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Investigation of Nitrogen-Doped Biomass as a Catalyst Support

for Polymer Electrolyte Membrane Fuel Cells

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Abstract

An active biomass carbon catalyst support was synthesized with the potential to enhance the activity of the platinum catalyst in PEM fuel cells. Garbanzo beans, an inexpensive source of nitrogen dense carbon, were used to produce the biomass carbon catalyst support, biosupport. The biosupport was synthesized by means of pyrolysis in the absence of oxygen in order to maximize nitrogen retention. To characterize the prepared biosupport, cyclic voltammetry experiments were conducted on the biosupport and a standard carbon support, Vulcan XC 72, by scanning the potential from -270 mV to 950 mV in both perchloric and sulfuric acid. The resulting cyclic voltammograms of the biosupport had a cathodic peak at 750 mV and an anodic peak at 220 mV whereas the Vulcan XC 72 had no significant peaks which is characteristic of an electrode in which no electrochemical activity is occurring. The peaks present on the cyclic voltammogram of the biosupport indicated a reversible oxidation and reduction processes taking place. The intensity of the cyclic voltammogram peaks, indicating reversible oxidation and reduction reactions for the biosupport, was greater in the perchloric acid, which indicates that the biosupport is more active, in regards to electrochemical reactions, in the perchloric acid. Cyclic voltammetry scans of synthesized 20% w/w platinum on the biosupport, by means of homogenous deposition using NaBH₄, showed compromised durability from a large decrease in the intensity of the hydrogen adsorption peak at 100 mV in perchloric acid after two rounds of scans. The durability of the synthesized 20% w/w platinum on the biosupport was less compromised in sulfuric acid, with significantly less decrease in the hydrogen adsorption peak at 100 mV. These results presented evidence for a negative correlation between the extent of the activity and durability of the biosupport.

Introduction

There is a growing demand for renewable energy sources and greener technologies surrounding energy production. The global dependence on fossil fuels has led to many issues surrounding energy production. Fossil fuels are a nonrenewable source of energy, meaning that at some point if the consumption of these fuels continues they will begin to run out. This would then lead to their costs skyrocketing. Along with not being a perpetual source of energy, the consumption of fossil fuels in energy production leads to the emission of greenhouse gases and other pollutants that plague the natural environment. In recent years, data suggests that the pollution caused by the consumption of these fuels is a leading cause to global warming as well as the deterioration of the atmosphere [1]. The resulting environmental concerns have been brought to the attention of many of the world's leaders, which in turn has spiked a growing interest in developing greener technologies for energy production. One of the leading technologies that offers a solution to many of the world's energy issues is fuel cells [1].

Since the early nineteenth century fuel cell theory and technology has been in development. A key breakthrough in harnessing chemical energy came from William Robert Grove in 1839, when he made the first gas voltaic battery [2]. This battery utilized the electrochemical reaction between hydrogen and oxygen to produce a current and was one of the earliest fuel cell technologies. NASA interest in fuel cells resulted in many technological breakthroughs by the chemists involved in the space program. Leonard Niedrach and Willard Grubb designed and implemented the first polymer electrolyte membrane fuel cell (PEM) [3]. Since then, the PEM type of fuel cell has been at the forefront of energy research and has been implemented in space missions, commercial vehicles, and power stations since the early 2000's [3].

Overall, the development and commercialized production of PEM fuel cells for energy production is limited at the current moment by their high costs. Within the continued development of fuel cell technologies, an area of popular research is improving the platinum catalyst efficiency in promoting the desired electrochemical reactions between hydrogen and oxygen while reducing costs. Platinum, the traditional catalyst material, being a large portion of the high cost of production. A core task in making needed improvements is developing catalysts and supports that improve catalyst activity, stability, durability, and alongside these things a reduction in costs. An area of catalyst research for PEMs that has a great potential in improving the overall cost effectiveness of the PEM fuel cell technology is catalyst supports. Now, the most effective and widely used fuel cell catalysts, for both the anode and cathode of the cell, are highly dispersed platinum nanoparticles [4]. The high cost of this noble metal continues to be a significant obstacle for the continued development and commercialization of PEM fuel cell systems. The industry standard catalyst supports are variations of Vulcan XC 72 carbon black that platinum is reduced onto [5]. While the use of this material has made improvements in lowering the costs of the technology, the costs of these materials and components for PEM fuel cell systems continues to dominate the overall value of the technology.

A recent development to improving fuel cell catalyst supports has been the exploration of nitrogen-doped carbons. Carbon materials that are doped with nitrogen have a variety of unique electrochemical properties such as high electric conductivity and mesoporosity [6]. These properties offer improvements to catalyst support technologies while also enhancing their durability. The durability of a polymer electrolyte membrane fuel cell and its membrane electrode assembly is directly related to its ability to prevent poisoning from carbon monoxide (CO). The addition of nitrogen helps to prevent poisoning, while also improving the catalytic

character. However, these improvements are also limited in their value due to the high cost of their synthesis and fabrication.

Biomass materials such as garbanzo beans are an abundant naturally occurring carbon source that contain high amounts of nitrogen [7]. Because of their abundance, these materials offer to be an inexpensive source of carbon catalyst support, for fuel cell technologies, that is rich in nitrogen. The high contents of nitrogen present in this source also offer favorable properties in their use in polymer electrolyte membrane fuel cell catalysts. This thesis project explores the synthesis of nitrogen-doped biomass carbon catalyst supports and evaluates their effectiveness as a catalyst support in fuel cell applications.

Literature Review

Overview of PEM Fuel Cells

All fuel cells operate off the basic principle that chemical energy, stored in chemical bonds or interactions, can be converted directly into electrical energy. Unlike the burning of fossil fuels for generating electrical energy, which utilizes the heat from the reaction to drive turbines or other mechanisms, PEM fuel cells are a direct method of generating electrical energy from chemical reactions. Fuel cells use a variety of methods in harnessing chemical energy. The most basic and commonly used fuel used in fuel cells is hydrogen, but oxygen is also required to allow the desired reactions to take place [8]. The benefit of using hydrogen and oxygen, two atmospheric gases, is that the emissions of most fuel cells is water and heat. Similar to batteries, fuel cells contain two functioning electrodes, the anode and cathode. In between the anode and cathode is a polymer membrane that contains an electrolyte. The function of the electrolyte membrane is to act as a transportation vector for charged particles that are produced in the

desired reactions from one electrode to the other. Another key component to the efficiency of fuel cells is the catalyst. Catalysts are placed at both the anode and cathode and their function in regards to the cells is to lower the energy needed for the desired reactions to take place. This lowering of the energy needed to facilitate the reactions accelerates the rates of reactions in the overall process occurring within the cell [9]. Each component plays a central role in the overall efficiency and effectiveness of a fuel cell, and the ineffectiveness of one component can diminish the overall operating capabilities of the entire system. This then means that there must be balance between the capabilities of all the components such that one area is not hindering others.

The efficiency of PEM fuel cells is also dependent upon its operating conditions. Polymer electrolyte fuel cells operate at a low temperature due to the nature of the reactions and components used in their operation. In its simplest form, PEM fuel cells operate most effectively when a hydrogen rich fuel such as hydrogen (H₂) is pumped at low pressure into a system where it interacts with the catalyst present at the anode. An oxidant such as oxygen (O₂) or air simultaneously interacts with the catalyst at the cathode. Before the interactions with the cathode and anode can occur, a gas diffusion layer may be employed. This layer allows for both the fuel, H₂, and oxidant, O₂, to more efficiently interact with the catalyst materials. This is a growing area of study due to diffusion layers also being useful for managing the water that is created as a byproduct of the reactions. For the fuel cell to operate efficiently some moisture is needed to facilitate the reactions but the reactions can be hindered in the presence of too much moisture, which has been termed as flooding.

