INTEGRATED BIPOLAR PLATE – GAS DIFFUSION LAYER DESIGN FOR POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Abstract


Bipolar plates compose a large portion of the weight and manufacturing costs in fuel cells. Bipolar plates are metal plates that separate each membrane-electrode assembly in a fuel cell stack. They provide structural strength, contain flow channels for fuel transport, and conduct electricity in the fuel cell. Electricity also flows through the gas diffusion layer (GDL) which lies next to the bipolar plate. Because the GDL is separate from the bipolar plate, there is a contact resistance as the electricity flows from one to the other. The scope of this thesis is to research an efficient way of manufacturing a cheap and lightweight bipolar plate-GDL combination. This is to be done by using materials such as exfoliated graphite, a binding resin, and sacrificial additives. Processing temperatures and pressures as well as component ratios are variables to be investigated in order to easily and quickly make bipolar plate-GDL combinations.
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A fuel cell is a type of electrochemical device that has similarities to both batteries and combustion engines. Like a battery, a fuel cell converts chemical energy directly to electricity. The fuel cell uses the chemical energy stored in the fuel on which it runs. So long as fuel is supplied, the fuel cell continues to operate. A combustion engine also runs on fuel and draws power from the chemical energy stored in the fuel. However, that is where the similarity ends. Through a combustion reaction, the chemical energy is converted first into heat and then into mechanical energy. If electricity is the desired output, the mechanical energy must be further converted. The use of so many stages of energy conversion introduces inescapable efficiency reductions. The chemistry inside a fuel cell is essentially a combustion reaction. However, the fuel cell controls the reaction to directly produce electricity. [1]

**Advantages and Disadvantages**

With fewer moving parts and no stage of conversion to heat energy, a fuel cell is theoretically much more efficient, longer lasting, and quieter than a combustion engine. Fuel cells scale well in both power, determined by the fuel cell size, and capacity, determined by the fuel reservoir size. For batteries, the power and capacity are normally
interrelated and do not scale well to large sizes. Also, fuel cells can run continuously with adequate fuel supply while batteries must be shut down and recharged. [1]

Fuel cells do have their disadvantages and technological challenges. Because of the materials and complexity, cost is a major concern for wide spread implementation. Availability and storage of fuel is another issue that needs addressed. The best fuel is hydrogen. However, it is a gas that is not widely available, and its low density makes it difficult to store in any significant quantity. Other fuels such as methanol and formic acid are easier to store but add difficulties to the system. They may cause reduced performance of the fuel cell or require additional reforming equipment. Fuel cells may also have limited operational temperature ranges and susceptibility to poisoning from environmental compounds. Depending on the materials used, corrosion and degradation with cycling can become a concern. [1]

**Chemistry**

In a combustion reaction, chemical bonds contained in the reactants are broken while new bonds of the products are formed. The reactants include both the fuel and the oxidant. The rearrangement of bonds occurs through the transfer and redistribution of electrons over a time span of picoseconds. The reaction proceeds because the final configuration of the bonds is at a lower energy than the starting configuration. The difference in energy is released from the reaction as heat. [1]

A fuel cell controls a reaction by harnessing the electrons as they move from the higher energy reactant configuration to the lower energy product configuration. Since the electron movements happen on such short time and distance scales, the only way to control the transfer is by separating the reactants and forcing the electrons to move over a
greater distance. Then as the electrons move from the fuel to the oxidant, they can be directed to produce an electrical current. [1]

A variety of fuel cell types exist that are categorized by the fuels they use and the configuration of cell components. These types include but are not limited to the polymer electrolyte membrane fuel cell (PEMFC), alkaline fuel cell (AFC), solid-oxide fuel cell (SOFC), direct methanol fuel cell (DMFC), and formic acid fuel cell (FAFC).

One of the most commonly researched types of fuel cells is one that runs on hydrogen, namely the PEMFC. The basic hydrogen combustion reaction is

$$\text{H}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{H}_2\text{O}.$$  

Equation 1.1

With the physical separation of the reactants, the formula for the combustion reaction can be split into two electrochemical half reactions, Equations 1.2 and 1.3.

$$\text{H}_2 \leftrightarrow 2\text{H}^+ + 2\text{e}^-$$  

Equation 1.2

$$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2\text{O}$$  

Equation 1.3

The separation of the two half reactions forces each electron to move through an external pathway and do work before it can complete the reaction. [1]

**Configuration and Operation**

The separation of the reactants is achieved through use of an electrolyte. An electrolyte is a solid or liquid through which ions can move but not electrons. A fuel cell contains one electrode for each of the half reactions. An electrode is composed of a gas diffusion layer (GDL) and a catalyst layer. The two electrodes are separated by an electrolyte layer commonly called the polymer electrolyte membrane or the proton exchange membrane. [1]
The electrons are produced where the electrode, electrolyte, and reactants all make contact. A fuel cell can be scaled by adjusting the total contact area where the reactions take place. To provide large surfaces and maximize the surface-to-volume ratio, the components for fuel cells tend to be made into planar structures. Porosity in the electrodes also increases the total surface area and allows the gaseous reactants access to the reaction sites. [1]

The electrode that is supplied with the fuel (e.g. hydrogen) is referred to as the anode. The electrode supplied with the oxidant (e.g. oxygen) is referred to as the cathode. A thin membrane, the electrolyte layer, separates the two electrodes and prevents electrons or reactants from passing directly between the electrodes. [1]
There are four critical steps that must occur for successful operation of a fuel cell.

The steps are:

1) Transport of reactant into the fuel cell
2) Electrochemical reaction
3) Conduction of ions through electrolyte and electrons through circuit
4) Removal of product(s) from fuel cell.

[1]

For a fuel cell to begin its operation, the fuel and oxidant must be delivered to it. The amount of current being drawn from a fuel cell relates directly to the amount of reactants it needs. If the reactants are not supplied quickly enough with a high current pull, the fuel cell can starve. The best way to deliver the reactants to the reaction area is first to use plates containing a grooved flow channel structure. The channels disperse the reactants across the electrode. The electrode is porous to allow the reactant access to the reaction sites while still providing an electrically conductive network to carry the electrons away. [1]

Once the reactants reach the reaction sites along the electrode, the electrochemical reactions begin. The rate at which these reactions occur directly affects the current produced by the cell. Faster reactions result in higher current output. In general, the kinetic limitations of electrochemical reactions are the greatest obstacle to efficient performance. To make it easier and more energetically favorable for the reactions to occur, catalysts are used. A catalyst is a material that promotes a chemical reaction to proceed while the catalyst itself remains unchanged. In a hydrogen fuel cell, platinum
helps to break the bond between the hydrogen atoms while capturing their electrons in the process. This is a reaction that would not otherwise occur spontaneously. [1]

Because the electrochemical half reactions are separated in the fuel cell, electrons and ions must be transported from the electrode where they are produced to the electrode where they are consumed. The electron transport is relatively easy as it simply requires an electronically conductive pathway. Ion conduction is more difficult because ions have greater size and mass than electrons. An electrolyte provides pathways for the ions which move using hopping mechanisms. These methods are much less efficient than electron transport, so ion conduction can account for significant resistance losses. To minimize the losses, the electrolyte is made as thin as possible. [1]

Once the electrochemical reactions are completed, the product species must be removed from the fuel cell. If the products are not removed, the buildup would eventually suffocate the cell and prevent any further reactions from occurring. A fuel cell running on hydrogen produces only one product, water. Other fuel cells may produce additional compounds such as carbon dioxide depending on the fuel used. Fortunately, the pore and flow channel structure used to supply reactants to the cell is useful for removing the products. Product removal does not tend to be a major problem for fuel cell design, but still should not be overlooked. [1]
Section 2: Bipolar Plates

In a fuel cell, most of the reactions that produce the electricity occur in the membrane electrode assembly (MEA). The MEA consists of the polymer electrolyte membrane and the surrounding electrodes. On each side of the MEA are plates that seal in the MEA and prevent unwanted species from entering or exiting. When multiple MEAs are combined to create a fuel cell stack, the separating plates are called by bipolar plates. [3]

Figure 1.2: Diagram of a simple fuel cell stack with 1: a bipolar plate, 2: end plates, and 3: MEAs with seals. [3]

Bipolar plates serve four main purposes in a fuel cell. The first is to contain channels that supply fuel to the cell and remove exhaust. The second task they perform is to collect the electrical current generated by the fuel cell. The third task is to cool the area where reactions occur. The final task is to provide structural strength to the fuel cell.
stack. Because of the material requirements placed on bipolar plates, they contribute to a significant portion of the cost, size, and weight of fuel cells. The plates can actually compose as much as 80% of the weight of a fuel cell. [4]

**Material Requirements**

In order to provide a significantly rigid structure for the fuel cell stack, the DOE has set a target for a minimum flexural strength of 25 MPa. [5] The material used for a bipolar plate is one that must be able to support a potentially complex system of grooves for supplying the fuel. Preferably, the grooves can be made in the plate material with minimal effort during the manufacturing process. This, however, is not always possible. [3]

![Figure 1.3: Various types of flow channel grooves used in fuel cells.](image)

To collect and transmit current efficiently, the material used in the bipolar plates needs to have a high electrical conductivity. The DOE target for electrical conductivity is a minimum of 100 S/cm. A good thermal conductivity is also desirable as fuel cells produce heat that must be removed. Bipolar plates provide the easiest method of removing the heat by conducting it away from the MEA. [3]

Electrochemical stability is important for a bipolar plate material. Depending on the type of fuel cell, a variety of chemicals may be present such as air, water, hydrogen,
carbon monoxide, carbon dioxide, strong acids, and various peroxides. Many of these chemicals create a corrosive environment that can degrade materials used in a bipolar plate. The more electrochemically stable a material is, the less it is likely to corrode. Thermal stability is also important. A material used for a bipolar plate needs to be able to maintain its strength through a range of temperatures from room temperature to 200°C. Through these temperatures, the material should preferably have a low coefficient of thermal expansion. If a bipolar plate would undergo significant changes in size as the temperature changes, the components attached to it could be severely damaged. [3]

To prevent fuel leakage, a material should have a low permeability to the chemicals it delivers to the fuel cell. Of major concern is hydrogen due to its small size. The DOE has set a limit of $2 \times 10^{-6} \text{cm}^3/(\text{s} \times \text{cm}^2)$ for hydrogen permeability at 80°C and 0.3μPa. Also to prevent leakage, the surface roughness of a bipolar plate near contacts and seals should be low, and the overall thickness of the plate should be uniform within 0.02 mm. [3]

The cost of a present working fuel cell is around $200/kW [6] with the cost of the bipolar plates being as much as 45% of that total [4]. In order to reduce the cost, the DOE has set a target goal of $5/kW by 2010 for the price of bipolar plate production and a target weight of less than 0.4 kg/kW. [5]

**Pure Metals**

For years, the bipolar plates in many fuel cells have been made of pure metals. Pure metals are attractive because they have a high conductivity, and they are mechanically strong. The high strength of metals means that the bipolar plates can be made thin, which helps to reduce the weight. Even when thin, metals have a low
hydrogen permeability. There are two main problems with pure metals; they are susceptible to deterioration in the corrosive environment in many fuel cells, and they are heavy. The first result of corrosion on many metals is the formation of an oxide layer that is electrically insulating on an order of $10^{12} \, \text{Ω} \cdot \text{cm}$. These layers contribute a significant contact resistance that detracts from the overall voltage of the fuel cell. Protective coatings related to corrosion are a major area of study for metal bipolar plates. These coatings must be made to cover reliably 100% of the surface to prevent opportunities for galvanic corrosion sites. [6] Besides deterioration of the bipolar plate, the other main danger of corrosion is that the metal cations freed in the process can pass into the MEA and poison the catalyst. [3] The catalyst particles promote the chemical reactions that occur to produce electricity. Poisoning of the catalyst means that it can no longer do its job and the efficiency of the fuel cell is severely degraded.

Stainless steel is one common metal for bipolar plates. It has good conductivity and strength, and it is easily machined when compared to other metals. It costs around $0.15/\text{lb}$, has an electrical conductivity of 10,000 $\text{S/cm}$, and has a thermal conductivity of 16.3 $\text{W/(m}\cdot\text{K})$. It has negligible permeability, and its density is 8 $\text{g/cm}^3$. [6]

Stainless steel bipolar plates could be mass produced into thin sheets by methods of rolling or batch stamping. The ability to be stamped allows for complicated gas channel structures to be easily formed. When stainless steel corrodes, an inert $\text{Cr}_2\text{O}_3$ layer forms on the surface. The problem with corrosive layers, even when inert, is that they add significant contact resistances to electrical conduction in the fuel cell. [6] One type of stainless steel that has been tested for use as bipolar plates is 316L. It is an alloy commonly used in medical implants. Despite the inert surface layer, stainless steels such
as 316L can still gradually deteriorate. Experiments showed that 316L used in a fuel cell degraded at 0.2% per day. Common metal ions present in steels that could poison the catalyst include iron, nickel, and copper. [3]

In order to prevent degradation of stainless steel, a different type of coating would be needed that could protect against corrosion and dispersion of chromium ions. In order to limit contact resistance, the coating should be at least somewhat electrically conductive. With the extra step of applying a coating added to the manufacturing process, it would be difficult to meet the low cost goals of bipolar plate production. [6]

Titanium is another metal that is being considered for use in bipolar plates. At 4.54 g/cm³ it has a lower density than stainless steel. It has an electrical conductivity of 1,500 S/cm and a thermal conductivity of 17.2 W/(m*K). It has negligible permeability to hydrogen and costs around $5/lb. [6] Titanium has good strength and hardness. Titanium can also have corrosion resistance, but only when it is in a very pure form that is costly to refine. Even then, pure titanium can corrode significantly in a fuel cell within 300 hours of runtime. Corrosion first forms an insulating oxide layer before the plate eventually degrades. Fortunately, titanium ions are not very poisonous to the catalyst. [3] When used to make bipolar plates, titanium should still be coated to help prevent corrosion. An example of such a coating is a titanium nitride finish. [6] Additionally, precious metal coatings may be used with an increase in cost. [7]

It takes longer to produce titanium than stainless steel because it is a two step process. The process starts with titanium oxide ore from which TiCl₄ is produced. This compound is then reduced to pure titanium metal. Bipolar plates then can be machined from the metal through a process such as power metallurgy. [3]
A metal that is attractive because of its low density is aluminum. It has a density of 2.7 g/cm³, an electrical conductivity of 376,000 S/cm, and a thermal conductivity of 205 W/(m*K). It has negligible permeability and costs about $2/lb. These values mean that aluminum is more conductive and less dense than both stainless steel and titanium. An insulating oxide layer forms on aluminum during corrosion similar to the oxide layer on titanium. Bipolar plates can be made from aluminum by casting, machining, etching, or stamping. It is expensive to coat aluminum in protective coatings because of the processes used. Ion sputtering and chemical vapor deposition require high temperatures and expensive equipment. With an alternate coating option of electrodeposition, only expensive materials such as gold, platinum, or palladium can be used. Also, during temperature cycling of the fuel cell, differences in the coefficient of thermal expansion may cause the protective layers to detach from the plate or even damage the MEA. [6] Fortunately, aluminum ions are not poisonous to the catalyst particles. If the corrosion problem could be solved simply, aluminum bipolar plates made by stamping foil would have the potential to be three times lighter, half as thick, and cheaper than bipolar plates made of carbon. [3]

Bipolar plates made of carbon or graphite are appealing because they have high conductivity and high corrosion resistance. Carbon is also not poisonous to the catalyst particles in the fuel cell. Single crystal graphite is rarely considered because it is expensive and exfoliates easily. Turbostrate graphite and glass carbon have good conductivity, good mechanical properties, and high impermeability to gas. The disadvantage again is that they are expensive materials. Glass carbon is also very hard
and thus, very costly to machine. Expensive methods such as laser etching are needed to cut the complex flow grooves. [3]

