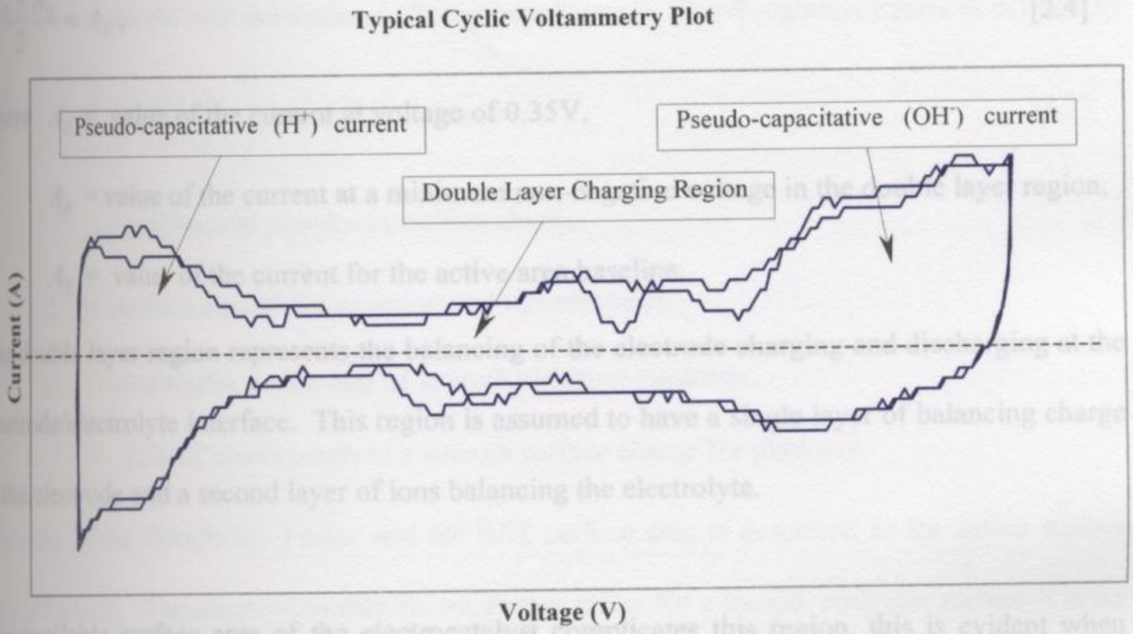

Figure 2-6 Typical performance curve of a cyclic Voltammetry experiment.

The electrochemically active surface area will be determined from the coulombic charge required for hydrogen adsorption or desorption on the platinum crystallites in the electrode. The amount of charge measured depends directly on the amount of adsorbed hydrogen being adsorbed during the anodic sweep. The pseudocapacitative current is defined for the reaction:

$$H^{+} + e^{-} + M \xrightarrow{cathodic} MH_{ads},$$
$$H^{+} + e^{-} + M \xleftarrow{anodic} MH_{ads}, \qquad [2.3]$$

where M is used to indicate the surface of the platinum electrocatalyst. The cyclic voltammetry sweep will be conducted from 1.00V to 0.15V, at a rate of 5 mV/Sec, for at least 10 repetitions. The pseudo-capacitative (H^{+}) current region is from a voltage of 0.15 volts to approximately 0.35

volts. The double layer region starts at approximately 0.35 volts and end at 0.7 volts and will be utilized to formulate the linear extrapolation required for the roughness factor. The line will be described by

$$\frac{A_A + A_B}{2} = A_X , \qquad [2.4]$$

where A_A = value of the current at voltage of 0.35V,

A_B = value of the current at a minimum non-negative voltage in the double layer region,

A_X = value of the current for the active area baseline.

The double layer region represents the balancing of the electrode charging and discharging at the electrode/electrolyte interface. This region is assumed to have a single layer of balancing charge to the electrode and a second layer of ions balancing the electrolyte.

The available surface area of the electrocatalyst complicates this region, this is evident when comparing PEMFC's with different catalyst loadings. As the particle size and available amount of surface area increase the double layer region reflects the increased amount of surface area. As the amount of electrocatalyst is increased the cyclic voltammogram will increase in area across the double layer region. The double layer region can mask the platinum hydrogen adsorption/desorption characteristics due to oxidation-reduction (redox) behavior of surface-active groups on carbon, i.e., quinone/hydroquinone [16]. This region can be skewed by additional organic contaminants complicating the masking effect of the surface-active groups. In addition, if the anodic limit is extended past the 1 volt RHE, oxidation of carbon occurs. The pseudo-capacitive (OH^-) current region is from a voltage of 0.7 volts to approximately 1.0 volt. In this anodic region, the reactions are governed by:

$$M + H_2O \rightarrow MO + 2H^{+} + 2e^{-}, \text{ and} \qquad [2.5]$$

$$M + H_2O \rightarrow MOH + H^{+} + 2e^{-}. \qquad [2.6]$$

The comparison of the experimental area, equating to a columbic charge, and analytical loading of the electrocatalyst will determine a "Roughness Factor". The Roughness Factor is defined by

$$\left[\frac{E_C\,(\mu C)}{S_T\,(cm^2)}\right]\left[\frac{S\,(cm^2)}{S_C\,220(\mu C)}\right] = \text{Roughness Factor}, \qquad [2.7]$$

E_C = experimental pseudo-capacitive charge,

S_T = surface area of the experimental test electrode,

S = one square centimeter of smooth platinum electrode,

S_C = 220 μC corresponds to a smooth surface charge for platinum.

The ratio of the Roughness Factor and the BET surface area is described as the active surface area utilization. The assumption that the roughness factor for a smooth platinum surface is unity will be utilized.

The percent utilization calculation is determined by the BET surface area of the electrode and compared against the unity smooth surface charge of platinum, which is assumed at 220μC. The percent utilization is defined by:

(*BET surface area for* 20% *loading*)

$$\left[\frac{112\,(m^2)}{1\,(g)}\right]\left[\frac{0.4\,(mg)}{(cm^2)}\right]\left[\frac{1.0(g)}{1000(mg)}\right]\left[\frac{1.0(cm^2)}{0.0001(m^2)}\right] = 448, \qquad [2.8]$$

(*BET surface area for* 80% *loading*)

$$\left[\frac{11\,(m^2)}{1\,(g)}\right]\left[\frac{5\,(mg)}{(cm^2)}\right]\left[\frac{1.0(g)}{1000(mg)}\right]\left[\frac{1.0(cm^2)}{0.0001(m^2)}\right] = 550, \qquad [2.9]$$

(*BET surface area for Pt Black*)

$$\left[\frac{28\left(m^2\right)}{1(g)}\right]\left[\frac{5\,(mg)}{\left(cm^2\right)}\right]\left[\frac{1.0(g)}{1000(mg)}\right]\left[\frac{1.0(cm^2)}{0.0001\left(m^2\right)}\right]=1400, \qquad [2.10]$$

$$\left[\frac{Roughness\ Factor}{(BET\ surface\ area)}\right]=Percent\ utilization \qquad [2.11]$$

The calculated linear area is based on a standardized linear interpolation of the raw data in the appropriate voltage ranges of 0.35 to 0.7 volts. The line defined by equation 2.4 was used to determine the baseline for the experimental area calculation. The experimental area was calculated using an integral defined by the raw data in the ranges of 0.15 to 0.35 volts.

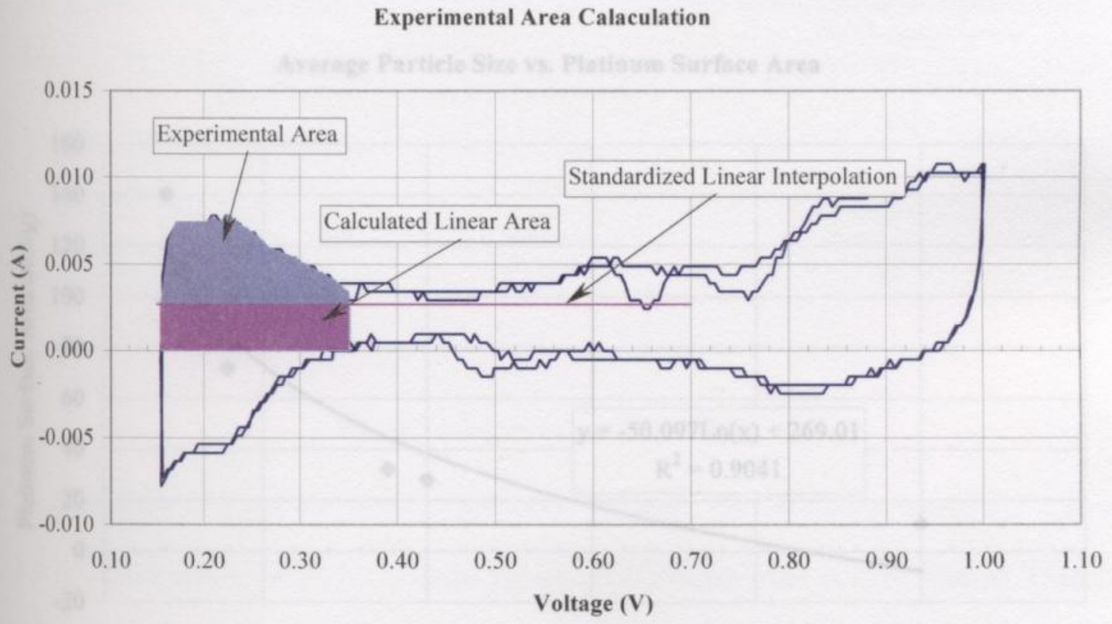

Figure 2-7 Experimental area calculation plot for a PEMFC electrocatalyst utilization.

The difference between the calculated linear area and the experimental area was utilized as the active surface area. Each timed experiment included a preliminary and post cyclic voltammetry sweep. The percent of electrocatalyst utilization, as determined by cyclic voltammetry, was correlated to a steady state current density vs. cell potential plot.

2.6 Correlation of Electrocatalyst Losses and Particle Size

Platinum is the standard electrocatalyst for most PEMFC systems. As the platinum loading on a carbon support increases, the platinum particles grow, thus reducing the available active surface area of the platinum. A correlation of the average particle size of platinum on Vulcan XC-72 and the electrocatalyst losses from the PEMFC was made. The use of different electrocatalyst loadings in the Timed Operation Under a Constant Electrical Load experiments will allow the observation of any relationships in electrocatalyst particle size, and electrocatalyst removal from the electrode.

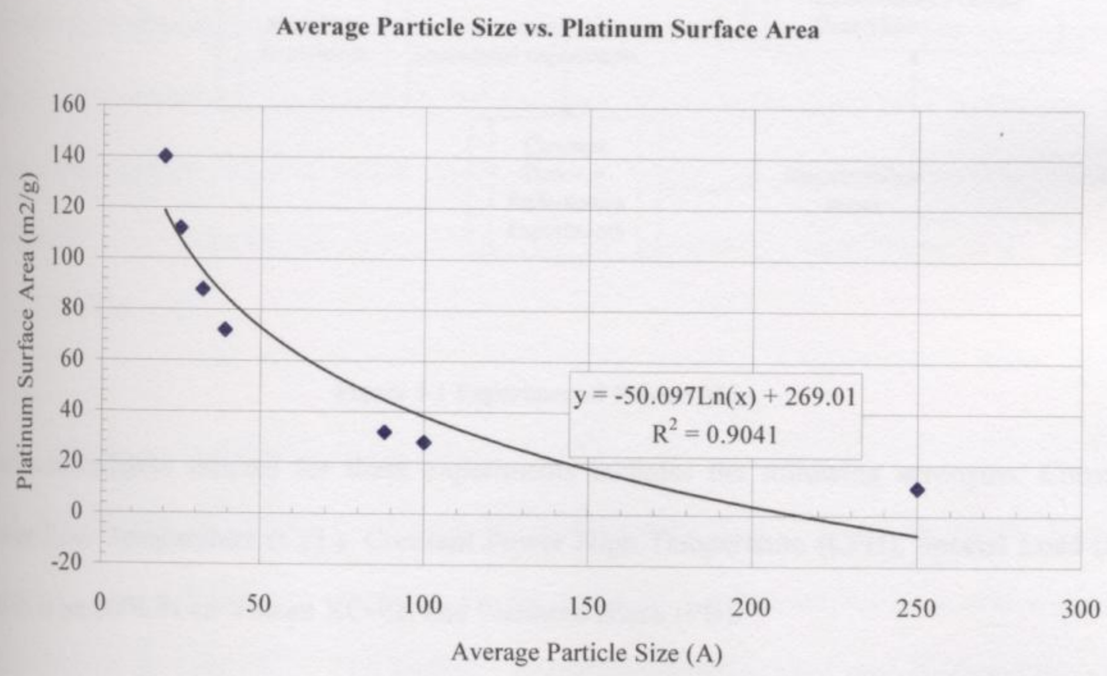

Figure 2-8 Average Pt particle size in Å in contrast to the platinum surface area.

Figure 2.8 shows the relationship between the platinum surface area and Pt particle size. These values in figure 2.8 are provided by E-Tek. It can be rationalized that the larger the particle the lower the expectation of removal from the electrode, however this parameter must be verified by experimental analysis. The smaller particles that are associated with the carbon supported on carbon with a 20% dispersion was compared to a large 250 angstrom particle and a smaller 100 angstrom particle to experimentally asses any dependence on the particle size.

3.0 RESULTS AND DISCUSSIONS

The experimental tasks include the electrode material removal, the mass flux experiment, and the timed operation under a constant electrical load. The parameters utilized for each experiment were dependent on the results of the previous experiment, therefore the order of operations and experimental results used for the subsequent experiment are detailed in Figure 3.1.

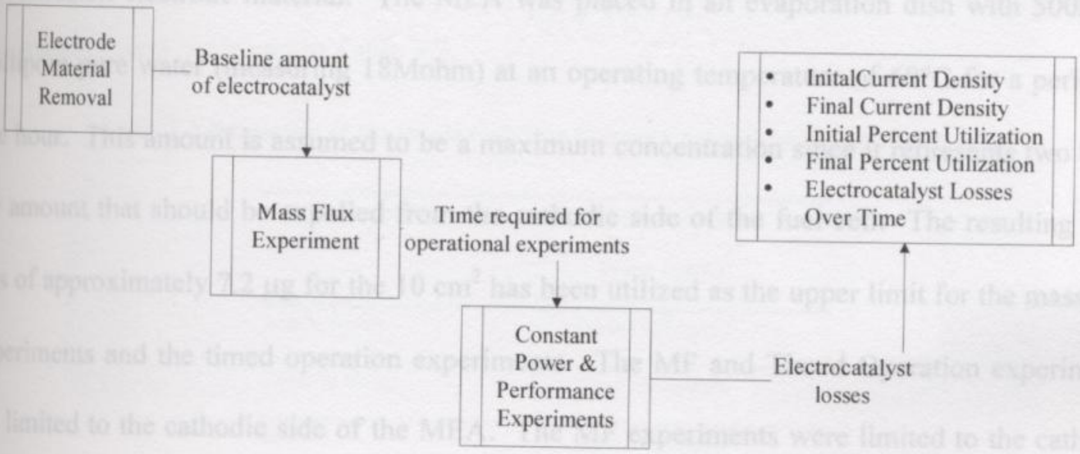

Figure 3-1 Experimental Process Map.

The nomenclature utilized for these experiments includes the following acronyms: Constant Power Low Temperature (CPL), Constant Power High Temperature (CPH), Special Load (SL) which is an 80% Pt on Vulcan XC-72, and Platinum Black (PB).

3.1 Electrode Material Removal (EMR)

The particle removal is described in Table 3.1. MEA1 and MEA2 were placed in a bath of 18M-ohm water and the temperature was increased to 60ºC at 1 atmosphere for a period of one hour. The solution was then analyzed on the Perkin-Elmer ICP mass spectrometer.

Table 3-1 Electrode particle displacement by hydrothermal manipulation.

MEA	Sample Volume (ml)	Pt 196 Concentration Mean (µg/L)	Concentration Standard Deviation (µg/L)	Pt Mass Lost (µg)	Platinum Electrocatalyst
MEA 1	500	14.3501	0.1329	7.18	0.4 mg/cm^2
MEA 2	500	14.4708	0.0948	7.23	0.4 mg/cm^2

The total concentration of the electrocatalyst in the material is representative of 10 cm^2 worth of gas diffusion electrode material. The MEA was placed in an evaporation dish with 500ml of Millipore pure water (measuring 18Mohm) at an operating temperature of 60°C for a period of one hour. This amount is assumed to be a maximum concentration since it represents two times the amount that should be expelled from the cathodic side of the fuel cell. The resulting mass loss of approximately 7.2 µg for the 10 cm^2 has been utilized as the upper limit for the mass flux experiments and the timed operation experiments. The MF and Timed Operation experiments are limited to the cathodic side of the MEA. The MF experiments were limited to the cathodic side of the fuel cell.

3.1.1 Membrane and Electrode Assemblies

Each gas diffusion electrode was impregnated with an electrolyte [17], (5% by weight, Nafion® solution). This solution was dispersed on the electrode's active surface to a total weight of approximately 0.6 mg/cm^2. The Nafion® membrane material used was Nafion 115. The electrode has a distribution of electrocatalyst per unit area based on a percentage of the electrocatalyst weight of the material. For example 20% Pt on Carbon at a distribution of 0.4 mg/cm^2 would indicate that for a 5cm^2 electrode there is a total of 2.0mg of the electrocatalyst/carbon mix and only 0.4mg of platinum present. However the actual amount of electrocatalyst present is only 20% of the 2.0 mg total, from the example above, in actual terms the amount of electrocatalyst present is 400μg.

A GlobeTech, Inc. single cell test fixture, shown in Figure 2.3 (model SSTF-5, 5cm^2 surface area test fixture), contained the test MEA. The carbon blocks of the test fixture were subjected to EMR experiment process to provide a baseline amount of platinum present in the block material. This information was compared against material test reports from the manufacturer. The amount of platinum found is present in Table 3.2.

Table 3-2 Properties of the Single Cell Test Fixture Carbon Plates and Test Stand.

Description	**Pt 196 Concentration Mean (μg/L)**
Anode Bottle	Non Detectable
Cathode Bottle	Non Detectable
Block 1	Non Detectable
Block 2	Non Detectable

There were no measurable traces of platinum in the system components when compared to the detectable limit based on the 0.625 ppb standard.

