The Development of Compression Moldable Polymer Composite Bipolar Plates for Fuel Cells

Brent Cunningham

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Committee Members:

Dr. Donald G. Baird, Chair

Dr. Judy S. Riffle

Dr. Garth L. Wilkes

Dr. Jack Lesko

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(ABSTRACT)

The development, design, and modeling of a rapid continuous processing scheme is developed to economically manufacture conductive polymer composite bipolar plates for fuel cells. Bipolar plates are required to possess several important properties for fuel cell operation, with the most sought after being electrical conductivity and mechanical strength. The polymer composite material generated at Virginia Tech is based on material generated by a wet-lay process and uses polyethylene terepthalate (PET) or polyphenylene sulfide (PPS) as the binder, although PPS is mainly used. In order to reach sufficient conductivity for use in generating bipolar plates, the polymer is doped with high levels of conductive graphite particles in the range of 70-80 wt%. The polymer system is reinforced with 6-9 wt% glass or carbon fibers. When compression molded into a solid, flat preform, the wet-lay material exhibits excellent bulk (in-plane) conductivity (> 250 S/cm). The material also exhibits tensile and flexural strengths of 57.5 and 95.8 MPa, respectively, higher than other polymer composite material being considered for bipolar plate production. However, formability and through-plane conductivity needs improvement.

The laminate bipolar plates developed at Virginia Tech are made using wet-lay material in the core and a thermoplastic/graphite mixture on the surfaces. The wet-lay material provides mechanical integrity, while a powder form of PVDF or PPS and graphite mixture added to the surfaces to improve through-plane conductivity and formability.

The manufacturing scheme for the production of laminate bipolar plates is based on the pre-consolidation of the wet-lay material, which establishes a solid, flat surface for the continuous addition of laminate powder. Because the laminate powder only requires heating, radiation heating is used in the process design to pre-heat the preform prior to compression molding. The heated preform passes underneath a press, where forming of channels takes place along with cooling of the bipolar plate. It is estimated that the entire process can take one minute to produce a bipolar plate. The cost of manufacturing a bipolar plate is estimated to be $8/kW, below the goal of $10/kW. The annual production is determined to be 250,000, with over 500,000 possible depending on certain design factors.

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Foremost appreciation goes to my parents, David and Tina Cunningham. It was your encouragement and support that made all of my accomplishments throughout life possible.

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Original Contributions

The following are considered to be significant original contributions of this research.

1. A clearer understanding of the role of the bipolar plate in an operating fuel cell. Gained significant knowledge about the variety of materials being considered for bipolar plate production and the advantages and limitations that each material possesses.

2. Using a unique product development approach to reach required properties. The wet-lay process is used to develop polymer composite preforms that provide a highly conductive, strong material comparable to any other composite material being considered for bipolar plate production.

3. The novel laminate design brings about the potential for development of a rapid, continuous processing scheme. Importantly, the PPS based laminate material shows improvements to the through-plane conductivity, half-cell resistance, and formability when compared to the wet-lay based material.

4. Most researchers working with polymer composite bipolar plates have neglected the measuring or reporting of mechanical strengths at elevated temperatures due to expected deceases in strength and modulus. However, it has been observed that the PPS based laminate material can maintain high flexural strengths that meet the target value at fuel cell operating temperatures of 100 ^{o}C.

5. It has been demonstrated by design and numerical modeling that the bipolar plate cost target of $10/kW. The manufacturing goal of generating a bipolar plate in 2-3 minutes is expected to be possible with the incorporation of the laminate structure plates, radiation heating, and compression molding, with an actual time estimate of 1-1 ½ minutes. The processing time also show room for improvement so that over 1,000,000 plates/year can be produced.

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1 Introduction

Preface

The following section introduces the fuel cell and the basics of its operation and role as an alternative source of power. The role of the bipolar plate in the operation of the fuel cell is also discussed. The section concludes with a statement of research objectives.

1 Introduction

1.1 Fuel Cells

A fuel cell is an electrochemical device that converts chemical energy into electrical energy. An ideal fuel cell does not undergo physical change or wear down like a dry-cell battery. It does, however, need to be recharged like a battery by adding more fuel. A fuel cell stack is a collection of bipolar plates and two monopolar end plates allowing for fuel, usually hydrogen and oxygen, to be carried on either side of the plate as shown in Fig. 1.1. The gaseous fuel flows through a channel network similar to the design shown in Fig. 1.2. Bipolar plates are connected in series with a Polymer Electrolyte Membrane (PEM) in between each bipolar plate. One side of the bipolar plate acts as an anode reaction site in a given cell while the other side acts as the cathode site in the adjacent cell. The PEM membrane electrode assembly (MEA) contains a catalyst to drive the reduction and oxidation reactions as well as allow the protons to pass through to the cathode site where the oxidized hydrogen protons react with the reduced oxygen molecules, producing water. Shown in Fig. 1.3 are the reduction and oxidation reactions that take place as well as the placement and composition of the PEM. Each individual cell produces approximately 0.7 V, so a collection of bipolar plates in series is required in order to generate large amounts of power.

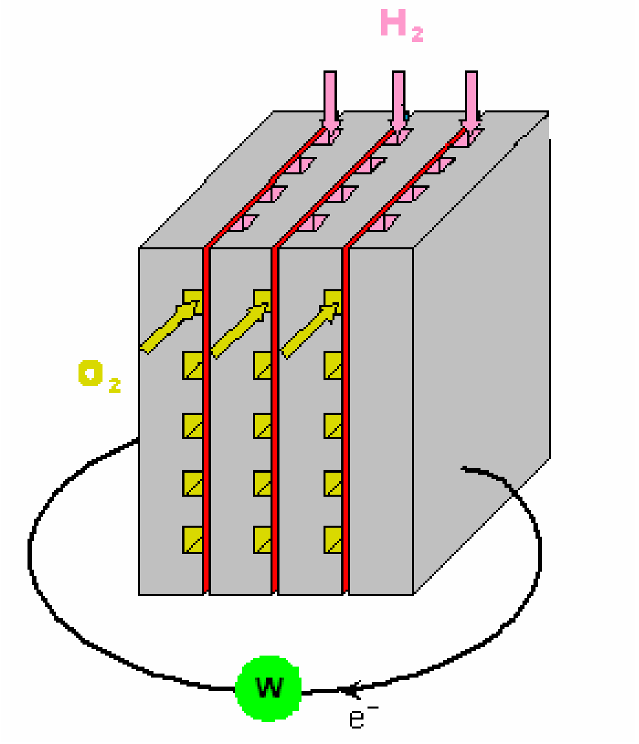

Figure 1.1 - Fuel cell stack with two bipolar plates and two monopolar end plates, showing inlets for hydrogen, oxygen and the collection of current.