One of the most common materials used for current bipolar plates is natural graphite. It is not nearly as expensive as single crystal graphite or glass carbon but has some similar properties. Graphite has a density around 2 g/cm$^3$, an electrical conductivity ranging from 110 to 680 S/cm, and a cost ranging from $0.50 to $1.00 /lb. The attractiveness of graphite is its low density combined with high conductivity. Unfortunately, pure graphite is brittle with a low flexural strength and has a porous structure. This creates permeability issues and means that the bipolar plates must be made thicker than with pure metals. It is also expensive and time consuming (several hours per plate) to machine channels into plates to create the flow field. Even production of the initial graphite for the plates is expensive. The raw graphite production requires weeks in a high temperature sintering process. To compensate for the porosity, the graphite may be vacuum impregnated with a resin. The plates must be ground and polished to create a smooth surface. Ensuring that graphite bipolar plates are fully sealed in the fuel cell can cost as much as $100/kW. [6]

**Carbon/Carbon**

Carbon/carbon bipolar plates are made from a carbon fiber material which is porous. To eliminate the porosity, additional graphitic carbon is deposited on the surface by chemical vapor infiltration. At 0.96 g/cm$^3$, the density is about half that of graphite. The electrical conductivity is between 200 and 300 S/cm. The process to produce these plates involves several steps. To start off, carbon fibers (or alternatively graphite powder) are combined with phenolic resin. The size of the carbon fibers is
approximately 400 μm by 10 μm. The fibers and resin are mixed in water in a ratio of around four to three, fiber to resin. The phenolic resin provides strength and stability. The slurry is vacuum molded and cured for several minutes at 150°C. Additional resin may be added after this to help seal the surface. Chemical vapor infiltration is performed with methane at 1400 to 1500°C and low pressure to further reduce permeability. If graphite powder is used in place of the carbon fibers, a slightly different process is followed. In a mixture of one to one, the graphite powder and phenolic resin are compression molded under an appropriate temperature and pressure to melt and partially cure the resin. The material is then placed in an inert atmosphere and heated to around 1000°C to carbonize the resin and convert it almost completely to vitreous carbon. The material is heated further to 2100°C to convert the carbon to graphite. This last step improves the corrosion resistance, electrical conductivity, thermal conductivity, and hydrogen impermeability. Both processes finally require flow channels to be machined into the surface. [6]

Carbon/carbon plates produced from carbon fibers have shown an excellent flexural strength around 175 MPa and a conductivity above 200 S/cm. Plates produced from graphite particles, however, had a flexural strength of 46.7 MPa and inconsistent conductivity measurements. The need for high temperatures and long processing times for both the carbonization and chemical vapor infiltration processes make them uneconomical for large scale production at present. [6]

**Polymer Composites**

History has shown that when a new material is needed that meets strict and sometimes contradictory requirements, the solution is often a composite. Composites for
bipolar plates would be made of a polymer, a thermoplastic or thermoset, and a noncorrosive, conductive filler such as graphite flakes or carbon fibers. The polymer generally does not compose more than 30 weight percent of the composite. Some requirements for the binding polymer used are a low permeability to gas, thermal stability throughout the fuel cell operating temperatures, a low coefficient of thermal expansion, and resistance to acids and oxidants. The binding polymer also cannot contain compounds that would poison the catalyst. [3] To improve mechanical properties, sometimes additional fillers such as carbon or glass fiber may be added. [6]

Thermoset resins include epoxies, phenolics, and vinyl esters. Thermosets are generally strong and tough materials that resist deformation under elevated temperatures. One benefit of thermosets is their low viscosity which allows for loading with large amounts of graphite or other conductive filler. Another benefit from the nature of thermosets compared to thermoplastics is that once formed, they do not require time to crystallize. Once the thermoset has cured in the mold, it can be removed while it is still hot. Thermoplastics take time to cool and crystallize. [6]

Experiments have been performed using epoxy resins mixed with graphite in ratios varying from 1:1 to 9:1 graphite to resin. They were cured in a mold in an oven at a temperature between 60°C and 140°C under pressure for eight hours. After the molded plate was removed from the oven and cooled, an additional, chemically resistant thermoset resin was added to the plate in areas not requiring electrical conductivity. This additional resin helped to create seals without the need for gaskets. The new resin was cured again for five hours at 100°C. Long processing times and low conductivities, around 3 S/cm, have made these epoxy composites unsuitable so far. [6]
Experimental results from a vinyl ester resin have shown more promise. To produce this type of bipolar plate, a liquid mixture is made of vinyl ester, graphite particles, and other catalyst or reinforcing fiber additives. This mixture is then compression molded under a pressure between 1000 and 2000 psi. With a good choice of temperature and catalyst for the resin, cure times can be less than ten minutes. Experimental results have shown the conductivity of a 75% graphite mixture to be 85 S/cm with a flexural strength of 38 MPa. [6]

An attractive composite using phenolic resin was developed by P. H. Maheshwari et al. The first step to making the composite involved creating a carbon fiber mat by paper making technology not discussed in detail. The mat was then coated in a slurry of phenolic resin, carbon black, and graphite powder dissolved in an acetone solvent. The mixture was dried and placed in a die mold where it was cured at 150°C for one hour. The composite contained 25 volume percent phenolic resin and 65 volume percent natural graphite powder. The remaining 10 volume percent consisted of varying amounts of carbon fiber and carbon black. [7]

Figure 1.4: SEM images of a) initial carbon fiber mat and b) fractured surface of 7.5 vol-% carbon fiber composite plate. [7]
Reported results showed that the composite with 2.5 volume percent carbon fiber had a conductivity of 309.6 S/cm and a flexural strength of 55 MPa. As the amount of carbon fiber increased to 10 volume percent, the conductivity dropped to 213.7 S/cm and the flexural strength rose to 82 MPa. It was noted, however, that no improvement in flexural strength was seen past 7.5 volume percent carbon fiber. The density of these composites was around 1.9 g/cm³. [7]

Thermoplastic composites generally involve graphite powder or carbon black. These composites are compression molded or, occasionally, injection molded. Price can be reduced by adjusting and optimizing processing procedures. Factors such as particle size and amount affect a balance between conductivity and mechanical properties. [6]

One thermoplastic that has been investigated is polyvinylidene fluoride (PVDF). Mixtures with varying loadings of graphite powder between 74% and 84% were blended for 25 minutes. The mixture was then compression molded at 300°C and 2000 psi. Conditions were then adjusted to 400°C and 300 psi and again adjusted to 290°C and 2000 psi. The 86% graphite mixture had a conductivity of 277 S/cm and a flexural strength of 9 MPa. The 74% graphite mixture had a conductivity of 119 S/cm and a flexural strength of 20 MPa. An alternate mixture was prepared with 64 weight percent graphite and 16 weight percent carbon fiber. This mixture had a conductivity of 109 S/cm and a much improved flexural strength of 42.7 MPa. [6]

Polypropylene and polyphenylene sulfide resins have been used to form composites with graphite powder and carbon black. Injection molding was used to form bipolar plates of these composites. A mixture of 40 to 45 weight percent polypropylene, 16.5 weight percent carbon black, 33 to 38.5 weight percent graphite powder, and 4
weight percent carbon fiber was shown to have a low conductivity of 3 S/cm and a flexural strength of around 43 MPa. When the amount of carbon fiber was increased to 5.5 weight percent, the conductivity did not change, but the flexural strength increased to 52 MPa. A mixture of polyphenylene sulfide with graphite and 4 weight percent carbon fiber showed a conductivity of 10 S/cm and a flexural strength of 84 MPa. So far, these injection molded composites have conductivities too low to be used for bipolar plate applications. [6]

Some investigations have been done on liquid crystal polymer and graphite mixtures. Due to the low viscosity of the liquid crystal polymer, these composites could also be injection molded. To form the composite, a liquid crystal polymer was mixed with a small amount of thermoplastic binder and graphite powder or nickel coated graphite fibers. The amount of graphite ranged from 30% to 50%. The length of the graphite fibers varied from 0.3 to 1.3 cm with diameters between 5 and 40 μm. The mixture was dried for 12 hours before being placed in an injection molding machine to mold the plate. Conductivities as high as 100 S/cm have been shown, but no mechanical properties have been reported. [6]

Figure 1.5: Schematic of process to form bipolar plate from a wet lay slurry. [6]
Another more promising thermoplastic is a wet lay composite. The process to form a wet lay composite, shown in Figure 1.5, is similar to the process used to make paper because the component materials are mixed with water to form a slurry. First, polyethylene terephthalate or polyphenylene sulfide polymer fibers in the range of 13 to 40 weight percent are mixed with one weight percent water in a pulper to form the initial slurry. In the pulper, graphite powder is added in the range of 60 to 80 weight percent. If the composite has less than 60 weight percent graphite, it has insufficient conductivity. If more than 80 weight percent graphite is used, the composite loses mechanical strength. For reinforcement, carbon fibers or glass fibers are added in the range of six to nine weight percent. The mixture is then sent to another tank where microglass is added at one weight percent. The microglass helps to attach the graphite to the reinforcing fibers. Preferably, the mixing process is done in such a way that all components are distributed uniformly throughout. The water must then be removed from the slurry. The majority of water is removed through a filtering screen with a vacuum underneath. Using the screen in this manner forms an entangled layer of material. The material is then moved into an oven where the heat evaporates the remaining water and fuses the material by partially melting the thermoplastic. After this step, the material can be rolled for storage. Compression molding could be used to form plates from the wet lay material. A specific number of sheets are cut and stacked on top of each other inside a mold. The number of sheets is chosen so as to provide the desired thickness after molding. [6]

Experimental results using polyethylene terephthalate with 65 weight percent graphite powder and seven weight percent glass fiber have given conductivities as high as 230 S/cm. The flexural strength was measured at 53 MPa. A bipolar plate made of
polyphenylene sulfide, 70 weight percent graphite powder, and six weight percent carbon fiber gave even better results. The conductivity was measured at 271 S/cm and the flexural strength was 95.8 MPa. Thus, the conductivity and flexural strength from this composite plate meet DOE requirements in those areas. [6]

One problem with the polyethylene terephthalate is that it can degrade in the presence of water (hydrolysis). As a result, investigations have been conducted looking for a polymer and graphite powder mixture that could coat bipolar plate cores made of polyethylene terephthalate. This protective layer would need to provide chemical resistance and electrical conductivity. The processing temperature would need to be close to that of the polyethylene terephthalate core, and there would need to be good adhesion at the interfaces. Polyvinylidiene fluoride meets these requirements; as such, a powder form of it called Kynar 761 was chose for testing. A plate of Kynar mixed with 74 weight percent graphite powder alone exhibited a conductivity of 119 S/cm and a flexural strength of 37.2 MPa. A laminate composite of Kynar and polyethylene terephthalate showed better properties and a lower cost since the latter has a lower cost. Such a composite was made with an overall loading of 68 weight percent graphite, a skin to core ratio of 20 to 80 weight percent, and a Kynar to graphite ratio of 20 to 80 weight percent. This composite had a conductivity of 163 S/cm and a flexural strength of 54.4 MPa. Another composite was made with an overall loading of 66.5 weight percent graphite, a skin to core ratio of 10 to 90 weight percent, and a Kynar to graphite ratio of 20 to 80 weight percent. This composite had better results with a conductivity of 171 S/cm and a flexural strength of 60.2 MPa. Another advantage of these composites due to the formability of polyvinylidiene fluoride is that they have produced clean, well formed
gas channels when compression molded. Also, because of the low melting temperature of polyvinylidene fluoride, the processing temperature of the composite can be lower which leads to less cooling time and a shorter processing cycle. [6]

There are various polymers that have been investigated for use in bipolar plate composites. Each has advantages and disadvantages. Fluoropolymers such as polyvinylidene fluoride have the advantage of chemical resistance and hydrophobicity and the disadvantages of high cost and high viscosity. [3] The cost of solid powder polyvinylidene fluoride is between $8.50 and $11 per pound. [6] Liquid crystal polymers have the advantage of high heat resistance and low viscosity and the disadvantage of high cost. [3] The cost of liquid crystalline polymers is around $10 per pound. [6] Polyphenylene sulfide has the advantages of high heat resistance and low viscosity and the disadvantage of high cost. [3] Its cost is around $5 per pound. [6] Polypropylene has the advantages of low cost and ready manufacturability and the disadvantage of a long extrusion cycle. Polyphenylene has the advantage of high heat resistance and the disadvantage of the need for additional hardening. Phenolic resins have the advantage of low cost and the disadvantage of only medium heat resistance. Vinyl esters have the advantage of ready manufacturability and the disadvantage of only medium heat resistance with hydrolysis above 100°C. [3] Cost of vinyl esters are around $5 to $10 per pound. Polyethylene terephthalate has the advantage of low cost and the disadvantage of hydrolysis. Cost of this polymer is around $2 per pound. For comparison, graphite particles or flakes generally cost around $2 to $3 per pound. [6]
**Thermally Expanded Graphite**

A novel material that has been developed in the past few years is thermally expanded graphite (EG), also referred to as foamed graphite or exfoliated graphite. This material is produced by heat treating intercalated graphite compounds. In the typical procedure, acceptor-type graphite flakes generally between 0.3 and 5 mm in size are bathed in a sulfuric acid and oxidant system to form the intercalated graphite compound. In the second step, hydrolysis is performed on the compound. Finally, by exposing the intercalated graphite flakes to a sufficiently high temperature, the layers of graphite are pushed apart forming a foamed compound. There are several advantages to such a foamed compound. It has a low bulk density and a large specific surface area. It can be molded without the use of binders such as polymers. It is resistant to aggressive chemicals, and because it is graphite, it has a high electrical conductivity. [3]

One use of this foamed graphite is to form graphite foils without the need to make a polymer composite first. These foils maintain all the properties of natural graphite in addition to new properties like elasticity and plasticity. Traditional uses of this material so far have included sealants, resistance heaters, and protection from heat and radiation. There are some drawbacks to the graphite foil, however. It is permeable to hydrogen and it exhibits anisotropic behavior in its electrical and thermal conductivity depending on direction through the foil. Nonetheless, it is an appealing material because of the possibility of producing thinner plates. Also, because the foil is soft, it has a lower contact resistance than with rigid materials and it can be easily machined. [3] Since such graphite foil is used in other applications as sealants, it indicates that when used in a fuel
cell as bipolar plates, the need for separate sealing gaskets would be reduced. [7] Graphite foil has a low density even when compared with natural graphite. [3]

To make graphite foils usable as bipolar plates, their mechanical properties would need to be improved and their gas permeability reduced. Since the foils can be made thin, there is the option to make multilayer carbon composites. These composites would have inner layers made of harder carbon to prevent gas penetration. Another option is to use binders such as phenolic resins, epoxy resins, furan, or polyacrylates to create a composite. [3]

A few methods are available to make channels in graphite foils. In one method, multiple layers of the foil would be put together. The outer layers would have a stenciled flow pattern in them. A carbonizing adhesive would be used to bond the layers after being clamped together. More traditional methods such as stamping, molding, or cutting are also available. [3]

![Figure 1.6: A bipolar plate made of thermally expanded graphite.](image)

Use of EG for bipolar plates is not limited to foils. S. R Dhakate et al. experimented with compression molded plates composed of EG and novolac phenolic resin powder. Various ratios of graphite and phenolic resin were used. They were
ground for 30 minutes to mix the materials. The mixture was placed in a hot press that was slowly heated and then maintained at a temperature of 150°C. Fourier transformed infrared spectroscopy results indicated that the novolac phenolic resin has hydroxyl and methylene linkages that can facilitate connections and bonding with EG. [8]

Various tests were run on the plates produced by Dhakate et al. including density, hardness, conductivity, and flexural strength.