3.2 Mass Flux (MF) Experiment

Placing a peristaltic pump in line with a volume of 18M-ohm purity water and mechanically pumping a specific volume of water through the single cell test fixture surmises the mass flux experiment, shown in Figure 3.2. A GlobeTech, Inc. (model GT-FLO) system was used to control the experiment parameters. The test fixture was mechanically cleaned and rinsed with 18M-ohm purity water repeatedly after every experiment to prevent cross contamination.

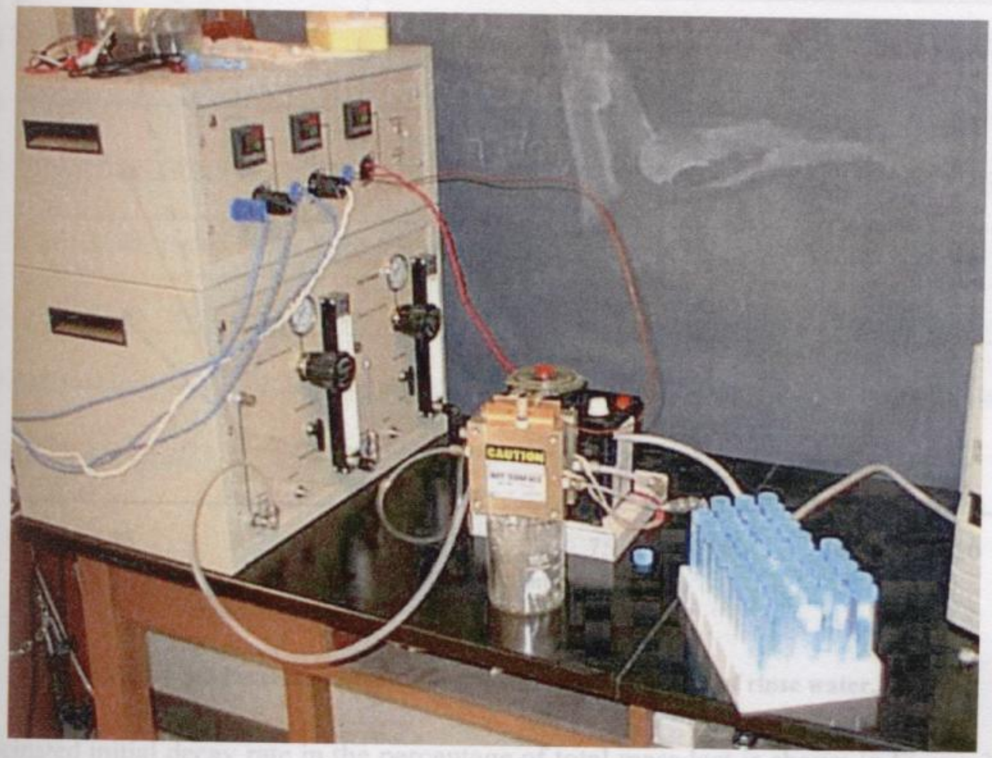

Figure 3-2 Mass flux experiment setup.

The Anode humidification bottle was increased to 65°C at 1 atmosphere, the cathode was 70°C at 1 atmosphere, and the single cell test fixture was 50°C. The peristaltic pump inlet was connected directly to the humidification bottle sight glass, thus allowing the water in the humidification bottle to be directly injected into the system at a rate of 4.0ml/min. The samples were collected in sterilized 15ml polypropylene vials. The raw data is located in Appendix C. Figure 3.3 shows the concentration of platinum that was mobile in the aqueous phase, thus mechanically removed from the gas diffusion electrode on the cathodic side of the fuel cell during the experiment.

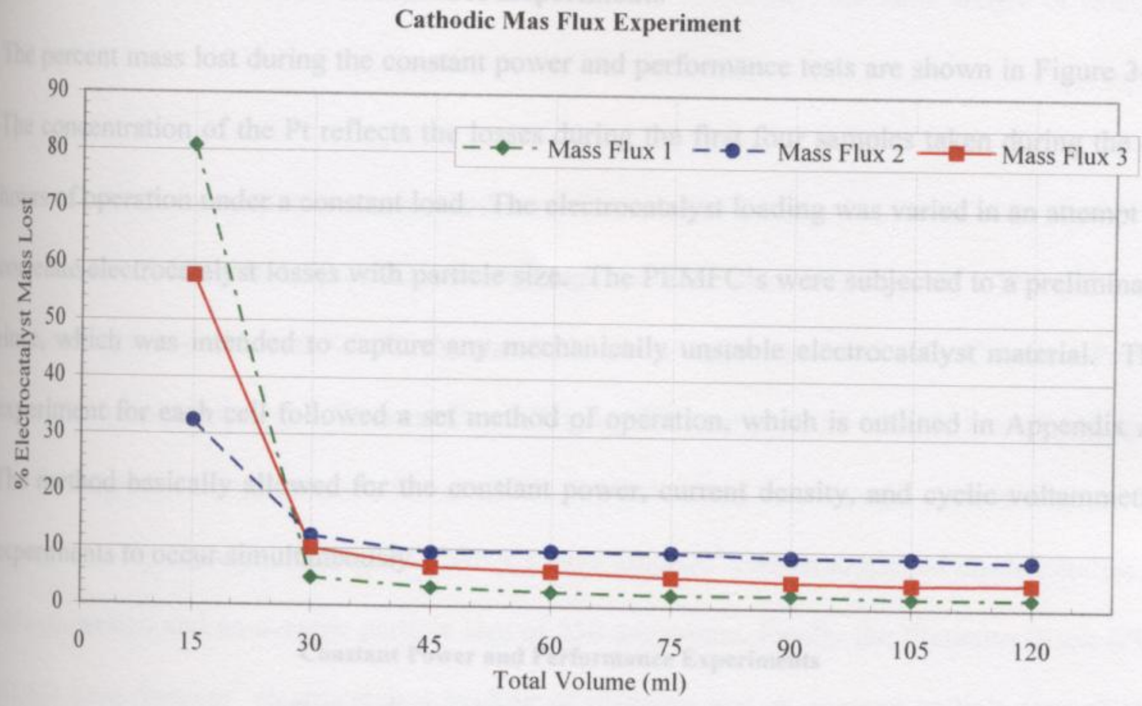

Figure 3-3 Percent electrocatalyst losses vs total volume of rinse water.

The anticipated initial decay rate in the percentage of total mass lost is shown in Figure 3.3. The amount of electrocatalyst lost in each 15ml sample volume of the experiments has been represented as a percentage of the total electrocatalyst lost during the mass flux experiment. The rapid decay over the first 30ml of volume that is passed through the cathodic side of the PEMFC was an expected result, in support of the theory that the electrocatalyst losses are a rinsing loss. The majority of the total electrocatalyst lost during the first 120ml of volume is in the first 30ml. As a result of the MF experimental indication that the first 30ml of water contains significant electrocatalyst losses the timed operation experiments were based on a 48-hour cycle, to allow reclamation of majority of the platinum lost during operation.

3.3 Constant Power and Performance Experiments

The percent mass lost during the constant power and performance tests are shown in Figure 3-4. The concentration of the Pt reflects the losses during the first four samples taken during the 48 hours of operation under a constant load. The electrocatalyst loading was varied in an attempt to correlate electrocatalyst losses with particle size. The PEMFC's were subjected to a preliminary rinse, which was intended to capture any mechanically unstable electrocatalyst material. The experiment for each cell followed a set method of operation, which is outlined in Appendix A. The method basically allowed for the constant power, current density, and cyclic voltammetry experiments to occur simultaneously.

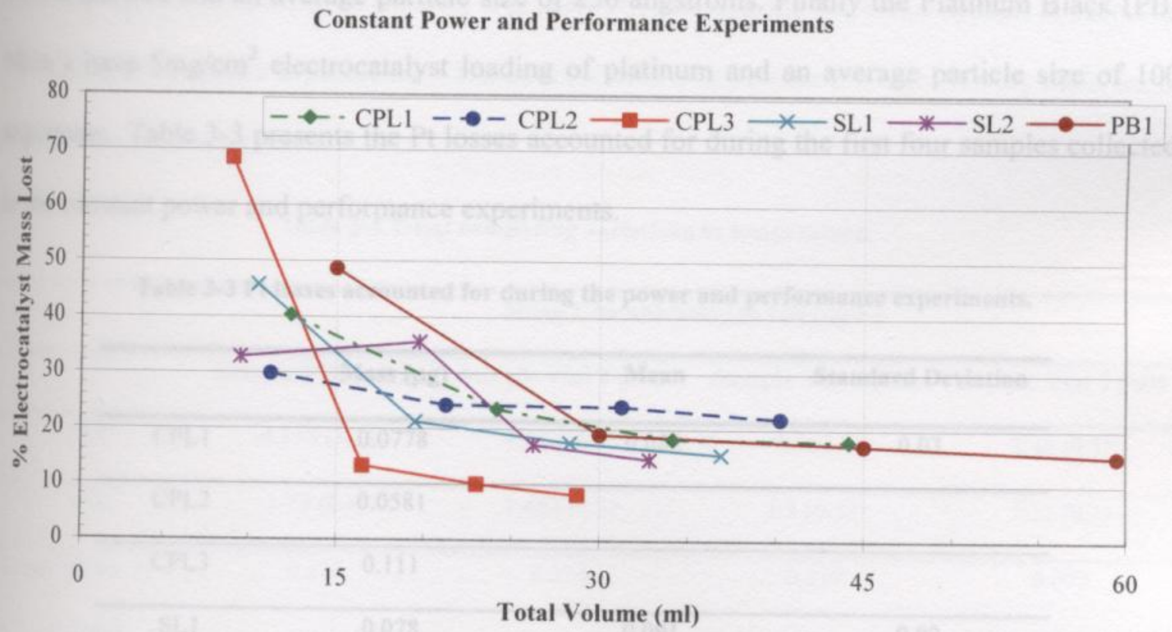

Figure 3-4 Percent electrocatalyst losses vs total volume of water produced

As indicated in Figure 3-4 the majority of electrocatalyst losses occurred within the first 30ml of water produced. The measurements for the SL2 experiment suggest the MEA did not immediately loose the electrocatalyst as the other had. Ultimately, the same weight of catalyst was lost.

3.3.1 Dependence of Electrocatalyst Losses on Particle Size

The vendor E-TEK Inc., provided the average particle size information. The platinum electrocatalyst is on Vulcan XC-72, the standard carbon support material. The Constant Power Low (CPL) temperature and Constant Power High (CPH) temperature MEA's have 0.4mg/cm^2 carbon supported electrocatalyst has at 20% dispersion and an average particle size of 25 angstroms. The Special Loading (SL) MEA's have 5mg/cm^2 carbon supported electrocatalyst at 80% dispersion and an average particle size of 250 angstroms. Finally the Platinum Black (PB) MEA's have 5mg/cm^2 electrocatalyst loading of platinum and an average particle size of 100 angstroms. Table 3-3 presents the Pt losses accounted for during the first four samples collected in the constant power and performance experiments.

Table 3-3 Pt losses accounted for during the power and performance experiments.

	Mass (µg)	**Mean**	**Standard Deviation**
CPL1	0.0778	0.082	0.03
CPL2	0.0581		
CPL3	0.111		
SL1	0.078	0.091	0.02
SL2	0.104		
PB1	0.125	0.0125	-

A one-way ANOVA was performed on this data and there were no significant differences (P=0.719) between the means of the Pt mass lost when comparing these loadings.

3.3.2 Dependence of Electrocatalyst Losses on Temperature

The temperature range that was used is based on typical fuel cell operations. The standard temperature conditions for nominal operation were conducted at 50 (cell), 65 (Anode), and 70ºC (Cathode) at 1 atmosphere. Lower temperature ranges of 25, 50, and 60°C (cell, anode, cathode) were used as a lower limit for the experiments, since a PEMFC will rise to this temperature on it own as a result of energy lost as heat. A higher range of 75, 85, and 90°C (cell, anode, cathode), were utilized as a high point. This avoids dehydration of the membrane material, since the system was not operated under pressure. The mass values for the high temperature experiments are not available, but statistical analysis was performed comparing the concentration in each vial for the two temperature experiments. The concentrations of Pt were not significantly different in any of the collection vials.

Table 3-4 T-test comparing variations in temperature.

	Mean Concentration in vial (μg/L)			
	Sample Vial 1 (SD)	**Sample Vial 2 (SD)**	**Sample Vial 3 (SD)**	**Sample Vial 4 (SD)**
50°C	4.159 (3.7)	1.642 (0.3)	1.5 (0.2)	1.46 (0.1)
75°C	1.79 (0.4)	1.404 (0.2)	1.3 (0.13)	1.21 (0.1)
T-tests (50 vs. 75°C) P-Value	0.456	0.374	0.219	0.059
Interpretation	NSD	NSD	NSD	NSD

NSD = No Significant Difference

SD = Standard Deviation

The Table 3.4 data provides evidence that there is no significant electrocatalyst loss associated with the size of the particle.

3.3.3 PEMFC Performance

These results have been grouped by MEA on a per page basis. The initial and final current densities vs. cell potential plots are displayed on the same graph. Figures 3.5 – 3.15 share the same basic characteristic of excessive resistive losses in the fuel cell. There is an activation energy problem associated with the majority of the initial sweeps, but this is an expected result since there is typically some organic contamination in the PEMFC at the site of the electrocatalyst. In general PEMFC's are operated at an elevated temperature and pressure, (85°C and 3 atmospheres), for 6-8 hours to remove any organic impurities.

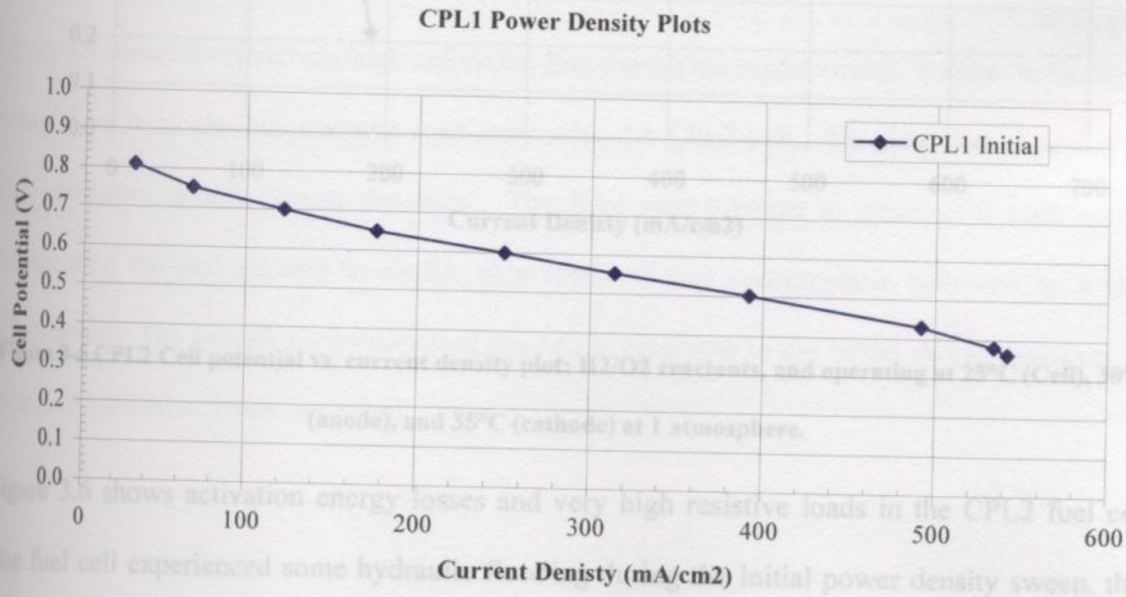

Figure 3-5 CPL1 Cell potential vs. current density plot; H2/O2 reactants, and operating at 25°C (Cell), 30°C (anode), and 35°C (cathode) at 1 atmosphere.

CPL1 developed a "pin-hole" and was destroyed during the experiment, thus there is no final power density sweep. Figure 3.5 indicates that there is an excessive amount of activation energy lost due to the Open Circuit Voltage (OCV) being 1.004 but the current density not being measurable until 0.810 V. Figure 3.5 also shows high resistive loads within the fuel cell.

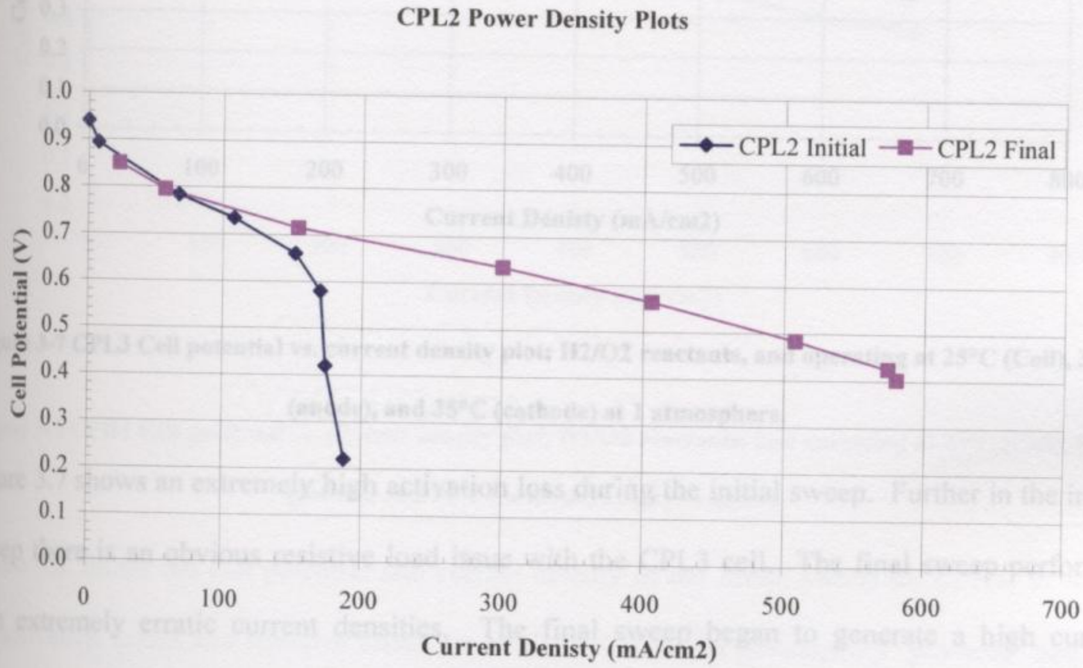

Figure 3-6 CPL2 Cell potential vs. current density plot; H2/O2 reactants, and operating at 25°C (Cell), 30°C (anode), and 35°C (cathode) at 1 atmosphere.