Moving more centrally to the electrodes, the anode and cathode of these fuel cells are comprised primarily of carbon structures. These carbon structures are commonly doped with platinum, ruthenium, and or palladium. The use of these metals in their bulk metallic forms is what allows the catalyst materials to lower the overall energy needed to facilitate the reactions and increase rates of reaction. The catalytic environments are an essential part of PEM fuel cell technology, and remain one of the most expensive and limiting components. In addition to their overall cost, the catalyst layers are hypersensitive to carbon monoxide contamination. Once traditional catalyst materials, those utilizing platinum, have been contaminated or poisoned by CO their ability to facilitate catalytic interactions with both O₂ and H₂ is terminated. Consequently, proton exchange membrane fuel cells require highly purified H₂ and O₂ gas in order for continued efficiency and stability of the cells [10].



Figure 1. Basic schematic of a fuel cell and the electrochemical reactions that take place within [11]. As shown in Figure 1, the interactions between the gases, cathode, and anode promote chemical reactions, which effectively can be directly harnessed to produce electrical energy. At the anode, the hydrogen fuel is oxidized so that the hydrogen ion, H⁺, can then move across an

electrolyte membrane. This disassociation also produces electrons. The oxidative reactions at the anode and the reduction reactions at the cathode establish an electrical potential difference between them. This difference allows an external circuit to promote ionic mass transport, while keeping both electrodes electrically isolated. The standard electrolyte membrane used is a fluoropolymer with Teflon-like chains. The chemical structure of this polymer promotes chemical, mechanical, and thermal stability alongside highly protonic conductivity. The protonic conductivity of the electrolyte membrane is directly dependent upon the water content present in the membrane. It is essential that this polymer electrolyte barrier be properly humidified to promote these characteristics. From an electrical point of view, there is a nonlinear relationship between the output impedance and operating conditions such as the humidity of incoming gases, the partial pressures of the incoming gases, the temperature of the system, and the electrical current [10].

The nonlinear relationship between the efficiency of the cell and the operating conditions makes the careful examination of each of these conditions crucial in determining the environment for which a cell works at its maximum efficiency [10]. In maintaining this optimum environment, the variability of these conditions must be kept to a minimum once the startup of the reactions has been completed. These conditions can be maintained using temperature control devices such as Peltier devices alongside water pumps, as well as other liquid cooled systems. In maintaining the constant partial pressures of gases, the use of pressure gauges and flow controllers are essential for the control going into the cell. Once the gases have been pumped into the cell, then an effective outlet system for holding pressure while allowing the release of built of gases maintains this internal pressure. The humidity present in the cell must be controlled. Before the gases, such as H_2 and O_2 , enter the fuel cell, they can be humidified through bubbling

the gases through deionized water. Once the overall reaction within the cell has taken place, one of the byproducts is water. This water slowly builds up within the cell and can cause oversaturation of the membrane, flooding. This flooding can cause major operational issues within the cells reactions. Methods for which a cell can effectively deal with the removal of this water are similar to the release gases through ports in the cell.

The reactions that take place in a PEM fuel cell are electrochemical half-reactions that take place simultaneously at the anode and cathode.

At the anode:

$$H_2 \rightarrow 2 H^+ + 2 e^-$$

At the Cathode:

 $\frac{1}{2}O_2 + 2 H^+ + 2e^- \rightarrow H_2O$

The Overall:

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

Equation 1. Oxidation and reduction half reactions with full redox reaction for PEMs.

The reaction taking place at the anode leads directly into the reaction taking place at the cathode through the electrolyte. The products of the oxidation of hydrogen, the hydrogen ions and the electrons move to the cathode side of the cell. For the hydrogen ions, this is done by passing through the electrolyte membrane, while the electrons travel through an external circuit that can be used as power. Once at the cathode the reduction of oxygen takes place. The reduction of oxygen at the cathode is the rate limiting step in the reaction [12]. This rate limiting step determines the efficiency of the fuel cell to catalyze the overall reaction. The byproducts of this reaction in total are water and heat. Heat is present in essence due to the overall reactions being the same as the combustion of hydrogen.

In regards to the reactions taking place at the two separate sides of the cell, the oxidation of hydrogen is accomplished rapidly with much ease using a platinum catalyst. On the cathode side, the reduction of oxygen takes place at a much slower rate when using a platinum catalyst. This causes a considerable overpotential in regards to the reaction. Researchers have deduced that the overpotential of this reaction at the cathode can be linked to the proton and electron transfer to both adsorbed oxygen or hydroxide, that are strongly bonded to the surface of the electrode [11]. This phenomenon then takes place when the cathode reaction is at equilibrium. In using a model designed by researchers the trends of thermodynamic limitations are present for possible electrode metals in question. This has allowed researchers to deduce that platinum is the best element to use as cathode catalyst material. Alongside this, the model has allowed improvements to be realized through alloying platinum [12]. This alloying can then be used to further improve the performance of the cathode in facilitating the wanted reaction, as well as lowering platinum costs.



Figure 2. Free-energy diagram for oxygen reduction [12].

The free-energy diagram for oxygen reduction begins to explain the limiting factors present at the cathode through the use of a free-energy diagram. This allows for the gas-phase hydrogen oxidation reaction to be better understood. When cell potential (U) is equal to zero the cell is being run under short-circuit conditions that is the oxygen and hydrogen electrodes are directly connected. In the short-circuit situation, the steps present are shown to be exothermic, meaning that the thermodynamics of the reaction are favored with the Gibbs free energy being negative. When the Gibbs free energy is negative, it means that the reaction is proceeding spontaneously. When the chemical potential is then shifted where U then equals 1.23 eV, it shows the fuel cell having maximum potential. In this situation, both the electron and proton transfer steps become unspontaneous and one of these two steps becomes rate-limiting [12]. From the rate-limiting step, the overpotential is then determined, the reaction proceeds spontaneously as the adsorbed oxygen and hydroxyl groups destabilize.

Catalysts and Support Structures

The role of the catalyst in the polymer electrolyte membrane is to aid in facilitating the reactions present at the anode and cathode. To date the most effective catalysts, make use of platinum metal in their structure. This is largely due to the fact that though other metals can catalyze these types of reactions, they cannot withstand the acidic as well as oxidizing environment that is present within a PEM fuel cell.



Figure 3. Trends in oxygen reduction activity [12].

The reaction within a fuel cell that is the most difficult to catalyze is the oxygen reduction at the cathode, as established earlier. Figure 3 shows the trend of oxygen reduction activity versus the cell potential, where platinum is the most suitable for catalytic work with palladium just beneath it. Non-precious metals have been stabilized and converted into useful nonmetallic forms such as metalorganic complexes, enzymes, oxides, and graphene based materials. These compounds and structures have shown activity around or even above that of platinum, but they are not stable in the acidic environments that are present in the fuel cell. Only platinum, gold, and iridium are thermodynamically stable enough in their metallic bulk forms to handle potentials greater than 0.9 V, but of these three, platinum has the best activity [13]. Most catalytic research in regards to platinum catalysts is in respect to enhancing the catalytic activity of the platinum. A common mixture between platinum and ruthenium is used to enhance a fuel cells durability, due to ruthenium's tolerance to CO being much higher than pure platinum. The mixture of platinum and ruthenium has commercialized limitations due to the increased cost of production. The most common catalyst layers present at the cathode contain Nafion, carbon particles, and platinum. Changing the concentrations of each of these components has drastic effects on the performance and cost efficiency of the cell. Increasing the concentration of Nafion present, helps to improve the ability of the proton to migrate as well as reduces the unfilled spaces necessary to facilitate gas exchange. This then reduces the ability of the cell to facilitate this gas exchange. Though increasing the platinum load directly increases the electrochemical capacities of the catalytic membrane, it greatly increases costs [14]. This can drastically impair the cost efficiency of a cell. A balance between these two loading percentages is the first necessary aspect of fabricating an efficient catalytic layer. Alongside this is the optimization of distribution of the platinum and Nafion within the membrane.