![Figure 1.7: Plots of density and Shore hardness with respect to EG composition. [8]](image1)

![Figure 1.8: Plot of the relationship between conductivity and EG composition. [8]](image2)
The bulk conductivity increased quickly with the addition of graphite to the phenolic resin. When the ratio was above 50% EG, the conductivity exceeded the DOE requirement of 100 S/cm.

![Figure 1.9: Plots of flexural strength and modulus with respect to EG composition. [8]](image)

The highest results for both the flexural strength and modulus were obtained in the 50% EG plate. The peak strength value was 54 MPa which is above the DOE requirement. [8]

Some other experimental results have shown bipolar plates made of thermally expanded graphite have a density of 2.1 g/cm$^3$, a flexural strength of 40 MPa, and an electrical conductivity of around 100 S/cm. [3] For a comparison, natural graphite flakes can have a conductivity as high as $10^4$ S/cm. [8]

X. Yan et al. compared the contact resistance of three different types of plates. The plate materials were pure graphite, metal composite, and expanded graphite. The metal composite plate consisted of a stainless steel supporting plate with layers of EG placed on the surface into which flow channels could be molded. The graphite plate contained machined flow channels. The EG plate was made with a thermosetting resin
and flow channels were stamped into its surfaces. Each plate was placed between gas diffusion layers, and various pressures were applied.

The results showed that the contact resistance decreased quickly as higher pressures were applied to the plate. In general, the EG plate exhibited slightly higher resistances. [9]

**Graphite and Carbon Composite Coatings**

Some initial investigations have been done into using carbon or carbon composite coatings to improve corrosion resistance of metal bipolar plates. A low cost and low density material such as aluminum or magnesium could be used to form a plate. Then a very thin layer of a conducting graphite-polymer mixture could be applied to the surface. One experiment used vapor deposition of graphite nanofibers to create a coating. The coating had the additional benefit of providing improved gas distribution because of better surface diffusion. Also, to improve conductivity of polymer composite plates, a coating of graphite could be applied to the surface. Often, electrical conductive fibers of carbon are embedded in a core and then coated with a carbon composite. The problem with these concepts is that manufacturing is difficult and expensive. [3]
Section 3: Electrodes

The membrane electrode assembly (MEA) is the heart of the PEMFC. It is composed of a proton exchange membrane sandwiched between two electrodes. An electrode consists of everything contained between the electrolyte membrane and the flow channels of the bipolar plate. Generally, an electrode contains a catalyst layer next to the electrolyte and a gas diffusion layer (GDL) next to the flow channels. [2]

Catalyst Layer

A catalyst layer is located on each side of the proton exchange membrane. It can either be applied to the membrane or the GDL. [2] The reactions in the cell occur around the catalyst particles in what are called triple phase zones. The triple phase zones are areas of intersection of gas-phase pores, the electrically connected catalyst, and the ion conducting electrolyte. The reactions only occur in these zones because they are the only areas prepared to handle the reactions. The pores supply the reactant in gas form. [1] These pores are normally on the order of a few hundred nanometers. [10] As the reaction occurs around the catalyst, the produced electrons are conducted from the catalyst into the electrically conductive network of the electrode. The ions that are produced in the reaction are conducted into the electrolyte. [1]

The optimization of a catalyst layer involves effectively distributing the available volume among the transport media for each the gas, electrons, and ions. Determining this
distribution is important in order to avoid transport losses that hurt cell performance. Meanwhile, the transport media must be configured such that each makes good contact at the catalyst particles. [2]

![Diagram of the configuration of the catalyst layer between the proton exchange membrane and the GDL. The transport of gases, protons, and electrons are illustrated.](image)

There are several requirements for the choice of catalyst in a fuel cell. The catalyst should have high mechanical strength, high electrical conductivity, high porosity, and high catalytic activity. The catalyst should also be resistant to corrosion and easily manufactured. Platinum is the best known and most commonly used catalyst for PEMFCs. [1]

Catalyst layer thickness is a parameter that must be carefully balanced. A thin layer allows better gas diffusion and better utilization of the catalyst. However, a thicker layer can hold more catalyst and contain more triple phase boundaries. Catalyst layers
are commonly between 10 μm and 50 μm in thickness. [1] One of the challenges to making commercially viable fuel cells has been reducing the catalyst loading. Platinum is an expensive material, so using less in a fuel cell can help to reduce the cost. [2] Some of the processes used to reduce the catalyst loading include sputtering and electrodeposition. These have successfully reduced loadings below 0.1 mg/cm². [11]

Most electrodes use a thin-film design. In such a design, catalyst particles are supported on larger carbon particles. A Nafion film binds the particles together. The presence of Nafion provides the necessary ion conducting pathways. The use of Nafion in the film has improved the performance of the catalyst layer when compared with previous designs such as the PTFE-bound layer. However, the Nafion layer is less durable. [2]

**Gas Diffusion Layer**

The gas diffusion layer serves several main purposes in the fuel cell. It provides strength to protect and reinforce the catalyst layer. It also conducts electrons from the catalyst layer to the current collecting bipolar plates. The conductivity is balanced with porosity which is needed to distribute the reactant gases to the catalyst layer. An increase in porosity decreases conductivity due to a reduction in electron pathways. One other role the GDL plays is water management within the fuel cell. [2]

The ability of a GDL to perform can be affected by a variety of factors. These factors include structure, porosity, hydrophobicity, hydrophilicity, gas permeability, transport properties, water management, and surface morphology. An understanding of properties such as these is important in order to characterize and optimize GDLs.
Hydrophobicity describes water expelling properties while hydrophilicity describes water retaining properties. These two characteristics must be balanced to maintain proper function of a fuel cell. [10] In order to work efficiently, the proton exchange membrane must stay hydrated. [1] The GDL helps water to reach and be held at the membrane. At the same time, water is constantly produced on the cathode side. If not removed, water can collect around the catalyst particles and prevent reactant gases from reaching them. Often PTFE is applied to the GDL to help control the movement of water. The downside of PTFE is that it is not electrically conductive and it can reduce the size of the pores. Thus, the use of PTFE must be balanced carefully with the other requirements of the GDL. [2] Over long term use, the water management capability of the GDL decreases leading to an increase in mass transport losses. This drop in performance is possibly related to the degradation of PTFE. [11]

Most often, GDLs are made from multiple layers of a porous carbon material. [10] The thickness of the overall layer normally ranges from 100 μm to 400 μm. [1] Most of the GDL contains macropores on the order of 1 μm to 100 μm. In addition to the macroporous layer(s) there is at least one microporous layer. The primary role of the microporous layer is to manage the movement of water. The microporous layer in the cathode ensures the product water is removed so that oxygen molecules can easily reach the reaction sites. [10]

Both woven and non-woven carbon materials can be used in constructing the GDL. [10] These include carbon cloth, felt, and paper. When the components of a fuel cell are combined, the various layers are put under a pressure due to the clamping force that holds the cell together. This pressure increases the mass transfer losses for both
woven and nonwoven materials. Under this pressure, the GDL can potentially cause high local stresses on the catalyst layer and the proton exchange membrane. [11]

Figure 1.12: SEM images of a GDL layer of carbon a) cloth, b) felt, and c) paper. [11]

S. Escribano et al. studied the effects of clamping pressure on carbon cloth, paper, and felt. Conductivity measurements showed a trend of decreasing resistance with increasing pressure. The measurements were conducted on a stack of 10 samples with and without PTFE and varied orientations of microporous layers. A single layer of carbon cloth had an area specific resistance of approximately 20 mΩ*cm². The carbon paper and felt had even lower resistances. [11]

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US patent 7,241,409 describes a process for creating a porous GDL from EG by using a sacrificial additive. It details various steps in the process of forming intercalated graphite, expanding it, and forming it into a flexible graphite sheet. In addition, it mentions that a resin may be used as a binder to improve the strength, stiffness, and moisture resistance of the sheet. Examples of such resins are acrylic-, epoxy-, and phenolic-based resins. The material used for the sacrificial additive can be mixed with the EG particles before or after expansion, depending on the thermal stability of the material. The sacrificial additive would be removed after the sheet is created to form a porous structure characteristic of a GDL. A solvent or the application of heat can be used to remove the additive depending on its properties. Some of the options for sacrificial materials are methylcellulose, paper fiber, buckminsterfullerenes, and microballoons made from materials such as pitch, polymers, and inorganic fibers. [12]
An opportunity exists to further this concept of using a sacrificial additive in fuel cell component construction. The goal of the present research is to experiment with combining the bipolar plate and GDL into a single component. Any time two separate objects are put into electrical contact, a contact resistance exists between them. Combining the bipolar plate and GDL would eliminate such a contact resistance. Besides eliminating contact resistance, use of readily available, low cost materials offers the ability to minimize the cost of the components. The combination of the components also means a combination of processes to form them which should reduce the cost as well.

The primary material for both the bipolar plate and GDL would be exfoliated graphite (EG) as described in [12] due to its low cost. EG has been investigated for use in numerous research projects such as those described in [8], [9], and [13]. The nature of the material makes it easily formable into various shapes through molding or pressing. It is commonly used in the making of seals and gaskets. Thus, the use of EG to make fuel cell components could reduce the need for additional gaskets within a cell. Sealing is important to ensure complete separation of the fuel and oxidant and thus the
electrochemical half reactions. Since EG is graphite, it would have a high resistance to corrosion while still maintaining a good conductivity.

In addition to EG, a binding resin would be used to improve the strength of the plate. Phenolic resin is such a resin that is readily available and has a low cost. Various literature [12, 8, 13, 14] describes its use in forming composites with EG. Phenolic resin was chosen as the primary binder for investigation in this research.

Flow channels in the bipolar plate exist between the plate and the GDL so that fuel can be distributed to the GDL. Often the channels are machined into the bipolar plate. With EG, the option exists of pressing or molding channels into the plate. [3, 9] In order to combine the bipolar plate and GDL as one component, a different method of forming the flow channels is required because the GDL would cover the surfaces of the plate into which the channels need to be pressed or machined. Use of a sacrificial additive offers a solution.

Application of a sacrificial additive as mentioned in [12] is useful not only to create a porous network for a GDL, but also to form flow channels within a plate. The planned flow channel pattern can be machined into a single mold. A sacrificial additive material or mixture of additives would be placed in the mold to form a flow channel insert. At least one of the sacrificial additives would need to be a polymer to make molding a reasonable possibility. When the bipolar plate and GDL combination are pressed from an EG mixture, the insert can be contained within the mixture such that it is trapped within the final plate. The sacrificial additive could then be thermally degraded or dissolved out of the plate leaving voids within the plate to serve as the flow channels. The final product would contain both a solid portion serving as the bipolar plate and a
porous layer serving as the GDL. Contained in between the layers would be the system of flow channels. Based on literature and patent searches of the terms “bipolar plate” and “gas diffusion layer,” there is no indication that a combination of these components through use of a sacrificial additive has yet been attempted.
Section 2: Materials

Exfoliated Graphite

Graphite is a form of carbon composed of multiple stacked layers. Each layer has covalently bonded carbon molecules arranged in a network of hexagons. The individual layers are commonly referred to as graphene. [15]

![Graphene layer and layer stacking](image)

Figure 2.2: Views of a graphene layer and layer stacking in graphite.

[15]

Carbon has a valence of four. When carbon atoms are arranged in the structure of a graphene sheet, each atom has only three permanent bonds. [15] Each atom takes on an sp²-hybridized orbital configuration. [16] The presence of only three bonds leaves one electron from each atom to become delocalized across the entire sheet. This delocalization gives graphite very good electrical conductivity because the electrons are free to move around the sheet. However, the direction of the conductivity in graphite is
limited to the two dimensions of the sheet. The delocalization affects each sheet individually and does not contribute to the movement of electrons between sheets. [15]

Exfoliated graphite (EG) is known by several other names including expandable graphite, thermally expanded graphite, intercalated graphite, and intumescent flake graphite. EG is formed using an intercalation process in which graphite particles or flakes are saturated with an intercalant material. Molecules of this material become inserted between the individual graphene layers in the crystal of the graphite particle. A variety of materials can be used as intercalants, but one of the most common is sulfuric acid. In addition to the acid, other oxidizing agents may be used to serve as catalysts. EG has found a wide variety of applications including gaskets and sealants, conductive fillers, fire retardants, and electromagnetic pulse and radiation shielding. [17]

The goal of intercalation is to give the treated graphite flakes the ability to undergo a volumetric expansion when exposed to heat. A simply way to visualize the expansion process is to consider the intercalant to be in the solid or liquid phase. The particles are locked in place between the graphene layers. High temperature from rapid heating causes the intercalant compound to vaporize. As it enters the gas phase, the intercalant expands by a factor of 1000. The pressure from the expansion delaminates and pushes apart the adjacent graphene layers. This process is illustrated in Figure 2.3. The resulting expanded flakes are sometimes referred to as worms because of their long twisting shape. [17]
Figure 2.3: a) The placement of intercalation compounds between graphene layers, and b) the expansion of the intercalation agent to exfoliate the layers. [17]

Figure 2.4: Scanning electron microscope (SEM) image of natural, unexpanded graphite flakes. [17]
During exfoliation, the volume of the graphite flakes increases by a factor of up to 300. With the increase in volume, the density decreases. The true density of an exfoliated graphite flake is around 2.2 g/cm³. However, the observed density of the bulk material is much lower due to the tangling of the worms and the resulting open space between uncompressed worms. [17]

The exfoliation process increases the surface area by a factor of ten. Increased surface area means that the expanded material has an increased chemical reactivity and thus, oxidizes more readily than normal graphite. [17] Oxidation of the graphene layers includes more than just the formation of carbon dioxide. Oxygen-based functional groups can attach to the exposed edges of the graphene sheets. These groups include hydroxyl, carboxyl, carbonyl, and epoxide functional groups. They can attach to both the basal and edge planes. Besides simply limiting the available conduction pathways for electrons, these functional groups can reduce conductivity by altering the graphene structure. The presence of the groups can shift the normal, planar, sp²-hybridized
geometry of the graphene to a distorted sp$^3$-hybridized structure. This bond structure takes away the delocalized electron present in the sp$^2$ structure. [16]

A variety of factors can affect the rate and extent of expansion of exfoliated graphite. These factors include the material and process used for intercalation, graphite particle size, temperature, and heating rate. [17]

To reach the maximum potential for expansion of a particular grade of intercalated graphite a rapid heating rate must be used. A slow heating rate results in little or no expansion. The expansion process uses the forces created by sudden vaporization of the intercalant. There is a threshold pressure that the gas must reach in order to cause expansion. If heat is applied slowly, the intercalant gasifies more gradually and does not exert as high of a force on the graphene layers. [17]

The size of the starting particles or flakes can have just as much of an impact on expansion as the rate of heating. In general, there is a directly proportional relationship between particle size and expansion ratio. The only space through which the vaporizing intercalant particles have to escape is at the edge of a flake between the graphene sheets. A flake can be modeled as a disk or cylinder of radius $r$ with a spacing between layers of height $h$ as illustrated in Figure 2.6. A circular assumption is a reasonable approximation since flakes actually tend toward a similar hexagonal shape. Also, assuming no defects, $h$ is constant at 3.35 Å. [17]
Figure 2.6: Diagram of the geometry of a graphite flake when modeled as a cylinder. [17]

With the disk model, the volume that the intercalant occupies is

\[ \pi r^2 h. \]  \hspace{1cm} \text{Equation 2.1}

The total area around the edge of this volume that gaseous intercalant has to escape is

\[ 2\pi rh. \]  \hspace{1cm} \text{Equation 2.2}

The ratio of escape area to occupied volume is then

\[ \frac{2\pi h}{\pi r^2 h} = \frac{2}{r}. \]  \hspace{1cm} \text{Equation 2.3}

The ratio of 2/r shows that as the radius decreases, the relative area for gaseous intercalant to escape increases significantly. This geometric analysis reveals that smaller particles provide a more efficient pathway for the intercalant to escape as it vaporizes. Easy escape prevents the necessary pressure buildup to push the graphene layers apart and limits expansion. [17]