Figure 3.6 shows activation energy losses and very high resistive loads in the CPL2 fuel cell. The fuel cell experienced some hydraulic flooding during the initial power density sweep, thus the slope of the line and mass transport limitation. Figure 3.6 does indicate an increased PEMFC performance during the final sweep.

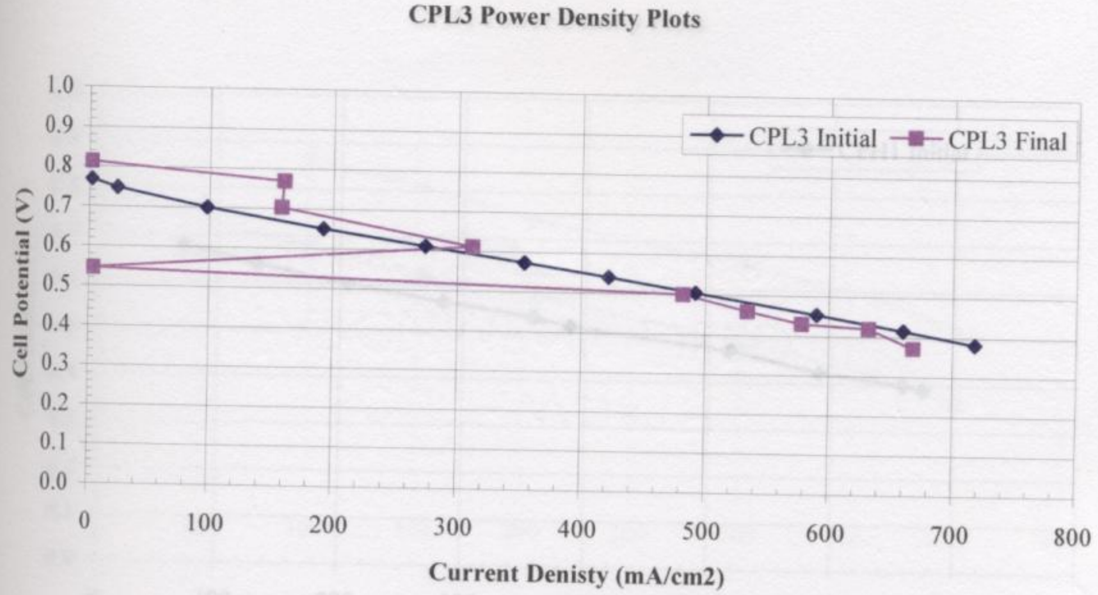

Figure 3-7 CPL3 Cell potential vs. current density plot; H2/O2 reactants, and operating at 25°C (Cell), 30°C (anode), and 35°C (cathode) at 1 atmosphere.

Figure 3.7 shows an extremely high activation loss during the initial sweep. Further in the initial sweep there is an obvious resistive load issue with the CPL3 cell. The final sweep performed with extremely erratic current densities. The final sweep began to generate a high current density then the cell appears to choke, as a result of fuel consumption, followed by a slow stabilization. The overall performance of the cell is equitable to the initial sweep, however the improved activation losses are noted.

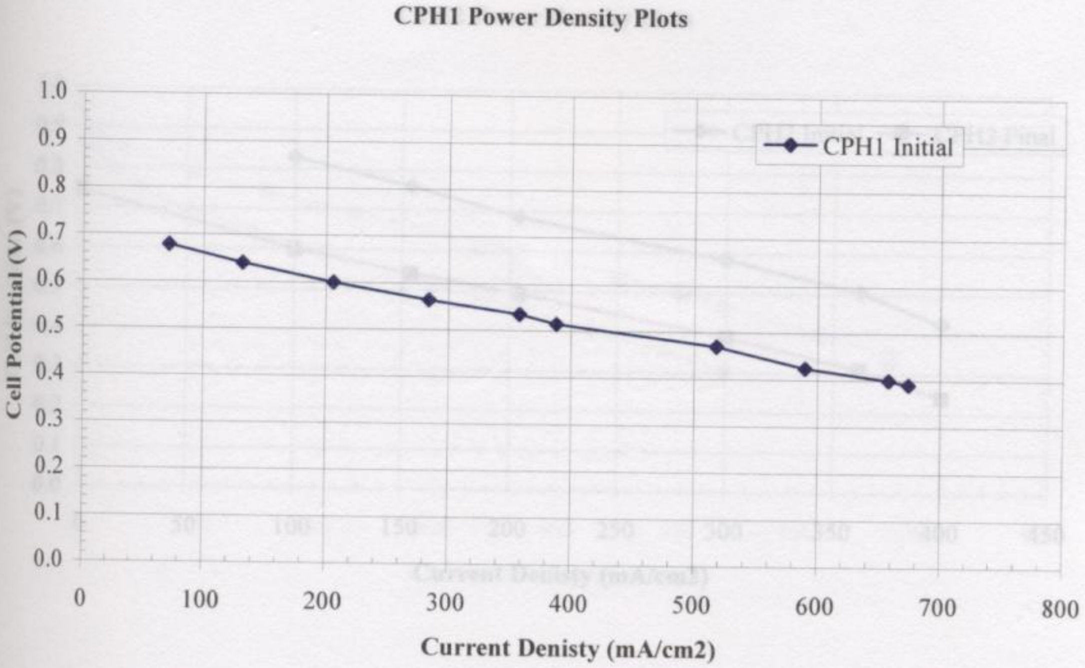

Figure 3-8 CPH1 Cell potential vs. current density plot; H2/O2 reactants, and operating at 75°C (Cell), 85°C (anode), and 90°C (cathode) at 1 atmosphere.

Figure 3.8 shows the cell potential and current density of the initial sweep for CPH1, in which the activation losses and resistive losses are evident. The MEA developed a "pin-hole" and was subsequently destroyed.

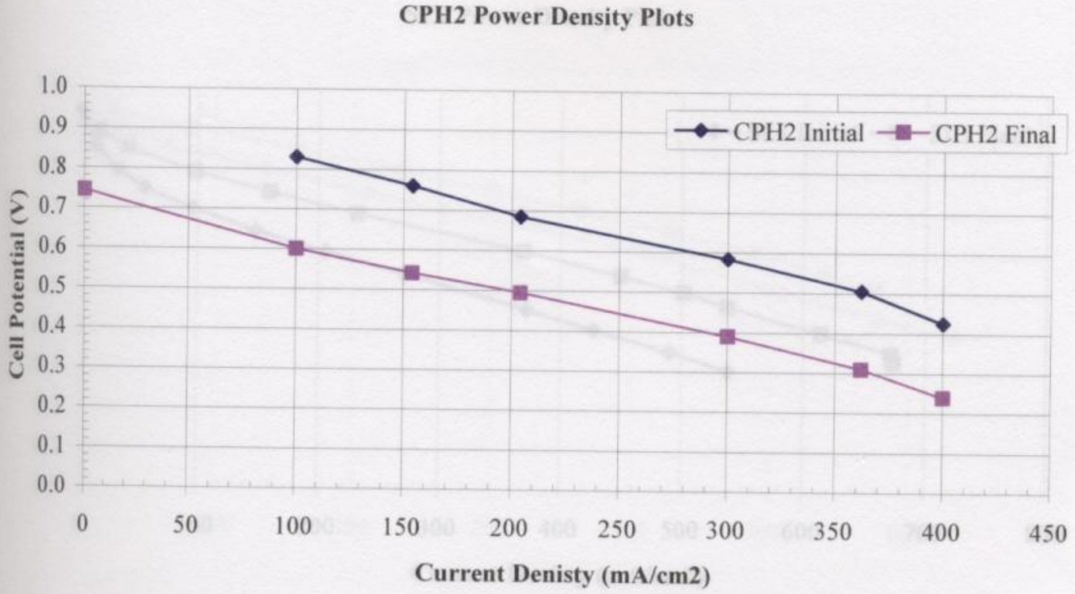

Figure 3-9 CPH2 Cell potential vs. current density plot; H2/O2 reactants, and operating at 75°C (Cell), 85°C (anode), and 90°C (cathode) at 1 atmosphere.

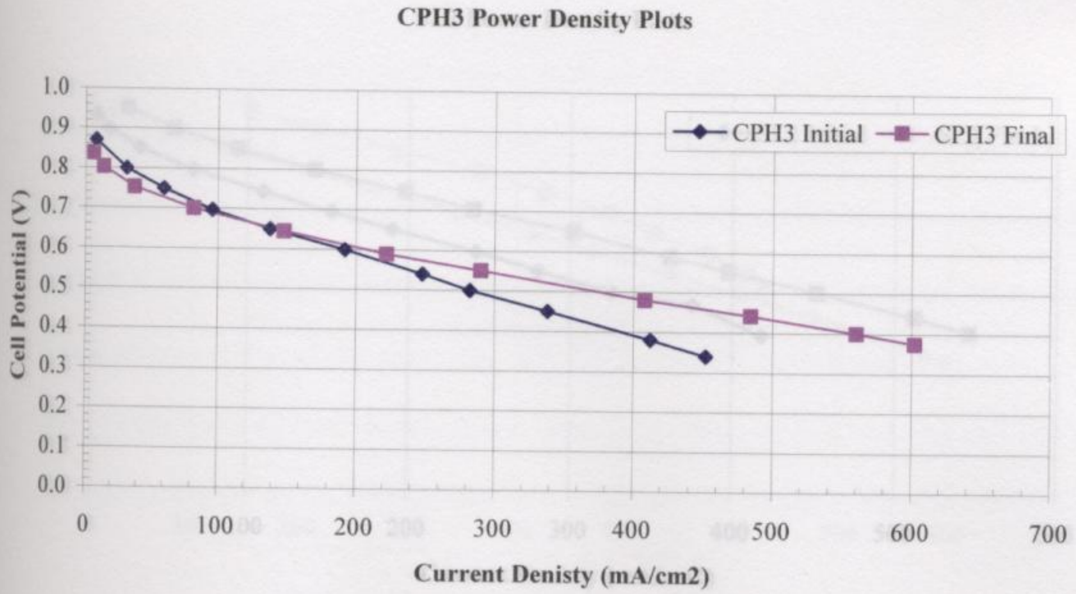

Figure 3-10 CPH3 Cell potential vs. current density plot; H2/O2 reactants, and operating at 75°C (Cell), 85°C (anode), and 90°C (cathode) at 1 atmosphere.

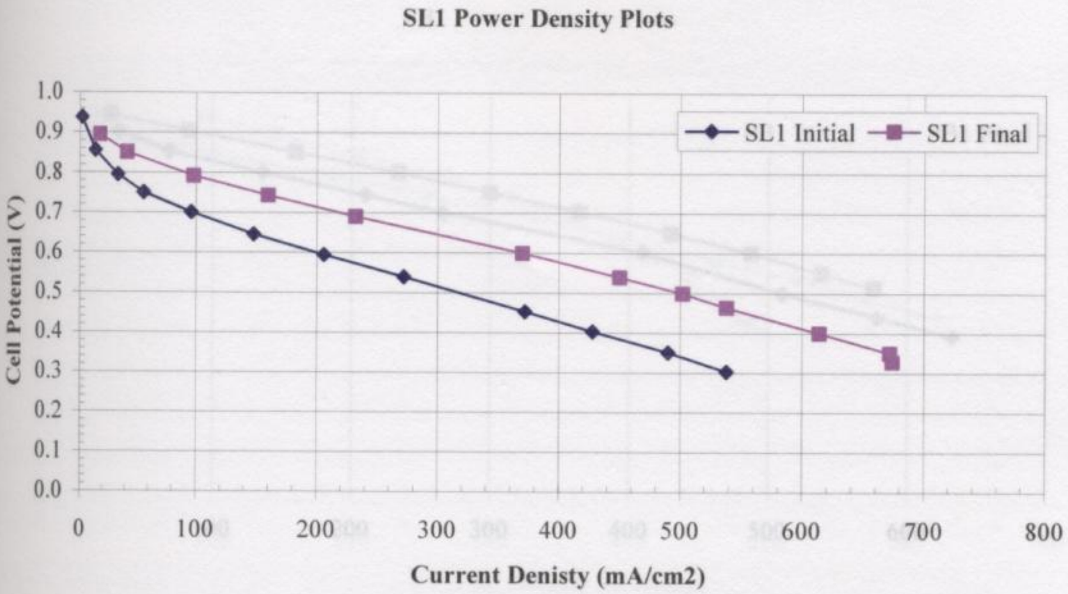

Figure 3-11 SL1 Cell potential vs. current density plot; H2/O2 reactants, and operating at 50°C (Cell), 65°C (anode), and 70°C (cathode) at 1 atmosphere.

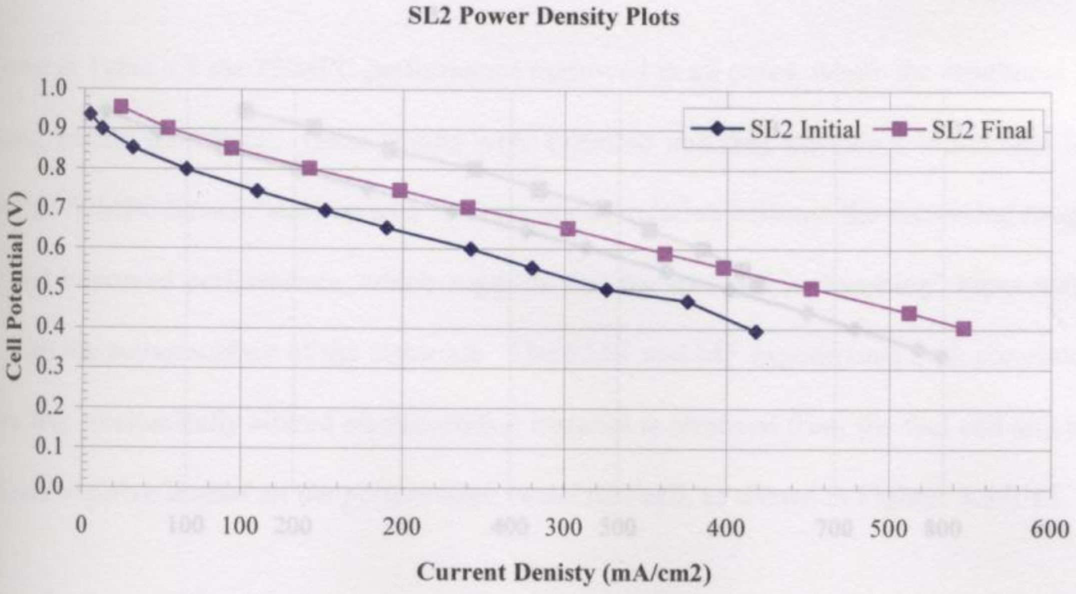

Figure 3-12 SL2 Cell potential vs. current density plot; H2/O2 reactants, and operating at 50°C (Cell), 65°C (anode), and 70°C (cathode) at 1 atmosphere.

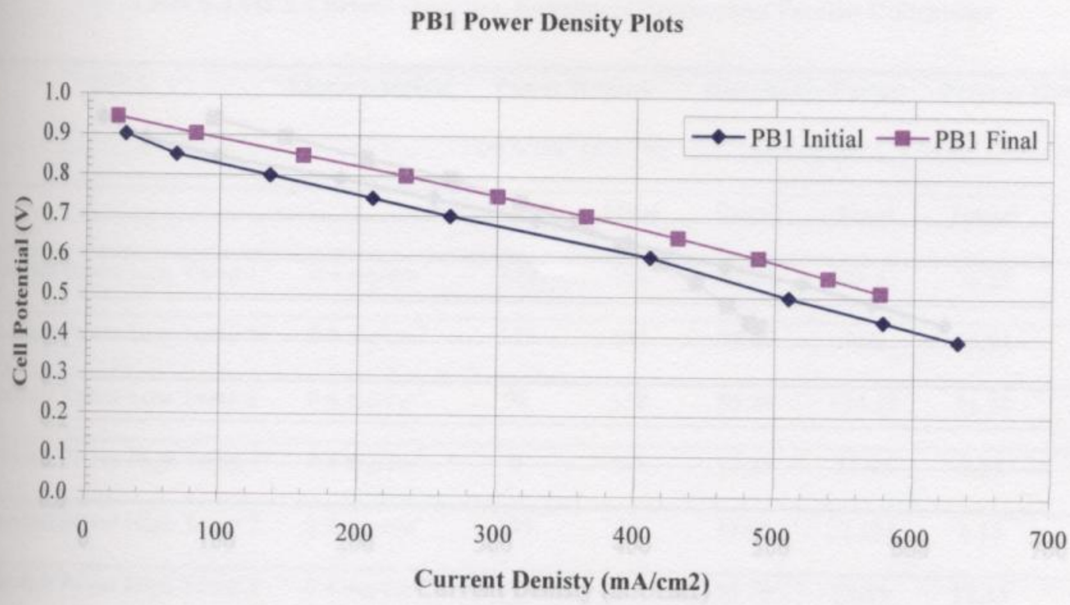

Figure 3-13 PB1 Cell potential vs. current density plot; H2/O2 reactants, and operating at 50°C (Cell), 65°C (anode), and 70°C (cathode) at 1 atmosphere.