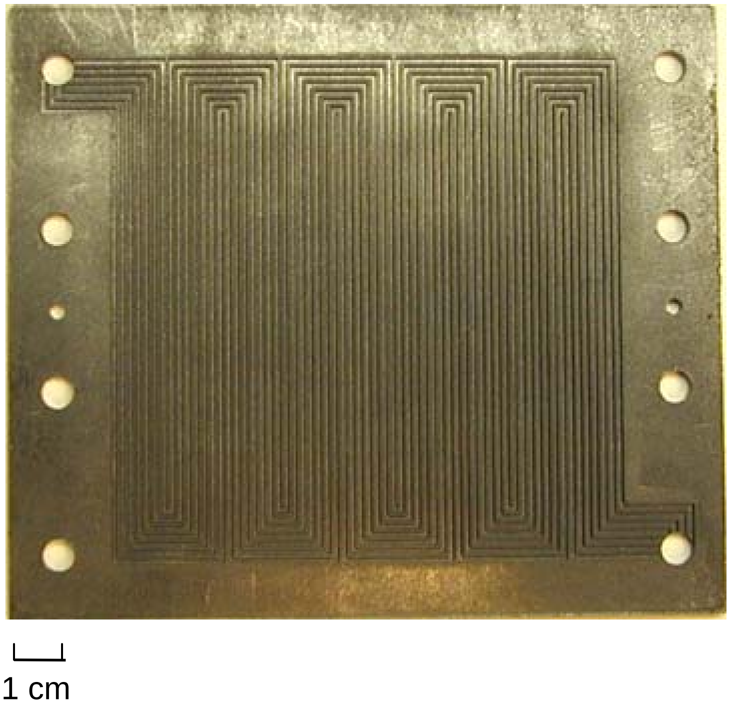

Figure 1.2 – Bipolar plate showing 0.8 x 0.8 mm parallel serpentine style grooves.

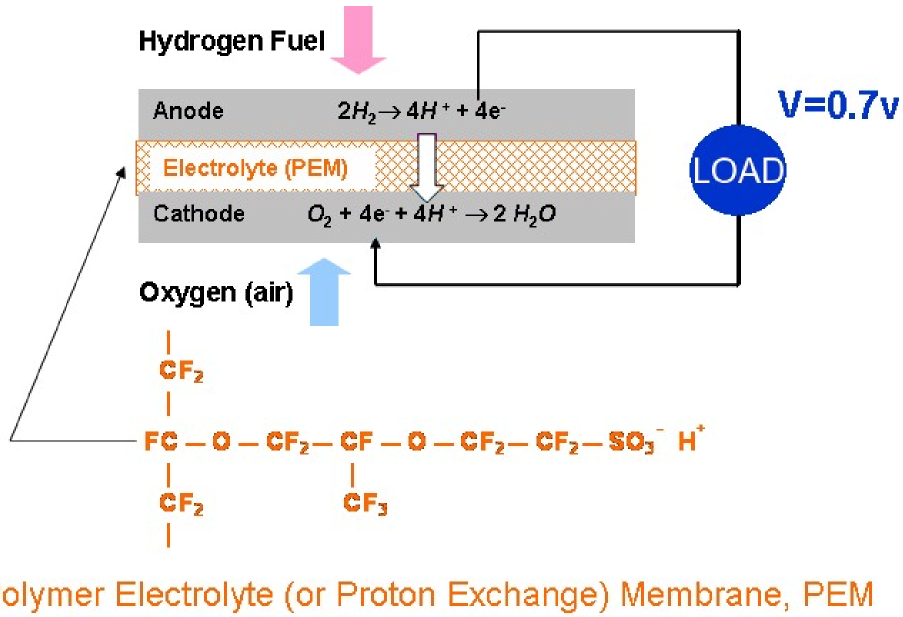

Figure 1.3 – Single cell fuel cell showing reduction and oxidation reaction sites and PEM membrane composition.

Fuel cells have advantages over gasoline engines including their high operating efficiency and near zero pollutant emission. The efficiency of gasoline engines in automobiles or other applications are limited to about 50% while the fuel cell has been estimated to be up to 90% efficient.[1, 2, 7] The fuel cell is not a combustion engine but rather a chemical conversion unit which can obtain near complete conversion of chemical energy into electrical energy. It is an efficient means of converting hydrogen into electrical power. In addition to an improved efficiency over gasoline engines, the emissions resulting from a fuel cell stack are near zero.[6, 8] When using hydrogen and oxygen as the fuel and oxidant, the reduction-oxidation set of reactions produces pure water as the product in addition to electrons. As such, the fuel represents a key element in efforts to demonstrate and implement hydrogen as a fuel for electric power generation.

The significant and growing interest in fuel cells for stationary power and transportation has been demonstrated by the attention these technologies are receiving from both government and industries.[6, 9] The first practical uses of the fuel cell began in the 1960's when the NASA space program used fuel cells as a small, portable source of power for astronauts. Currently, efforts are being made to commercialize fuel cells in the automotive industry.

The operating requirements and conditions for a fuel cell stack are numerous. The size of a fuel cell stack will vary depending on the amount of power a cell can provide. Many automotive applications require at least 200 V DC as the stack output.[5] Since one cell typically produces 0.7 V, it is necessary to require as much as 300 cells in a stack. Fuel cells should be able to operate at temperatures up to approximately 80 ^{o}C with quantities of water present. Therefore, chemical compatibility of the bipolar plates is important in the operation of a fuel cell.

1.2 Bipolar Plates

Bipolar plates are by weight, volume, and cost one of the most significant parts of a fuel cell stack.[10, 11] In Fig. 1.4 is shown the current DOE cost estimate breakdown of a fuel cell. The bipolar plate holds a large portion of the cost at 29%. The total cost of a working fuel cell is typically about \$200/kW, with the DOE goal set at \$35/kW for the automotive industry. This leaves the cost target for bipolar plates currently at about \$10/kW.

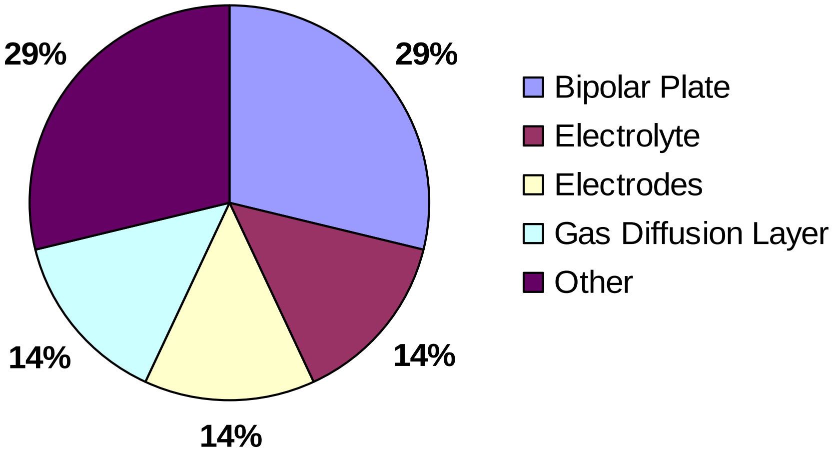

Figure 1.4 – Cost breakdown of a fuel cell stack.

Not only do bipolar plates represent a large fraction of the cost associated with a fuel cell stack, but their performance is also a key element in the operation of a fuel cell. The bipolar plate has three main functions: distribution of gases homogeneously over the whole area of the single cells; separation of the fuel and oxidant gases and the prevention of gas leakage; and collecting the current produced in the electrochemical reactions.[12-14] The ability of a bipolar plate to pass electrons is based on its conductivity. Graphite has been the standard material in which bipolar plates have been developed due to the high conductivity it possesses, but graphite plates typically have poor mechanical strength due to porosity and are expensive to manufacture into bipolar plates.[9, 15] Many other materials are being researched to optimize a balance of both of these properties, along with maintaining low gas permeability and corrosion resistance. The motivation towards the development of bipolar plates to meet these rigorous demands has been a set of specified requirements issued by the Department of Energy (DOE) summarized in Table 1.1. These targets are considered to be the minimum acceptable performances required if the bipolar plates are to be competitive.

Table 1.1 - Summarized DOE specified targets for bipolar plates.