For the present research, expandable graphite flakes have been obtained from Asbury Graphite Mills, Inc.
Phenolic Resin

Phenolic resin is a thermoset polymer that helped to give birth to the synthetic polymer industry in the early twentieth century. [18] A thermoset is a class of polymeric materials. Such materials are initially solid or liquid at room temperature. When sufficient heat is applied, a thermoset experiences a brief drop in viscosity before hardening. This hardening is called curing. The key to thermosets is that after they are cured and cooled, they do not melt upon the reapplication of heat. Therefore, they cannot be reshaped. [19]

Phenolic resin is formed from the reaction between the phenol and aldehyde families of compounds. The characteristic of phenols is that they have a hydroxyl group bonded directly to an aromatic ring. The most common compound in the phenol family that is used to produce phenolic resins is phenol. [18]

![Diagram of a phenol molecule](image)

Figure 2.7: Diagram of a phenol molecule. It consists of a hydroxide ion attached to a benzene ring. [20]

Pure phenol has a melting point of 40.9°C, but mixing with water can lower that temperature. For every 0.1% water in a mixture with phenol, the melting point is lowered approximately 0.4°C. For the production of phenolic resin, phenol is typically mixed with water in a 90% to 10% ratio which makes it a liquid at room temperature. There is a limit to how much water can uniformly be mixed with phenol at room temperature.
However, when the mixture is heated above 65.3°C, water and phenol can be mixed in any ratio. [18]

Formaldehyde is the only aldehyde used for the production of any standard phenolic resins. Formaldehyde is a colorless, pungent, and toxic gas whose chemical formula is CH₂O. For industrial and commercial applications, it is commonly dissolved into an aqueous solution. [18]

![Diagram of a formaldehyde molecule.](image)

Phenolic resins are formed through step-growth polymerization of monomers. The monomers specifically used are phenols which have an average functionality of 2.31 and formaldehyde which is a difunctional monomer. There are three stages in the overall process to produce phenolic resin. The first step is the addition of formaldehyde to phenol. The next step is the chain growth or prepolymer formation. The last step is the curing process in which the polymer chains are cross-linked to form the final thermoset product. [18]

The temperature and pH under which the polymerization reactions occur have a significant effect on the properties of the final product. The rate of the reaction between phenol and formaldehyde is proportional to ion concentration. When the reaction is carried out in a solution that has a pH between 1 and 4, the hydrogen ion is the controlling factor. However, at a pH of 5 and above, there is a change in the reaction mechanism. The hydroxyl ion concentration affects the rate at those higher pH values.
The difference in reaction mechanisms means that two different prepolymer types can be formed that are referred to respectively as novolacs and resoles. [8]

Curing is a progressive polymerization process characterized by cross-linking of mostly linear polymer chains. The occurrence of cross-linking leads to gelation. The individual polymer molecules combine to form a large scale network and a macroscopic molecule. At this point, the system loses fluidity because the gel is insoluble. [18]

In phenolic resins, the most common site for cross-links to form is the methylene bridge because it is the most thermodynamically stable site. [18]

![Diagram of the cross-linking in a phenolic resin.](image)

Theoretically, a ratio of 1.5 mol of formaldehyde to 1 mol of phenol would be needed for thorough, three dimensional cross-linking. However, as cross-linking proceeds and molecule size increases, formaldehyde is unable to access some reactive sites because of limited space and molecular shielding. Typically, excess formaldehyde is supplied in commercial resins. [18]
For some commercial applications, a supply of an uncured resin mixture is desired. When such a mixture is provided, it can be cured through the application of heat and pressure. Three steps occur in this curing process. These steps in order are melting, flow, and gelation. For heat curing, typical temperatures range between 130°C and 200°C. [18]

Phenolic resin based on phenol and formaldehyde is recognized as a temperature resistant polymer. However, it will degrade with sufficient heat. The degradation can be divided into three stages. These stages are characterized by changes in weight and volume. [18]

The first stage occurs with heat application up to 300°C. Minimal amounts of gases are released which include water vapors and unreacted monomers left over from prepolymer formation. The second stage occurs between 300°C and 600°C where decomposition begins. Scission occurs randomly in the polymer chains, but complete depolymerization does not occur. Gases consisting of water, carbon monoxide, carbon dioxide, methane, phenol, cresols, and xylenols are released. There is minimal loss in volume, but porosity increases. In the final stage above 600°C, a majority of the remaining gases are released from large-scale breakdowns in the polymer. These freed compounds include carbon dioxide, methane, water, benzene, toluene, phenol, cresols, and xylenols. Density of the remaining solid increases as volume and porosity decrease. Electrical conductivity has been shown to increase when temperatures reach 600°C to 700°C. [18]

Bakelite phenolic resin granules from IASCO are used for the present research. This is a form of uncured phenolic resin. The raw material ranges in size from a fine
powder to over a millimeter in diameter. Phenolic resin was selected for use as a binder due to its low cost and common use as a binder in research of graphite composites. [8, 12, 13, 14]

**Polypropylene Carbonate**

Polypropylene carbonate (PPC) is a colorless amorphous thermoplastic. [23] A thermoplastic is a polymer that is solid at room temperature. Application of heat causes the plastic to soften or melt. Unlike thermosets, a thermoplastic can be shaped or reshaped at any time by simply heating and cooling the material. There is no curing to change the structure of the polymer. [19] The appeal of PPC is that it can degrade and burn uniformly and quickly at relative low temperatures. Since it leaves minimal ash residue after burning, it is a useful material for binder and sacrificial additive applications. The products remaining after degradation, mainly carbon dioxide and water, are not toxic to the environment. [23]

PPC is formed from the reaction of an epoxide, such as propylene oxide, with carbon dioxide in the presence of metallic catalysts, such as double metal cyanide catalyst. [23, 24]

![Figure 2.10: Diagram of the chemical reaction used to produce PPC.](image)

The selection of the catalyst and processing system can produce a very pure product which leads to simple and clean burnout. [23]
The glass transition temperature of PPC is around 37°C. Thermal gravimetric analysis experiments have shown degradation to occur consistently above 200°C. [23]

A sample of polypropylene carbonate was obtained for testing from Novomer. The material was an opaque white with a soft, foam-like texture. The size of the particles varied from a fraction of a millimeter to approximately 3 millimeters across. One disadvantage of PPC compared with other materials investigated in this research is its cost. The price is around $100/lb.

**Polystyrene**

The characteristic of the polystyrene is an attached benzene ring to the carbon polymer backbone.

![Figure 2.11: Repeating unit of polystyrene.](image)

The addition polymerization mechanism is used to form the polymer chains of the bulk material. The large size of the benzene ring attached to the carbon backbone limits the ability of the molecule to bend or form into any large scale organized pattern. Since crystallinity in a polymer relates to an organized series of bends, polystyrene is entirely amorphous. Polystyrene is colorless and transparent because light passes through its amorphous structure with minimal refraction. [19]

A yellow flame and dark, soot-filled smoke are characteristic of burning polystyrene. It burns easily since the aromatic rings are attached to the polymer backbone and not directly within it. The onset of glass transition begins around 100°C.
Thermal decomposition occurs above 250°C, but some degradation may be observed with sustained temperatures as low as 150°C. [19]

Polystyrene pellets were obtained from IASCO. They were colorless and transparent with a smooth and hard texture. The pellets had a consistent size distribution around 2 millimeters.

**Polyvinyl Alcohol**

Figure 2.12: Structure of the repeating unit of PVA. [26]

Polyvinyl alcohol (PVA) is a water soluble polymer. Water is a polar solvent and PVA is a polar molecule. This behavior agrees with the traditional chemistry expression of “like dissolves like” referring to the interaction between similar types of compounds. [19]

The first stage of interaction between a solvent and a polymer of similar type involves swelling. Because the chemical nature of the two compounds is similar, hydrogen bonds or van der Waals forces form at certain sites along the polymer. The bonding forces cause solvent molecules to cluster around these sites. Gathering of a large amount of solvent can push open the structure of the polymer. As the individual polymer chains are pushed apart, the bulk material begins to swell. This swelling process is also called plasticizing. It is a method sometimes used to making stiff polymers soft and pliable for processing. [19]

For some polymers and solvents, their similarity is so great that their interaction continues beyond swelling. As solvent molecules continue to gather around the
energetically favorable sites in the polymer, they can exert sufficient force to break secondary bonds between adjacent polymer chains. The breaking of these bonds allows the individual chains to become disentangled and to move apart. The polymer is considered dissolved once the polymer molecules can move freely with respect to each other. This is the process that occurs when PVA dissolves in water. [19]

**Sodium Chloride**

Sodium chloride, or salt, is an ionic compound that is readily soluble in water. The sodium chloride used in the present experiments was obtained from two sources. The large grain salt was produced by Gordon Food Services. The small grain salt was produced by the McDonald’s Corporation. Both contained some minor additives in addition to the basic sodium chloride. Since the salt was ultimately to be dissolved out of the samples, these additives were not considered to be a major factor.
Section 3: Material Preparation

Exfoliated Graphite

The expandable graphite flakes used for the present experiments were obtained from Asbury Graphite Mills, Inc.

Figure 2.13: Expandable graphite flakes before expansion.

The flakes were expanded in a Lindberg tube furnace that was preheated to 1050°C. For each batch of graphite expanded, a few grams of unexpanded flakes were placed in one of the furnace’s quartz tubes. The tube was shaken so as to disperse the flakes along the length of the tube. The tube was then inserted horizontally into the tube furnace. Having the furnace already at temperature allowed for a maximum heating rate and thus a high expansion ratio. The tube furnace was located under a fume hood for removal of the acidic vapors released during expansion. A temperature as high as 1050°C was not necessary for expansion, but it was set to compensate for a temperature drop with insertion of the tube. A minimum temperature of 700°C was desired for expansion.
Layers of oxidation can inhibit conductivity by limiting the electron pathways. Conduction in samples made of compressed worms relies on contact between the worms. A coating of oxidation can create a contact resistance among worms within a sample.

Initial batches of EG were expanded with heating for 1 to 2 minutes under a normal atmospheric air mixture. Since exfoliated graphite is more susceptible to oxidation than natural graphite especially at higher temperatures, later batches were expanded with nitrogen or argon flowing through the tube. The goal of the inert atmosphere flow-through was to limit the amount of oxygen in the tube during expansion and thus, reduce oxidation.

The setup for the inert gas flow-through involved connecting a pressurized tank of the gas, nitrogen or argon, to the tube containing the EG. The quartz tubes used for the tube furnace were longer than the furnace itself. This allowed the ends of the tube to be kept outside of the furnace. One end of the tube was sealed with a compressed piece of high-temperature insulation. A small PTFE tube was passed through this insulation to introduce the inert gas into the larger quartz tube. PTFE was used due to its resistance to
deforming or degrading at high temperatures. Since the end of the quartz tube was kept outside of the tube furnace, the PTFE was not subjected to the full heat of the furnace.

The PTFE tube was connected to the gas tank through a control valve. The opposite end of the quartz tube was closed off with a piece of insulation to prevent escape of the EG as it expanded. A small gap was left in this insulation to allow the flow-through gas and evolving acid vapors to escape the tube. Since this end was also outside of the tube furnace, the gases could escape directly to the fume hood.

In a further attempt to limit oxidation, a few batches of expanded graphite were kept in the furnace for an additional 30 minutes. The extended heating time was investigated for the possibility of removing or burning away any oxidation that was not initially prevented.

Expanded graphite worms were not the final desired form of graphite for fuel cell components. They were simply one stage to make further production steps easier than they otherwise would be with natural graphite. EG was compressed into stronger and more compact samples for experimental investigation. The pressing was similar to the process that would be used for actual commercial production of fuel cell components.

**Phenolic Resin**

Bakelite phenolic resin granules from IASCO ranged in size from a fine powder to over a millimeter in diameter. For some initial trials, unaltered granules were used when mixing with the EG. In an attempt to obtain a better distribution of the phenolic resin throughout the EG, the particle size was reduced. A coffee grinder was used to grind the mixture of granules entirely to a fine powder.
Mixing

Obtaining a sufficient mixture of phenolic resin with the EG was one of the primary challenges faced in the preparation of samples. Initially, a magnetic stir bar was used to mix the desired ratio of phenolic resin and EG. Total amounts, mixing time, and mixing speed were varied in an attempt to obtain an even distribution. However, because of the difference in particle size and density between the phenolic resin and EG, the phenolic would tend to settle to the bottom of the beaker. Both the larger granule form and the reduced-size powder form of the phenolic resin were used in trials.

For trials where the plate-making assembly was used, the phenolic powder and EG were mixed by hand. Alternating between the two materials, EG and phenolic were added in pinches to the assembly. Slight agitation was used to encourage further mixing. The agitation was either shaking of the assembly or shifting the material with a mixing spoon. Ball milling was also attempted as a mixing method.
Section 4: Measurement Methodology and Calculations

Conductivity

Conductivity tests are used as the primary quantitative method of evaluating samples produced in this research. In basic terms, conductivity is inversely proportional to the resistance of a material and also takes geometry into consideration.

\[ \sigma = \frac{L}{RA} \]  

Equation 2.4

The conductivity is represented by \( \sigma \), and \( R \) is the resistance. The sample’s length over which the charge carriers move is \( L \), and the sample’s cross-sectional area is \( A \). [1]

Conductivity is a measurement of the ability of a material to allow the movement of charges through it when under the influence of an electric field. There are two main factors that affect conductivity. They are the number of charge carriers present in the material and how easily those carriers can move about. The equation which shows the relationship of these factors for a particular charge carrier is

\[ \sigma = |z|Fcu \]  

Equation 2.5

where \( c \) is the molar concentration of the charger carrier and \( u \) is its mobility within the material. Faraday’s constant, \( F \), is used to convert the charge number, \( z \), of the charge carrier to coulombs. For the components of a fuel cell, both electrons and ions must be considered for charge carriers. Not only does the structure of the material affect
conductivity, but also the conduction mechanism, which varies significantly between electronic and ionic conduction, plays a role. [1]

In the free-electron model for electron conduction, valence electrons become detached from the atoms in a metal’s lattice. The electrons freely shift through the metal while the ions remain in place. The readily available collection of detached electrons can easily move when an electric field is applied. [1]

Ion conduction in a crystalline lattice uses a hopping mechanism. The lattice contains both positively and negatively charged ions. Ion conduction relies on a migration of defects from one site to another in the crystal lattice. These defects can be vacancies, missing atoms in the lattice, or they can be interstitials, extra atoms between lattice sites. The nature of this mechanism leads to much lower carrier concentrations and mobilities for ions than for electrons. [1]

**Conductivity Measurement**

Since conductivity is directly related to resistance, determining the conductivity of a sample involves measuring its electrical resistance. Resistance can be found by using Ohm’s Law.

\[ R = \frac{V}{I} \]  

Equation 2.6

When a known current, I, is sourced across a sample, a voltage, V, results and can be measured. From these two values, the resistance, R, can be calculated. [27]

When measuring a conductive material, the resulting voltage is very small. For low signal levels, offset voltage and noise can impact the measurements. Thus, caution must be taken to reduce these quantities. With a normal DC stimulus, the actual measured voltage is more than just the desired induced voltage across the sample. It also
contains components of lead and contact resistance, thermoelectric voltage, white noise, and other 1/f noise contributions. [27]

Lead resistance, which would be measured by the voltmeter across the source leads, is eliminated by instead using four separate leads. Two leads would be attached to each side of the sample, one for the current source and one for the voltage measurement. Also, choosing appropriate equipment and applying filters can reduce signal noise. Compensating for thermoelectric voltages tends to be more difficult, and these voltages present the greatest challenge to low voltage measurements. [27]

Thermoelectric voltages can cause offset and drift errors in measurements. Any point in an experimental setup where dissimilar metals touch forms a thermocouple. When one of these junctions encounters a temperature difference, voltage errors are introduced to the circuit. Rapidly changing thermoelectric voltages can even exceed the magnitude of the desired voltage measurement across the sample. Sometimes simply increasing the applied current can negate the thermoelectric errors. However, increased current may also raise temperatures in the circuit or sample which then changes resistance values. [27]

A change in the measurement technique offers a way to improve accuracy. Measuring voltage at both a positive and negative test current can cancel a constant thermoelectric voltage. The variation of the test current is referred to as a delta reading. This variation also increases the signal-to-noise ratio which reduces susceptibility to noise. When the thermoelectric voltage is not constant, a similar technique can be used. Thermoelectric drift can be treated as a linear function whose slope can be determined from consecutive voltage readings. Since the slope is constant, it can be eliminated by
making two delta measurements which involves alternating the current source two times. In order to approximate the function as linear, data must be collected using a rapidly alternating current source, and the voltmeter must be able to make accurate voltage measurements in a short time interval. [27]

For the present conductivity measurements, a Keithley 2400 SourceMeter was used as the current source, and the voltage was measured by a Keithley 2182A Nanovoltmeter. These devices were run in conjunction to perform delta measurements by alternating quickly between positive and negative currents. Groups of samples were taken to the facility containing the equipment four separate times. The equipment was turned on at least two hours prior to testing to allow adequate warm-up time for uniform temperature of the measuring devices.