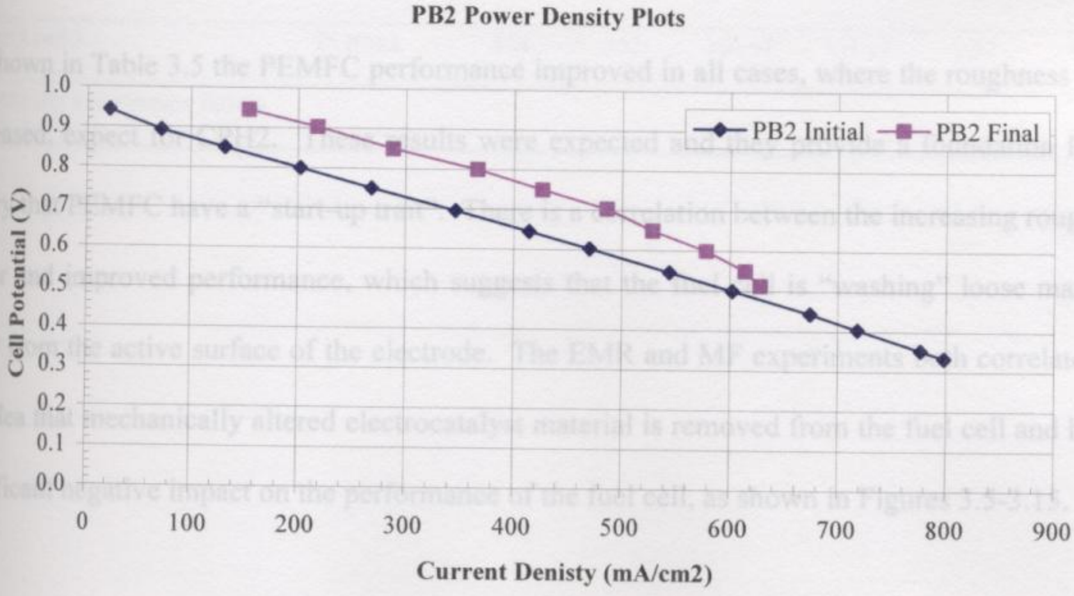

Figure 3-14 PB2 Cell potential vs. current density plot; H2/O2 reactants, and operating at 50°C (Cell), 65°C (anode), and 70°C (cathode) at 1 atmosphere.

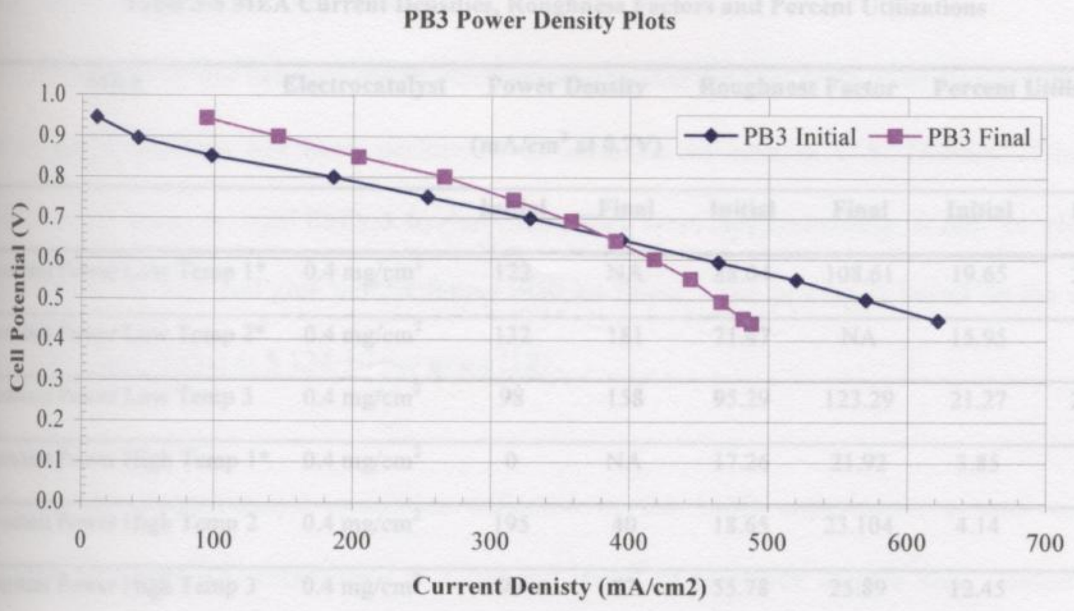

Figure 3-15 PB3 Cell potential vs. current density plot; H2/O2 reactants, and operating at 50°C (Cell), 65°C (anode), and 70°C (cathode) at 1 atmosphere.

As shown in Table 3.5 the PEMFC performance improved in all cases, where the roughness factor increased, expect for CPH2. These results were expected and they provide a foundation for the theory that PEMFC have a "start-up trait". There is a correlation between the increasing roughness factor and improved performance, which suggests that the fuel cell is "washing" loose materials away from the active surface of the electrode. The EMR and MF experiments both correlate with the idea that mechanically altered electrocatalyst material is removed from the fuel cell and has no significant negative impact on the performance of the fuel cell, as shown in Figures 3.5-3.15.

Table 3-5 MEA Current Densities, Roughness Factors and Percent Utilizations

MEA	Electrocatalyst	Power Density (mA/cm² at 0.7V)		Roughness Factor		Percent Utilization	
		Initial	Final	Initial	Final	Initial	Final
Constant Power Low Temp 1*	0.4 mg/cm²	122	NA	88.04	108.61	19.65	24.24
Constant Power Low Temp 2*	0.4 mg/cm²	132	181	71.47	NA	15.95	NA
Constant Power Low Temp 3	0.4 mg/cm²	98	158	95.29	123.29	21.27	27.52
Constant Power High Temp 1*	0.4 mg/cm²	0	NA	17.26	21.92	3.85	4.89
Constant Power High Temp 2	0.4 mg/cm²	195	40	18.65	23.104	4.14	5.16
Constant Power High Temp 3	0.4 mg/cm²	93	82	55.78	25.89	12.45	5.78
Special Load 1	5 mg/cm²	96	230	45.42	97.35	8.26	17.7
Special Load 2	5 mg/cm²	150	242	74.93	86.12	13.6	15.7
High Load 1	Pt Black	266	369	131.17	111.12	9.37	7.94
High Load 2	Pt Black	342	284	114.75	49.72	8.20	3.55
High Load 3	Pt Black	328	352	126.95	131.17	9.07	9.36

* Indicates a membrane failure

4.0 ECONOMIC ANALYSIS

In consideration of the value of the Pt electrocatalyst value for fuel cells, specifically PEMFC's, an economic analysis has been performed to ascertain its cost in U.S. Dollars. Since the experimental analysis was limited to fuel cells that were approximately 5 cm^2 in electrode surface area the fuel cell area extrapolation shall be linear. The pricing is based on the current cost of Pt black (98%) at \$ 134.10 per gram [18].

Utilizing the electrocatalyst quantities collected in the EMR experiment, a total mass of electrocatalyst loss was established at 7.2μg for 10cm^2 of electrode surface area. Based on an approximation of 0.72μg per cm^2 can be calculated by dividing the surface area by the total mass of electrocatalyst losses. With this assumption Table 4.1 has been developed.

Table 4-1 Electrocatalyst quantities for liner extrapolation of economic analysis.

MEA Size (cm^2)	Quantity (g)	Price of Platinum (USD)
10	0.000007	\$ 0.00
100	0.000072	\$ 0.01
1,000	0.000720	\$ 0.09
10,000	0.007200	\$ 0.97
100,000	0.072000	\$ 9.65
1,000,000	0.720000	\$ 96.55
10,000,000	7.200000	\$ 965.52
100,000,000	72.000000	\$ 9,655.20
1,000,000,000	720.000000	\$ 96,552.00
10,000,000,000	7200.000000	\$ 965,520.00

Commercial products similar to those in Table 4.2 are an example of size and cell quantity.

Table 4-2 Commercially available BCS Fuel Cells Inc. product sizes and power densities.

Cell Stack	Area (cm^2)	Current (A)	Voltage (V)	Power (W)
10-cell	64	25	6	150
21-cell	64	25	12	300
32-cell	64	25	20	500
24-cell	245	70	15	1000
48-cell	245	70	30	2000
72-cell	245	70	45	3000

The typical residential application would use 5-10 kilowatts at a minimum. Hence the amount of cost recovery from 6000 watts (2:3000 watt stacks) would be \$ 3.41, which is based on multiplying the surface area of the cell (245), number of MEA's (144), 0.72µg per cm^2, and \$134.10 per g. As fuel cells are scaled up to accommodate larger residential areas the scale of economy will come into play and the dollar amount may become equitable.

The amount of environmentally distributed platinum has an economic value associated with its cleanup and risk assessment. Currently the World Health Organization estimates that the ambient air concentrations of platinum range [19] from 0.05 pg/m^3 to 0.09 ηg/m^3, which is based on an average emission rate for vehicle catalytic converters of approximately 20 ηg/km. Comparatively the peak concentration of 14 µg/L (at fuel cell start-up), or 14 ηg/m^3, established during this research is relatively high.

5.0 CONCLUSIONS

This research examined the "start-up" conditions in a PEMFC. This research has provided evidence that supports quantitative electrocatalyst losses, performance analysis, and possible environmental and economical consequences. The quantitative amounts of platinum rejected from the fuel cell were analyzed utilizing the EMR experiment. The rate of electrocatalyst loss from the PEMFC was established with mass flux analysis. The performance criteria of the fuel cells were established and reviewed with cyclic voltammetry and cell potential vs. current density graphs.

5.1 Quantitative Electrocatalyst Isolation

The Electrode Material Removal process resulted in a baseline amount of electrocatalyst being liberated from the surface of the membrane and electrode assembly. The EMR experiments did result in a functional baseline for the mass flux experiments. The quantative amount of 14.39 μg/L proved to be an accurate peak range for the ICP mass spectrometer analysis.

Ambient air concentrations of platinum are estimated at 0.05 pg/m^3 to 0.09 ηg/m^3, which is based on an average emission rate for vehicle catalytic converters of approximately 20 ηg/km. The peak concentration of 14 μg/L, or 14 ηg/m^3, established during this research is relatively high when compared to the ambient air concentrations. Conclusively the environmental risk associated with large-scale distribution of PEMFC's will exacerbate the environmental concerns associated with Pt.

5.2 Mass Flux Experiment

The results, as displayed in Figure 3.3, indicate a drop over the first 30ml of refuse collected for all three MEA's that were analyzed. The results present have indicated that the constant load experiments need not exceed a 48-hour period, as the first 30ml of water was produced within this time interval. The rate of electrocatalyst depletion was determined during the constant power and performance experiments and indicates that the electrocatalyst losses are immediate. This immediate removal of material provides a strong correlation for compressive losses due to the fabrication process. Under the traditional PEMFC fabrication procedure the electrode is subjected to high pressures, which can affect the mechanical structure of the electrode. The losses of electrochemical material are electrochemically negligible and probably due to the method of fabrication technique of the MEA. As a result of the MF experimental indication that the first 30ml of water contains the majority of electrocatalyst losses the timed operation experiments were based on a 48-hour cycle.

5.3 Fuel Cell Performance

Electrocatalyst loses are independent of particle size, as indicated in Table 3-3. Temperature also had no significant effect on the amount of electrocatalyst lost from the PEMFC, as indicated in Table 3-4. A rather high Ohmic resistance in the fuel cells was observed, however the slope is comparative to other published data thus the fuel cells performed as expected. The PEMFC performance improved in all cases, where the roughness factor increased, expect for CPH2. The results support the theory that PEMFC's have a "start-up trait". The EMR and MF experiments both correlate with the idea that mechanically altered electrocatalyst material is removed from the fuel cell and has no significant negative impact on the performance of the fuel cell.

The research suggests that the removal of the mechanically unsound material correlates with improved performance of the fuel cell. The amount of electrocatalyst lost from the PEMFC's was irrelevant to the cell performance. In most cases the cell performance increased after the samples were collected. The increase in performance suggests that the electrocatalyst is not participating in the membrane surface electrochemistry, specifically it does not have an electrochemical contact to the membranes proton exchange surface.

5.4 Further Research

Investigations into fabrication techniques, other than the traditional pressing method for PEMFC are necessary to further the research and development of PEMFC's. Any further research in this area would benefit from utilizing an electronic load and a highly precise relative humidity meter for the anode and cathode gases. The assessment of Pt losses in a closed loop regenerative fuel cell system is a research task that would also be of tremendous value in our understanding performance characteristics of PEMFC's.

There is a definite need for this research, as the PEMFC has not reached commercial production levels and the environmental impact of PGE materials is under scrutiny [20]. This research indicates that merely a 24-hour test for platinum losses were adequate to ascertain the initial losses of platinum from the fuel cells.

In conclusion the PEMFC electrocatalyst losses are predominantly during the first 24-hours of operation and specifically during the first 30ml of water volume transferred through the fuel cell.

There is some indication that the method of fabrication has a role in the electrocatalyst losses, however this would require further investigation. This research shows no indication that particle size or temperature have an impact on the amount of losses or the rate of loss from the fuel cell.

The amount of environmentally distributed platinum has an economic value associated with its cleanup and risk assessment. Anthropogenic emissions of PGE are currently being studied in Europe, and the United States, as a result of the dramatic increase in quantitative environmental impacts. As indicated by this research, the commercial introduction of PEMFC into the next generation of vehicles may result in a similar pattern of anthropogenic emissions being introduced into the environment and exacerbate the environmental impact associated with PGE. This environmental travesty may be avoided entirely simply by insisting that the Original Engineering Manufacture (OEM) use a recovery process during the production of fuel cell systems.

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APPENDIX A - PROCEDURES

Constant Power & Performance Experiment Methodology

Materials Needed

- Resistive Load
- Multi-meters
- PEMFC
- PC controlled auto-sampler or an exhaustive amount of time.
- Bipotentiostat
- PC for data acquisition
- Fuel Cell Test Station
- Single Cell Test Fixture

Procedure

1. Rinse MEA's for loose material removal.
   1.1. Insert the MEA into a non-contaminated sample vial.
   1.2. Add 15ml of nanopure water.
   1.3. Place on test tube mixer for 30 seconds.
   1.4. Remove MEA from sample vial and store properly until insertion into the single cell test fixture.
2. Clean Single cell test fixture with kemwips, nanopure water (18mohm), and small brush
   2.1. Rinse the gas distribution blocks with nanopure water
   2.2. Use the brush to remove any loose items which may be present
   2.3. Continue to rinse the block
   2.4. Use a kemwip, or equilivent non-contaminating wipe, to dry the blocks.
3. Insert the MEA following standard procedures.
4. Attached the single cell test fixture to the fuel cell test station per standard procedures
5. Provide a sample vial to capture and water that is "washing" the electrode during the system start-up.
6. Start the fuel cell test station and bring the experiment up to the operational variables.
7. Perform the cyclic voltammetry experiment.
8. Perform a Current density sweep.
9. Place the system under a constant load.
   9.1. Using a resistive load lower the cell potential to 0.6-0.7 volts and record the current.
10. Start the auto-sampling system for the appropriate duration of the experiments
11. Perform the cyclic voltammetry experiment.
12. Perform a Current density sweep.
13. Analyze the Samples for electrocatalyst content.

Cyclic Voltammetry Experiment

Materials Needed

- Bi-potenistat Pine Instrument Model AF-CBP1
- PC with recommended National Instruments data acquisition Card and cable.
- Pine© Software.
- Single Cell Test Fixture (GlobeTech, Inc. single cell test fixture SSTF), reference electrode is optional.
- 3 Reference Cables, 18 AWG minimum.
- High purity Nitrogen
- High purity Hydrogen
- MEA

Procedure

14. Fuel cell preparation and Instrument setup
    14.1. Insert of the test MEA into the SSTF
    14.2. The SSTF must be void of all oxygen prior to conducting any testing.
        14.2.1. The recommendation is to pass an inert gas, Nitrogen in this case, on the cathodic side of the fuel cell and apply a load until the cell no longer registers a potential.
    14.3. The counter electrode is attached to the anodic side of the fuel cell.
    14.4. The reference electrode is connected to the anodic side of the fuel cell, the reference wire from the Pine Instrument has two leads a red and black lead, both are connected to the anodic side of the fuel cell. The red part of the Instrument reference wire should be connected to the reference electrode if one is present.
    14.5. The working electrode is connected to the cathodic side of the fuel cell test fixture.
15. Gas
    15.1. Chromatographic grade Hydrogen and Nitrogen must be used during this experiment, with hydrogen passed on the anodic side of the fuel cell and nitrogen on the cathodic side of the fuel cell.
    15.2. The gases should be humidified, if using a non self-humidified PEMFC, and introduced into the cell at a low flow rate at the operating temperature of the experiment. The typical operating temperatures were 50, 65, and 70°C for the Cell, Anode, and Cathode respectively.
    15.3. The gases should be allowed to pass for a period of one hour, during which time it is appropriate to apply a small load to the fuel cell to expedite the removal of any oxygen present in the fuel cell.
16. Instrument settings
    16.1. Use an analog sweep experiment, as optioned by the software.
    16.2. Variables:
        16.2.1. Sweep Rate of 5 mV/s or 10mV/s
        16.2.2. Lower voltage limit of 150 mV
        16.2.3. Upper voltage limit of 1000mV
        16.2.4. The number of sweeps performed should be at least 10, starting at the upper limit and moving towards the lower limit.

16.2.5. This arrangement only utilizes one working electrode in this experiment, thus K2 has no bearing on the experiment outcome.

17. Interpretation of the Data

17.1. The plot of the voltage, x-axis, against the current of the working electrode (I1) shows the typical cyclic voltammetry sweep of the fuel cell. On this plot the first peak on the positive side of the chart is the hydrogen/electrocatalyst interface. The area under this curve represents the columbic charge associated with the fuel cell.

17.2. Roughness Factor – determined by dividing the experimental charge by the fuel cell surface area and then by further dividing by .000220 (c), the surface charge of 1 cm^2 worth of smooth platinum. This dimensionless number is the Roughness Factor.

17.3. Percent Utilization – determined by dividing the roughness factor by the BET surface are of the equivalent loading. The vendor of the electrode material typically provides the BET surface area number.

Organic Impurity Removal for Water Electrolyzer

Materials Needed

- 100ml beaker.
- Ti mesh 120 x 120, 0.04mm diameter, or 150 x 150, 0.01.
- 120ml Reagent Grade Acetone.
- Hot Plate.
- Ventilation system for flammable vapor removal.