There are several different methods of reducing platinum loading, such that costs are reduced, while also increasing the overall utility of the catalytic membrane. These methods include thin film, electrodeposition, sputter deposition, dual ion-beam assisted deposition, electrolysis deposition, nano-carbon as catalysts electrodeposition, supercritical deposition. Each of these methods is characterized having different benefits and drawbacks, which is shown in Table 1.

| Preparation methods | Pt loaded supports or substrates (applied electrode) | Pt loading (mgPtcm ⁻²) | Pt utilization (gPtkW ⁻¹) | Comments |
|--------------------------------------|--|--|---|--|
| Modified thin film | NCI (both) | 0.1* | 0.14 ^{b,c} | Pt loading can be reduced to as low as 0.05 mgPt cm ⁻² at both electrodes |
| Electrodeposition | NCL (cathode) | 0.32 based on cathode 0.72^a (anode = 0.4) | 0.33 ^d based on cathode 0.75 ^{d,c} | Possible to increase the Pt/C ratio up to 75 wt.% near the surface of the electrode resulting in a 5 µm thick catalyzed layer |
| | Nafion-bonded NCL (cathode) | 0.50 based on cathode | - | Better performance than those of a conventional electrode with loadings of 0.1 mgPrcm ⁻² |
| Sputter deposition | Membrane; Nafion 117 (both) | 0.04ª | 1.21°.°, 8° (commercial) | Performance is extremely sensitive to sputtered platinum thickness and membrane texture |
| | GDL, membrane, MEA; NCI + membrane (both) | 0.027 at one layer; 0.162 (six layers at MEA) | 0.26 ^f based on one layer; 1.59 ^{fc} | Of the three substrates, sputter-depositing Pt on the GDL showed the best performance |
| | GDL (both) | 0.054 (SGL), 0.107 (ETEK) (not clear whether based on one electrode or MEA) | 0.285 (SGL), 0.535 (ETEK) based on one electrode; 0.568-0 (SGL); 1.068-0 (ETEK) | Catalyzed layers sputter-deposited onto GDL are a very important factor to reduce the Pt loadings |
| | MEA; NCI+membrane (anode) | 0.1 (three layers at anode); 0.4 ^a (cathode=0.3) | 0.51 th based on anode; 2.57 ^{f,c} | Multi-layers of Pt sputter-deposited on the gas diffusion layer provide better performance than sputtering one |
| Dual ion-beam assisted deposition | GDL (both) | 0.04 at one electrode 0.08² | 0.297ic | IBAD gas diffusion electrodes have the potential to create highly customized products, therefore also revolutionizing the micro-fuel cells mudert |
| Electroless deposition | Carbon-supported Ru nanoparticles (anode) | 0.017 (Pt), 0.18 (Ru) based on anode; Cathoda (not dare) | 0.70 ^j gPrRs kW ⁻¹ based on anode | Only a small degradation in performance was recorded after |
| Nano-carbons as cataly | sts | Cullione (Instatus) | | 1000 h cropsillion |
| Electrodeposition | Amorphous supermicroporous carbons (cathode) | 0.0175 based on cathode; 0.0575ª (anode =0.4) | 0.1kc | Further research on the improvement of Pt dispersion and on ASC supports prepared from |
| Supercritical deposition | Carbon aerogel (cathode) | 0.1 based on cathode; anode; PtRu (not clear) | 0.125 ¹ based on cathode | different precursors are needed Better penetration of Nafion particles into the pores of the aerogel carbon support and better coverage of the membrane surface with a lower Pt content |

Table 1. Methods of reducing Pt loading and increasing Pt efficiency [15].

The industry standard method of dispersing platinum catalysts is electrodeposition. This method as shown in Table 1 allows for a thicker dispersion of platinum to be present on the electrode. Though this method is favorable due to its high conductivity and better dispersion of platinum throughout the electrode, it is limited by the cost of carbon catalyst support materials.

Nitrogen-Doped Carbon Catalyst Supports

Nitrogen rich carbon materials can be used as the catalyst support structure for platinum to adhere onto. Nitrogen-doped carbon catalysts produce a more robust environment for the electrochemical reactions to take place in [16]. There is a variety of carbon materials that can be used in the doping of nitrogen. These materials include carbon nano-cages, nano-fibers, graphene, and nanotubes. At a molecular level each of these materials are made of pure carbon bonded such that they create specific cage-like or fibrous materials. The use of these materials greatly enhances the conductivity and porosity of the catalyst when incorporated in the membrane electrode assemble (MEA) [17]. Graphene is a single layer of pure carbon atoms that is most widely used and manipulated to create these nano-cages and nano-fibers. The use of these materials in fuel cell technology has been limited thus far due to the high cost and low output of its production commercially [18].

When nitrogen is then added to these highly organized pure carbon materials, it enhances many of the functional characteristics of the highly organized carbon support material. The addition of nitrogen expands the pH range for which catalytic interactions are favorable [17]. This is favorable in increasing the stability of the PEM fuel when operating, because of the variability of pH in the operating environment when the cell is functioning. As stated earlier, the conductivity and durability of the catalyst and MEA are enhanced with the addition of nitrogen to the carbon catalyst support. This phenomenon can be contributed to the stability that is brought by the nitrogen species to its bonding through the use of pi bonds [17]. In the carbon molecular network, the addition of pi bond systems reduces the chance of catalyst poisoning from CO and allows for the flow of electrons to take place with more efficiency.

The most enticing improvement that the addition of nitrogen offers is the enhanced catalytic activity seen in the oxygen reduction reaction. As stated earlier, the reduction of oxygen at the cathode is the rate limiting step, and therefore limits the efficiency of the entire fuel cell to produce an electric current from the harnessing of energy in chemical bonds. When nitrogendoped carbon supports are used without the addition of platinum or other metallic catalysts, oxygen reduction properties are more prevalent than in pure carbon supports [17]. The oxidation reduction properties present the nitrogen-doped carbon support demonstrates that this type of support is active in aiding the catalytic interactions of platinum. Traditional carbon supports do not present this activity and have been characterized as being more inert in their reactions. Though an active catalyst support can be viewed as advantageous in supporting platinum in its catalytic interactions, at the present moment this activity is also characterized as having downfalls in stability and durability [17]. When the addition of platinum is synthesized, such as in PEM fuel cell catalysts, this combination lowers the overpotential found at the cathode, where the reduction of oxygen takes place. This lowering of the overpotential increases the efficiency of the catalyst as well as the fuel cell.

Electrochemistry Background Information

Cyclic Voltammetry

In order to better understand and characterize the electrochemical reactions taking place at the electrodes, cyclic voltammetry has been used. Cyclic voltammetry is a method of potentiodynamic electrochemical measurement. A typical set up for this type of measurement incorporates an electrochemical cell with two to four electrodes. For measuring the activity of catalytic reactions for catalyst materials in PEM fuel cells a three electrode setup is utilized. For this type of setup there is a working electrode, reference electrode, and counter electrode. The working electrode is the electrode where the chemical reactions of interest take place. The reference electrode is an electrode that has a known stable potential. The reference electrode then allows the potential of the cell to be known in order to manipulate it as desired for experiments. Lastly, the counter electrode, auxiliary electrode, is the electrode in which the current of the electrochemical cell is expected to flow through. In order to make measurements of the working electrode the counter electrode is needed such that the only currents related to electrochemical processes or reactions are measured at the working electrode. This three electrode setup is then placed into a solution that is applicable to the desired experiments being run. To measure the activity of a catalyst material such as platinum in adsorbing and reducing hydrogen ions by means of cyclic voltammetry aqueous solutions containing hydrogen ions are used. These solutions are commonly sulfuric and perchloric acid.



Figure 4. (a) Schematic of a typical voltage sweep; (b) typical plot of current versus voltage [19].

Figure 4b illustrates the ideal shape of a cyclic voltammetry scan. Cyclic voltammetry scans are constructed through sweeping the cell potential (V) back and forth between two voltages limits while recording the current. The voltage is swept at a constant rate as illustrated above in Figure 4a. The cell starts at a desired minimum potential and the potential is then increased steadily to a maximum value and then steadily allowed to return to the minimum potential, all while the current at the working electrode is measured, Figure 4b. Peaks in the cyclic voltammogram, Figure 4b, occur because of the presence of electrochemically active species and can be used to determine the activities of catalytic material.