Through-Plane Conductivity

There are two types of electrical conductivity that are measured for fuel cell components. These types relate to the direction of conduction and require different experimental techniques to measure each.

Through-plane conductivity is the conductivity of electrons directly through a sample from one side the other. Through-plane conductivity was measured by placing each sample within a specialized assembly. The assembly was sized to fit a sample of one square inch and variable thickness. Thus, all of the samples tested were cut to fit within the assembly. Because of the destructive nature of this type of test, the through-plane conductivity test was the last test done to each sample.

The assembly contained electrically insulative plastic around the sample. A copper plate measuring one inch by one inch touched each face of the sample. A current
source wire and voltage probe were attached to each copper plate. For the first set of
tests, this assembly was not used because it had not yet been fabricated. Instead, just the
copper plates were used with the wires attached. Electrical tape held the plates around
each sample and insulated them as they were being pressed.

For the first round of tests, carbon fiber sheets were placed between the sample
and each copper plate. Carbon sheets are sometimes used in conductivity testing to
improve contact between a sample and the plates used for measuring. The sheets were
not used in later tests because the softness of the samples ensured good contact with the
plates. The presence of the sheets also introduced the possibility of additional contact
resistance that could affect the measurements.

The measurement assembly with a sample inside was placed within a Carver
hydraulic press. The nature of the assembly allowed for a force to be applied to it and
transmitted directly to the sample inside. The sample was put under a force of 1000
pounds (lbf) for the measurements.

For most samples, five conductivity measurements were taken. Between each
measurement, the force from the press was released and reapplied. For each voltage
measurement recorded by the voltmeter, at least 100 data points were taken and averaged
by the meter. For initial measurements, 500 data points were taken. However, because
there was little variation among the individual data points, the number of points was
reduced to 100 for later measurements.

Through plane conductivity is ultimately calculated by combining equations 2.4
and 2.6.

\[ \sigma = \frac{L \cdot I}{A \cdot V} \]

Equation 2.7
Here, L is the thickness of the sample, and A is the contact area between the sample and the copper plate.

For the first, third, and fourth sets of measurements, the voltage was also measured across the equipment without a sample present. This measurement was taken to determine the system resistance that was separate from the sample. The system resistance was then subtracted from the resistance given by Equation 2.4 for each trial. The conductivity was calculated from this adjusted resistance using Equation 2.6.

For the second set of measurements, a different method was used to determine the system resistance. Two pure EG samples of different thicknesses were both tested. A plot of their average resistance versus thickness was created. The plot was extrapolated to find the y-intercept which should be the theoretical resistance as thickness approaches zero. The system resistance with this method was found to be 3.22 mΩ.

<table>
<thead>
<tr>
<th>thickness (cm)</th>
<th>R_avg (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.086</td>
<td>0.003636</td>
</tr>
<tr>
<td>0.295</td>
<td>0.004646</td>
</tr>
</tbody>
</table>

Figure 2.15: Values used for the calculation of the system resistance.
Both methods of determining the system resistance should yield reasonable and comparable values. The direct measurement value was preferred for most trials because it was an actual experimental value. Also, the plotting method requires having at least two samples of the same consistency and different thicknesses each time the calculation is to be performed. Such samples were not available for each set of measurements.

**Bulk Conductivity**

Bulk, or in-plane, conductivity relates to the movement of electrons across the surface of a sample. Measurement of bulk conductivity requires a more complicated physical setup than through-plane conductivity. Commonly a four point probe is used. The probe contains four in-line metal points that are touched to the surface of a sample. The current is applied across the two outermost probes while the voltage is measured across the two innermost probes. [28]

Bulk conductivity was measured by a Lucas Labs 302 Resistivity Stand.
The four point probe was connected to the Keithley 2400 SourceMeter, which provided the source current, and the Keithley 2182A Nanovoltmeter, which measured the output voltage.
At least five measurements were made on each face of each sample by touching the four point probe to both the top and bottom sides of the samples in various locations. Similar to the through-plane conductivity tests, each voltage measurement recorded by the voltmeter averaged least 100 data points. For initial measurements, 500 data points were taken. However, because little variation was seen among the individual data points, the number of points was reduced to 100 for later tests.

The equation used for calculation of bulk conductivity can vary depending on the shape and geometry of the sample being tested. For an infinitely large and thin sample, bulk conductivity is calculated from the equation

$$\sigma = \frac{1}{\ln 2} \cdot \frac{\pi \cdot cf \cdot V}{I \cdot L}$$

Equation 2.8

where $V$ is the measured voltage, $I$ is the provided current, $L$ is the thickness of the sample, and $cf$ is a correction factor. The derivation of the conductivity equation and the resulting final equation varies for different sample dimensions, shapes, and positions of probes. [30]

The correction factor is based on the dimensions of the sample and is a function of the ratio of the thickness of the sample to the spacing between individual probe tips. It approaches 0 for an infinitely thick sample and 1 for an infinitely thin sample. The availability of different equations and the use of a correction factor compensates for varying electron pathways when the edge of the sample is sufficiently near the location of the measurement. [30] For the present measurements, the correction factor was set as one based on the advice of Dr. James Guo in order to ensure calculation of conservative values.
Results from each test for through-plane and bulk conductivity were compiled and calculations were performed in Microsoft Excel. Standard deviation was calculated based on the program’s built-in equation

\[ sd = \sqrt{\frac{\sum (x - \bar{x})^2}{n-1}} \]

Equation 2.9

where \( x \) represents the measurements under consideration and \( n \) is the total number of measurements. The standard deviation was displayed as error bars on any plots used to relate conductivity among samples.
CHAPTER 3
Experimental Trials and Results

Section 1: Sacrificial Additives

Two options exist for a type of sacrificial additive, and these options relate to the method of removal of the additive. Material can be removed from within an EG sample by either thermal degradation or dissolution.

Thermal degradation involves heating the sample past a certain temperature at which the sacrificial material would begin to decompose and vaporize. The mass of the material is removed from the sample through the conversion to and evolution of the vapors. This method requires a pathway out of the sample for the vapors to escape.

Dissolution involves bathing a sample in a solvent such as water to dissolve the sacrificial material. As the solid dissolves, it disperses into the liquid solution and leaves the confines of the sample. This method requires access into the sample by the solvent in order to reach the material to be dissolved.

Flow Channels

Basic thermal degradation trials served as the first step toward investigating sacrificial materials for use as a flow channel insert. A variety of trials was run on several different materials. Ideally, degradation of the sacrificial material would occur
around 300°C or below in order to limit any degradation of the phenolic resin binder.

Thus, most degradation trials were run around 300°C.

A few pellets of material were placed on a piece of aluminum foil for each trial. The mass of the pellets and foil were measured before and after placement in the oven. The trials below 300°C were heated in a Cascade Tek vacuum oven because of the capability to vent the released gases to the fume hood. Trials at or above 300°C exceeded the capacity of the vacuum oven and were run in a nearby Lindberg oven. Samples were kept in the oven for at least 40 minutes to ensure adequate time for heating and degradation.

Figures 3.1 and 3.2 show the results of the degradation trials, indicating the temperature of the trial and the percentage by weight of the material lost.

<table>
<thead>
<tr>
<th>Temp °C</th>
<th>Change in Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-0.6</td>
</tr>
<tr>
<td>200</td>
<td>-0.6</td>
</tr>
<tr>
<td>250</td>
<td>-0.5</td>
</tr>
<tr>
<td>300</td>
<td>-39.4</td>
</tr>
<tr>
<td>350</td>
<td>-67.4</td>
</tr>
<tr>
<td>PPC</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>-10.3</td>
</tr>
<tr>
<td>200</td>
<td>-99.7</td>
</tr>
<tr>
<td>250</td>
<td>-99.7</td>
</tr>
<tr>
<td>280</td>
<td>-100.4</td>
</tr>
<tr>
<td>300</td>
<td>-100.2</td>
</tr>
<tr>
<td>LDPE</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>-22.2</td>
</tr>
<tr>
<td>PVA</td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>-37.5</td>
</tr>
</tbody>
</table>

Figure 3.1: Tabulated results of the thermal degradation trials.
Figure 3.2: Chart displaying the relation between temperature and percent mass lost due to thermal degradation.

The thermal degradation results indicate that PPC far exceeds the other materials in the temperature range investigated. At a temperature as low as 200°C, nearly all of the mass of PPC is removed as vapor. Only a small brown residue is left.

The polystyrene only begins degrading once the temperature passes 300°C. Higher temperatures than the desired range are needed for full degradation. PVA shows a similar weight loss at 300°C to that of PS. Low density polyethylene has minimal weight loss at 300°C.

In order to use a sacrificial material to create flow channels, the material must first be molded into a shape resembling the desired flow channel pattern. The resulting molded piece would then be placed as an insert within a mixture of material that is to be pressed into an experimental sample or plate.
The first attempt to mold flow channels involved a cross pattern (+) machined into an aluminum block. PVA powder was placed in the grooves of the mold and then the mold was placed in a Lindberg oven at 200°C. The powder did not melt into the channels. Instead it only began to carbonize and take on a brown color. This was the only time this mold was used because the trial indicated that pressure was also needed. All future experiments were designed such that both heat and pressure could be applied to the material being molded.

The next step in investigating sacrificial additives involved a mold to be used in the Buehler Simplimet 3 Mounting Press. A pure phenolic disk was first formed in the mounting press at normal pressing conditions of 150°C and 4200 psi for 2 minutes. Then a basic flow channel pattern was ground into the disk by hand with a Dremel rotary tool.

The mounting press was used because many of the initial sample trials were prepared in the mounting press. Thus, sizing was appropriate for testing of the inserts.

The mold was placed in the mounting press with a layer of silicone spray to serve as a mold release. The sacrificial material was then placed along the grooves of the mold. The press was set to a temperature appropriate for the material, and pressure was applied.
PPC, PS, and PVA were investigated with the mounting press mold. All three materials were pressed at 4200 psi for 5 minutes. A temperature of 100°C was used for PPC. A temperature of at least 110°C was used for PS. A temperature of 150°C, which matches the curing temperature used for the phenolic disk, was used for PVA.

Several PPC inserts were successfully formed using the mounting press mold. The temperature used was above the glass transition temperature for PPC, so with the application of pressure, the material filled the groves. After heating, the PPC took on a translucent appearance. Even after cooling, the insert remained somewhat flexible.

Only one PS insert was successfully formed with this mold. Once the PS cooled, it became very brittle, and it was difficult to extract the insert from the mold in one piece. The extraction had to be attempted while the material was still warm and somewhat flexible.

No usable PVA inserts were obtained as the particles of material did not fully merge within the channels. The insert was not uniform and crumbled when attempting to remove it from the mold. Higher temperatures were needed which means a material other than phenolic resin was needed for the mold.

Actual results of trials including the inserts within disks are described in Section 3.2 under the subheading *Flow Channels*.

Since some difficulty was encountered extracting molded inserts from the phenolic mold, another method of forming inserts with the mounting press was investigated. Several different materials were added without a mold to the mounting press with the intention of cutting a flow channel pattern out of the disk that would result from pressing. A mixture of two materials was tried in order to experiment with reducing
the amount of polymer needed. In such a situation, the sacrificial polymer also serves as a binder.

The first attempt involved placing a mixture of 50% PVA and 50% NaCl. Such a mixture would be dissolved out of a sample rather than thermally degraded. Minimal silicone spray was used for the mold release in an attempt to avoid dissolving some of the sample material before pressing. The resulting disk displayed a high adhesion to the pressing surfaces of the mounting press. Simple application of force would not separate the two metal pieces joined by the sample material. The pieces were removed from the mounting press and placed in a water bath to dissolve the sample. This did not remove much of the material. Some NaCl was dissolved and the PVA swelled. Eventually, a saw was used to cut the sample material out from between the press components.

Two more samples were made of a mixture of PVA and salt. The first was 10% PVA and 90% NaCl. Wax paper was used as a mold release to ensure easy removal from the mounting press. The resulting disk was too brittle to be cut and the wax paper adhered to it. The second sample used 20% PVA with 80% NaCl. Aluminum foil was used as a mold release. The edges of the disk crumbled as though there was not sufficient heat to cause the PVA to bind the material together at the edges. The center was more solid but still too brittle to cut. The distribution of PVA and NaCl across the disk did not seem uniform.

When portions of the 10% PVA disk were placed in a water bath, they never fully dissolved. Some soft clumps of polymer remained visible even after several days.

Another attempt to combine a polymer with NaCl was made with a disk composed from 30% PPC and 70% NaCl. It was pressed at 100°C and 4000 psi. The
PPC worked better as a binder than the PVA. The resulting disk was softer and easier to cut. This trial indicated that adding salt in a mixture with PPC would be an option to reduce cost. PPC is a moderately expensive material so using less would be advantageous. One problem is that the use of salt requires a second dissolution step in addition to thermal degradation.

In preparation to make plates that combined the various facets of this research, a mold was machined from 12L14 carbon steel that could form flow channel inserts for the plates. This steel was chosen based on the advice of machinist John Lawless because of its increased strength over aluminum.

![Figure 3.4: Flow channel mold to make inserts for plates.](image)

The mold was composed of two pieces. The lower half contained a simple flow channel pattern machined into it. The height and width of the channels were designed to be around 0.06 in. Small holes were drilled at the intersection of the channels to facilitate removal of the insert. The holes allowed a pushpin to be used to eject the molded part if necessary.
A simple cap was made to fit over the lower half of the mold both to contain the material being used and to apply pressure to force it into the channels. For mass production, a more complex and efficient injection mold design would likely be developed.

PPC was placed in the mold along the grooves. Silicone spray was used on both the upper and lower halves of the mold to ensure good release of the final part. The mold was pressed in the hot press at 2000 lbf for approximately 30 minutes. The temperature was set such that the mold was heated to around 100°C.

Two inserts were successfully made using the mold. The inserts were removed while the mold was still warm. They were flexible and pulled out of the mold without suffering any damage. The plates made with these inserts are described in Section 3.3 under the subheading *Cumulative Plates*.