Procedure

1. Place 60ml of Acetone in the 100ml beaker.
2. Cut the Ti mesh into an electrode of test size. (This procedure is intended for a small cell 5-10cm^2)
3. Insert the Ti mesh into the beaker and place the beaker on the hot plate.
   3.1. The hot plate and beaker should be located in the vent hood to remove vapor.
   3.2. Increase the temperature of the hot plate to the boiling point of the acetone.
   3.3. Boil the mesh for a period of one hour
4. Remove the beaker from the hot plate.
5. Rinse the electrodes with DI water.
6. Follow the Inorganic contaminant removal process immediately.

Inorganic Impurity Removal for Water Electrolyzer

Materials Needed

- 100ml beaker.
- Ti mesh 120 x 120, 0.04mm diameter, or 150 x 150, 0.01.
- 160ml 1N Hydrochloric acid.
- Hot Plate.
- Ventilation system for vapor removal.
- Hydraulic press with temperature control.

- Oven.

Procedure

1. Place 80ml of 1N HCL in the 100ml beaker.
2. Cut the Ti mesh into an electrode of test size. (This procedure is intended for a small cell 5-10cm^2)
3. Insert the Ti mesh into the beaker and place the beaker on the hot plate.
    3.1. The hot plate and beaker should be located in the vent hood to remove vapor.
    3.2. Increase the temperature of the hot plate to the boiling point of the 1N HCL.
    3.3. Boil the mesh for a period of one hour
4. Remove the beaker from the hot plate.
5. Rinse the electrodes with 18Mohm water.
6. Insert the electrodes into a hydraulic press and apply 2 metric tons of pressure, at 85°C, to the wire mesh to make the surface uniform. Please note the surface finish of the material must be very high tolerance to insure an even distribution.
7. Air Dry the electrode in an over at 105°C for a period of 6 hours
8. Place 80ml of 1N HCL in a clean 100ml beaker.
9. Insert the Ti mesh into the beaker and place the beaker on the hot plate.
    9.1. The hot plate and beaker should be located in the vent hood to remove vapor.
    9.2. Increase the temperature of the hot plate to the boiling point of the 1N HCL.
    9.3. Boil the mesh for a period of 30minutes.
10. Remove the beaker from the hot plate.
11. Rinse the electrodes with 18Mohm water.
12. The electrodes may be stored at this point, utilizing 18Mohm nanopure water. The entire electrode should be submersed in a storage vessel with a predetermined weight.

Platinum Black Plating and Electrocatalyst Application Procedure

Materials Needed

- 100ml beaker.
- Ti mesh 120 x 120, 0.04mm diameter, or 150 x 150, 0.01. which has been Organically and inorganically cleaned.
- 80ml 1N Hydrochloric acid.
- 5.0 mg of dihydrogen hexachloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) CAS 26023-84-7
- 5cm of Platinum wire.
- 10V DC, 10-Ampere (100 Watt) power supply.
- Small Brush.
- 5% Nafion Solution
- Ventilation system for vapor removal.
- Oven.

Procedure

1. Dissolve 5.0mg of the $H_2PtCl_6 \cdot 6H_2O$ in a 100ml beaker with 10 ml of 1N HCL.
2. Volumetrically increase the 1N HCL/ $H_2PtCl_6 \cdot 6H_2O$ solution to 80ml with 1N HCL.

3. Attach each of 2 Ti mesh electrodes to 2.5cm of platinum wire and immerse into the 80ml of 1N HCL/ $H_2PtCl_6 \cdot 6H_2O$ using care not to immerse the platinum wire into the solution beyond the requirements for mesh.
    3.1. Attach one electrode to the positive terminal of the power supply.
    3.2. Attach the other electrode to the negative end of the power supply.
4. The platinum were deposited galvanostatically by passing a current of 5-10mA per cm^2 of electrode for a period of 1-6 hours, periodically verifying the weight of the electrode in solution using weigh by difference methods.
5. Once the desired deposition has been acquired the power supply terminals should be inverted and the step 4 repeated for the alternate electrode.
6. Upon plating completion the electrodes should be rinsed with 18Mohm water and the excess water should be blotted away with a Kemwip®.
7. The electrocatalyst used for this experiment will be a 5% Nafion Solution with an equivalent weight of 1100.
8. The Nafion solution will be weighed out and applied directly to the electrode using a brush.
9. The electrode must then be placed in an oven at 105°C for a period of 1 hour.
10. The brushing process should be continued until the desired amount of Nafion has been dispersed onto the electrode.
11. The electrodes are now ready to be hot pressed onto the membrane material using standard MEA fabrication techniques.

Nafion Membrane Cleaning Procedure

Materials Needed

- Pyrex dish capable of a basal surface area equivalent to the surface area of the membrane material.
- Nafion membrane cut to MEA specifications.
- 1L of 3% Hydrogen Peroxide.
- 2L of 18Mohm water.
- 1L of 10-15% solution of Nitric Acid.
- Hot plate.

Procedure

1. Immerse the membrane material in 3% hydrogen peroxide and bring to a boil.
    1.1. Maintain this temperature for a period of 30 minutes.
2. Immerse the membrane material in 18Mohm water and bring to a boil.
    2.1. Maintain this temperature for a period of 60 minutes.
3. Immerse the membrane material in 10-15% solution of Nitric Acid and bring to a boil.
    3.1. Maintain this temperature for a period of 30 minutes.
4. Immerse the membrane material in 18Mohm water and bring to a boil.
    4.1. Maintain this temperature for a period of 60 minutes.
5. Immerse the membrane material in 18Mohm water bath just prior to pressing and bring to a boil for a period of 30 minutes.

APPENDIX B – SAMPLE CALCULATIONS

Cyclic Voltammetry Calculations

$$\frac{V_A+V_B}{2}=V_X, \qquad [2.2]$$

Sample Calculation:

$$\frac{0.001953+0.00098}{2}=0.000488$$

,which yields a line equation of

$$0.00098+0.000488 \quad or \quad y=0.001456$$

that will be utilized by the integration program for the area calculations.

Roughness Factor

$$\left[\frac{E_C\ (\mu C)}{S_T\ (cm^2)}\right]\left[\frac{S\ (cm^2)}{S_C\, 220(\mu C)}\right]=Roughness\ Factor, \qquad [2.3]$$

Sample Calculation:

$$\left[\frac{19000(\mu C)}{5\,(cm^2)}\right]\left[\frac{1\,(cm^2)}{220(\mu C)}\right]=17.27\ ,$$

which is inserted in the percent utilization calculation.

Percent Utilization

$$\left[\frac{Roughness\ Factor}{(BET\ surface\ area)}\right]=Percent\ utilization\ . \qquad [2.4]$$

Sample Calculation:

$$\left[\frac{17.27}{448}\right][100]=3.85\%$$

APPENDIX C – RAW DATA

Table C.1 Experimental Data for MEA Properties

	Standard E-Tek Electrodes			
	Electrocatalyst	**Electrode 1 (g)**	**Electrode 2 (g)**	**Membrane (g)**
Constant Power Low Temp 1	0.4 mg/cm2	0.1865	0.1747	0.8553
Constant Power Low Temp 2	0.4 mg/cm2	0.1901	0.1742	0.9373
Constant Power Low Temp 3	0.4 mg/cm2	0.2094	0.2053	1.0381
Constant Power High Temp 1	0.4 mg/cm2	0.1444	0.1289	0.93
Constant Power High Temp 2	0.4 mg/cm2	0.1276	0.1394	0.7435
Constant Power High Temp 3	0.4 mg/cm2	0.1459	0.145	0.7939
Special Load 1	5 mg/cm2	0.1442	0.1536	1.0106
Special Load 2	5 mg/cm2	0.1315	0.1345	0.8385
High Load 1	Pt Black	0.1285	0.1198	0.7238
High Load 2	Pt Black	0.1432	0.1301	0.8638
High Load 3	Pt Black	0.1314	0.1346	0.8716

	Electrocatalyst	**Pre-Press Sum. (g)**	**Post-Press Total (g)**	**Difference (g)**
Mass Flux 1	0.4 mg/cm2	1.3876	1.3826	0.0050
Mass Flux 2	0.4 mg/cm2	1.216	1.2034	0.0126
Mass Flux 3	0.4 mg/cm2	1.2222	1.2012	0.0210
Constant Power Low Temp 1	0.4 mg/cm2	1.2165	1.1869	0.0296
Constant Power Low Temp 2	0.4 mg/cm2	1.3016	1.3116	-0.0100
Constant Power Low Temp 3	0.4 mg/cm2	1.4528	1.41318	0.0396
Constant Power High Temp 1	0.4 mg/cm2	1.2033	1.1854	0.0179
Constant Power High Temp 2	0.4 mg/cm2	1.0105	0.9928	0.0177
Constant Power High Temp 3	0.4 mg/cm2	1.0848	1.084	0.0008
Special Load 1	5 mg/cm2	1.3084	1.2994	0.0090
Special Load 2	5 mg/cm2	1.1045	1.0887	0.0158
High Load 1	Pt Black	0.9721	0.9722	-0.0001
High Load 2	Pt Black	1.1371	1.1298	0.0073
High Load 3	Pt Black	1.1376	1.128	0.0096

Table C.2 Experimental Data for MF experiment 1

	Mass Flux Experiment 1						
	Vial Number	Flow Rate	Pt Concentration	SD	Units	Sample Vol. (ml)	Total Vol. (ml)
Anodic Side	1	4.0 ml/min			ug/L	15	15
	2	4.0 ml/min			ug/L	15	30
	3	4.0 ml/min			ug/L	15	45
	4	4.0 ml/min			ug/L	15	60
	5	4.0 ml/min			ug/L	15	75
	6	4.0 ml/min			ug/L	15	90
	7	4.0 ml/min			ug/L	15	105
	8	4.0 ml/min			ug/L	15	120
	9	4.0 ml/min			ug/L	15	135
	10	4.0 ml/min			ug/L	15	150
Cathodic Side	11	4.0 ml/min	3.24	0.0816	ug/L	15	15
	12	4.0 ml/min	0.197	0.002	ug/L	15	30
	13	4.0 ml/min	0.133	0.00482	ug/L	15	45
	14	4.0 ml/min	0.105	0.00372	ug/L	15	60
	15	4.0 ml/min	0.0885	0.0064	ug/L	15	75
	16	4.0 ml/min	0.0942	0.00746	ug/L	15	90
	17	4.0 ml/min	0.0763	0.0048	ug/L	15	105
	18	4.0 ml/min	0.0754	0.00488	ug/L	15	120
	19	4.0 ml/min	0.0652	0.00423	ug/L	15	135
	20	4.0 ml/min	0.0641	0.0059	ug/L	15	150

Table C.3 Experimental Data for MF experiment 2

	Mass Flux Experiment 2						
	Vial Number	Flow Rate	Pt Concentration	SD	Units	Sample Vol. (ml)	Total Vol. (ml)
Anodic Side	1	4.0 ml/min	0.707	0.0145	ug/L	15	15
	2	4.0 ml/min	0.264	0.00576	ug/L	15	30
	3	4.0 ml/min	0.201	0.00715	ug/L	15	45
	4	4.0 ml/min	0.173	0.0082	ug/L	15	60

	Mass Flux Experiment 2						
	Vial Number	Flow Rate	Pt Concentration	SD	Units	Sample Vol. (ml)	Total Vol. (ml)
	5	4.0 ml/min	0.171	0.00554	ug/L	15	75
	6	4.0 ml/min	0.153	0.00814	ug/L	15	90
	7	4.0 ml/min	0.137	0.00757	ug/L	15	105
	8	4.0 ml/min	0.132	0.00525	ug/L	15	120
	9	4.0 ml/min	0.124	0.00689	ug/L	15	135
	10	4.0 ml/min	0.0641	0.0059	ug/L	15	150
Cathodic Side	11	4.0 ml/min	0.192	0.0132	ug/L	15	15
	12	4.0 ml/min	0.0728	0.00592	ug/L	15	30
	13	4.0 ml/min	0.0558	0.00321	ug/L	15	45
	14	4.0 ml/min	0.0578	0.00428	ug/L	15	60
	15	4.0 ml/min	0.0575	0.00502	ug/L	15	75
	16	4.0 ml/min	0.0538	0.00282	ug/L	15	90
	17	4.0 ml/min	0.0534	0.00437	ug/L	15	105
	18	4.0 ml/min	0.0501	0.00343	ug/L	15	120
	19	4.0 ml/min	0.0498	0.00702	ug/L	15	135
	20	4.0 ml/min	0.0631	0.00506	ug/L	15	150

Table C.4 Experimental Data for MF experiment 3

	Mass Flux Experiment 3						
	Vial Number	Flow Rate	Pt Concentration	SD	Units	Sample Vol. (ml)	Total Vol. (ml)
Anodic Side	1	4.0 ml/min	0.54	0.0175	ug/L	15	15
	2	4.0 ml/min	0.139	0.00905	ug/L	15	30
	3	4.0 ml/min	0.114	0.00505	ug/L	15	45
	4	4.0 ml/min	0.0962	0.00191	ug/L	15	60
	5	4.0 ml/min	0.0877	0.0022	ug/L	15	75
	6	4.0 ml/min	0.0711	0.00266	ug/L	15	90
	7	4.0 ml/min	0.0691	0.00448	ug/L	15	105
	8	4.0 ml/min	0.0602	0.00457	ug/L	15	120
	9	4.0 ml/min	0.0617	0.00427	ug/L	15	135
	10	4.0 ml/min	0.0587	0.00609	ug/L	15	150

	Mass Flux Experiment 3						
	Vial Number	Flow Rate	Pt Concentration	SD	Units	Sample Vol. (ml)	Total Vol. (ml)
Cathodic Side	11	4.0 ml/min	0.866	0.00617	ug/L	15	15
	12	4.0 ml/min	0.152	0.00417	ug/L	15	30
	13	4.0 ml/min	0.103	0.00566	ug/L	15	45
	14	4.0 ml/min	0.0935	0.00394	ug/L	15	60
	15	4.0 ml/min	0.0804	0.00394	ug/L	15	75
	16	4.0 ml/min	0.0695	0.00524	ug/L	15	90
	17	4.0 ml/min	0.0647	0.00473	ug/L	15	105
	18	4.0 ml/min	0.0675	0.00275	ug/L	15	120
	19	4.0 ml/min	0.124	0.00343	ug/L	15	135
	20	4.0 ml/min	0.0641	0.0059	ug/L	15	150
	21	4.0 ml/min	0.0674	0.00171	ug/L	30	180
	22	4.0 ml/min	0.0524	0.00733	ug/L	30	210
	23	4.0 ml/min	0.057	0.00526	ug/L	30	240
	24	4.0 ml/min	0.0503	0.00171	ug/L	30	270
	25	4.0 ml/min	0.0494	0.0023	ug/L	30	300
	26	4.0 ml/min	0.0484	0.00533	ug/L	30	330
	27	4.0 ml/min	0.0563	0.00516	ug/L	30	360
	28	4.0 ml/min	0.206	0.00113	ug/L	30	390
	29	4.0 ml/min	0.06	0.00287	ug/L	30	420
	30	4.0 ml/min	0.0569	0.00296	ug/L	30	450
	31	4.0 ml/min	0.0484	0.00297	ug/L	30	480
	32	4.0 ml/min	0.043	0.00176	ug/L	30	510

Table C.5 Experimental Data for Constant Power Low Temperature Number 1

Constant Power Low Temperature Number 1

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.004			OCV			
	0.980						
	0.810	0.160	32.000				
	0.753	0.340	68.000				
	0.700	0.610	122.000				
	0.650	0.880	176.000				
	0.600	1.250	250.000				
	0.553	1.570	314.000				
	0.502	1.960	392.000				
	0.430	2.460	492.000				
	0.380	2.670	534.000				
	0.361	2.710	542.000				

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
CPL1-1		2.526	0.0278	75
CPL1-2		1.5581	0.0118	30
CPL1-3		1.4174	0.0074	
CPL1-4		1.3897	0.0051	
CPL1-5		1.3576	0.0063	

Table C.6 Experimental Data for Constant Power Low Temperature Number 2

Constant Power Low Temperature Number 2

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.025			OCV	1.023		
	0.940	0.001	0.200		0.990		
	0.893	0.040	8.000		0.850	0.120	24.000
	0.784	0.340	68.000		0.795	0.290	58.000
	0.735	0.540	108.000		0.715	0.770	154.000
	0.660	0.760	152.000		0.635	1.500	300.000
	0.580	0.850	170.000		0.565	2.030	406.000
	0.420	0.870	174.000		0.485	2.540	508.000
	0.220	0.940	188.000		0.425	2.870	574.000
					0.403	2.900	580.000

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
CPL2-1		1.5401	0.0166	75
CPL2-2		1.41	0.0069	30
CPL2-3		1.398	0.0039	
CPL2-4		1.4143	0.0124	

Table C.7 Experimental Data for Constant Power Low Temperature Number 3

Constant Power Low Temperature Number 3

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	0.969			OCV			
	0.969				0.813	0.010	2.000
	0.768	0.010	2.000		0.770	0.800	160.000
	0.748	0.120	24.000		0.703	0.790	158.000
	0.701	0.490	98.000		0.612	1.560	312.000
	0.651	0.960	192.000		0.546	0.020	4.000
	0.611	1.370	274.000		0.501	2.410	482.000
	0.574	1.770	354.000		0.460	2.670	534.000
	0.541	2.110	422.000		0.430	2.890	578.000
	0.505	2.460	492.000		0.420	3.160	632.000
	0.453	2.950	590.000		0.372	3.340	668.000
	0.415	3.300	660.000				
	0.382	3.590	718.000				

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
CPL3-Wash		6.1201	0.0165	
CPL3-1		8.4121	0.1261	75
CPL3-2		1.9578	0.0305	30
CPL3-3		1.7153	0.026	
CPL3-4		1.5696	0.0217	
CPL3-5		1.524	0.0338	

Table C.8 Experimental Data for Constant Power High Temperature Number 1

Constant Power High Temperature Number 1							
Initial	**Volts**	**Amp**	**mAmp/cm2**	**Final**	**Volts**	**Amp**	**Amp/cm2**
OCV				OCV			
	0.945						
	0.760						
	0.678	0.360	72.000				
	0.640	0.660	132.000				
	0.600	1.030	206.000				
	0.564	1.420	284.000				
	0.535	1.790	358.000				
	0.515	1.940	388.000				
	0.470	2.590	518.000				
	0.425	2.950	590.000				
	0.400	3.290	658.000				
	0.391	3.370	674.000				

Notes: The sample had 5 mil of wash through prior to power. I anticipate some distortion effects, sample 1 s all wash through. Some samples have over run the volume of the tube.