Plate Property	**DOE specified target**
Conductivity	> 100 S/cm
Corrosion	< 16 mA cm^2
H_2 permeability	$< 2 \times 10^{-6}$ cm^3/cm^2 s

The major difficulty in the production of bipolar plates suitable for commercialization in the automotive industry is the production of a material which simultaneously meets the property requirements and can be readily processed. Bipolar plates can be made from many different materials to be discussed in section 2.3. Each material possesses the ability to meet one or more of the recommended DOE target requirements, but it has been shown to be very difficult to find a material that can reach high conductivity coupled with high mechanical strength, while still allowing for a cost effective, rapid production scheme in which channels can be formed into the surfaces.

1.3 Research Objectives

Although the knowledge base for the use of polymer composites in the production of bipolar plates is increasing due to a considerable amount of ongoing research, this work focuses mainly on the use of compression moldable thermoplastic composite materials. The ability to select a polymer composite system that will optimize material properties and processing conditions requires a thorough understanding of material characteristics and processing scenarios. Therefore, successful completion of several objectives is required to accomplish the primary goal. The first objective is to develop a material that meets material property target values suitable to be used in a fuel cell stack. The second objective is to determine the best processing method for the selected material that will allow for rapid channel formation into the surfaces. This objective is comprised of the development of an overall production scheme involving heat transfer models as well as a physical process design. The final objective is to perform estimates on processing cost and bipolar plate production rates for effective use for commercialization in the automotive industry.

1.4 References

1. Igot, F., Face Off: Internal Combustion Engine versus the Hydrogen Fuel Cell. Montgomery College Student Journal of Science & Mathematics, **1**, (2002), 1-10.

2. http://www.fuelcells.org/basics/benefits.html.

3. Landis, L., Tucker, Jonathan L., *Bipolar Plate Components Move to the Forefront*. R&D Magazine. October, (2002), 36-38.

4. Cooper, J. S., *Design Analysis of PEMFC Bipolar Plates Considering Stack Manufacturing and Environment Impact*. J. Power Sources. **129**, (2004), 152-169.

5. Doughty, D. H., Vyas, Brijesh, Takamura, Tsutomu, Huff, James R., *Materials for Electrochemical Energy Storage and Conversion-Batteries, Capacitors and Fuel Cells*, Mat. Res. Soc. Symp. Proc., April 17-20, San Francisco, Ca, (1995), 150-155.

6. Cleghorn, S. J. C., Ren, X., Springer, T.E., Wilson, M.S., Zawodzinski, C., Zawodzinski, T.A., Gottesfeld, S., *PEM Fuel Cells for Transportation and Stationary Power Generation Applications*. Int. J. Hydrogen Energy**. 22**(12) (2002), 1137-1144.

7. Larminie, J., Dicks, Andrew, Fuel Cell Systems Explained. 2nd ed., Editor: John Wiley & Sons, (2003), 30-43.

8. Thomas, S., Zalbowitz, Marcia *Fuel Cells - Green Power*; Los Alamos National Laboratory: Los Alamos, New Mexico, Sept. 23, (1999), 1-33.

9. Huang, J., Baird, Donald G., McGrath, James E., *Development of Fuel Cell Bipolar Plates from Graphite Filled Wet-lay Thermoplastic Composite Materials*. J. Power Sources, **150**, (2005), 110-119.

10. Middleman, E., Kout, W., Vogelaar, B., Lenssen, J., de Waal, E., *Bipolar Plates for PEM Fuel Cells.* J. Power Sources, **118**, (2003), 44-46.

11. Bar-On, I., Kirchain, Randy, Roth, Richard, *Technical Cost Analysis of PEM Fuel Cells,* J. of Power Sources, **109**, (2002), 71-75.

12. Balko, E., N., Lawrance, Richard J., US 4,339,322, (1982).

13. Lawrance, R. J., US 4,214,969, (1980).

14. Thring, R. H., Fuel Cells for Automotive Applications. Editor: R. H. Thring, (2004), 6-9.

15. Mepsted, G.O., Moore, J.M., *Performance and Durability of Bipolar Plate Materials*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd., (2003), 286-293.

2 Literature Review

Preface

This chapter provides a review of literature pertinent to this research project. The key topics discussed in this chapter include: materials used for bipolar plates and their processing methods, and molding and heating technologies used to process polymeric materials.

2 Literature Review

This chapter contains a review of research that is relevant to the progress and development of bipolar plates for fuel cells. In section 2.1 is discussed important requirements that must be met for bipolar plates to be used commercially. In section 2.2, an overview of two different conductivity measurements is discussed. In section 2.3, a thorough review of materials that are being considered for bipolar plate production is discussed. Processing technologies of polymer composite material are discussed in sections 2.4 and 2.5. The review concludes in section 2.6 with a restatement of research objectives and questions to be answered, with an emphasis on tying together the previous work found in the literature review with the objectives for this work.

2.1 Bipolar plate requirements

The motivation behind the development of a material suitable to commercialize the production of bipolar plates is based on a set of rigorous targets listed below:[1]

- Electric conductivity (>100 S/cm)*
- H_2 Permeability ($< 2\times10^{-6}$ cm^3/cm^2-sec)
- Corrosion resistance (<16 μA/cm^2)
- Flexural strength >59 MPa (Plug Power target)
- Tensile Strength > 41 MPa (Plug Power target)
- Thermal Stability up to 120 ^oC
- Chemical Stability in the presence of fuel, oxidant, water, and acidic conditions
- Low thermal expansion
- Thermal conductivity >10 W/mK (Plug Power target)
- Low cost (<$10/kW)
- Rapid manufacturing

*Data in brackets show current Dept. of Energy (DOE) targets.

Materials used for bipolar plate production have been able to meet one or more of these targets, but no material has yet been able reach each property simultaneously.

Electrical conductivity and mechanical properties are probably most frequently reported for bipolar plates. The DOE conductivity target is for bulk, or in-plane conductivity. Several other research organizations report through-plane conductivity but no requirement has been set for this specific value. Generally for mechanical data, flexural strength and tensile strength are reported with an occasional report on impact strength. DOE has not specified mechanical targets, although several research organizations have developed their own estimations on strength targets such as Plug Power, a leading company in the research of fuel cell technology. Fewer reports have been made concerning other targets such as permeability, corrosion resistance, thermal conductivity, etc. mainly due to the focus put on conductivity and strength.

The last two goals are low cost and rapid manufacturing. Attempts to reach both of these goals have shown to be difficult. The cost target for bipolar plates is \$10/kW, with the current estimate of cost at \$60-65/kW.[2] Manufacturing times do not currently have specific targets although it is known that machining channels into graphite material can take several hours. More favorable molding techniques for polymer composites have shown a manufacturing time within 10 minutes, so it is likely that a processing time of several minutes will generate much attention.

2.2 Overview of electrical measurements

One of the most sought after properties of bipolar plates is conductivity. Conductivity is directly calculated from resistance measurements of the plates. The two types of resistance measurements are in-plane, or bulk (along the surface) and through-plane (perpendicular to surface). The more important measurement is through-plane resistance because this is the direction the electrons must travel in a fully operating fuel cell. However, the DOE target specifies only a bulk conductivity target, and most results only report bulk conductivity. To understand the difference between in-plane and through-plane resistance, the measurement techniques will be discussed first.

Measurements of in-plane resistance are done using a four-point probe technique (Fig 2.1), which actually is a measure of resistivity of the material in accordance with ASTM Standard F76-86 test method. The resistance, R_S, is obtained from two measured characteristic resistances, R_A and R_B by numerically solving the Van der Pauw equation, (1).[1]

$$\exp(-\pi\, R_A/R_S) + \exp(-\pi\, R_B/R_S) = 1 \tag{1}$$

where:

$$R_A=V_{AB}/I_{DC}=V_{DC}/I_{AB} \tag{2}$$

$$R_B=V_{BC}/I_{AD}=V_{AD}/I_{BC} \tag{3}$$

where the resistivity is defined as $\rho = R_S d$ (Ω cm) and conductivity is defined as $\sigma = 1/\rho$ (S/cm). The parameter d represents the thickness of the specimen.