The reaction for overall catalyst characterization of interest in PEM fuel cells is the adsorption of hydrogen onto the catalyst material present at the working electrode. The top curve in figure 4b is a result of reduction processes (the removal of electrons) and is called the cathodic curve. The potential value of the peak depends on the specific chemical reaction occurring, for hydrogen reactions the peaks should occur near zero. The bottom curve is the anodic curve that results from the addition of electrons (oxidation); the desorption of hydrogen at the working electrode peak occurs near zero as well. The current at the peak values provides an evaluation of the amount of material being oxidized or reduced.

The cyclic voltammogram can be used to determine the reversibility of an electrochemical process by comparing the cathodic peak to the anodic peak. If they are the same size, this indicates a reversible process. For the PEM fuel cells, the overall adsorption and desorption of hydrogen on the catalyst material needs to be reversible or else the catalytic activity will decrease over time and lower the overall efficiency of the catalyst material.

Electrochemically Active Surface Area

An important property of electrochemically active catalyst is the surface area of the catalytic material that is available for facilitating the desired reaction, the electrochemically active surface area (ECA). The ECA relates the specific activity of a catalyst material, determined by a method like cyclic voltammetry to the activity of specific surface area. The ECA is a crucial property of a catalyst in catalyzing a desired reaction and it directly relates to determining the activity and overall efficiency of a material in catalyzing a reaction.

In regards to platinum catalysts for PEM fuel cells, there is much interest in maximizing the ECA of catalyst materials, such that less platinum is needed to have a similar or better activity. When ECAs are analyzed with regards to platinum loadings the overall efficiency of a catalyst can be compared to other potential materials.

Determination of Electrochemically Active Surface Area

The ECA can be measured using cyclic voltammetry and differential electrochemical mass spectrometry [20]. Due to the limited ability of most labs to conduct differential electrochemical mass spectrometry, cyclic voltammetry has been the standard electrochemistry method of determining ECA. To quantify the electrochemically active surface area, the region of the cyclic voltammetry curve where peaks are present that are related to the adsorption of a single layer of hydrogen onto the working electrode is analyzed (that is the peaks near zero), and the area under these peaks is directly related to the charge needed to facilitate this process by the Equation 2.

$$ECA = \frac{Q_H}{195 \,\mu C/cm^2} = \frac{\int \frac{idE}{v}}{195 \mu C/cm^2}$$

Equation 2. Calculation of electrochemically active surface area [20].

By integrating the current (i) in regards to the cell potential (E) from where the peak begins and ends, as shown in Equation 2, a charge (Q) can be calculated. This charge, related to the charge needed to adsorb a single layer of hydrogen onto the working electrode, is then divided by the number of electrons transferred by the reaction relating to this peak, which is 1 for all of the experiments conducted using aqueous hydrogen ions as the analyte, multiplied by the scan rate (v). Using a value for the charge density of bulk polycrystalline platinum prepared by flame annealing in prior peer reviewed research of 195 μ C/cm², an approximate electrochemically active surface area can be calculated for comparison purposes [20].

Experimental Overview

A preliminary characterization of biomass carbon catalyst support, from dried garbanzo beans, as well as industry standard materials was achieved in this research. The biomass carbon catalyst support was synthesized using a modified procedure for pyrolysis of biomass materials such that the retention of nitrogen species in the carbon particles was maximized. Following this, the synthesis of the platinum nanoparticles using the biomass carbon catalyst support and the industry standard Vulcan XC 72 carbon catalyst support was achieved. This synthesis utilized the reduction of platinum particles onto the carbon catalyst material in an aqueous solution using NaBH4. Cyclic voltammetry experiments were then done on purchased platinum nanoparticles on Vulcan XC 72, synthesized platinum nanoparticles on purchased Vulcan XC 72 carbon, and synthesized platinum nanoparticles on biomass carbon in order to determine the effectiveness of the procedure for running cyclic voltammetry scans, determine the effectiveness of the procedure for synthesizing platinum nanoparticles, characterize and compare the activity and durability of the biomass carbon catalyst support to industry standard materials. Cyclic voltammetry experiments were then conducted on the biomass carbon catalyst support and Vulcan XC 72 carbon catalyst support to better characterize their activity. Following these characterizations, the fabrication of membrane electrode assemblies for PEM fuel cells was initiated in order to refine a procedure for hot-pressing membrane electrode assemblies.

Materials and Methods

Synthesis of Biomass Carbon Catalyst Support Material

The first stage of this project was to refine the technique and procedures for obtaining biomass carbon black to later be used as catalyst support materials. The biomass material used for this synthesis was dried garbanzo beans, a renewable organic material. These beans are readily available at a low cost at most grocery stores. Dried garbanzo beans were first inspected for any signs of damage or decay that could adversely affect their pyrolysis. Next, the beans were thoroughly ground into smaller particles using a coffee grinder. These ground dried garbanzo beans were then further ground and pulverized into finer particles using an agate mortar and pestle. This fine powder was then placed into ceramic crucibles such that the powder was several millimeters thick and the bottom of the container was completely covered. Nitrogen (N₂) was then pumped into the crucible and the beans were left to sit under this inert gas for ten minutes. The material was placed under nitrogen to prevent any unwanted oxidation during the pyrolysis. Once the biomass had been under nitrogen for the required time, the bean materials were then placed into a muffle furnace.



Figure 5. Thermo Scientific Muffle Furnace model number: F6018.

The procedure for the pyrolysis of the biomass was to place the crucible with the biomass under nitrogen into the muffle furnace, pictured in Figure 5, at temperatures between 100 °C to 150 °C and to ramp the temperature to 600 °C at a rate of 10 °C min⁻¹. Once the furnace reached 600 °C, it was held there for 15 minutes. The sample crucible was then removed from the furnace carefully and allowed to cool before the lid was removed. This was done in order to prevent unwanted oxidation of the biomass and maintain the system under nitrogen while still at combustible temperatures. In published experimental results, this procedure yielded a 9-46% retention of nitrogen in charred biomass [21].

Synthesis of Platinum Nanoparticle on Carbon Catalyst Support

The next step in this project was to refine the synthesis of platinum nanoparticles on carbon black. Though there are several techniques and procedures for the synthesis of these platinum nanoparticle complexes, the homogeneous deposition of platinum nanoparticles on carbon black was achieved through the use of NaBH₄ reduction. This method of synthesis is common in PEM fuel cell research [22]. This method had also been implemented in our research with success in synthesizing platinum nanoparticles on biomass carbon black. The carbon black produced in the previous section was used to refine the procedure and techniques for the implementation of platinum reduction onto carbon black using NaBH₄, due to its lost cost and greater availability.



Figure 6. Branson 1800 Sonicator.

In synthesizing a 20% w/w platinum load on the carbon black, 32.5 mg of carbon black was added to 200 mL of deionized water and sonicated for 30 minutes in a Branson 1800 Sonicator, pictured in Figure 6, to ensure an even dispersion of the carbon black in solution. 5 mL of 0.05 M H₂PtCl₆ aqueous solution was then added, and the mixture was stirred for 3 hours to ensure efficient dispersion of platinum in the solution. The pH of the mixture was then adjusted to 7-8 by the dropwise addition of 0.4 M KOH. A solution of aqueous NaBH₄ was then added, with a molar ratio of NaBH₄ to Pt being 10:1. The mixture was then left to stir for several days in the absence of light. Once the stirring was complete, the catalyst was then be filtered using vacuum filtration and quantitative filter paper. The resulting platinum nanoparticle catalyst materials, the materials were carefully scraped off the surface of the filter paper and placed into vials for storage and later use.