Both the phenolic disk mold and the plate mold used channels designed to reach to the edge of the disk or plate sample. This was for evaluation purposes so that the channels could be seen without cutting open the sample. The flow channel pattern was
not actually designed to be functional in a fuel cell. It was only meant to simulate the basic geometry of flow channels.

**Porosity**

A sacrificial additive used for porosity needs to be in a powder form in order to offer the potential to create a network of pores. The powder would need to be mixed and distributed in a sample mixture in a manner similar to the phenolic resin. If too little powder is used, the resulting pores would not connect. Connection between pores is essential for migration of fuel through the layer.

The issue of creating porosity within samples was addressed after first investigating options for creating flow channels. The first material used for porosity related trials was PVA powder. Later experiments used NaCl. Both of these materials would be removed by dissolution in water. Actual trials with disks are described in Section 3.2 under the subheading *Porosity*.

Another material considered for porosity trials was PPC which would be removed by thermal degradation. The size of the larger particles and the overall particle size distribution in the sample PPC from Novomer were too large to make them feasible for use in creating porosity. A reduced particle size was necessary, so an attempt was made to grind some PPC in a coffee grinder to reduce the particle size. Due to the low density and foam-like nature of the sample, the material clung readily to the edges of the grinder making recovery of the material difficult. Also, the softness caused the particles to resist breaking when impacted by the blade. No useful powder was produced.
Section 2: Disks

Basic Trials

The initial approach to break down the problem presented by this thesis research involved gaining an understanding of mixing exfoliated graphite with phenolic resin as a binder. The mixing stage was followed by application of pressure and heat to the mixture to compress the EG and cure the phenolic resin. The resulting samples were designed to have the basic characteristics of a bipolar plate such as strength, impermeability, and conductivity.

Since the goal of the initial trials was to understand the behavior of the materials to be used, actual functional plates were not generated. Instead, a Buehler Simplimet 3 Mounting Press was used to form disks. The mounting press could be set to automatically apply pressure and heat. For most of the disk samples, the magnetic stir bar was used first to mix the EG and phenolic resin.

A naming convention was established to identify each disk sample. The convention was a simple $d$ for disk followed by a number. Numbers were assigned to the disks in the order in which they were made.

Common conditions used for curing phenolic resin in the mounting press are the application of a temperature of 150°C and a pressure of 4200 psi for 2 minutes. This pressure is the result of the application of force to a circular pressing ram with a diameter
of 1.25 inches. Most disk samples prepared for this research used these same conditions for their pressing.

The first several sample disks that were prepared experimented with variation of the ratio of EG to phenolic resin. The mixture for the first disk sample prepared, \( d01 \), contained 70% EG by weight and 30% phenolic resin granules by weight. All percentages given in this paper are assumed to be a percentage by weight unless otherwise stated.

The mixture for \( d01 \) was mixed with a magnetic stir bar for 2.5 hours. The EG worms were largely broken apart and compacted. The breaking apart of the worms introduced the concern that conductivity could be decreased since electron conduction relies on contact within the worms and between the worms. Most future samples were only mixed for 10 to 15 minutes to reduce breaking of the worms.

Breaking of the worms means more total particles are present in a sample which results in more contact points when the sample is pressed. An increase in the relative number of particles increases the likelihood of additional contact resistances within a sample. Keeping worms whole should provide better connections for electrons within the material.

At the edges of some of the disks, especially disks with a lower concentration of phenolic binder, striations were noticed. They appeared as gaps between layers in the material like a delamination effect. These gaps can hurt conductivity by decreasing available electron pathways in a sample.

Difficulties were encountered with the first few disks when attempting to remove them from the mounting press without damage. The disks would tend to stick to the
pressing surfaces. Efforts to remove them left some pieces of the disk surface behind. Additional silicone spray was used in future samples to minimize damage to the disk during removal. Damage and roughness on the surface would decrease bulk conductivity which relies on conduction at the surface.

The silicone spray had a strong smell, and this smell was detected on the sample disks even days after removal from the press. Since it appeared that some of the silicone spray was remaining trapped in the sample disks, concerns were raised that the silicone could be reducing conductivity. The silicone had opportunities to migrate in between mixture particles during pressing. The trapped spray could be obstructing electron pathways between the numerous EG particles in the disks. Thus, steps were taken to remove the excess silicone spray from later disk samples.

After pressing, the disks were placed in the vacuum oven at 115°C for at least 30 minutes. A partial vacuum was applied to the oven several times to encourage outgassing of the residual silicone spray. A strong odor of silicon spray was evident when the oven was opened after each removal attempt.

After the conductivity was measured in the first series of disks, a recommendation was made by Dr. James Guo to repress samples after taking them out of the mold. This would help to prepare the samples for through-plane conductivity tests and thus provide better accuracy. Also, use of the vacuum oven introduced the potential to deform samples slightly. If any air was trapped inside a sample when placed in the oven under vacuum, the pressure could push outward on the sample and deform the surface. Repressing of the samples would ensure compaction of the material and level out any deformations.
Most samples were repressed at 2000 lbf in a hydraulic press. For samples with minimal or no phenolic binder, repressing caused some material to be squeezed out and away from the disk at the edges. This occurrence was an indication of the reduced strength of samples with little or no binder.

The next series of sample disks experimented with properties besides simple component ratios. Some disks were made with EG that had been expanded under a nitrogen flow-through. Some disks had been placed in a vacuum oven to remove the silicone spray. Extended mixing was revisited for some mixtures using the magnetic stir bar for a duration of at least an hour.

One attempt was made to investigate the use of PS as a binder. PS pellets were ground in a coffee grinder. The resulting powder was mixed in with EG in a manner similar to the phenolic powder. Disks were pressed at both 200°C and 100°C. The corresponding pressures were 4400 psi and 2000 psi.

Figure 3.6: Picture of the surface of $d_{27}$ which was pressed at 200°C and 4400 psi.
The surfaces of the produced disks were very uneven. Noticeable depressions were present and were likely the result of the PS deforming and migrating during pressing. Once the PS would shift or disperse, the structure of the graphite around it would collapse.

**Flow Channels**

Flow channel inserts for investigation with disk samples were formed using the phenolic mold disk described in Section 3.1. The first disk to include a PPC insert was d12. It used a ratio of 70% EG with 30% phenolic resin. The insert was successfully pressed within the disk.

Following the pressing of the insert within the disk, the sample was placed in the vacuum oven for approximately 40 minutes to degrade the insert out of the disk. Although PPC could degrade around 200°C, the maximum temperature of the vacuum oven, around 280°C, was used in order to ensure sufficient heat to degrade the entire insert.

When the sample was removed from the oven, it was evident that the insert had been successfully removed. The sample was cut open to visually inspect the channels.
The channels were present through the entire sample. The inconsistent width shows how the insert deformed somewhat when heat and pressure were applied to form the disk.

Bulges were observed on the surface of the sample. It is possible that some bulging was caused by the vaporizing PPC. However, due to the location of the bulges and the temperature used, it is most likely that the bulging was the result of some components of the phenolic resin vaporizing and trying to escape. The binding strength of the phenolic should not have been affected because the vapors were probably unreacted materials left over from the initial resin formation.

Another disk was made with a PPC insert for conductivity testing. The insert was degraded out of the disk, and bulging occurred again. The disk was repressed at 2000 lbf to remove the bulges and prepare it for through-plane conductivity testing. The repressing crushed the flow channel voids.

One trial was run including a PS insert within a disk, d22. When the disk was pressed, the insert severely deformed and pushed out of the sample. The structure of the graphite over what would have been the flow channel collapsed during the initial disk pressing. Depressions matching the flow channel insert formed on the surface in a similar manner to the depressions formed from the trials with PS as a binder.
Porosity

A few trials were run investigating the potential for PVA powder to be used as a sacrificial additive to create porosity. For one of these trials, *d16*, a ratio of 70% EG and 30% phenolic resin powder was prepared. A weight of PVA equivalent to the weight of the other non-sacrificial components for the disk was added to the mixture. The components were mixed for 1.5 hours with the magnetic stir bar. After the mixture was pressed, the disk was placed in a warm water bath.

The problem with dissolving PVA is that it is a polymer with long molecules composed of many atoms. Before the polymer dissolves, the collecting of solvent molecules around the polymer chains causes the material to swell. [19] This is what happened in *d16*. 

Figure 3.8: Picture of the flow channel depression on the surface of *d22* resulting from deformation of the PS insert.
Swelling of the PVA occurred when the disk was placed in the water bath. The swelling caused severe distortion of the disk. Figure 3.9 shows the damaged disk after the water evaporated from the sample. The evaporation of the water reduced the swelling, but the damage remained.

Later trials investigated sodium chloride as an option to create porosity. Since NaCl is not a polymer, no swelling occurred when a water bath was used to remove it from the samples. One of the samples, d21, was made from a mixture of 70% EG and 30% phenolic. A total of four times the mixture’s permanent mass in large grain salt was added. The removal of the salt from d21 left behind a large network of open pores. However, as is evident from Figure 3.10, the salt was not evenly distributed within the sample.
It was determined from various trials, that the amount of powder needed to generate sufficient porosity is a mass more than equal to that of the permanent material of the sample. A perfect pore network was not formed, so the ideal amount of salt was not determined.

**Conductivity**

The conductivity from two different sets of disks was measured. The first set investigated the role of the ratio of EG to phenolic resin. The second set considered factors such as EG expanded under an inert atmosphere, mixing methods, and use of the vacuum oven. In the following figures, wt% is the percentage by weight, \( \sigma \) represents conductivity, and sd represents standard deviation.

For each sample on which conductivity tests were performed, bulk conductivity was measured first. The use of the four point probe did not cause damage that would
prohibit other testing from being done afterward. Bulk conductivity measurements were taken on both the top and bottom surfaces of each disk.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG</th>
<th>Top σ_avg [S/cm]</th>
<th>sd [S/cm]</th>
<th>Bottom σ_avg [S/cm]</th>
<th>sd [S/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>d04</td>
<td>50</td>
<td>16.4</td>
<td>1.3</td>
<td>52.6</td>
<td>5.5</td>
</tr>
<tr>
<td>d06</td>
<td>60</td>
<td>6.5</td>
<td>6.9</td>
<td>49.5</td>
<td>5.6</td>
</tr>
<tr>
<td>d03</td>
<td>70</td>
<td>43.7</td>
<td>5.6</td>
<td>66.9</td>
<td>8.0</td>
</tr>
<tr>
<td>d05</td>
<td>80</td>
<td>10.2</td>
<td>1.4</td>
<td>54.6</td>
<td>3.4</td>
</tr>
<tr>
<td>d07</td>
<td>90</td>
<td>38.5</td>
<td>4.2</td>
<td>51.8</td>
<td>13.7</td>
</tr>
<tr>
<td>d02</td>
<td>100</td>
<td>42.2</td>
<td>0.9</td>
<td>39.0</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Figure 3.11: Numeric tabulation of disk bulk conductivity as it varies with material ratios.

Figure 3.12: Plotted results of disk bulk conductivity as it varies with material ratios. Error bars indicate the standard deviation of each averaged point.

The bulk conductivity for each sample varied between the top to bottom surfaces. The reason for this variation was likely due to the inadequate mixing of the EG and phenolic resin. Size and density differences between the EG and phenolic resin caused
much of the phenolic resin to settle to the bottom of the container during mixing. When
the mixture was poured into the mounting press, there was then a higher concentration of
phenolic at the top of the sample. An increased ratio of phenolic resin reduced electron
pathways in the EG and decreased conductivity at the surface. As expected, the bulk
conductivity on the top and bottom of the sample without phenolic resin is nearly the
same.

<table>
<thead>
<tr>
<th>Sample</th>
<th>side 1</th>
<th>side 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>σ_avg</td>
<td>σ_avg</td>
</tr>
<tr>
<td></td>
<td>S/cm</td>
<td>S/cm</td>
</tr>
<tr>
<td></td>
<td>sd</td>
<td>sd</td>
</tr>
<tr>
<td>d08 70% EG, mix</td>
<td>112.1</td>
<td>128.6</td>
</tr>
<tr>
<td></td>
<td>7.6</td>
<td>6.6</td>
</tr>
<tr>
<td>d10 70% EG, N2, mix</td>
<td>84.6</td>
<td>75.5</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>8.7</td>
</tr>
<tr>
<td>d13 70% EG, N2, vac, ppc</td>
<td>119.8</td>
<td>122.9</td>
</tr>
<tr>
<td></td>
<td>8.7</td>
<td>3.5</td>
</tr>
<tr>
<td>d11 100% EG, N2</td>
<td>98.5</td>
<td>132.3</td>
</tr>
<tr>
<td></td>
<td>2.3</td>
<td>13.3</td>
</tr>
<tr>
<td>d14 100% EG, N2</td>
<td>286.3</td>
<td>265.9</td>
</tr>
<tr>
<td></td>
<td>14.2</td>
<td>23.5</td>
</tr>
<tr>
<td>d09 100% EG, N2, vac</td>
<td>276.9</td>
<td>245.2</td>
</tr>
<tr>
<td></td>
<td>40.5</td>
<td>21.0</td>
</tr>
</tbody>
</table>

Figure 3.13: Numeric tabulation of disk bulk conductivity as it varies
with properties investigated in the second set of trials.

There was no direct evidence within the second round of trials that the parameters
varied had any significant impact on the bulk conductivity of the samples. Namely, these
parameters were the inert atmosphere flow-through during exfoliation (N2), use of the
vacuum oven for removal of the excess silicone spray or PPC (vac), mixing with the
magnetic stir bar for over an hour (mix), and the inclusion and degradation of a PPC
insert (ppc).

All of the bulk conductivities from the second round were greatly improved from
values measured in the first round. It is possible that some of the parameters varied in the
second round contributed to the improved results. Another factor was probably an
increased proficiency in preparing and testing the samples that was the result of practice.
Better removal of the samples from the mounting press would have left them with
smoother surfaces. A better quality surface could easily have produced higher conductivities.

Following the bulk conductivity test for each sample, through-plane conductivity was measured.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG</th>
<th>σ_avg</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>d04</td>
<td>50</td>
<td>30.3</td>
<td>0.7</td>
</tr>
<tr>
<td>d06</td>
<td>60</td>
<td>30.1</td>
<td>0.5</td>
</tr>
<tr>
<td>d03</td>
<td>70</td>
<td>48.3</td>
<td>1.6</td>
</tr>
<tr>
<td>d05</td>
<td>80</td>
<td>55.5</td>
<td>0.9</td>
</tr>
<tr>
<td>d07</td>
<td>90</td>
<td>69.4</td>
<td>2.2</td>
</tr>
<tr>
<td>d02</td>
<td>100</td>
<td>78.7</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Figure 3.14: Numeric tabulation of disk through-plane conductivity as it varies with material ratios.

Figure 3.15: Plotted results of disk through-plane conductivity as it varies with material ratios. Error bars indicate the standard deviation of each averaged point.

The through-plane conductivity results follow a more expected trend than the bulk conductivity results. The conductivity increases from the low EG concentrations to the
pure EG. More EG means that a greater ratio of the sample is composed of conductive material. Thus, a pure EG sample should be more conductive than a 50% EG sample. Since these measurements look at the entire sample at once, the placement of the phenolic resin in the sample does not affect the through-plane conductivity in the same way it does the bulk conductivity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{\text{avg}}$ S/cm</th>
<th>sd S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>d08 70% EG, mix</td>
<td>16.1</td>
<td>4.2</td>
</tr>
<tr>
<td>d10 70% EG, N2, mix</td>
<td>15.6</td>
<td>3.1</td>
</tr>
<tr>
<td>d13 70% EG, N2, vac, ppc</td>
<td>16.0</td>
<td>2.9</td>
</tr>
<tr>
<td>d11 100% EG, N2</td>
<td>34.3</td>
<td>4.9</td>
</tr>
<tr>
<td>d14 100% EG, N2</td>
<td>71.1</td>
<td>92.8</td>
</tr>
<tr>
<td>d09 100% EG, N2, vac</td>
<td>23.3</td>
<td>9.6</td>
</tr>
</tbody>
</table>

Figure 3.16: Numeric tabulation of disk through-plane conductivity as it varies with properties investigated in the second set of trials.