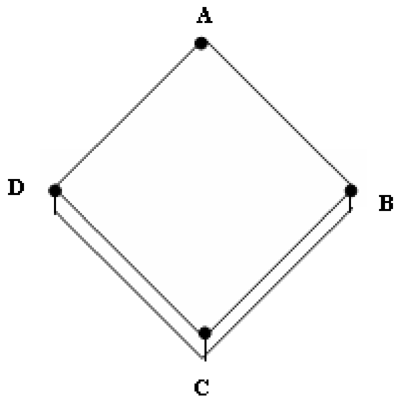

Figure 2.1 – Probe location for in-plane resistance tests.

Measurements of through-plane conductivity follow the method proposed by L. Landis and J. L. Tucker[3] with some modifications. Through-plane resistance is measured on a slab of material with no channels or design in the surface. The procedure by Huang & co-workers[1] was to cut a 25.4 mm x 25.4 mm sample and place it between gold-plated copper electrodes. Between the electrodes and both surfaces a graphite diffusion layer (GDL) paper was added to help improve electrical contact of the sample with the electrode. The test cell was placed under pressure to simulate conditions similar to those in a fuel cell stack. The system was initially preconditioned at 1500 psi for three cycles and then the resistance of the test cell was measured several times in order to calculate the average. The sample was removed, and the resistance of the test cell with GDL papers measured under the same conditions to obtain a baseline resistance. Subtracting the baseline resistance from the total resistance gives the sample resistance. The resistivity is calculated by equation 4, with conductivity calculated as previously done, being equal to the reciprocal of resistivity.

$$\rho = R_S A/L = (R_T - R_B)A/d \qquad (4)$$

where:

ρ - resistivity (Ω cm)

R_T – total resistance (Ω)

R_B – baseline resistance (Ω)

A – cross-sectional area of sample (cm^2)

d – thickness of sample (cm)

To measure the half-cell resistance, an experimental apparatus similar to the one used for measuring through-plane conductivity was used as shown in Fig. 2.2.[1] A single-sided bipolar plate (monopolar plate) 12.1 cm x 14.0 cm x 0.32 cm and an active area of 100 cm^2 was placed between gold-plated copper electrodes. Carbon paper (Toray TGP-H-120) was placed between the sample and electrodes. The size of the carbon paper was 10 cm x 10 cm on the channel side to cover only the active area, while a 12.1 cm x 14.0 cm section was placed on the flat side of the plate. While a constant current (typically 250 mA) was passed through the current collectors, the potential drop between the collectors was measured. The half-cell resistance was then calculated based on Ohm's law. The baseline resistance, that is the resistance of the testing circuit excluding the monopolar plate, was measured every time after testing the plate. This was done to ensure the stability of the baseline of the instrument and to evaluate the contribution of the bipolar plate to the while half-cell resistance.

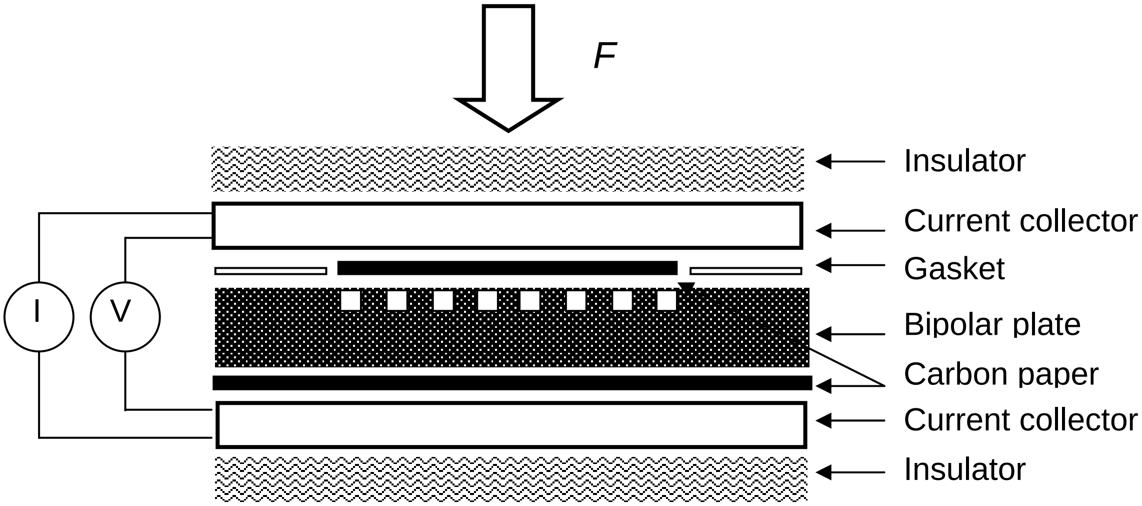

Figure 2.2 – Schematic of the half-cell resistance test using a monopolar plate.

2.3 Materials for bipolar plates and their processing methods

The search for a suitable material for bipolar plates that meets all DOE requirements has been challenging evidenced by the number of studies done in recent years. An array of materials has been investigated and each material displays some, but not all of the properties required for a good working fuel cell. The choice of material is a balance between cost, durability, and electrical performance. Initially graphite plates were constructed because of their low weight and good conductivity properties. Recently many other materials have been investigated such as stainless steel, aluminum, and polymer composites as alternatives to help relieve the costs associated with manufacturing graphite plates.

The difficulty with graphite, metal and carbon/carbon plates is that the introduction of channels requires machining or etching, a very costly and time consuming step. Typical costs for the machining step alone are \$20-\$78/kW.[4] Machining times can take as long as several hours to complete. In addition, post processing (such as resin impregnation) is needed to make graphite plates impermeable to the fuel and oxygen.[1] Due to poor corrosion resistance in metal plates, a conductive coating must be applied to the surfaces of the plates to form a protective layer, which has been found to be very difficult to accomplish.[5] Carbon/carbon plates developed at Oak Ridge National Laboratory (ORNL) claim to have high electrical characteristics along with excellent mechanical properties.[6] The manufacturing process consists of multiple steps, including the production of carbon fiber/phenolic resins preforms from slurry-molding followed by densification by chemical vapor infiltration. The process is likely to be too complicated and costly to be applied to automotive applications. Because material and machining costs for with graphite, metal, and carbon/carbon plates are prohibitive for at least the automotive industry, extensive efforts have been made to develop alternative materials for bipolar plate production.

As an alternative, polymer composite plates have been considered if conductivity and mechanical requirements can be met. Processing of composite materials has exhibited the possibility for a more favorable molding technique where channels are formed directly into the surface at a considerably shorter length of time and at a reduced cost. The plates are heated above the melting temperature of the polymer allowing for channels to be molded directly into the surfaces eliminating much time and costs associated with machining. Typically, injection and compression molding are used to form thermoplastics and thermosets. Molding techniques for polymer composite plates have shown the greatest potential in reducing time and cost in bipolar plate production. Molding channels is preferred over machining or etching due to the lower cost and faster processing times. Choosing which molding method to use depends mainly upon how the material will flow when heated. The use of fibers and particles inhibits the flow of the material making them unsuitable for certain applications. Each molding technique is similar in that the goal is to form a melt and then introduce it to a cold mold and have it shaped or formed quickly. Molding techniques can reduce production times to several minutes. The production of bipolar plates using polymer composites at a cost of about \$10/kW has been accomplished.[2, 7] Manufacturing costs have been estimated to be as low as \$6/kW using a molding technique rather than machining or etching of channels, a significant improvement in manufacturing cost.[7]

2.3.1 Graphite bipolar plates

Current plate designs are generally based on graphite material primarily because of its high electrical conductivity, excellent corrosion resistance, and low density relative to that of metal.[8] Specific properties are summarized in Table 2.1. Bulk conductivities for graphite plates are in the range of 110-680 S/cm, well above the target of 100 S/cm. (Note: S/cm – Siemens/cm or the reciprocal of resistivity in Ω cm). Hydrogen and oxygen permeability results for typical plates are $< 2 \times 10^{-5}$ cm^2/s. This is comparable to the permeability goal of $< 2 \times 10^{-6}$ cm^2/s, but graphite bipolar plates are still considered to be slightly permeable to gases.[9]

Table 2.1 – Properties of graphite plates compared to the target properties.[9-11]
*Plug Power target for flexural strength.