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
CPH1-Wash		2.9373	0.0405	
CPH1-1		3.8251	0.0843	75
CPH1-2		4.6532	0.0656	30

Table C.9 Experimental Data for Constant Power High Temperature Number 2

Constant Power High Temperature Number 2

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.028			OCV			
	0.983				0.745	0.000	0.000
	0.830	0.030	100.000		0.601	0.500	100.000
	0.760	0.100	154.000		0.542	0.770	154.000
	0.685	0.230	204.000		0.495	1.020	204.000
	0.584	0.580	300.000		0.390	1.500	300.000
	0.505	1.050	362.000		0.310	1.810	362.000
	0.425	1.640	400.000		0.240	2.000	400.000
	0.340	2.200					
	0.250	2.350					

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
CPH2-Wash		3.3235	0.0141	
CPH2-1		2.052	0.0408	75
CPH2-2		1.5194	0.0266	30
CPH2-3		1.3721	0.0731	
CPH2-4		1.265	0.0087	
CPH2-5		1.2274	0.0078	

Table C.10 Experimental Data for Constant Power High Temperature Number 3

Constant Power High Temperature Number 3

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	0.996			OCV	0.956		
	0.870	0.040	8.000		0.837	0.030	6.000
	0.800	0.160	32.000		0.803	0.070	14.000
	0.750	0.300	60.000		0.753	0.190	38.000
	0.696	0.480	96.000		0.700	0.410	82.000
	0.650	0.690	138.000		0.645	0.740	148.000
	0.600	0.960	192.000		0.590	1.110	222.000
	0.540	1.240	248.000		0.550	1.450	290.000
	0.500	1.410	282.000		0.480	2.040	408.000
	0.450	1.690	338.000		0.442	2.420	484.000
	0.380	2.060	412.000		0.400	2.800	560.000
	0.340	2.260	452.000		0.375	3.010	602.000

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
CPH3-Wash		3.1077	0.0704	
CPH3-1		1.5272	0.0098	75
CPH3-2		1.2895	0.0239	30
CPH3-3		1.1832	0.021	
CPH3-4		1.1468	0.0028	
CPH3-5		1.1386	0.0059	

Table C.11 Experimental Data for Special Loading Number 1

Special Loading Number 1

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.010			OCV	1.017		
	0.937	0.010	2.000		0.895	0.090	18.000
	0.855	0.070	14.000		0.851	0.210	42.000
	0.795	0.170	34.000		0.792	0.490	98.000
	0.750	0.280	56.000		0.743	0.800	160.000
	0.701	0.480	96.000		0.691	1.160	232.000
	0.646	0.740	148.000		0.600	1.850	370.000
	0.595	1.030	206.000		0.540	2.250	450.000
	0.540	1.360	272.000		0.500	2.510	502.000
	0.453	1.860	372.000		0.464	2.690	538.000
	0.403	2.140	428.000		0.400	3.070	614.000
	0.351	2.450	490.000		0.350	3.360	672.000
	0.303	2.690	538.000		0.328	3.370	674.000

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
SL1-Wash		3.6427	0.0232	
SL1-1		3.3965	0.0287	75
SL1-2		1.8361	0.0135	30
SL1-3		1.5528	0.0081	
SL1-4		1.3988	0.0139	
SL1-5		1.3528	0.0106	
SL1-wash2		27.3282	0.3403	

Table C.12 Experimental Data for Special Loading Number 2

Special Loading Number 2

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.021			OCV	1.086		
	0.936	0.020	4.000		0.954	0.120	24.000
	0.900	0.060	12.000		0.902	0.270	54.000
	0.853	0.160	32.000		0.852	0.470	94.000
	0.799	0.330	66.000		0.802	0.710	142.000
	0.745	0.550	110.000		0.748	0.990	198.000
	0.696	0.760	152.000		0.705	1.200	240.000
	0.653	0.950	190.000		0.653	1.510	302.000
	0.600	1.210	242.000		0.590	1.810	362.000
	0.553	1.400	280.000		0.555	1.990	398.000
	0.500	1.630	326.000		0.504	2.260	452.000
	0.470	1.880	376.000		0.443	2.560	512.000
	0.395	2.090	418.000		0.405	2.730	546.000
	0.347	2.290	458.000		0.382	2.820	564.000

Notes: The concentration of the SL2-1 Vial is a combination of the SL2 wash2 1.3276 number and 2.253, the experimental value. This justification comes as a result of the wash2 being the collection of water made during the temperature adjustment period.

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
SL2-Wash		3.5676	0.0794	
SL2-1		3.5806	0.0267	75
SL2-2		3.5961	0.101	30
SL2-3		2.7332	0.0886	
SL2-4		2.284	0.0554	
SL2-5		1.7859	0.0105	
SL2-wash2		1.3276	0.011	

Table C.13 Experimental Data for Platinum Black Number 1

Platinum Black Number 1							
Initial	**Volts**	**Amp**	**mAmp/cm2**	**Final**	**Volts**	**Amp**	**Amp/cm2**
OCV	1.034			OCV	0.964		
	0.901	0.150	30.000		0.944	0.120	24.000
	0.851	0.340	68.000		0.903	0.410	82.000
	0.800	0.680	136.000		0.850	0.800	160.000
	0.743	1.050	210.000		0.800	1.170	234.000
	0.700	1.330	266.000		0.750	1.500	300.000
	0.600	2.050	410.000		0.703	1.820	364.000
	0.500	2.550	510.000		0.650	2.150	430.000
	0.440	2.890	578.000		0.600	2.440	488.000
	0.391	3.160	632.000		0.550	2.690	538.000
					0.513	2.880	576.000

Notes:

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
PB1-wash		8.2583	0.1286	
PB1-1		4.0407	0.0496	75
PB1-2		1.5819	0.0164	30
PB1-3		1.4182	0.0424	
PB1-4		1.3038	0.0089	
PB1-5		1.3578	0.0087	
PB1-wash2		2.7083	0.0209	

Table C.14 Experimental Data for Platinum Black Number 2

Platinum Black Number 2

Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.062			OCV	0.895		
	0.943	0.110	22.000		0.795	0.770	154.000
	0.893	0.360	72.000		0.750	1.090	218.000
	0.850	0.660	132.000		0.695	1.440	288.000
	0.800	1.010	202.000		0.648	1.830	366.000
	0.750	1.340	268.000		0.600	2.130	426.000
	0.695	1.730	346.000		0.544	2.430	486.000
	0.645	2.070	414.000		0.504	2.640	528.000
	0.603	2.350	470.000		0.450	2.890	578.000
	0.545	2.720	544.000		0.405	3.070	614.000
	0.500	3.010	602.000		0.373	3.140	628.000
	0.443	3.370	674.000				
	0.404	3.590	718.000				
	0.353	3.880	776.000				
	0.333	3.990	798.000				

Notes: This MEA died, I am unable to make consistent time sampling and the sampling was stopped in vial number 2.

Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
PB2-Wash		5.0836	0.056	
PB2-1		2.8609	0.0334	75
PB2-2		7.4979	0.0813	30
PB2-wash2		2.3562	0.0334	

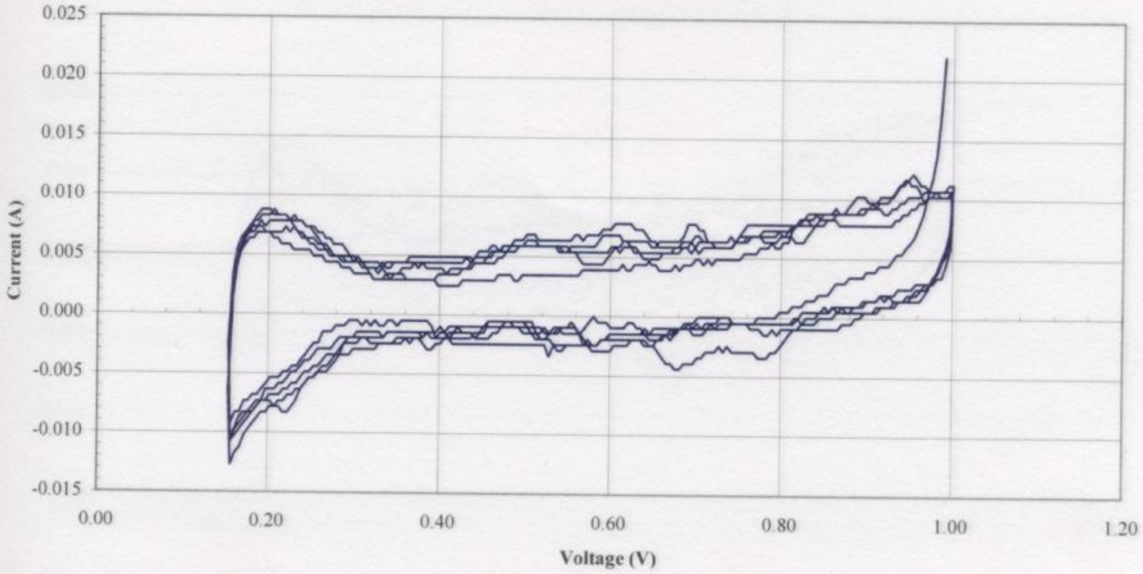
Table C.16 Experimental Data for Platinum Black Number 3

Platinum Black Number 3

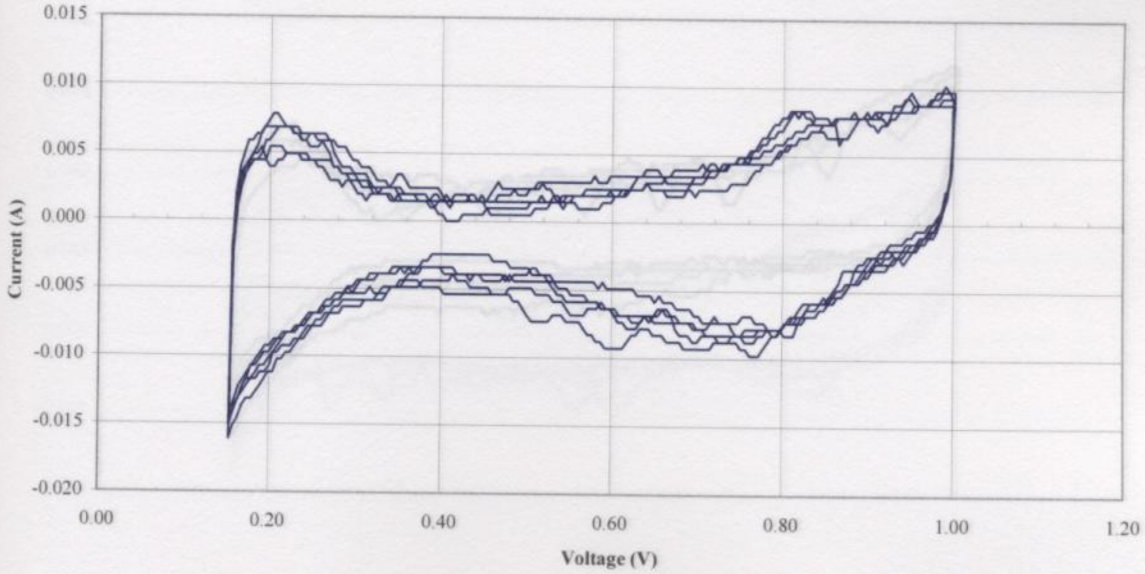
Initial	Volts	Amp	mAmp/cm2	Final	Volts	Amp	Amp/cm2
OCV	1.064			OCV	1.163		
	0.946	0.060	12.000		0.945	0.470	94.000
	0.895	0.220	44.000		0.900	0.730	146.000
	0.852	0.490	98.000		0.850	1.020	204.000
	0.800	0.930	186.000		0.801	1.330	266.000
	0.751	1.270	254.000		0.745	1.580	316.000
	0.700	1.640	328.000		0.694	1.790	358.000
	0.648	1.970	394.000		0.645	1.950	390.000
	0.593	2.320	464.000		0.600	2.090	418.000
	0.550	2.600	520.000		0.551	2.220	444.000
	0.501	2.850	570.000		0.495	2.330	466.000
	0.450	3.110	622.000		0.453	2.410	482.000
					0.443	2.440	488.000

Notes:

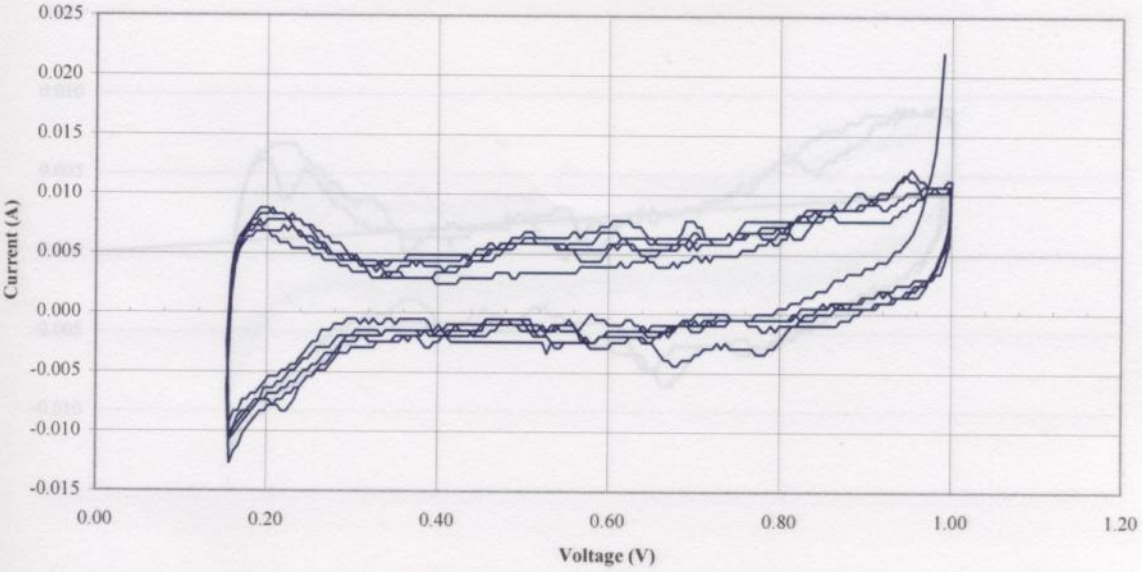
Vial Number	Sample Volume (ml)	Pt Concentration (ug/L)	Plasma SD	Temp (C)
PB3-Wash		5.2102	0.0502	
PB3-1		2.0736	0.0134	75
PB3-2		1.3313	0.0112	30
pb3-wash2		4.4138	0.0492	