Preparation of Working Electrode

A glassy carbon rotating disc electrode was used to prepare the working electrodes. Known amounts of catalyst material or catalyst support material were placed into 7 mL of water. This mixture was then sonicated for 30 minutes to ensure better dispersion in the solution. Periodically while sonicating, the mixtures of catalyst and water were stirred using a vortex mixer on its highest setting. This solution, similar to a black ink, was then applied in various amounts to a cleaned and polished glassy-carbon electrode. This thin layer was then dried at room temperature under an argon stream for 1 hour. The argon stream was used to speed the drying times for the electrodes. Next, $20 \,\mu$ L of 5.0% w/w Nafion was added as a drop onto the catalyst layer to form a thin protective film. The drop of Nafion polymer was added such that no air bubbles were created. This protective layer prevents the catalyst from detaching from the electrode during the cyclic voltammetry scans. The attached layers to the glassy-carbon electrode were then dried for 1 hour at room temperature such that they sufficiently hardened [20]. Following the addition of the Nafion an argon stream was not used to lessen dry times, due to the tendency of the thin Nafion layer to crack and peal up at the edges.

Cyclic Voltammetry Experimental Setup

The cyclic voltammetry experiments were completed using a Gamry Potentiostat with a Pine Rotating Disk Electrode. In preparing the cyclic voltammetry cell for experimentation, 0.1 M HClO₄ or 0.05 M H₂SO₄ was placed into an electrochemical reaction vessel. Next, while stirring using a magnetic stir bar, nitrogen was bubbled through the acid solutions for 10 minutes to purge the electrochemical cell of unwanted oxygen. Oxygen species, if not sufficiently purged, in the solution react at the working electrode resulting in unwanted reactions. Once this was completed a three electrode setup was achieved using a platinum counter electrode, Ag/AgCl reference electrode, and a prepared glassy carbon working electrode. Attached to the working electrode was a working and working sense input. Attached to the platinum counter electrode was an auxiliary input. Attached to the Ag/AgCl reference electrode was a reference input. All voltage limits for the desired scans were adjusted in reference to the Ag/AgCl reference electrode being utilized. Next, the working electrode was activated using chrono-amperometry set at -270 mV for 120 seconds with the disc rotating at 1500 rpm. This activation acted as a cleaning period, where unwanted particles and debris on the working electrodes surface were stripped off such that a steady current was achieved before subsequent scans could be run. Following this activation and cleaning, cyclic voltammetry scans of the catalyst were performed at scanning rates of 75, 50, and 20 mV s⁻¹ at voltage boundaries of -270 mV to +950 mV with the disc rotating at 1500 rpm [20]. For each sample three continuous scans were ran at each scan rate starting with 75 mV s⁻¹ and proceeding to 50 then 20 mV s⁻¹. This set of scans was then repeated once more at each scan rate. This procedure was repeated for the catalyst samples as outlined later in Table 2 as well as with the catalyst support materials. The experimental setups were run using Gamry software, and the subsequent data was analyzed using Gamry Echem Analyst software [23].

Characterization of Platinum Nanoparticles on Catalyst Supports

Following the synthesis of platinum nanoparticles on both biomass carbon black and Vulcan XC 72 carbon black, these catalyst complexes were characterized and analyzed alongside 20% w/w platinum on Vulcan XC 72 purchased from Fuel Cell Store Inc., pictured in Figure 7 [24]. The purchased 20% w/w platinum on Vulcan XC 72 was used as a standard to compare the efficiency and effectiveness of the homogeneous deposition method.



Figure 7. Purchased 10% w/w and 20% w/w Pt catalyst on Vulcan XC 72 carbon, Vulcan XC 72 carbon, and Nafion membranes.

Using cyclic voltammetry methods, the differences in the catalyst activity between purchased 20% w/w platinum on Vulcan XC 72, synthesized 20% w/w platinum on purchased Vulcan XC 72, and synthesized 20% w/w platinum on synthesized biomass carbon catalyst support were measured in HClO₄. Next, the durability of the synthesized biomass catalyst material was measured in HClO₄. Following this, the activity of the Vulcan XC 72 carbon support and the biomass carbon support without the addition of platinum was characterized in both HClO₄ and H₂SO₄ solutions. Then, the durability of the synthesized biomass catalyst material was characterized in H₂SO₄. Lastly, the catalytic activity of purchased 20% w/w platinum on Vulcan XC 72, Synthesized 20% w/w platinum on purchased Vulcan XC 72, and synthesized 20% w/w platinum on synthesized biomass carbon catalyst support were measured in H₂SO₄.

Refinement of Membrane Pressing and Fabrication

The fabrication of membrane electrode assemblies for PEM fuel cells using the synthesized platinum catalyst from the previous section was developed. The fabrication technique that was utilized for the preparation of the membrane electrode assembly was hot-pressing. Using Nafion polymer sheets as an electrolyte, carbon cloth as a support, and the

purchased 20% w/w platinum on Vulcan XC 72 as an electrochemical catalyst, an initial fabrication procedure for MEAs was developed. The thickness of the Nafion membranes used was 212, and the duration for which the MEAs were pressed as well as the temperatures for which they were pressed were varied.

The first step in fabricating the MEA was preparing the Nafion electrolyte membrane. This was accomplished through three steps. First, the membrane was cleaned by boiling it in deionized water for 1 hour. Next, the membrane was cleaned using a 3% hydrogen peroxide, H₂O₂, solution. Following the first two cleaning steps, the membrane was then activated through boiling it in a 0.5 M H₂SO₄ solution [25]. Once the membrane had been cleaned and activated, the fabrication of the gas diffusion electrode could take place.

The initial step of fabricating the gas diffusion electrode was to cast a thin layer of Polytetrafluoroethylene (Teflon or PTFE) and Vulcan XC 72 carbon onto the carbon cloth, creating a microporous layer. A PTFE and carbon black solution of 30% w/w PTFE in isopropyl alcohol was then painted onto the cloth such that the load of PTFE/C is 3.5 mg cm⁻² [25]. The microporous layer was then dried to the carbon cloth on only one side using a muffle furnace. The next step was to cast the catalyst layer onto the thin PTFE/C layer produced in the previous step. This was achieved through the use of a catalyst suspension using the 20% w/w platinum on Vulcan XC 72 and 5% Nafion solution in isopropyl solvent. The Nafion content in this solvent was 33% w/w with a platinum load of 0.2 mg cm⁻² [25]. This suspension was then brushed onto the PTFE/C layer. Following these steps, a 2.0 mg cm⁻² Nafion solution was then brushed onto the catalyst layer in order to enhance the contact between the membrane and catalyst. These layers were then dried to solidify their structural integrity. Once both the membrane and gas diffusion electrodes had been prepared, the MEA could then be pressed.



Figure 8. MEA hot-pressing apparatus.

Figure 8 shows the hot-pressing apparatus used. The hot-pressing apparatus used was a Mestra hydraulic dental press, model number: 030350, custom-fitted with temperature controlled REX-C100 heating press plates. The hot pressing parameters used for this project were a pressure of 500 psi at 100-120 °C for 90-120 seconds [26].

Results and Discussions

Synthesis of Biomass Carbon Catalyst Support Material

Carbon catalyst support material was synthesized from dried garbanzo bean biomass using pyrolysis under N₂.



Figure 9. Biomass carbon black synthesized through the pyrolysis of dried garbanzo beans and Vulcan XC 72 carbon.

Figure 9 pictures biomass carbon black catalyst materials that were successfully synthesized under N₂. When compared to biomass synthesized under O₂ it can be seen that there is significantly less oxidation in the N₂ sample. The biomass synthesized under N₂ was similar in color to the Vulcan XC 72 carbon. The carbon black catalyst material synthesized using biomass from dried garbanzo beans was unique in its physical features from Vulcan XC 72 in regards to particle size and consistency between particles. While Vulcan XC 72 carbon has a consistently small particle size, the biomass carbon black was observed as having a larger particle size in addition to a much broader range of particle sizes. In addition to the irregularities in size observed for the biomass support, irregularities in size may also be present. Increased particle size or irregularities in particle shape may account for the observed instability of the biomass particles.