	Graphite	Goal
Bulk Conductivity	110 - 680 S/cm	> 100 S/cm
Electrical Resistivity	.009-.02 Ω cm^2	< 0.2 Ω cm^2
Permeability	$< 2 \times 10^{-5}$ cm^2/s	$< 2 \times 10^{-6}$ cm^2/s
Density	1.8 - 2 g/cm^3	N/A
Cost	> $200/kW	$10-30/kW
Thickness	5-6 mm	< 3 mm
Flexural Strength	< 25 MPa	> 59 MPa*

The main problems with graphite plates are their brittle and porous structure, and the cost associated with machining channels into the plates. The brittleness and porosity can be overcome if the plates are made thick enough. Due to porosity, graphite plates are limited to a minimum plate thickness of about 5-6 mm. This is about twice the thickness goal of 3 mm.[12, 13] Brittleness and porosity lead to a low flexural strength which is well below the target of 59 MPa. Of the three problems, the biggest obstacle in the use of graphite is the expensive and time consuming process of machining flow channels. The machining step can take as long as several hours to complete for one bipolar plate.

Channels are usually around 1.0 mm deep and 1.0 mm wide, an example of which is shown in Fig 1.3 of section 1.2.

Not only is the machining of a graphite plate expensive, but the production of graphite blocks is costly. First raw graphite is used to make a block by means of a high-temperature sintering process that takes several weeks and results in some porosity and distortion of the material. Then the block is cut into slabs, vacuum-impregnated with resin filler for gas-tightness, and ground and polished to the desired surface smoothness.[10, 14]

Sealing the porous graphite plates is another additional expense. This process can cost as much as \$16/plate for a standard 160 cm^2 plate.[4] Fuel cell stacks suitable for automotive use have been estimated to require several hundred bipolar plates. This is over \$6,000/stack just for the sealing process, or over \$100/kW.

2.3.2 Metal bipolar plates

Metals such as stainless steel, aluminum, and titanium are considered for use in the manufacture of bipolar plates because of their excellent electrical conductivity and mechanical properties.[5, 8] In Table 2.2 are comparisons between the properties of metals commonly used for bipolar plate production, in addition to graphite. They range from about 10-100 times higher in conductivity than graphite. In addition, because of their high strength and rigidity, it is possible to make metal plates as thin as 1-2 mm. This is about a third of the thickness of graphite plates, making the total volume of a fuel cell stack significantly less.

Table 2.2 – Properties for common metal bipolar plates

	Titanium	Aluminum	Stainless Steel	Graphite
Bulk Conductivity	1500 S/cm	376,000 S/cm	10,000 S/cm	110-680 S/cm
Corrosion prone	Yes	Yes	Yes	Low
Density	4.54 g/cm^3	2.70 g/cm^3	8.0 g/cm^3	1.8-2.0 g/cm^3
Thermal Cond.	17.2 W/m K	205 W/m K	16.3 W/m K	N/A
Thickness	1-2 mm	1-2 mm	1-2 mm	5-6 mm
Permeability	Negligible	Negligible	Negligible	Low, near target
Cost ($/lb)	4.50	2.00	0.15	0.50-1.00

The significant drawback with the metal bipolar plates is corrosion problems on the surface. Corrosion problems arise from the formation of an oxide coating from chemically reactive metals.[5, 8] These oxide layers are electrically insulating, usually on the order of 10^{12} ohm-cm, which imparts high contact resistance leading to a voltage drop in the fuel cell, which cannot be accepted. To avoid this voltage drop, the formation of such a resistive layer has to be prevented by coating the metal surface. The protective coating must be conductive and provide complete corrosion protection.[5] The coating must also be chemically and mechanically stable in a fuel cell environment. The application of such a conductive, low-cost coating has been found to be very difficult to accomplish.

It has been shown that stainless steel might meet all the necessary requirements in fuel cell stacks due to its conductivity, strength, and ease of machining when compared to other metal plates.[5, 15] It is a relatively low cost material with good thermal conductivity and minimal permeability. Stainless steel is amenable to techniques of mass production and could be fabricated into bipolar plates in large quantities by continuous rolling or by batch stamping. Uncoated stainless steels have received little attention because of concerns surrounding chemical instability in the fuel cell environment and surface oxide effects. The inert oxide layer that forms on stainless steel is Cr_2O_3. Plates produced by means of stainless steel can be suitable for use in fuel cells provided protective layers against corrosion and chromium ion leaching are applied.[5, 16] The combination of the metallic bipolar plate and coating makes it difficult to meet the cost requirement. The major challenge in successfully utilizing stainless steel in the production of a bipolar plate lies in either the reduction, control, or modification of the oxide layer and the development of low-cost coatings to prevent ion leaching which contaminates the Pt catalyst in the Polymer Electrolyte Membrane (PEM) membrane.

Titanium possesses a number of the desirable properties that are required for bipolar plates and may be more suitable than stainless steel.[5, 17] The density of titanium is about 55% that of steel. It also maintains good strength and is easily fabricated. Titanium has excellent corrosion resistance to most dilute acids, impermeable to hydrogen, and excellent thermal conductivity. Titanium is not a particularly good conductor when compared to other metals but has a conductivity that is 30 times higher than graphite. The production rate of titanium is several times less than that of stainless steel because it requires a two-stage process, first creating $TiCl_4$ from its oxide ore, followed by reduction of the halide to titanium metal. Like stainless steel, titanium is also chemically reactive. Titanium can be made sufficiently corrosion-resistant by coating it with a titanium nitride finish which is actually electrically conductive. Even so, the production of titanium bipolar plates is very expensive and time consuming.

Aluminum also possesses a number of desirable properties including good strength, simple fabrication, and low density that is about 60% that of titanium. Its bulk conductivity is several orders of magnitude better than that of titanium, and the thermal conductivity is higher than that of both stainless steel and titanium. The material costs of aluminum are considerably less than those of other metals. Aluminum bipolar plates can be manufactured by casting, machining, and etching. The same type of electrically insulating oxide layer that forms on titanium also forms on aluminum. Aluminum can be coated by ion sputtering or chemical vapor deposition (CVD). Both of these processes require high temperatures and expensive capital equipment. One other process is electro-deposition, but the only electrically conductive materials that can be used are gold, platinum, and palladium. All three are uneconomical for a fuel cell application.