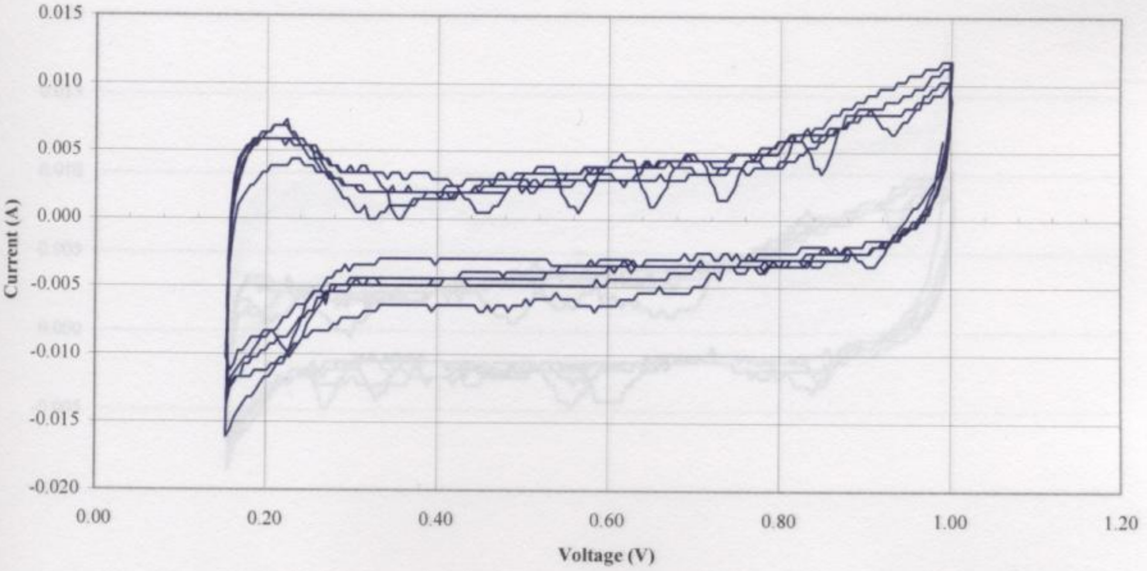


Constant Power Low Temperature 1 Initial Cyclic Voltammatery Sweep

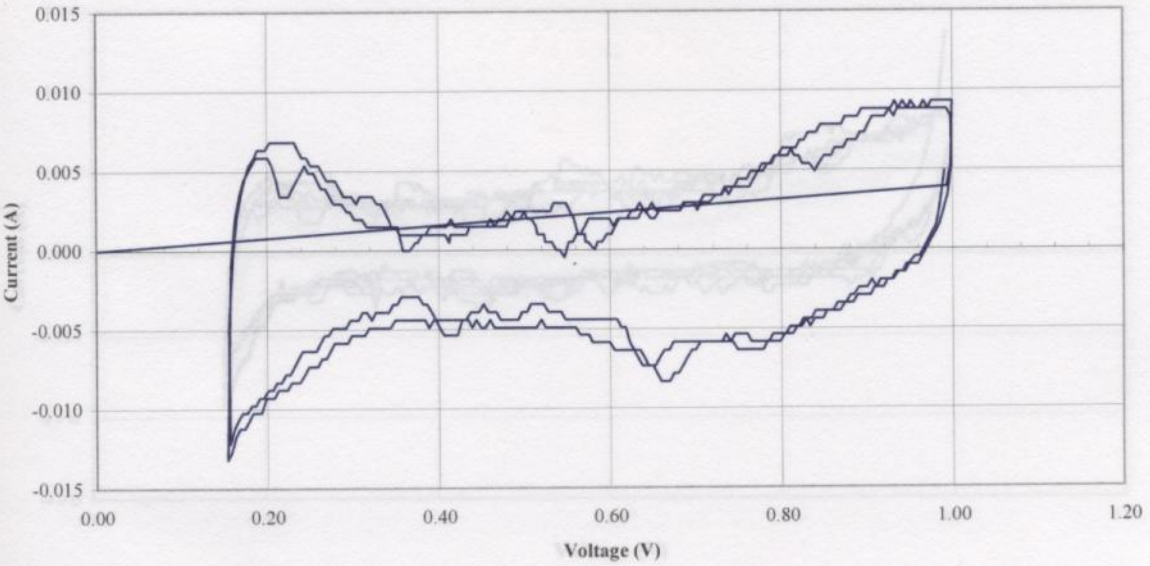


Constant Power Low Temperature 1 Final Cyclic Voltammetry Sweep

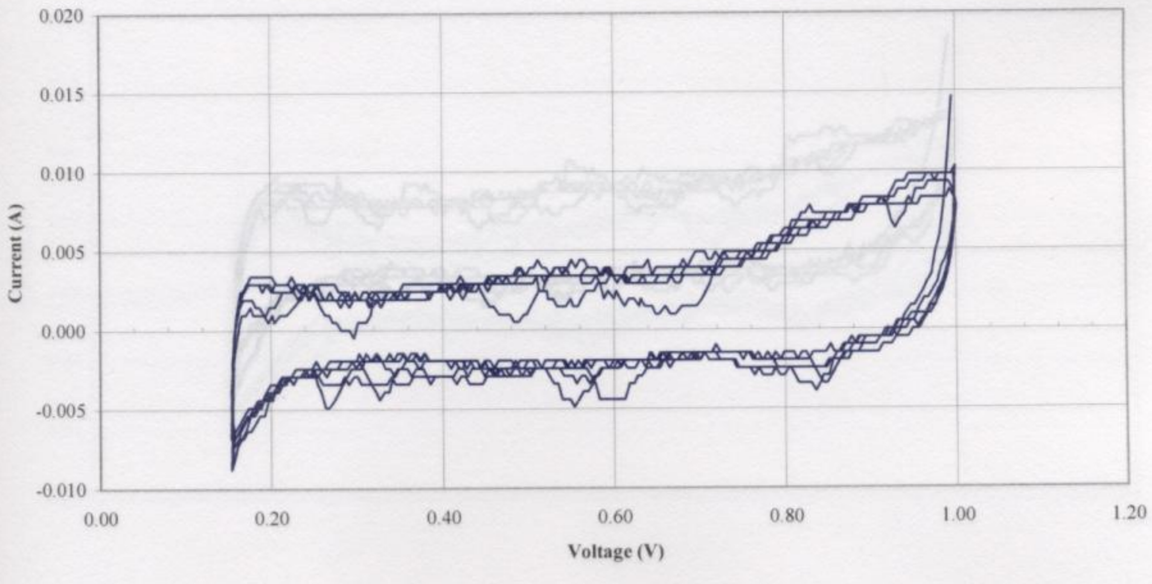

Constant Power Low Temperature 2 Initial Cyclic Voltammetry Sweep


Constant Power Low Temperature 3 Initial Cyclic Voltammetry Sweep

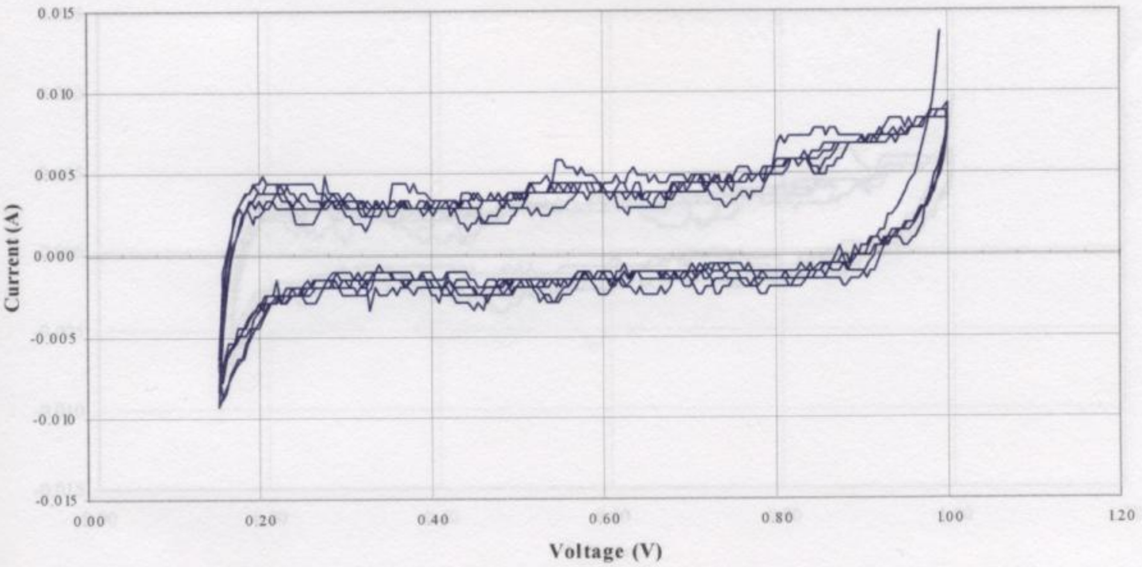
Constant Power Low Temperature 3 Final Cyclic Voltammetry Sweep



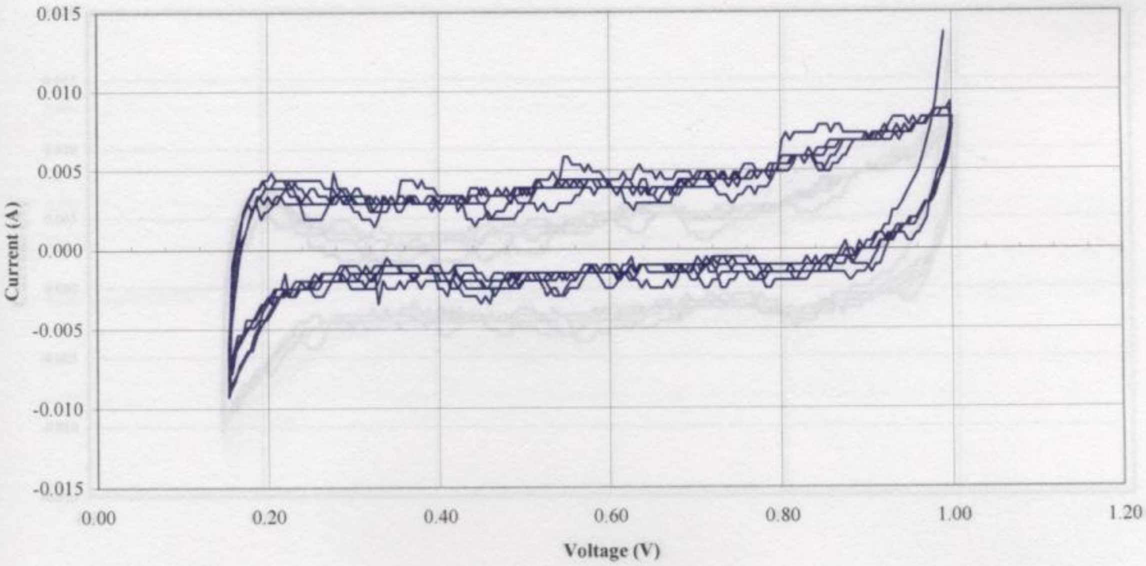
Constant Power High Temperature 1 Initial Cyclic Voltammetry Sweep

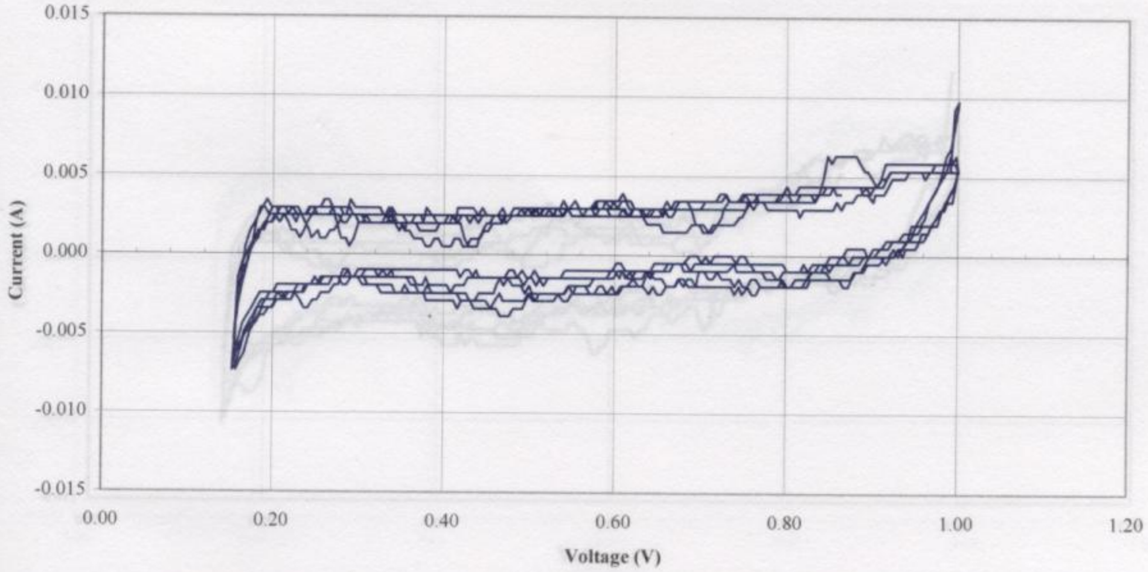


Constant Power High Temperature 1 Cyclic Voltammetry Final Sweep

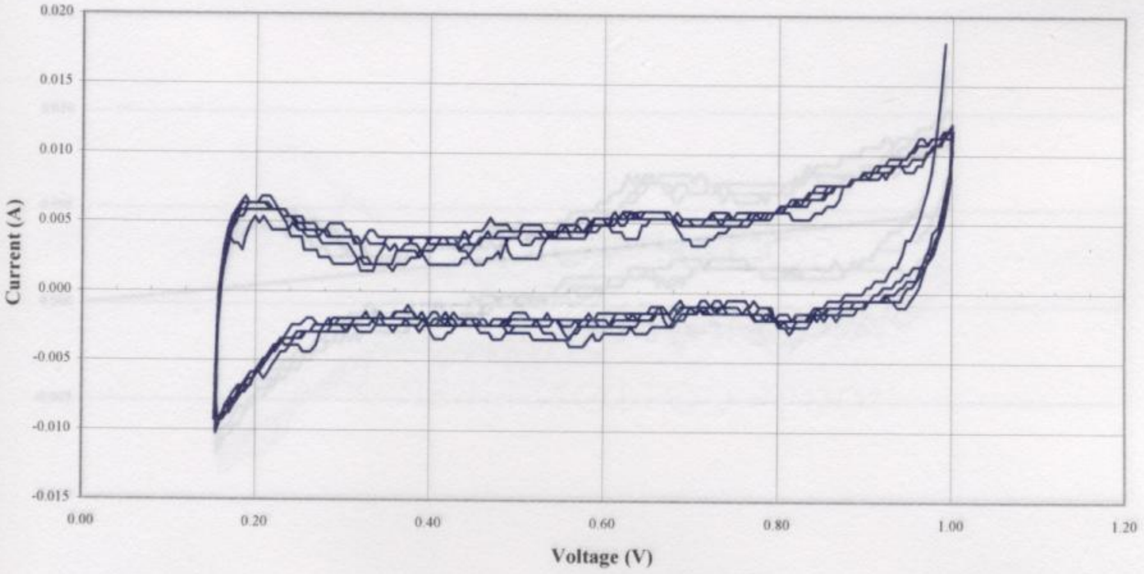


Constant Power High Temperature 2 Initial Cyclic Voltammetry Sweep



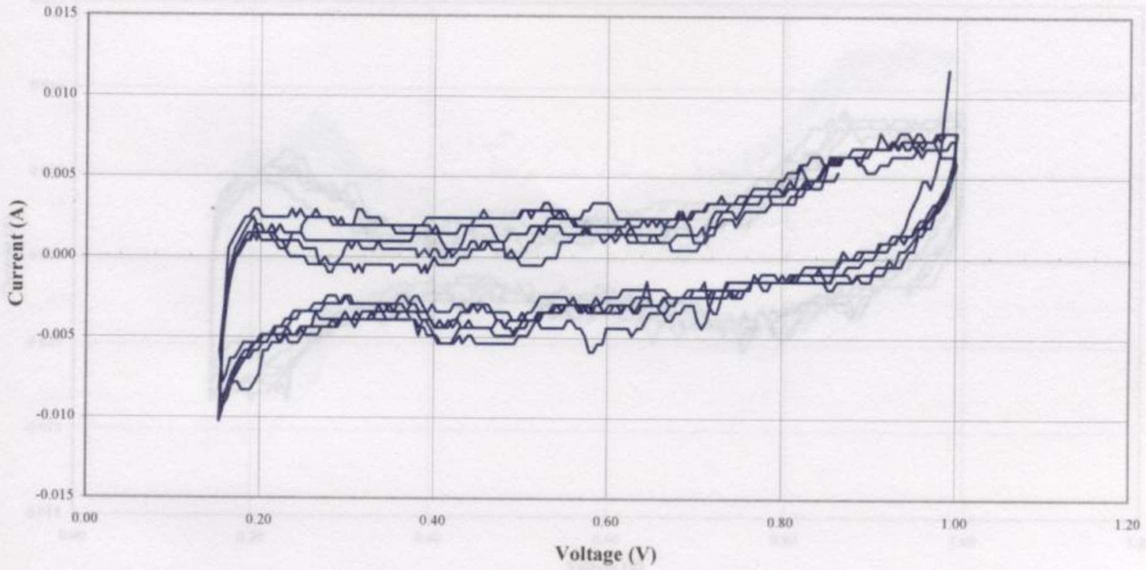


Constant Power High Temperature 2 Final Cyclic Voltammetry Sweep

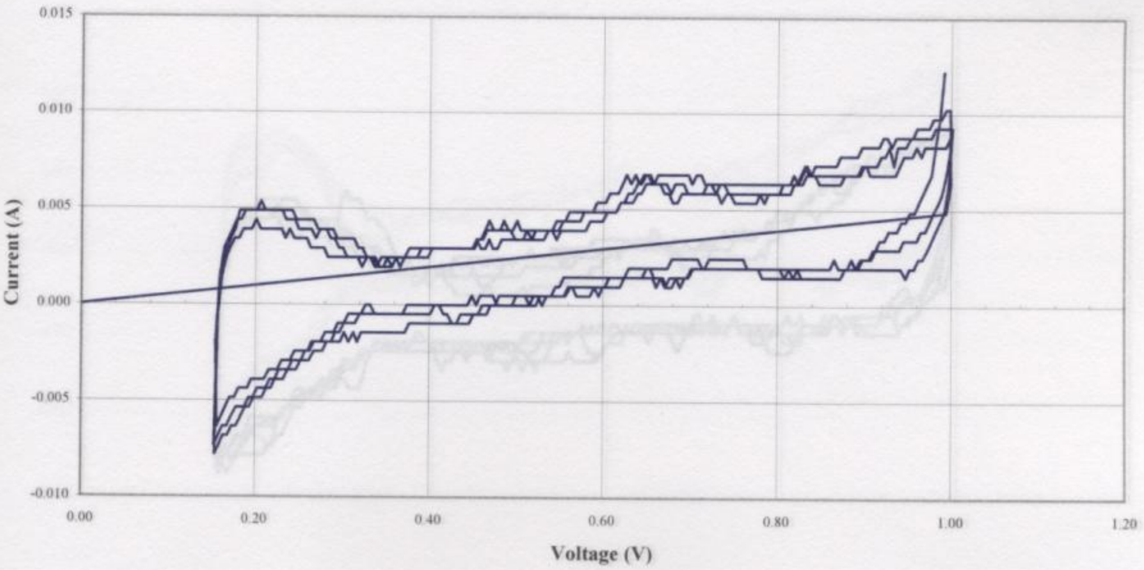


Constant Power High Temperature 3 Initial Cyclic Voltammetry Sweep

Constant Power High Temperature 3 Final Cyclic Voltammetry Sweep



Special Loading 1 Initial Cyclic Voltammetry Sweep



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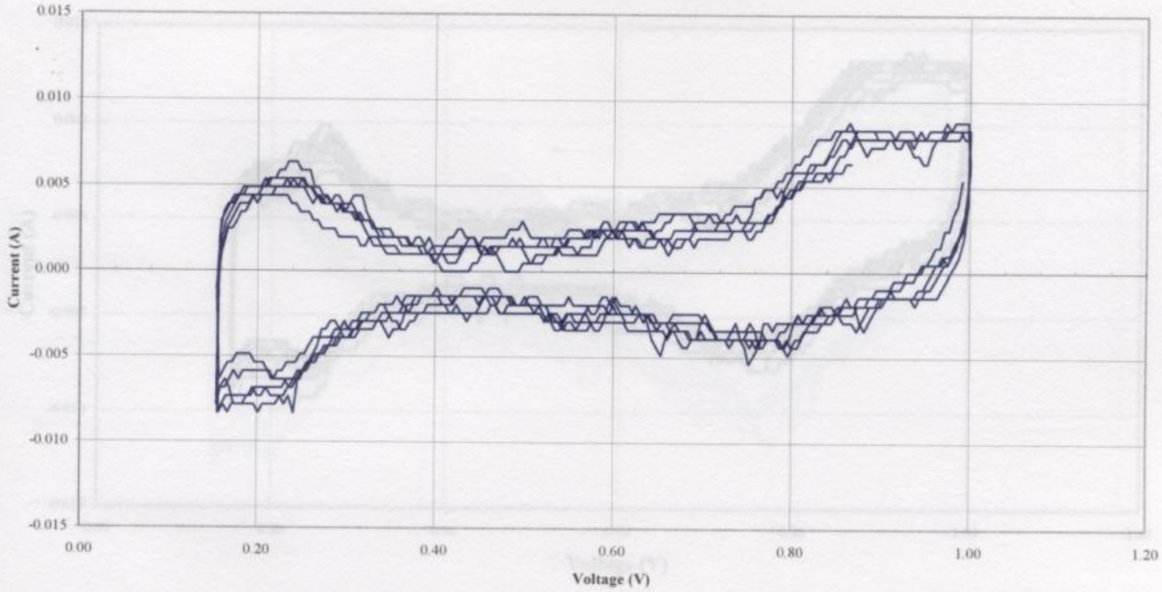