Again, there was no direct evidence within the second round of trials that the parameters varied had any significant impact on the bulk conductivity of the samples. As expected, the conductivities of the pure EG samples were higher than the 70% EG samples.

With each separate measurement for a particular sample, the through-plane conductivity would decrease. Each measurement involved the release and reapplication of pressure to the sample. Each time the pressure was applied, the structure of the sample would change or shift slightly in a manner that tended to reduce its conductivity.

While the bulk conductivity results overall increased from the first to second set of trials, the through-plane conductivity results decreased. It is unclear what caused the decrease in conductivity. One possibility relates to the slight change in equipment setup. The first round of trials simply used copper plates to press on the sample. The second round used a more convenient, specialized assembly to press and measure the disks.
Also, carbon fiber sheets were used between the copper plates and the sample for only the first round. It is possible but unlikely that the presence or absence of the carbon sheets caused such a significant change in conductivities.
Section 3: Plates

Pressing Assembly

The first step to making plate samples that resemble bipolar plates was creating an assembly in which the material mixtures could be pressed. An assembly was designed with several considerations in mind. First, the design was kept simple by evaluating available metal stock and configuration that would minimize the need for machining. Next, the assembly needed to be thermally conductive so that the applied heat would reach the phenolic resin inside. The assembly also needed to be tall to allow for addition of low density EG inside of it without requiring the sample material to be pressed multiple times before the final pressing. Multiple pressings could create smooth surfaces within a sample that reduce cohesion of the final sample. The size of the assembly was limited by the size of the Carver hydraulic hot press that was to be used for heating and pressing. Finally, there needed to be a simple way to extract each sample from the assembly without destroying the sample or the assembly.

The assembly was made from several pieces of aluminum which has low cost and high thermal conductivity.
Square metal tubing with a 2 inch inner diameter was used for the open portion of the assembly where sample mixtures would be contained. The tube sat in a groove in a base block. It was secured into this block by a pin that could be easily inserted and removed. The separation of the tube and base allowed for easy removal of the sample plates once pressed. A small hole was drilled into the base plate to allow for a thermocouple to be inserted. This hole location was near the surface where the curing would be occurring in the sample, and allowed for an accurate temperature reading. A ram was designed to fit inside of the tube to apply pressure to the sample. The ram height was the same as the height of the tubing above the base plate. The height agreement allowed for visual determination of the thickness of the sample during pressing.
Basic Trials

A different mixing procedure was used for production of the plates than was used for the disks. One reason for the difference is the use of more material to make the plates than the disks. The larger quantity would have been harder to mix with the magnetic stir bar. Also, the larger opening size of the assembly allowed for an alternative method. Instead of mixing the sample components before placing in the press or assembly, the components were added by hand to the assembly in alternating pinches. In other words, a small amount of EG would be added to the assembly. Then some phenolic powder would be sprinkled on top of it. Again, a pinch of EG would be placed in the assembly. This
procedure, while time consuming, allowed for a more even distribution of phenolic resin throughout the EG. Before adding any material to the assembly, a generous amount of silicone spray was applied to ensure smooth release of the final plate.

Unless otherwise noted, all plates were pressed at approximately 160°C and 5000 lbf for at least several minutes. The hot press was set at a temperature slightly above 160°C to compensate for some convective heat loss along the length of the assembly. The thermocouple confirmed that the desired temperature was reached at the surface of the plate being formed.

Similar to the sample disks, a naming convention for the sample plates was adopted using $p$ followed by a number assigned to each plate in the order in which it was made.

All plate samples except the first one, $p01$, used EG that had been expanded under an inert atmosphere. All plates were also placed in the vacuum oven at 115°C for at least 30 minutes. A partial vacuum was applied to the oven several times to encourage outgassing of any residual silicone spray.

The first few plate samples were formed simply to understand the behavior of the EG and phenolic when being pressed in the assembly and hot press. For initial trials, a mixture of 75% EG and 25% phenolic was used. The assembly was removed from the press immediately after the application of temperature and pressure was complete. This amounted to a total time in the press of less than half an hour. Once the assembly had cooled, the plate was removed.

Similar to some of the disk samples, striations were noticed along the edges of the plates. Even repressing the plates did not fully close these gaps. Such voids within a
sample would be detrimental to conductivity because they limit and sever electron conduction pathways.

Figure 3.19: Picture of the side of plate p01 showing striations that remained after repressing.

An attempt was made to drill a hole in one of these plates. This was an experiment to evaluate the plates for basic machinability with the intent to use them in some simple fuel cell tests. The plate deformed and tore with the application of the drill.

When seeking a solution for the striation problem, advice was given by machinist John Lawless that the plate should be left under pressure while it cools. He suggested that the striations resembled defects in molded parts that are removed from their molds before having sufficient time to set.

The next sample plate, p03, was prepared with a mixture of 70% EG and 30% phenolic powder. After pressing and heating was complete, the pressure was maintained as the entire assembly cooled overnight. The plate was removed from the cooled press the next day. It was fully compacted with no evidence of striations. All future plates were left under pressure as they cooled.

During the repressing of p03, an attempt was made to press a long, wide, and shallow groove into one side of the plate. A simple piece of sheet metal was placed between the one plate of the press and the sample plate to create the indentation. The pressing of this groove was another step to investigate the possibility of using sample plates in a fuel cell experiment. The indentation was successfully formed.
Another attempt was made to drill a hole in the newly pressed plate. This time, the drill cut cleanly through the plate without disturbing the surrounding material. Successful drilling indicated that the two factors changed since the previous drilling attempt made a significant difference in the strength of the plate. Those two factors were a slight increase in the amount of phenolic resin binder, and the extended application of pressure while the sample was cooling.

**Conductivity**

Conductivity measurements were carried out on the sample plates in a similar manner to the tests performed on the disks. Measurements were taken on three different sets of plates. The first two series experimented with ratios of EG to phenolic. The third series contained attempts to improve through-plane conductivity.

Bulk conductivity was measured first on each sample. Several readings were taken on both the top and bottom of each plate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG %</th>
<th>Top $\sigma_{\text{avg}}$ $S/cm$</th>
<th>sd $S/cm$</th>
<th>Bottom $\sigma_{\text{avg}}$ $S/cm$</th>
<th>sd $S/cm$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p08</td>
<td>50</td>
<td>144.2</td>
<td>18.1</td>
<td>214.4</td>
<td>30.6</td>
</tr>
<tr>
<td>p07</td>
<td>70</td>
<td>155.9</td>
<td>12.6</td>
<td>189.2</td>
<td>18.0</td>
</tr>
<tr>
<td>p06</td>
<td>75</td>
<td>207.3</td>
<td>37.4</td>
<td>256.1</td>
<td>33.5</td>
</tr>
</tbody>
</table>

Figure 3.20: Numeric tabulation of plate bulk conductivity as it varies with material ratios as measured in the first set of trials.
Figure 3.21: Plotted results of plate bulk conductivity as it varies with material ratios as measured in the first set of trials. Error bars indicate the standard deviation of each averaged point.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG</th>
<th>Top (\sigma_{avg}) S/cm</th>
<th>sd S/cm</th>
<th>Bottom (\sigma_{avg}) S/cm</th>
<th>sd S/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>p10</td>
<td>50</td>
<td>224.7</td>
<td>18.6</td>
<td>290.5</td>
<td>31.9</td>
</tr>
<tr>
<td>p11</td>
<td>60</td>
<td>290.5</td>
<td>37.5</td>
<td>352.4</td>
<td>25.1</td>
</tr>
<tr>
<td>p12</td>
<td>70</td>
<td>337.4</td>
<td>28.8</td>
<td>297.1</td>
<td>23.5</td>
</tr>
<tr>
<td>p13</td>
<td>75</td>
<td>323.5</td>
<td>40.0</td>
<td>297.1</td>
<td>67.8</td>
</tr>
<tr>
<td>p14</td>
<td>80</td>
<td>393.4</td>
<td>26.6</td>
<td>352.4</td>
<td>44.1</td>
</tr>
<tr>
<td>p15</td>
<td>90</td>
<td>497.1</td>
<td>40.0</td>
<td>478.6</td>
<td>47.0</td>
</tr>
</tbody>
</table>

Figure 3.22: Numeric tabulation of plate bulk conductivity as it varies with material ratios as measured in the second set of trials.
The bulk conductivities followed a general trend upward with an increasing ratio of EG as would be expected with an increase in conductive material. There was a slight variation from one side to the other in the conductivity values. The mixtures for the plates were more uniform than for the disks. However, since the mixing is done by hand, there is a distinct possibility for some variation in distribution during the addition process to the assembly. A variation in the composition could account for the difference in conductivity between sides. The second round of trials exhibited higher conductivity results than the first. This was perhaps due to an increased proficiency in preparing the samples.

Following bulk conductivity tests, through-plane conductivity was measured on each sample.
Figure 3.24: Numeric tabulation of plate through-plane conductivity as it varies with material ratios as measured in the first set of trials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG</th>
<th>σ_avg</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>p08</td>
<td>50</td>
<td>6.8</td>
<td>1.2</td>
</tr>
<tr>
<td>p07</td>
<td>70</td>
<td>9.2</td>
<td>1.2</td>
</tr>
<tr>
<td>p06</td>
<td>75</td>
<td>16.6</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Figure 3.25: Plotted results of plate through-plane conductivity as it varies with material ratios as measured in the first set of trials. Error bars indicate the standard deviation of each averaged point.

Figure 3.26: Numeric tabulation of plate through-plane conductivity as it varies with material ratios as measured in the second set of trials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG</th>
<th>σ_avg</th>
<th>sd</th>
</tr>
</thead>
<tbody>
<tr>
<td>p10</td>
<td>50</td>
<td>8.8</td>
<td>0.3</td>
</tr>
<tr>
<td>p11</td>
<td>60</td>
<td>12.0</td>
<td>0.3</td>
</tr>
<tr>
<td>p12</td>
<td>70</td>
<td>13.0</td>
<td>1.6</td>
</tr>
<tr>
<td>p13</td>
<td>75</td>
<td>11.5</td>
<td>0.3</td>
</tr>
<tr>
<td>p14</td>
<td>80</td>
<td>11.2</td>
<td>0.5</td>
</tr>
<tr>
<td>p15</td>
<td>90</td>
<td>11.3</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 3.27: Plotted results of plate through-plane conductivity as it
varies with material ratios as measured in the second set of trials. Error
bars indicate the standard deviation of each averaged point.

The first round of trials displays a trend of increasing through-plane conductivity
with increasing proportion of EG. The second round of trials, however, indicates that
past 60% EG, there is little or no improvement in conductivity by increasing the ratio.
Those measured values also show the 70% mixture as having the highest conductivity.

With each separate measurement for a particular sample, the through-plane
conductivity would decrease. Each measurement involved the release and reapplication
of pressure to the sample. Each time the pressure was applied, the structure of the sample
would change or shift slightly in a manner that tended to reduce its conductivity.

The final series of sample varied parameters such as pressing force, increased
exposure time of the EG worms to heat under an inert atmosphere, inclusion of graphite
powder in the mixture, and use of ball milling as a mixing method. All samples were
made with a mixture of 70% EG and 30% phenolic except the one sample in which the mass of EG was reduced (45%) and replaced with graphite powder (25%).

As EG is pressed, the exfoliated graphene layers tend to orient themselves parallel to the pressing surfaces. For through-plane conduction, electrons have difficulty moving as they must jump perpendicularly from one graphene plane to another. For bulk conductivity, the electrons can move more easily along the planes. This concept explains why the through-plane conductivity is lower than the bulk conductivity.

In an attempt to improve through-plane conductivity, graphite powder was mixed with the EG and phenolic powder used in the making of a plate. Powdered graphite has a slightly different structure than EG and should not be as susceptible to reorientation during pressing. It’s inclusion in the plate offers a possibility to provide better electronic pathways through a plate.

The pressure under which the plates were pressed was varied simply to investigate the influence of pressure on conductivity. Also, ball milling was investigated as a possible method of mixing phenolic resin with EG.

The results from this set of trials are compared to the two other 70% EG plates (normal) tested in the previous two experimental series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% EG</th>
<th>Top</th>
<th>Bottom</th>
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<td></td>
<td>%</td>
<td>σ_avg (S/cm)</td>
<td>sd (S/cm)</td>
<td>σ_avg (S/cm)</td>
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<td>245.3</td>
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<td>32.9</td>
<td>283.9</td>
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<td>6.7</td>
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<td>45</td>
<td>187.5</td>
<td>32.5</td>
<td>178.9</td>
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<tr>
<td>p21</td>
<td>70</td>
<td>185.9</td>
<td>18.4</td>
<td>189.7</td>
</tr>
</tbody>
</table>

Figure 3.28: Numeric tabulation of plate bulk conductivity of samples with certain varied parameters.
Figure 3.29: Comparison plot of plate bulk conductivity of samples with certain varied parameters. Error bars indicate the standard deviation of each averaged point.

Figure 3.30: Numeric tabulation of plate through-plane conductivity of samples with certain varied parameters.
The increased pressing force improved the bulk conductivity slightly from the other plates tested. There was no large improvement or drop in conductivity seen across the samples.

None of the altered parameters improved the through-plane conductivity compared to the previous two 70% EG plates. The conductivity actually noticeably decreased.

Cumulative Plates

The last two plates produced, $p22$ and $p23$, combined the all of the concepts investigated in this research into one sample. These concepts were the combination of the bipolar plate with flow channels and the GDL layer with porosity. Technically, the plates were not bipolar since they only contained channels on one side, but the methodology for production would be the same.
The plate p22 was prepared as a mixture of 70% EG and 30% phenolic powder. The EG used for this plate was material that had been kept in the tube furnace for 30 minutes under an Ar flow-through. First mixture portion with a total weight of 4g was added to the assembly by alternating pinches of each material. The ram was used to level the surface of the mixture so that a PPC flow channel insert could be laid on top of it. The ram was used again to level the insert. During this process, the EG was not significantly compacted.

![Image](image.png)

Figure 3.32: View inside the assembly of the PPC insert laid on top of the nonporous portion of the plate mixture.

On top of the insert, another mixture was placed to create a porous layer. This layer also contained a 70% EG and 30% phenolic mixture. This EG had also been exposed to the 30 minutes of Ar flow-through. Added to the mixture was small grain salt in an amount of 2.5 times the weight of the EG and phenolic mixture. The large size of the EG worms compared to salt particles can make it difficult to form a porous network through the entire layer. Thus, the EG for the GDL portion was placed in a coffee
grinder for 5 seconds. This reduced the size of the worms by breaking them up. However, the grinder was not run long enough to turn the EG to powder or significantly compress the worms. The three materials for the GDL were also added by alternating pinches.

Once the placement of the mixture in the assembly was completed, it was pressed in the hot press at the standard conditions for plates. Once the temperature reached 160°C, the heat was shut off and the assembly was left under pressure to cool overnight.

The next day the plate was removed from the assembly and placed in the vacuum oven at 275°C for 2.5 hours. The oven was partially evacuated several times to extract the released vapors. A metal block was placed on top of the plate during the time in the oven in order to apply a small amount of pressure to the plate. The pressure was meant to hinder any bulging in the surface of the plate.

![Figure 3.33: Side view of plate p22 showing the flow channel voids.](image)

Inspection of the plate after degradation of the insert showed successful formation of flow channels. The channels were distorted from their original cross-sectional shape during pressing since the plate was heated past the glass transition temperature of PPC.