Synthesis of Platinum Nanoparticle on Carbon Catalyst Support

The homogeneous deposition of platinum onto carbon and biomass support was performed by NaBH₄, 20% w/w. Two varieties of catalyst were synthesized: the first utilized the biomass carbon black catalyst support, synthesized in the lab, while the second utilized Vulcan XC 72 carbon support purchased from the Fuel Cell Store Incorporated [24]. The Vulcan XC 72 for this experiment was used as a standard to compare the biomass carbon support to, due to Vulcan XC being an industry standard carbon catalyst support [22]. Both procedures were identical with the exception of the carbon black source onto which the platinum nanoparticles was being reduced.



Figure 10. Platinum nanoparticle synthesized in the spring of 2016.

Figure 10 pictures synthesized platinum nanoparticles on biomass carbon black catalyst support after being filtered and dried. Similar to the biomass catalyst support material, these catalyst particles were not uniform in their overall shape or size. In order to better characterize the adherence patterns of the platinum onto this catalyst material, analysis using electron microscopy needs to be pursued, as well as atomic absorbance to determine the concentration of platinum in the biomass carbon catalyst material.

Standardization of Purchased Catalyst Material

Using the solution of 20% w/w Pt on Vulcan XC 72 established in Table 2, three sets of three working electrodes were prepared.

| Catalyst or Catalyst | Amount of material in | Electrodes | Electrodes prepped | Electrodes prepped |
|-----------------------|-----------------------|------------------|--------------------|---------------------|
| Support | 7 mL solution (mg) | prepped using 20 | using 30 uL of | using 40 uL mixture |
| | | uL of mixture | mixture | |
| Purchased 20% Pt on | 5.3 | 6 | 3 | 3 |
| Vulcan XC 72 carbon | | | | |
| Synthesized 20% Pt on | 5.6 | 6 | N/A | N/A |
| Vulcan XC 72 Carbon | | | | |
| Synthesized 20% Pt on | 5.4 | 6 | N/A | N/A |
| Biomass Carbon | | | | |
| Vulcan XC 72 Carbon | 4.4 | 4 | N/A | N/A |
| | | | | |
| Biomass Carbon | 4.3 | 4 | N/A | N/A |
| | | | | |

Table 2. Concentration of catalyst and support mixtures with loadings for working electrodes.

Table 2 shows the amount of each catalyst used as well as the number of electrodes prepared using that amount. The first set utilized 20 μ L of solution, the second set utilized 30 μ L of solution, and the third set utilized 40 μ L of solution. Each of these electrodes was then run using the cyclic voltammetry experimental setup established prior in a 0.1 M HClO₄ solution by sweeping three times between -270 mV and +950 mV. Shown in Figure 11 are representative voltammograms first scans for each loading collected at the scan rate of 75 mVs⁻¹.



Figure 11. Standardization of purchased 20% w/w Pt on Vulcan XC 72 in HClO4 for various platinum loadings.

From the known concentration of the catalyst solution and the known amounts of the solution deposited onto the electrode, the platinum loadings for the three different sets of electrodes were calculated as being 77.2, 115.7, and 154.3 μ g/cm². When the cathodic curves of each loading were analyzed focusing specifically on the region from -0.26 to 0.10 V, an increase in the area under these peaks can be noticed as platinum loading increased. As mentioned earlier, the peaks in this region of the curve are related to adsorption of hydrogen onto the catalyst material present at the working electrode. This area under the curve is also related to the electrochemically active surface area present at the working electrode. When the areas under the curve are analyzed in Figure 11, it can be seen that as the loading of platinum, catalyst material, is increased, the electrochemically active surface area also increases.

Using the Gamry Electrochemistry Analysis software, the exact areas under the curves related to the adsorption of hydrogen onto the working electrode were calculated for all of the samples ran [23]. The curves selected were a result of the first round of scans run at 75 mVs⁻¹. Next, the calculated areas under the curve were averaged, and this average valued was used to calculate the electrochemically active surface area for each set of platinum loadings.



Graph 1. Electrochemically active surface areas for purchased 20% w/w Pt on Vulcan XC 72 in HClO₄ using various Pt loadings.

Graph 1 plots the average electrochemically active surface areas for the purchased 20% w/w Pt on Vulcan XC 72 based upon their platinum loadings. From the graph, it can be seen that when the ECA is quantified in relation to platinum loading, there is a linear trend of increase. When a trend line is fitted to the data running through the origin, the 0.95 R^2 indicates that there is a linear relationship between the amount of catalyst added and the ECA. This was expected and ensures that the utilized procedures are effective in characterizing the electrochemically active surface area of a desired catalyst material for comparison purposes.

Characterization of Synthesized Catalyst Materials

Following the standardization of the purchased 20% w/w Pt on Vulcan XC 72 industry standard catalyst materials, the characterization of the synthesized 20% w/w Pt on Vulcan XC 72 and 20% w/w Pt on biomass was completed. The working electrodes for both sets of samples were prepared using 20 μ L of catalyst solution, such that platinum loadings for the samples run were nearly identical to the standard run using 20 μ L of purchased 20% w/w Pt on Vulcan XC

72. Cyclic voltammetry scans were then run using the identical procedure to the sets ran in the previous standardization, and the average curve from each set for the first round of scans at 75 mVs^{-1} is shown in Figure 12.



Figure 12. Cyclic voltammetry scans for synthesized materials and standards at similar platinum loadings in HClO₄.

In first comparing the curves for the purchased 20% w/w Pt on Vulcan XC 72 and synthesized 20% w/w Pt on Vulcan XC 72 it can be seen that the curves have a similar shape and peak in the region related to the adsorption of hydrogen ions and the electrochemically active surface area. Next, when the synthesized 20% w/w Pt on biomass is compared to the purchased 20% w/w Pt on Vulcan XC 72 it can be seen that they have similar characteristics in regards to their shape, but the peaks for the biomass catalyst material show significantly less ability to adsorb hydrogen and ECA. This trend may be explained by the observation that the biomass carbon support particles were far less uniform in size, and larger in size then the Vulcan XC 72 carbon particles. The size of the particle having an inverse effect on the surface area available for the hydrogen to adsorb onto for similar Pt loadings.

The ECAs for the two synthesized catalyst materials were calculated using the methods established prior. A plot of the ECAs for the synthesized Pt on biomass and Vulcan XC 72 is shown in Graph 2.



Graph 2. Electrochemically active surface areas for standards and synthesized 20% w/w Pt on Vulcan XC 72 and biomass in HClO₄.

When the trends discussed earlier, in regards to the comparison of the purchased standard and synthesized catalyst materials, are quantified, as shown in Graph 2, the catalytic activities of the synthesized materials can be better understood. The ECA of the synthesized 20% w/w Pt on Vulcan XC 72 is slightly less for a similar platinum loading. The similar ECAs between the purchased and synthesized Pt on Vulcan XC 72 for similar Pt loadings shows similarities in the materials in their catalytic characteristics. From this, the effectiveness of the procedure utilized in synthesizing 20% w/w Pt nanoparticles on carbon supports can be analyzed. The ability of the established procedure to synthesize 20% w/w Pt nanoparticles on carbon black can be seen as being effective, due to similarities between the purchased and synthesized platinum nanoparticles on Vulcan XC 72. When the ECA of the synthesized 20% w/w Pt on biomass is compared to the purchased standard Pt on Vulcan XC 72 it can once again be seen that the ECA is significantly lower. The ECA present for the synthesized Pt nanoparticles on biomass carbon catalyst support is similar to the expected ECA of the purchased standard at nearly half the Pt loading. The lower ECA is once again likely due to the larger particle size of the biomass carbon materials.

Durability of the Biomass Catalyst in HClO₄

Following the characterization and comparison of the synthesized catalyst materials to the purchased industry standard catalyst materials, the durability of the synthesized 20% w/w Pt on biomass was analyzed. The durability of the catalyst material was analyzed through the comparison of the first and second rounds of scans achieved at the scan rate of 75 mVs⁻¹ in HClO₄.



Figure 13. Initial and subsequent rounds of cyclic voltammetry scans for average synthesized 20% w/w Pt on biomass sample in HClO₄ at a scan rate of 75 mVs⁻¹.