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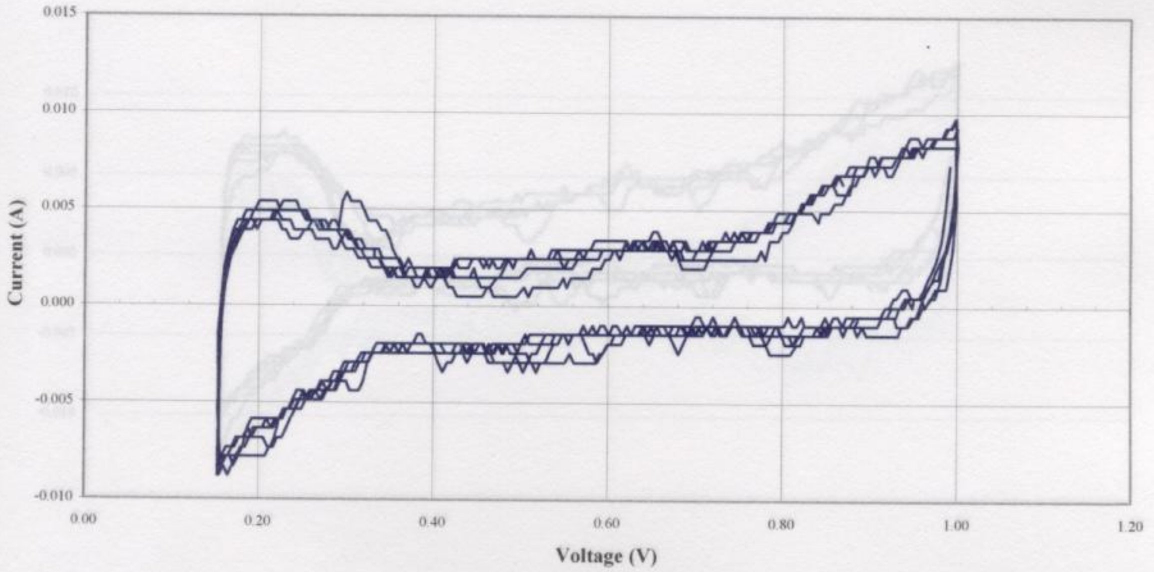
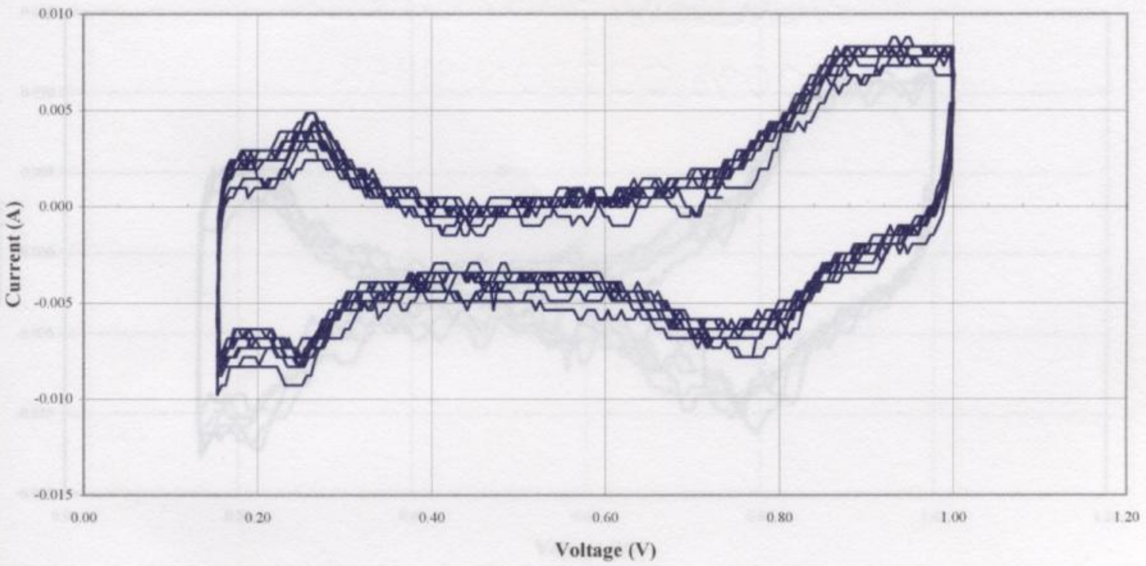
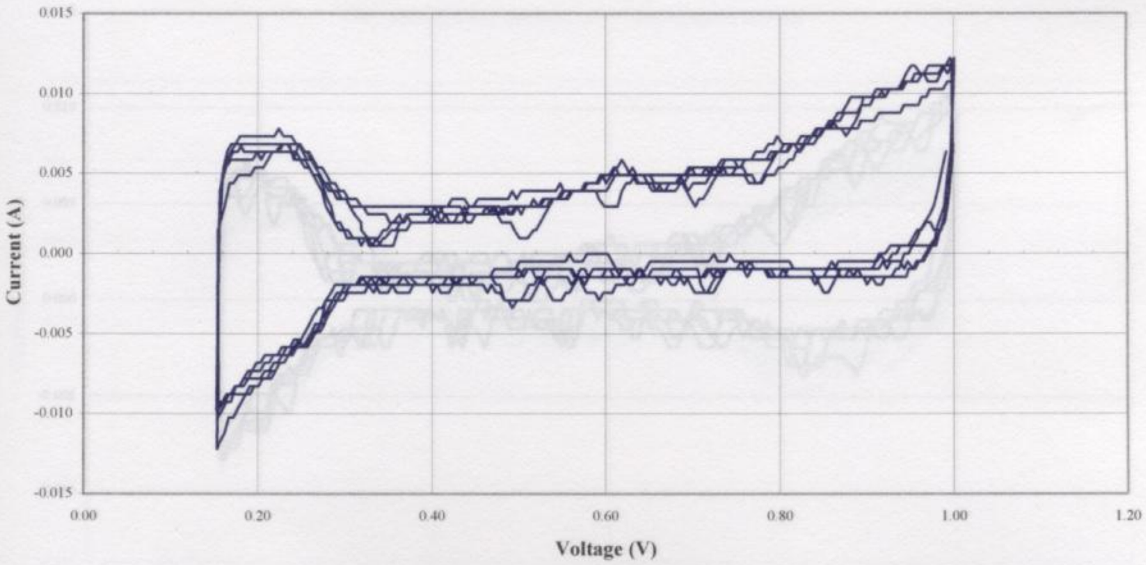
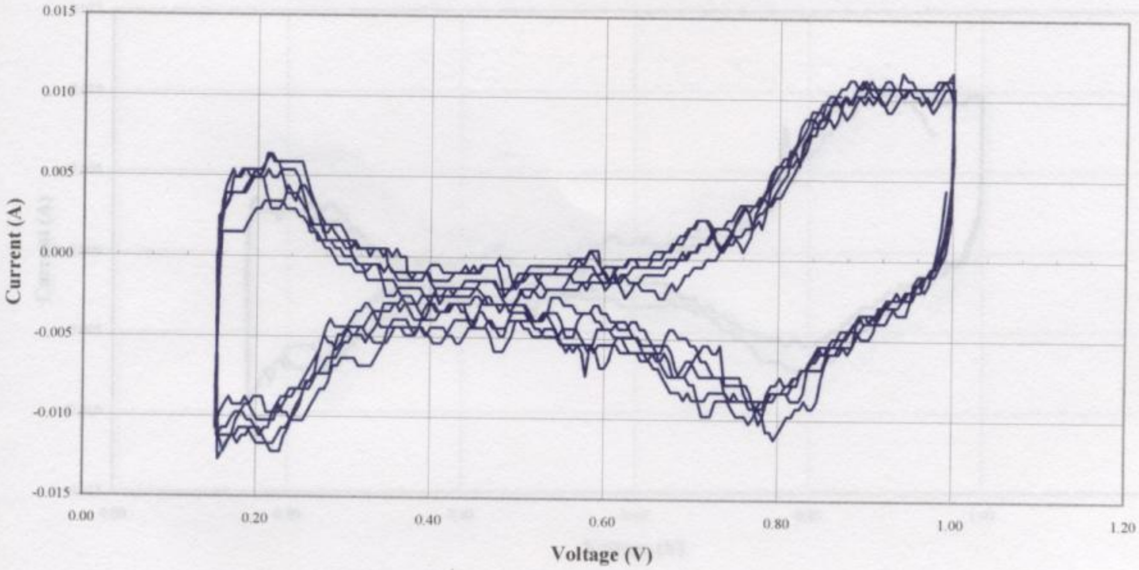


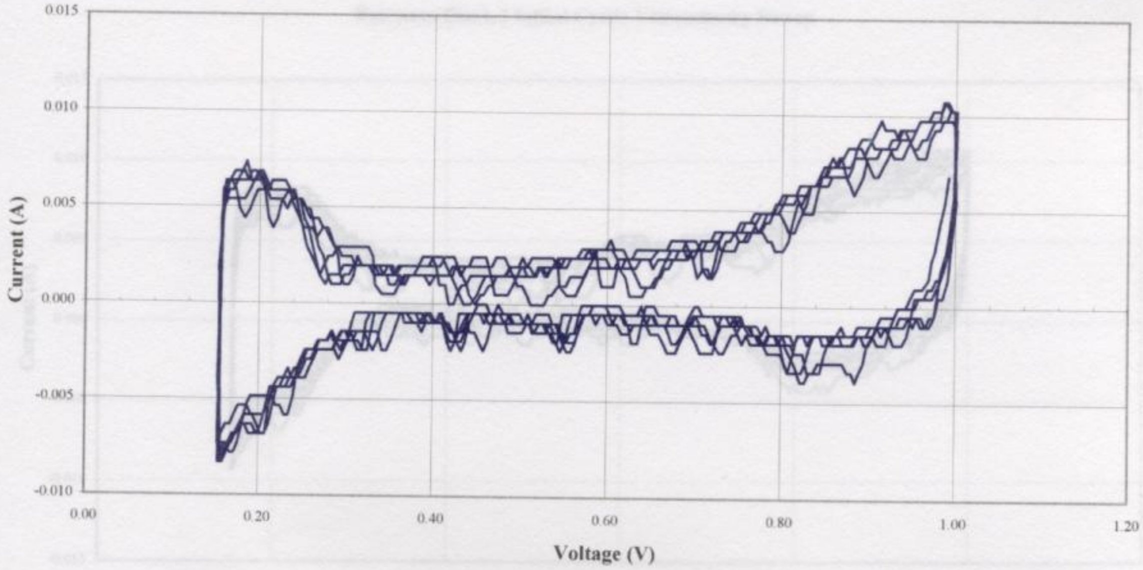

Special Loading 2 Final Cyclic Voltammetry Sweep

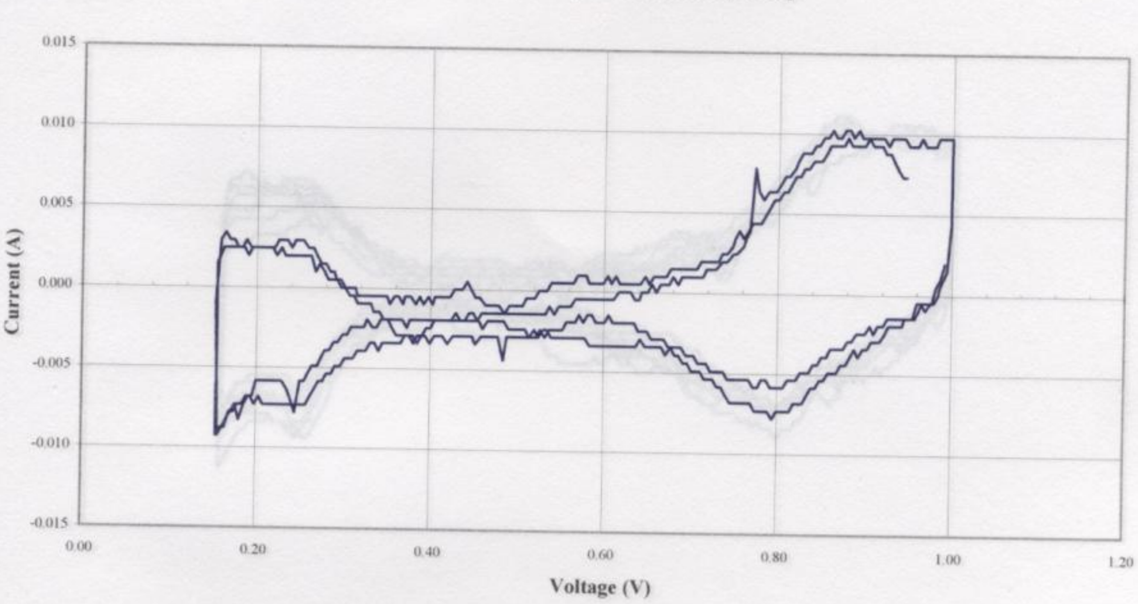

Platinum Black 1 Initial Cyclic Voltammetry Sweep

Platinum Black 1 Final Cyclic Voltammetry Sweep

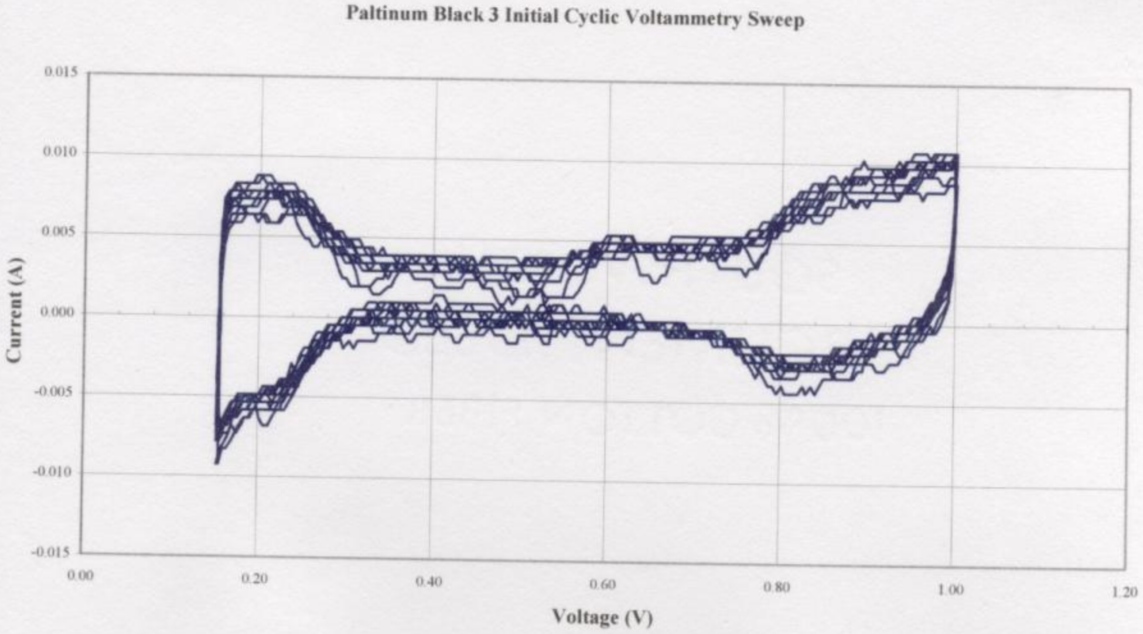


Paltinum Black 2 Initial Cyclic Voltammetry Sweep

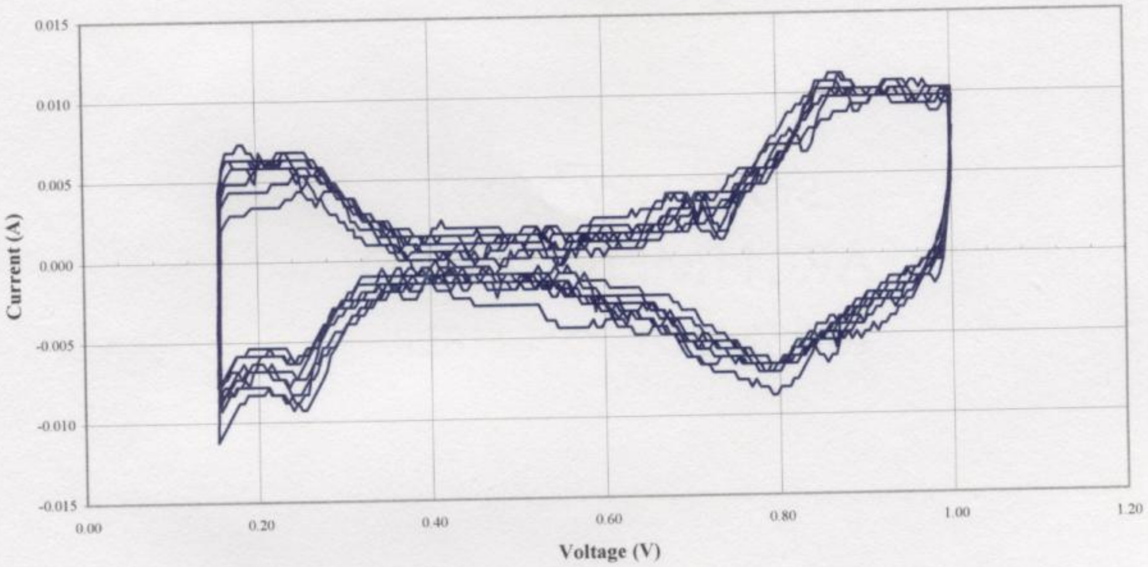




Paltinum Black 2 Final Cyclic Voltammetry Sweep



Paltinum Black 3 Initial Cyclic Voltammetry Sweep



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