Because metals possess superior conductivity, mechanical strength, and are available for batch stamping, a large amount of research has been carried out to protect the surface of stainless steel bipolar plates. With all metals, it is important that the applied coating possess minimal interfacial resistance, reduces the corrosion current, and covers 100% of the area because any discontinuities provide galvanic corrosion sites. If there is not 100% coverage, the fuel cell deteriorates rapidly and may become inoperable in a matter of hours.[5, 8] Unfortunately, most conventional coating methods are too expensive for PEM fuel cell stack commercialization or tend to leave pinhole defects, which result in accelerated local corrosion and unacceptable performance.[18] A possible solution to this problem is nitridation of an alloy specifically designed to form a protective nitride surface layer. First, because nitriding operates at elevated temperatures, pinhole defects are not expected because thermodynamic and kinetic factors favor complete conversion of the metal surface to nitride. Second, nitridation is a relatively inexpensive, well-established industrial technique and is viable for covering complex geometries such as bipolar plate flow field features. Third, the alloy can be formed into a final shape by inexpensive metal forming techniques such as batch stamping. Thermal and plasma nitrided base alloys (Tribocor and 316L stainless steel) have exhibited relatively low corrosion currents[18, 19]. Unfortunately, there are still concerns with passive films forming over the nitrided layer, weight loss of the nitrided layer after submersion into acidic environments, and defects occurring on the surface which affect the performance and interfacial contact resistance of the bipolar plate. Tawfik et al.[20] have developed a high corrosion resistant coating which was fabricated of a full densification carbide based alloy and applied to both aluminum and stainless steel bipolar plates. The carbide based coating applied on the aluminum bipolar plates showed excellent durability for harsh corrosive environments inside a fuel cell. During 1000 hours of operation in a single cell stack, the carbide based coated bipolar plates showed negligible formation of an oxide or passive layer, negligible metal ion poisoning, and negligible tarnishing of the catalyst. Further studies have been recommended to analyze the coating durability and integrity, along with the possibility of coating de-lamination due to differences in the coefficient of thermal expansion between coating and metal. Polypyrrole has been researched for use as a protective coating for 316L stainless steel bipolar plates.[21, 22] The bipolar plates are coated with polypyrrole by polymerization onto stainless steel using galvanostatic and cyclic voltammometric methods. The coated plates have exhibited a decrease in corrosion current density by one order of magnitude. However, in a simulated cathode environment of a PEMFC, the reduction in corrosion current was not seen because polypyrrole can be oxidized at 0.6 V. In a simulated anode environment, the current density becomes negative right away because the corrosion potential is increased after the polypyrrole coating. A negative current can provide cathodic protection for the 316L stainless steel bipolar plates. However, SEM images on polypyrrole coated 316L have revealed pinholes and cracks in the surfaces. There have been numerous studies on protective coatings for metal bipolar plates that can reduce the interfacial contact resistance, corrosion current, and the potential for defects to occur on the surface, but it has been difficult to develop a suitable coating that is inexpensive and flawless for large scale production.

Even with the corrosion problems associated with metal bipolar plates, major fuel cell developers are still uncertain which material pathway will be favored in the long run. Additionally, metal bipolar plates incorporate considerable weight and machining costs, but these problems can be avoided by using the correct material or combination of materials. The current costs for metal bipolar plates are estimated to be a minimum of \$65-\$100/kW, over 6 times the target cost.[2]

Similar to graphite, a significant drawback in the mass production of bipolar plates from metals is the machining or etching of channels. Channels can be generated by several different methods. They can be etched with a strong acid, cut by a water-jet or laser, or hollow embossed.[5] The conventional method of machining can be applied even to precut titanium foils which are diffusion bonded together to create complex channels. Hollow embossing of thin metal sheets is the preferred manufacturing process, largely due to the low cost. The structure of one plate side (e.g. the side fuel flows through) directly influences the opposite plate side (e.g. coolant), of the plate leading to greater restrictions on the design. Etching or massive embossing permits an independent design of each plate side. The hollow embossing process leads to a reduction of the material thickness of the plate. In practice, there is often a local high reduction spot which can crack the plate. The radial geometry of the channel depth must be sufficiently large to prevent a failure of the plate. The embossing or etching process is a slow and expensive way to form channels into metal plates, which makes it an unlikely candidate for a full scale cost effective production process.

2.3.3 Carbon/carbon bipolar plates

Carbon/carbon plates are developed from a porous carbon fiber material that is sealed by a chemical vapor infiltration (CVI) technique in which carbon is deposited on the surface of the material in sufficient quantity to make it hermetic.[6] Carbon/carbon bipolar plates have exhibited high bulk electrical conductivities (200-300 S/cm) and a low density (0.96 g/cm^3).[6] The material is hermetic with respect to through-thickness leakage and has high electrical conductivity as a result of the deposited graphite carbon. Carbon/carbon bipolar plates have been shown to possess the following properties:[6]

- A density about half that of graphite
- Very high electrical conductivity
- Very low cell resistance
- Gas impermeability

Processing carbon/carbon preforms has shown to be difficult and time consuming. Carbon/carbon preforms are made by molding a conductive filler such as graphite powder or carbon fibers along with phenolic resin.[6, 23] Carbon fibers are the most common type of conductive filler in the production of carbon/carbon bipolar plates and are combined with phenolic resin forming a slurry. The carbon fibers are ~400 μm long and 10 μm in diameter, which are suspended in water containing a phenolic resin in a ratio of approximately 4:3, fibers:phenolic resin.[6] The phenolic resin binder provides strength and geometric stability. A vacuum-molding process produces an 18 vol % fiber, isotropic preform material that is then cured for several minutes at 150 ^{o}C. Additional phenolic resin is spread by a doctor blade to reduce surface porosity and help seal the surface. The surfaces are further sealed by CVI. The CVI technique is performed at 1400-1500 ^{o}C, using methane at low pressures to deposit carbon on the near-surface fibers in order to make it hermetic. This provides an impermeable surface as well as a conductive plate. The CVI technique tends to warp the plate slightly (<5%) due to the non-uniformity of carbon dispersion. However, even the warped plates were pressed and flexed in a fuel cell stack without cracking or leaking. Long-term results may show that when held under stress at long times that the warped plates will not perform as well as other materials.[22, 24] Although carbon fibers are typically used as the filler for carbon/carbon plates, graphite powder has been used with a slightly different production method.[23] Instead of using a vacuum-molding process to produce a preform, a mixture of approximately 1:1 graphite powder:phenolic resin is compression molded under pressure and temperature to melt and partially cure the resin. Furthermore the CVI process is replaced by a carbonization technique. The preform is carbonized (resin converted into vitreous carbon) by stacking them in a suitable gas-tight enclosure where they are heated in an inert atmosphere. When the temperature reaches approximately 1000 ^{o}C, the resin has almost completely converted to vitreous carbon. In order to obtain adequate corrosion protection and to improve electrical resistivity and thermal conductivity, and to reduce hydrogen permeability, the plate must be further heated to at lest 2100 ^{o}C to convert the carbon into graphite. The final step for both of these methods is to machine channels into the surface of the plates.

Carbon/carbon plates have shown to have a good balance of conductive and mechanical properties. For a 4:3 ratio of carbon fibers:phenolic resin, bulk conductivities were measured in the range of 200-300 S/cm.[6] Flexural strength was measured to be approximately 175 MPa. For the carbonized plates using graphite powder, bulk conductivity was determined to be 59 S/cm.[23] Through-plane conductivity was measured to be very high at 310 S/cm. The flexural strength of the carbonized plates however was measured to be 46.7 MPa. The plates generated from carbon fibers have exhibited high bulk conductivities as well as flexural strength, but the plates generated from graphite powder have exhibited a more unbalanced set of conductive and mechanical properties. While it appears that carbon/carbon plates have shown potential in meeting a balance between conductivity and mechanical strength, the carbonization and CVI process requires extremely high temperatures and long processing times making it too uneconomical for a large scale operation.