From Figure 13, a change in the ability of the biomass catalyst to facilitate the adsorption of hydrogen and the resulting ECA can be seen from the first to second round of scans. When the

second scan is analyzed in more depth, there is a large decrease in the intensity of the hydrogen adsorption peak and the region between 100 mV to 950 mV lacks peaks. These results indicate there is a drastic decrease in the catalytic activity of the 20% w/w Pt on biomass in the second scan. From this decrease, it can be determined that the durability of the synthesized Pt on biomass is compromised in HClO₄. When the same analysis was achieved for the catalyst materials utilizing Vulcan XC 72 carbon, the durability of these materials was not compromised in the HClO₄. The lesser observed durability of the biomass catalyst material may be explained due to the biomass carbon material being less uniform and processed than the Vulcan XC 72 carbon. Vulcan XC 72 goes through many processes in its manufacturing that enhance its durability, and the application of these processes to the biomass carbon is an area of research that should be pursued.

Characterization of the Carbon Catalyst Support Materials

In order to further characterize the activity of the catalyst support materials, cyclic voltammetry scans were conducted utilizing the previously established procedure with solutions containing only Vulcan XC 72 carbon in water or biomass carbon in water. The concentrations of carbon in the solutions was identical to the concentrations of carbon in the catalyst solutions. These scans were conducted in aqueous solutions of 0.1 M HClO₄ and 0.05 M H₂SO₄.



Figure 14. Cyclic voltammetry scans of Vulcan XC 72 carbon in HClO₄ and H₂SO₄ solutions at a scan rate of 50 mVs^{-1} .

Figure 14 presents the cyclic voltammetry scans of Vulcan XC 72 carbon catalyst support without the addition of any platinum in two different aqueous solutions containing hydrogen ions. When the curve ran in H₂SO₄ is analyzed, it can be seen that the resulting anodic and cathodic curves are nearly parallel and lack any significant peaks. This shape is characteristic of scans for which there are no electrochemical reaction. When the curve ran in HClO₄ is viewed, it also shows a similar shape, with slightly more deviations. This shape shows that some very minor processes are occurring between the Vulcan XC 72 and the HClO₄, but overall the material is electrochemically unreactive under these conditions. The slightly less inert characteristic of the Vulcan XC 72 can most likely be explained by the detail that HClO₄ has a greater oxidizing potential.



Figure 15. Cyclic voltammetry scans of biomass carbon in HClO₄ and H₂SO₄ solutions at a scan rate of 50 mVs⁻¹.

The characterization of the biomass carbon catalyst support by means of cyclic voltammetry in aqueous solutions of HClO₄ and H₂SO₄ is shown in Figure 15. From Figure 15, it is clear that the biomass carbon catalyst support does not follow the inert trends of the Vulcan XC 72 carbon in identical solutions. The curve for the biomass carbon collected in the HClO₄ is more characteristic of a classical cyclic voltammogram. The peaks present on the anodic and cathodic curve provide evidence that reversible oxidation reduction reactions are being facilitated by the biomass carbon. The peaks are not present in the regions characteristic of catalytic activity with hydrogen. The evidence of oxidation and reduction processes being facilitated by the biomass, presents the material as being an active catalyst support material. The active, and not inert, characteristic is desirable in not only supporting but assisting the platinum in carrying out its catalytic activities. When the curve achieved in the H₂SO₄ solution is analyzed and its dimensions are increased a similar shape is seen, but to a lesser extent. This is evidence that the biomass carbon catalyst support is more active in HClO₄ rather than H₂SO₄. This

increased activity may account for the decreased durability of the biomass carbon when platinum catalyst is placed onto it.

Durability of the Biomass Catalyst in H₂SO₄

Following the characterization and comparison of the catalyst support materials, the durability of the synthesized 20% w/w Pt on biomass was analyzed once more. The durability of the catalyst material was again analyzed through the comparison of the first and second rounds of scans achieved at the scan rate of 75 mVs⁻¹, but instead in H₂SO₄.



Figure 16. Initial and subsequent rounds of cyclic voltammetry scans for average synthesized 20% w/w Pt on biomass sample in $HClO_4$ at a scan rate of 75 mVs⁻¹.

From Figure 16, a smaller decrease in the ability of the biomass catalyst to facilitate the adsorption of hydrogen and the resulting ECA can be seen from the first to second round of scans. When the second scan is analyzed in more depth, the tail end of the curve no longer shows inert characteristics. Overall, there is a slight decrease in the catalytic activity of the 20% w/w Pt on biomass in the second scan, but it is not nearly as significant as the decrease seen in HClO₄.

From this smaller decrease, it can be determined that the durability of the synthesized Pt on biomass is less compromised in H_2SO_4 . The greater observed durability of the biomass catalyst material in H_2SO_4 may be explained due to the biomass carbon material being less active in H_2SO_4 , and this should be tested in future research.

Characterization of Catalyst Materials in H₂SO₄

Lastly, purchased 20% w/w platinum on Vulcan XC 72, synthesized 20% w/w platinum on Vulcan XC 72, and synthesized 20% w/w platinum on synthesized biomass carbon catalyst support were characterized using cyclic voltammetry in 0.05 M H₂SO₄. Identical preparation and experimental setups were used as with the samples in HClO₄ to acquire the cyclic voltammetry data. The curves were then analyzed using the Gamry analysis software and ECAs were calculated using the previously established method [23].



Graph 3. Electrochemically active surface areas for catalyst materials in H₂SO₄ and standardization in HClO₄. Graph 3 shows the differences in ECAs for purchased 20% w/w platinum on Vulcan XC 72, synthesized 20% w/w platinum on Vulcan XC 72, and synthesized 20% w/w platinum on synthesized biomass carbon catalyst support in H₂SO₄ as well as the standardization of purchased 20% w/w platinum on Vulcan XC 72 in HClO₄. In first viewing the ECA for purchased 20% w/w platinum on Vulcan XC 72 in H₂SO₄, it can be seen that this value nearly matches the value of the identical material in HClO₄, by being only slightly less. In regards to synthesized 20% w/w platinum on Vulcan XC 72 the calculated ECA in H₂SO₄ fits on the linear trend of the purchased 20% w/w Pt on Vulcan XC 72 in HClO₄. The ECA for the synthesized 20% w/w platinum on biomass once again was significantly lower than that of the other catalyst materials with similar platinum loadings. Overall, the trends from Graph 2 are again present in Graph 3, with the ECA of the synthesized 20% w/w platinum on biomass being near half the platinum loading of that needed using purchased 20% w/w platinum on Vulcan XC 72. In future research, the standardization of purchased materials in H₂SO₄ should be pursued.

Refinement of Membrane Pressing and Fabrication

In regards to the development and refinement of a procedure for the hot-pressing of MEAs for PEM fuel cells, more development is needed in the ability to consistently cast microporous layers and catalyst layers onto carbon cloth with known amounts of material. The current method of casting these layers utilized wells that the layers were added to, with the carbon cloth sealed at the bottom, and resulted in the consistent loss of materials due to leaks in the seals. In regards to the actual ability of the custom made heated press to hot-press membranes, the press was able to consistently adhere purchased gas diffusion electrodes to prepared electrolyte membranes for the established pressing temperatures and durations at 500 psi. Overall, this is an area of research that should be expanded upon and refined by future work.

Conclusions and Recommendations

Biomass carbon black catalyst support was effectively synthesized using the pyrolysis under N₂, but uniformity of shape and size was not observed. As this research continues, ways to decrease the biomass particle size and improve the uniformity of the biomass particles should be investigated. In addition to further processing, characterization should be done using both electron microscopy and atomic absorbance to better determine the composition, shape, and size of the biomass carbon. Increased particle size or irregularities in particle shape may account for the observed instability of the biomass particles. The synthesis of platinum nanoparticles using homogeneous deposition of platinum was effective, as shown by the similarities in characterizing the purchased and synthesized platinum nanoparticles on Vulcan XC 72. The synthesized platinum nanoparticles on biomass need to be further characterized using electron microscopy and atomic absorbance spectroscopy, to better determine the platinum deposition and concentration characteristics of the biomass catalyst material.