Despite use of the metal blocks to apply pressure to the plate during heating in the vacuum oven, some bulging on the surface was detected. The bulging was the likely result of unreacted components of the initial phenolic resin vaporizing within the sample and pushing outward in an attempt to escape.
The plate was placed in a warm water bath at 67°C that used a magnetic stir bar to circulate the water. The plate was left in the bath for a week, and the water was changed several times. The water dissolved the salt particles and opened all pores to which the water had access.

The final plate produced, p23, was made with pure EG. The idea was to make a plate which did not require heat to press it. Without heat, the flow channel insert would
not undergo any significant deformation and full size channels could be observed. The same basic procedure was used to place the raw materials in the assembly for p23 as for p22. The EG for the bipolar plate portion was added first. The EG for this plate had been expanded under Ar but not left in the oven for 30 minutes. The surface was leveled before placing the insert into the assembly. Finally, pinches of slightly ground EG and large grain salt were added alternating between the two.

The plate was pressed at a slightly elevated temperature of 40°C and 5000 lbf for 10 minutes. The elevated temperature was due to residual heat in the press from molding the PPC insert prior. The plate was then placed in the vacuum oven for 2.5 hours at a temperature of 275°C. The oven was partially evacuated several times to extract the released vapors. Again, a metal block was placed on top of the plate to apply pressure and hinder bulging.

The flow channel voids that resulted had a shape very similar to the initial insert.

![Figure 3.36: Side view of plate p23 showing the flow channel voids.](image)

However, the surface of the final plate was very rough and uneven. Outlines and raised impressions of individual EG worms were evident. The GDL layer was pushed upward along the lines of the PPC insert while similar depressions were present on the bipolar plate side. The thickness varied from one location to another on the plate. There was also some irregularity of the structure around the voids produced by the insert that appeared as small striations. This plate made evident the importance of maintaining pressure over a long period of time when pressing a plate from EG.
Less total material was used for the GDL portion in $p_{23}$ than in $p_{22}$. The layer was still sufficiently thick in $p_{23}$. A thinner layer is beneficial when dissolution is used to create the porosity because there is less depth into which the solvent must gain access.

To remove the salt particles, the plate was placed in a warm water bath at 67°C. A magnetic stir bar was used to circulate the water. The plate was left in the bath for a week, and the water was changed several times.
Section 4: Experimental Fuel Cell

Two sample plates were pressed with the intent to construct an in-house fuel cell for testing. The plates were combined with the Masters research of John Holtkamp which dealt with catalyst preparation for formic acid fuel cells.

The mixtures for the plates were composed of 70% EG and 30% phenolic. The EG had been expanded under a nitrogen flow-through. The plates were placed in the vacuum oven after pressing to remove excess silicone spray. When the plates were repressed, a sheet metal insert was included between the plate of the hydraulic press and the sample plate. This formed an indentation approximately 1 inch wide and 1.5 inches tall on one side of each plate. Holes were drilled in the plates to pass bolts through.

The plates were secured with PTFE bolts to hold them together in the cell configuration. Use of PTFE for the bolts instead of metal prevented the formation of a direct conduction pathway between the plates. A gasket was used to separate the surfaces of the plates. In order to produce electricity from the cell, the plates had to be kept isolated so that electrons could be routed through an external circuit in a pathway from one plate to the other.

A palladium catalyst ink was applied to pieces of carbon cloth to form electrodes. The electrodes were separated with a piece of absorbent foam that was used to wick the formic acid fuel into the cell. The electrodes and foam were placed in the gap between...
the plates created by the indentations. Holes were also cut in both plates around the location of the electrodes to provide oxygen for the reaction and an escape pathway for the reaction products.

Figure 3.37: View of the side of the fuel cell showing the foam extending from the gap created by the indentations in the plates. The foam was used to supply fuel to the cell.

Figure 3.38: View of one side of the fuel cell.
An open circuit voltage of 224 mV was measured from the cell, but no appreciable current was drawn from it. Unfortunately, with this cell configuration trying two new concepts at once, it is hard to establish the exact reason for the inability to draw current. It is known that the plates are conductive, so it is likely the problem was with the fuel cell MEA design. A foam layer was used in place of an actual proton exchange membrane. The foam layer, despite being saturated with an aqueous ionic solution, may not have been able to serve sufficiently as an ionic conductor.

Nonetheless, the ability to construct the cell showed that it is reasonable to use plates made from EG for fuel cell applications.
CHAPTER 4
Conclusions

Section 1: Experimental Conclusions

Experimental trials have shown that EG is a promising material for use in forming fuel cell components due to its low cost and ease of processing. Use of a binder such as phenolic resin helps to hold the compressed material together and improve its strength. The softness of EG means that plates pressed from it do not exhibit the same brittleness as pure graphite.

One of the fundamental concepts investigated in this thesis research has involved mixture ratios. Deciding on a ratio of EG and phenolic resin to use becomes a balancing act. The graphite provides conductivity while the resin gives strength. More of either component may increase one property of the final product but at the cost of the other.

Some basic machining trials indicated that a mixture of 70% EG with 30% phenolic provided reasonable strength for a plate while still maintaining a high ratio of EG. Conductivity measurements of 70% EG samples showed that the mixture had reasonable conductivity, though not as high as pure EG.

Since EG is a form of graphite, it is electrically conductive like metals, yet it resists corrosion. Conductivity tests have shown that the bulk conductivity of EG samples exceeds the DOE goal of 100 S/cm for a bipolar plate. The through-plane
conductivity is lower. Conductivity is a material property, so it remains constant for a given type and composition of material. Looking at Equation 2.4, if the thickness, \( L \), of a sample is reduced, the resistance, \( R \), of the sample also decreases. This relation is true when evaluated samples have a constant cross-sectional area, \( A \), and when a consistent material mixture is used such that the conductivity is the same. Thus, the impact of the low through-plane conductivity can be minimized if plates can be made thin.

The conductivity from one set of trials to another even for similar samples tended to vary. While practice and increasing proficiency may have contributed to some improved results, other factors were probably also at play. It is possible that experimental setup and the environment around it, such as temperature fluctuations, also affected the results.

One of the largest problems encountered during sample making is determining a way to adequately mix the materials for a sample. This problem is mainly due to the size and density difference between the EG and phenolic particles. Using a magnetic stir bar helps somewhat to mix. However, the phenolic still tends to settle to the bottom. The distribution of phenolic through the EG is improved when mixing by hand in the assembly for pressing plates, but other problems are present. Mixing by hand is subject to human perception and inaccuracy. Thus, the distribution can vary from beginning to end of the sample addition process. Also, it is difficult to ensure that the phenolic resin is spread equally from center to edges of the plate sample when sprinkling the material into the tall assembly. Some phenolic powder clings to the sides of the assembly which slightly reduces the ratio along the edges of the plates. Similar to the situation with phenolic resin, distribution of sacrificial salt particles was inconsistent.
Difficulties with placement of materials into the plate pressing assembly cause problems besides just uneven material distribution. There is no way ensure that a consistent amount or depth of material is deposited from side to side during the entire adding process. Figure 3.33 shows how the individual GDL and bipolar plate layers vary in thickness from one side to the other.

Shortly after the making of plate samples began, it was discovered that maintaining pressure during cooling was essential to produce a fully compacted plate. However, the last plate produced, p23, from pure EG made evident that application of pressure for an extended time is important even when heating and resin curing is not involved.

There are likely two processes occurring during the pressing of a plate that need the time to complete. The various particles and graphene layers from the worms shift and settle during pressing. Once the pressure is fully applied, the settling into a final orientation is not instantaneous. Time is needed for various pieces to migrate to their final positions. Also, air may be trapped between the EG worms and within the structures of the worms themselves. The trapped air would hinder quick settling of the worms into a final orientation. Since EG is sometimes used for seals and gaskets, it is not conducive to easily releasing any trapped air. High pressure for a long period of time would provide an opportunity for the air to slowly escape.

The soft nature of the EG worms makes them pliable and causes them to deform and spread outward when pressed. While this property is essential for their use in making bipolar plates, it is not necessarily good when creating a porous layer. The EG can tend to spread around the powder being used to form the porosity, especially when the worms

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are much larger than the powder. If it spreads sufficiently, it can isolate a particle from being part of a network. When large numbers of particles become isolated, a full, porous network is never formed. Even at the surface of the disk, if enough worms lay on top of the sacrificial powder, entire portions of the network can be sealed inside the sample. When this happens, the solvent never has access to remove the sacrificial material, and porosity is never formed. EG worms can be ground before pressing to limit their ability to coat sacrificial particles. However, after grinding, they lose at least some of their ability to compress into a firm plate or layer.

There were several results from various experiments that indicated that PVA was far from an ideal choice for a sacrificial additive. When the sample of PVA with NaCl became trapped between the pressing surfaces of the mounting press, it could not be fully dissolved away. This situation actually resembled a flow channel insert within a plate. With so little surface area exposed to the solvent, the PVA was not eager to dissolve. It only swelled. Similarly, a flow channel insert pressed into a plate would be resistant to dissolving. Then, material would be left trapped within the plate and the desired flow channels would be blocked from allowing reactants to pass.

Sample disks, such as d16 in Figure 3.9, contained PVA powder in an investigation of forming a porous network. When bathed in water, the polymer swelled significantly and caused deformation of the disks. Such swelling indicates that soluble polymers like PVA are not practical for use as a soluble sacrificial additive because of their potential to swell and destroy the sample in which they are used.

Trials with PPC and NaCl used as sacrificial materials have shown they have much more promise than PVA. To be removed from a sample, NaCl can easily be
dissolved in water. When considering solvents, water is good because it is nontoxic and
does not require the special handling that some solvents do. Both NaCl and water are
inexpensive and readily available. PPC thermally degrades quickly, completely, and at
relatively low temperatures. As a polymer, it can be easily formed or molded into any
desired shape. The main downsides are the high cost and the low glass transition
temperature. Inserts tend to deform when contained within a plate that is being heated
and pressed for curing of a binder.
Section 2: Future Work

Several issues and concepts remain to be investigated in order to make bipolar plate – GDL combinations a commercially viable option. First, a more accurate and automated process would be needed for mixing component materials in preparation to form a plate. Also, a reliable method would be needed to ensure even distribution of material within a pressing assembly. Such investigations would address the issues of inconsistent conductivity and layer thickness.

When PPC is used as a flow channel insert, it tends to deform at the temperature and pressure used for the curing of phenolic resin. A series of experiments could be run to investigate phenolic behavior with a variation of steps used in the curing process. It is possible that the pressure and temperature could be applied separately. If the high pressure could be applied first, the heating for phenolic curing and PPC degradation could potentially be combined within the same step. Some pressure would still be needed in this step to prevent bulging of the sample. The heating stage investigation would require a balancing of the amount of pressure so as to ensure a smooth plate without crushing the flow channels.

Another factor to research is the formation of uniform porosity among the soft EG worms. The shifting of the EG during pressing currently blocks some pores from
forming. The size of the worms likely needs to be reduced without harming the ability of the EG to form a secure and compact layer.
References


### APPENDIX

#### Section A: Sample List

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<tr>
<th>Sample</th>
<th>Component Ratios</th>
<th>Other Specifications</th>
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<tbody>
<tr>
<td>d01</td>
<td>70% EG 30% phenolic granules</td>
<td>magnetic mix 2.5 hr</td>
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<td>d02</td>
<td>100% EG</td>
<td>pressed at 30°C for 3.5 min</td>
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<td>70% EG 30% phenolic granules</td>
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<td>50% EG 50% phenolic granules</td>
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<td>d05</td>
<td>80% EG 20% phenolic powder</td>
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<td>d06</td>
<td>60% EG 40% phenolic powder</td>
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<td>90% EG 10% phenolic granules</td>
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<td>repressed at 2000 lbf</td>
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<tr>
<td></td>
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<td>tube furnace to degrade PPC</td>
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<td>repressed again at 2000 lbf</td>
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<td>Day</td>
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<td></td>
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<td></td>
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<td>Treatment</td>
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<td>p02</td>
<td>75% EG, N2, 25% phenolic</td>
<td>pressed at 6000 lbf and 160°C first to let cool overnight under pressure repress with metal insert at 2500 lbf drilled holes</td>
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<td>70% EG, N2, 30% phenolic</td>
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<td>70% EG, N2, 30% phenolic</td>
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</tr>
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<tr>
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<td>80% EG, N2, 20% phenolic</td>
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<tr>
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<td>70% EG, N2, 30% phenolic</td>
<td>pressed at 1000 lbf vacuum oven repressed at 1000 lbf</td>
</tr>
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<td>p22a</td>
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<td>PPC insert press at 40°C and 5000 lbf vacuum oven to degrade at 275°C</td>
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<td>100% EG, Ar, ground *500% NaCl large grain</td>
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All samples were pressed at the standard conditions for disks or plates unless otherwise noted.

Disks: 150°C, 4200 psi, 2 minutes
Plates: 160°C, 5000 lbf, ~5 minutes

*Percentage of sacrificial additive indicates ratio of mass of additive to mass of permanent material in sample.
Section B: Sample Calculation Tables

The following tables are examples of the spreadsheet calculation tables used for calculating bulk and through-plane conductivity of the various samples tested. These tables contain values for several plate samples.
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<th>Sample</th>
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<th>Bottom</th>
<th>V mA mV S/cm</th>
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Figure A.1: Bulk conductivity calculations for sample plates.
## Through-Plane

<table>
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<tr>
<th>Sample</th>
<th>L (cm)</th>
<th>A (cm²)</th>
<th>I (mA)</th>
<th>V (mV)</th>
<th>R (ohm)</th>
<th>R_adjust (ohm)</th>
<th>σ (S/cm)</th>
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<td>100</td>
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</table>

### p10

| 50% EG  | 0.126  | 6.4516 | 100 | 0.22210774 | 6.4516 | 100 | 0.22366444 | 6.4516 | 100 | 0.21989968 | 6.4516 | 100 | 0.22946661 | 6.4516 | 100 | 0.23847964 | AVG 0.128 | 8.779381 |

### p11

| 60% EG  | 0.127  | 6.4516 | 100 | 0.15420178 | 6.4516 | 100 | 0.15870340 | 6.4516 | 100 | 0.16345070 | 6.4516 | 100 | 0.16705490 | AVG 0.124 | 12.00384 |

### p12

| 70% EG  | 0.137  | 6.4516 | 100 | 0.13641535 | 6.4516 | 100 | 0.13587030 | 6.4516 | 100 | 0.13645070 | AVG 0.137 | 13.01603 |

### p13

| 75% EG  | 0.140  | 6.4516 | 100 | 0.17993463 | 6.4516 | 100 | 0.18350256 | 6.4516 | 100 | 0.18741338 | AVG 0.137 | 11.48876 |

### p14

| 80% EG  | 0.101  | 6.4516 | 100 | 0.13333513 | 6.4516 | 100 | 0.13699894 | 6.4516 | 100 | 0.14746462 | AVG 0.101 | 11.18705 |

### p15

| 90% EG  | 0.096  | 6.4516 | 100 | 0.12721514 | 6.4516 | 100 | 0.12433819 | 6.4516 | 100 | 0.14139063 | AVG 0.098 | 11.29012 |

### vac

| 6.4516 | 100     | 0.00050351 | 6.4516 | 100     | 0.00051527 | 6.4516 | 100     | 0.00057769 | 6.4516 | 100     | 0.00057841 |
| AVG    | 6.4516 | 100     | 0.00054647 | 6.4516 | 100     | 0.00055745 | 6.4516 | 100     | 0.00055745 | 6.4516 | 100     | 0.00055745 |

**Figure A.2**: Through-Plane conductivity calculations for sample plates.