The major drawback in developing carbon/carbon bipolar plates is the extreme processing time and cost. The CVI process alone is estimated to cost around \$6-\$8/kW in a large scale batch processing of at least 30,000 plates.[6] What makes the CVI process so unattractive is the extremely high temperature of 1400-1500 ^{o}C along with an equally unappealing processing time of 5 hours. Furthermore, like graphite and metal, channels are machined into the surfaces of carbon/carbon plates. Combining machining costs, materials, and the complex processing scheme, carbon/carbon plates are likely to be too expensive for production of bipolar plates suitable for use in the automotive industry.

2.3.4 Polymer Composite Bipolar Plates

Traditionally, the majority of bipolar plates have been designed with stainless steel or graphite due to their high conductivity. However, the cost of these plates is too high for transportation applications, principally because of the costly gas channel machining step. Even the work with carbon/carbon plates has shown potential, but the plates still require machining of channels, and the CVI process appears to be too expensive and complex for use in the transportation industry. A solution may exist in the use of polymer composite bipolar plates in which a polymer resin and conductive fillers are combined. The main conductive filler is graphite powder due to its high conductivity. Some polymer composites may use additional fillers such as carbon or glass fiber to help improve plate properties. Furthermore, these materials may be amenable for the rapid and economical production of bipolar plates. The two different types of polymer resins that can be used in bipolar plate production are thermoplastic and thermosetting.

2.3.4.1 Thermosets

Various types of thermosetting resins such as epoxies and vinyl esters have been studied as possible materials for making bipolar plates.[25] There are a number of benefits in using thermosets. During processing they are low viscosity and, hence, can be loaded with high levels of conductive filler. Thermosets are typically strong, tough materials that require only heating of the polymer composite when forming channels. They do not require subsequent cooling during the manufacturing of the plates while thermoplastics require time for crystallization to occur. Once the thermoset is heated and cured, the part can be removed from the mold while it is still hot.

Bipolar plates based on epoxy resin can be produced by simply curing the polymer between temperature of 60-140 ^{o}C.[25] Again graphite powder is used as the conductive filler at ratios of 1:1 to 9:1 graphite to resin. The mixture is placed in a mold under pressure and cured in an oven for 8 hours. After extracting and cooling the bipolar plate, the plate is coated with a chemically resistant thermosetting resin on the areas that would not be in electrical contact with the PEM membrane. This coating helps seal the plates in a fuel cell stack without the use of gaskets. Then curing takes place again at 100 ^{o}C for 5 additional hours. These epoxy/graphite plates have exhibited poor conductivity values, with through-plane conductivity only reaching just over 3 S/cm. Additional conductivity and mechanical properties are unknown for these bipolar plates, but the long processing times they require make them unsuitable for fuel cell applications in the automotive industry.

Bipolar plates generated from vinyl ester resin at Los Alamos National Laboratory have exhibited better properties than the epoxy plates and a much more attractive production method than using phenolic resins.[26, 27] Vinyl esters are methacrylated epoxy difunctional polyesters generally viewed as a cross between a polyester and epoxy. In addition to being well known for excellent resistance to corrosion, vinyl esters are lightweight, strong, tough, and commercially available at low cost. In the production of vinyl ester bipolar plates, graphite is embedded into a vinyl ester resin matrix. The liquid component is formulated by incorporating various additives (e.g., catalyst, inhibitor, mold release, thickener) into the resin. Then the liquid is mixed with the graphite powder along with any other desired reinforcing fibers. The compound is compression molded in the range of 1000-2000 psi. Typical cure times of less than 10 minutes can be obtained with appropriate selection of temperature and resin/catalyst system, a significant improvement over the cure times for epoxy plates. Once cured, the plates can be removed from the mold while hot, thus potentially offering shorter cycle times than thermoplastics. Vinyl ester plates have been measured to have a bulk conductivity of 30 S/cm at a 68% graphite loading level. When the graphite level increases to 75%, the bulk conductivity jumps up to 85 S/cm while retaining a tensile and flexural strength of 25 MPa and 38 MPa respectively which are both still below their respective goals.

A major drawback in using thermosets is the long cure times and the poor mechanical properties. Curing of epoxies have typically exhibited a time frame of at least 8 hours, although vinyl ester matrices have shown to cure in only 10 minutes.[28, 29] Conductivity and mechanical strengths remain a concern with the vinyl ester plates as they are both well below their respective goals.

2.3.4.2 Thermoplastics

Bipolar plates based on the use of thermoplastics have been developed generally using two different types of conductive fillers in the form of powder, fibers, or a combination of both. Graphite powder and carbon black are common fillers because of their high conductivity and potential for use with injection molding depending on the wt. % of powder. Carbon fibers or glass fibers are used with some thermoplastics but are typically combined in small weight percents with a higher loading level of graphite powder. These composite materials typically require compression molding due to their poor flow characteristics, but injection molding has been used with limited success with polymer composites containing carbon fibers.

Composite bipolar plate cost requirements can be achieved by optimizing the process conditions, yielding a shorter and less expensive manufacturing scheme.[13] Gas distribution channels can be formed by compression molding, injection molding, or a combination of the two. This eliminates the need for a separate and costly machining step. Additionally, polymer composites offer potential advantages in lower cost, lower weight, and greater ease of manufacture than the traditional graphite and metal plates.[13, 29-31] Even though the raw material costs are generally comparable to graphite and metals, polymer composites are much more economically viable because they do not require expensive coatings, sealing procedures, and are suited to a less expensive molding step.

Characteristics of composite plates are dependent upon a number of factors, including the type and relative amounts of conductive filler. Also, there is usually a trade-off between conductivity and mechanical strength. Graphite creates a conductive network connecting the surfaces of the plate, but contributes to brittleness of the overall plate.[30, 32] Electrical conductivity is dependent on graphite size, distribution, and the ability to form a homogeneous mixture with the polymer resin. Electrical properties normally improve with increasing amounts of graphite or carbon black, while mechanical properties decrease, requiring a compromise in composition.[8] Composite plates typically contain at least 50% graphite, with a maximum of about 80%.

In some cases thermoplastics such as PVDF and injection grades of polypropylene (PP) and polyphenylene sulfide (PPS) and only graphite powder (no reinforcing fibers) have been used to produce bipolar plates.[33-35] PVDF composite plates were developed using a range of 74%-86% graphite powder.[34, 35] The mixture was blended for 25 minutes to provide a thoroughly homogenized mixture of graphite and PVDF. The mixture was then poured into a mold, heated to 300 ^{o}C, and compression molded at a pressure of 2000 psi. The pressure was reduced to 300 psi, temperature brought up to 400 ^{o}C, and pressure increased back to 2000 psi. The temperature was reduced to 290 ^{o}C and held for 5 minutes. The final step was to reduced the pressure to 300 psi and allow the mold to cool to room temperature. Bulk conductivity values for 86% graphite loadings reached 277 S/cm, but flexural strength was only 9 MPa, much lower than the goal of 50 MPa. Plates generated with 74% graphite loading exhibited conductivities of approximately 119 S/cm and a flexural strength of approximately 20.0 MPa. Carbon fibers have also been added to the PVDF/graphite mixture in an attempt to improve structural properties.[34] Keeping a high graphite weight percent of 64 % and adding 16 wt % carbon fibers, the conductivity remained consistent at 109 S/cm with the flexural strength increasing to 42.7 MPa, still below the target. While PVDF/graphite plates meet the target for bulk conductivity, their mechanical strength is poor. The polymer resins PP and PPS mixed with carbon black and graphite powder have been used in an injection molding process to develop bipolar plates.[33] Experiments have also been done using the same mixture with the addition of carbon fibers. Normally about 40-45 wt % of polymer is used with 16.5 wt % of carbon black. Additionally, 33-38.5 wt % graphite powder is added to the mixture. Carbon fibers in the range of 4%-5.5% were added in some cases. Bulk conductivities for PP and graphite powder fillers reached only as high as 3 S/cm with flexural strengths of 43-45 MPa. With the addition of 5.5%

carbon fiber, conductivity did not change significantly but flexural strength reached 52 MPa. Injection molded PPS with graphite powder and 4% carbon fibers reached a bulk conductivity value of 10 S/cm and flexural strength of 84 MPa. The bulk conductivity of the injection molded plates is very low, an order of magnitude less than the goal, with the flexural strength often fluctuating near the target of 50 MPa.