In regards to the ability to characterize catalyst materials using cyclic voltammetry, the established procedures and methods were shown to be effective based upon the strength of the linear trend in the standardization of the purchased platinum on Vulcan XC 72 being an R^2 value of 0.949. The characterization of the synthesized platinum nanoparticles on the biomass catalyst support showed lower ECAs, which is believed to be due to the increased size and irregularity of shape found in the biomass carbon material; further characterization is needed to make this conclusion. The durability of the synthesized platinum nanoparticles in HClO₄ was shown to be compromised based upon the significant degradation between the first and second round of cyclic voltammetry scans. This trend was not seen to the same extent in H₂SO₄, which significantly less degradation between the rounds of cyclic voltammetry scans and a preservation

of the overall activity based upon the shape of the curves. When the catalyst materials were then characterized using H_2SO_4 , it was seen that the overall trends in the ECAs were similar based upon their relation to the standardization in $HClO_4$, but a standardization in H_2SO_4 need to be achieved in order to better conclude upon this trend.

In regards to the characterization of the catalyst support materials using cyclic voltammetry methods, it was shown that the Vulcan XC 72 carbon acts as an inert support based with flat, parallel cyclic voltammograms in solutions of H₂SO₄ and HClO₄. This trend did not continue with the biomass carbon catalyst support, as evidence of oxidation reduction processes occurring was present. The presence of the oxidation reduction processes in H₂SO₄ and HClO₄ allow it to be concluded that the biomass carbon catalyst support is an active support. Further characterization of the biomass carbons activity is necessary to better understand the nature of its activity and its usefulness in aiding platinum in its catalyst activity. Based upon the extent of the activity in relation to the durability of catalyst support material, it can be concluded that as activity increases, for the biomass carbon, the durability decreases. Further research needs to be conducted to strengthen this conclusion.

Lastly, the fabrication of MEAs needs to be further explored in order to refine an effective procedure, such that the use of the biomass catalyst material may be characterized and compared in its effectiveness as a PEM fuel cell catalyst.

References

- [1] Seip, K.; Thorstensen, B.; Wang, H.; Environmental Impacts of Energy Facilities: Fuel Cell Technology Compared with Coal and Conventional Gas Technology. *Journal of Power Sources.* **1991**, 35, 37-58.
- [2] Grove R.; On a new voltaic combination of gasses by platinum. *London and Edinburgh Philosophical Magazine*. **1839**, *14*, 128–130.
- [3] Lucia U.; Overview on fuel cells. *Renewable and sustainable energy reviews.* **2014**, 30, 164-169.
- [4] Acres, G.; Frost, J.; Hards, G.; Potter, G.; Ralph, T.; Thompsett, D.; Burstein, G.; Hutchings, G.; Catal. *Today*. **1997**, 38, 393-400.
- [5] Lazaro, M.; Calvillo, L.; Celorrio, V.; Pardo, J.; Perathoner, S.; Moliner, R.; Study and Application of Carbon Black Vulcan XC-72R in Polymeric Electrolyte Fuel Cells. *Carbon Black: Production, Properties and Uses.* 2011, 1-28.
- [6] Datta, K.; Balasubramanian, V.; Ariga, K.; Mori, T.; Vinu, A.; *Journal of Chemistry Europe*. **2011**, 41, 3390-3397.
- Bidlack, J.; MacKown, C.; Rao, S.; Dry Weight and Nitrogen Content of Chickpea and Winter Wheat Grown in Pots for Three Rotations. *Journal of Plant Nutrition*. 2007, 30, 1541-1553.
- [8] Vielstich W.; Gasteiger H.; Lamm A.; Handbook of Fuel Cells Fundamentals, Technology, Applications. *New York: Wiley*; **2003**.
- [9] Larminie J, Dicks A.; Fuel cell systems explained. *Chichester: John Wiley & Sons*; 2000.
- [10] Kunusch C.; et al.; PEM fuel cell systems. Sliding-mode control of PEM Fuel Cell. 2012, 13-33.
- [11] Eastman S.; Energy Storage and Delivery. 2016.
- [12] Norskov J.; Rossmeisl A.; Logadottir A.; Lindqvist L.; Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode. *Journal of Physical Chemistry. American Chemical Society* 2004.
- [13] Report of the Hydrogen Production Expert Panel: A Subcommittee of the Hydrogen & Fuel Cell Technical Advisory Committee.; *United States Department of Energy*. **2013**.
- [14] Song D.; Wang Q.; Liu Z.; Eikerling M.; Xie Z.; Navessin T.; Holdcroft S.; A Method for Optimizing Distributions of Nafion and Pt in Catyhode Catalyst Layers of PEM Fuel Cells. *Electrochimica acta*. 2005.

- [15] Wee J.; Lee K.; Kim S.; Fabrication Methods for Low-Pt-Loading Electrocatalysts in Proton Exchange Membrane Fuel Cell Systems. *Journal of Power Sources*. 2007.
- [16] Zhao X.; Zhu J.; Liang L.; Li C.; Liu C.; Liao J.; Xing W.; Biomass-Derived N-Doped Carbon and its Application in Electrocatalysis. *Applied Catalysis B: Environmental*. 2014.
- [17] Shao, Y.; Sui, J.; Yin, G.; Gao, Y.; Nitrogen-Doped Carbon Nanostructures and Their Composites as Catalytic Materials for Proton Exchange Membrane Fuel Cell. *Applied Catalysis B: Environment.* 2008, 79, 89-99.
- [18] Shao, Y.; Zhang, S.; Wang, C.; Nie, Z.; Liu, J.; Wang, Y.; Lin, Y.; Highly Durable Graphene Nanoplatelets Supported Pt Nanocatalyst for Oxygen Reduction. *J Pow Sour*. 2010, 195, 4600-4605.
- [19] Wu, J.; Yuan, X.; Wang, H.; Blanco, M.; Martin, J.; Zhang, J.; Diagnostic Tools in PEM Fuel Cell Research: Part I Electrochemical Techniques. *International Journal of Hydrogen Energy.* 2008, 33, 1735-1746.
- [20] Mayrhofer, K.; Strmcnik, D.; Blizanac, B.; Staenkovic, V.; Arenz, M.; Markovic, N.; Measurement of Oxygen Reduction Activities via the Rotating Disc Electrode Method; From Pt Model Surfaces to Carbon-Supported High Surface Area Catalysts. *Electrochemia Acta.* 2008, 53, 3181-3188.
- [21] Darvell, L.; Brindley, C.; Baxter, X.; Jones, J.; Williams, A.; Nitrogen in Biomass Char and Its Fate during Combustion: A Model Compound Approach. *Energy Fuels*. 2012, 26, 6482-6491.
- [22] Fang, B.; Chaudhari, N.; Kim, M.; Kim, J.; Yu, J.; Homogeneous Deposition of Platinum Nanoparticles on Carbon Black for Proton Exchange Membrane Fuel Cell. *J Am Chem Soc.* 2009, 131, 15330-15338.
- [23] Gamry Instruments. 734 Louis Drive Warminster, PA 18974. Phone (215) 682-9330. https://www.gamry.com/
- [24] The Fuel Cell Store. 1902 Pinon Drive, Suite B, College Station, Texas 77845. Phone (979) 703-1925. http://www.fuelcellstore.com/
- [25] Therdthianwong, A.; Manomayidthikarn, P.; Therdthianwong, S.; Investigation of Membrane Electrode Assembly (MEA) Hot-Pressing Parameters for Proton Exchange Membrane Fuel Cell. *Energy*. 2007, 32, 2401-2411.
- [26] Tang, H.; Wang, S.; Jiang, S.; Pan, M.; A Comparative Study of CCM and Hot-pressed MEAs for PEM Fuel Cells. *J Pow Sour.* 2007, 170, 140-144.