Liquid crystalline polymer/graphite mixtures have been a promising material for bipolar plate production because of their ability to be used with injection molding due to the low viscosity of the polymer.[36] Liquid crystalline polymers are typically mixed with a conductive graphite filler in powder form, or more preferably, nickel-coated graphite fibers. Additionally a thermoplastic binder is added in the weight percent of 0.1%-20%. The conductive fillers are most preferably in the range of 30%-50%. The length of the graphite fibers are typically in the range of 0.3-1.3 cm in length with a diameter of 5-40 μm. The mixture of material is tumble dried for approximately 12 hours before pouring into the hopper of an injection molding machine. The polymer in the mixture undergoes melting, and the mixture is then conveyed into a mold followed by cooling and ejection of the part. Bulk conductivities have reached as high as 100 S/cm, just reaching the minimum target, but no reports on mechanical properties or through-plane conductivity were reported.

Another thermoplastic composite material that uses reinforcing fibers in addition to graphite fillers is a wet-lay composite containing either PET or PPS fibers.[1, 14, 37] The wet-lay process (shown in Fig. 2.3) is similar to a paper-making process where the raw materials are mixed with water at 1 wt % forming a slurry. The polymer fibers are mixed with water in a pulper, where reinforcing fibers and graphite are added. The slurry is then pumped into another tank where microglass is added. Microglass is used to help bond the graphite particles onto the fibers, and is added at 1% by weight of total solids (fibers & graphite). The slurry is then pumped into a head box containing a screen which removes the solids from the water while using a vacuum underneath to help remove excess water forming an entangled mat. The mat continues to pass through an oven to evaporate the remaining water and partially melt the thermoplastic fibers in order to fuse the material together. Finally, the material is rolled for storage and later processing. When the wet-lay material is prepared for compression molding, a pre-determined number of sheets are cut to fit directly inside of a mold. The sheets of wet-lay are stacked on top of each other to provide the desired thickness of plate after compression molding.

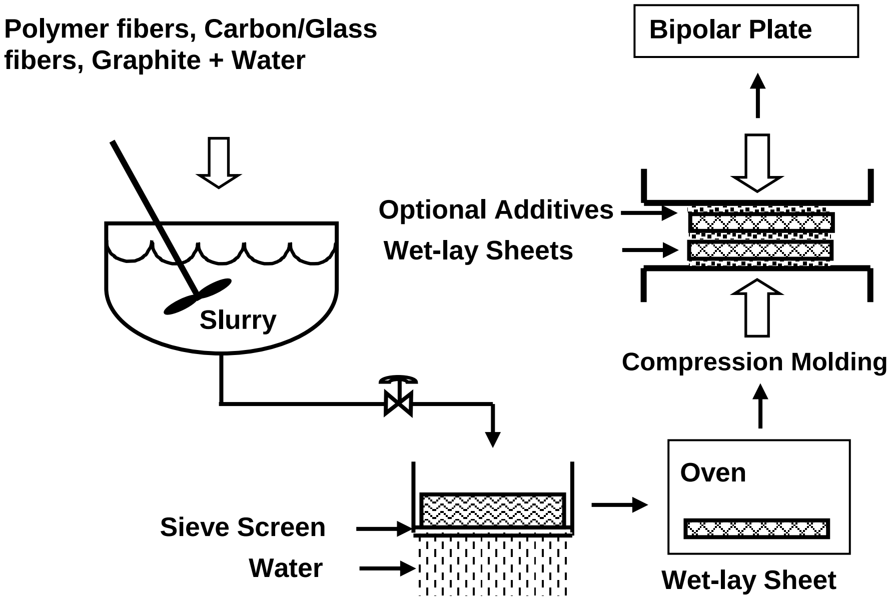

Figure 2.3 – Schematic of the wet-lay slurry production and subsequent forming process.[1]

Various ratios of components have been used in the production of wet-lay material. PET or PPS fibers are added at 13-40 wt %.[37, 38] Graphite powder is the main conductive filler composing 50-80 wt %. Carbon or glass fibers are used at a level of 6-9 wt %. Microglass is used at 1 wt % to enhance the loading level of graphite. The wet-lay material ideally is a uniform distribution of polymer and reinforcing fibers with graphite particles evenly distributed throughout the material. In order to process wet-lay material, the sheets are cut to fit inside a mold for compression molding. A pre-determined number of sheets are then stacked together which will provide the desired volume, or thickness of product.

Bipolar plates that are made using material generated by means of the wet-lay process have exhibited excellent mechanical properties and competitive conductive properties.[1] However, as with all other polymer composite materials, there are continuous efforts to balance both conductivity and strength simultaneously. To reach optimum levels of both conductivity and mechanical properties simultaneously, graphite is typically used in the wt % range of 60%-80%. Reducing graphite content further than 60 wt % compromises conductivity, while excessive graphite over 80 wt % compromises mechanical strength. PET plates with 65% graphite powder and 7% glass fibers have shown bulk conductivities as high as 230 S/cm, over twice the target. Tensile and flexural strengths have been measured to be 36.5 MPa and 53.0 MPa, respectively. PPS plates with 70% graphite and 6% carbon fibers have exhibited even higher properties. Bulk conductivities improved to 271 S/cm with excellent tensile and flexural strengths of 57.5 MPa and 95.8 MPa, respectively.

The main drawback in using polymer composite materials is their relatively low conductivity when compared to graphite and metal plates. While mechanical strength exceeds that of graphite plates, polymer composite plates exhibit a much lower strength than that of metal plates. Most polymer composite plates typically exhibit in-plane conductivity in the range of 55-120 S/cm, with PET based plates reaching 230 S/cm.[1] This is still several orders of magnitude lower than metal, and about half that of graphite. Through-plane conductivities for most polymer composite plates range from 19-50 S/cm. The wet-lay generated plates have a through-plane conductivity of 18-25 S/cm while the vinyl ester plates have exhibited values up to 50 S/cm. Through-plane conductivity is the one area where the wet-lay generated bipolar plates are lower than vinyl esters.

The manufacturing cost of polymer composites is a recurring topic of interest for their commercialization. Molding of channels and material costs for polymer composite bipolar plates have been estimated to be as low as \$10-30/kW.[2] The current cost estimate of machined graphite bipolar plates is \$60-65/kW, even superseding that amount due to additional coatings or sealants. Development of polymer composite plates that reach the DOE cost target of \$10/kW has been successful in a small batch process.[7] The development of a continuous process is highly anticipated to meet the \$10/kW target. On a cost basis primarily, polymer composite plates are a favorable material for bipolar plate production.

Raw material costs among the polymers used to produce bipolar plates are an important consideration in evaluating their economical compatibility. PET is generally inexpensive, less than \$2/lb with PPS a little more costly at \$5/lb. PVDF powder is sold in the range of \$8.50-11/lb.[39] Vinyl Esters cost around \$5-10/lb. Liquid crystalline polymers, useful with injection molding bipolar plates, typically cost around $10/lb. Graphite particles themselves cost around $2-3/lb.

In Table 2.3 the conductivity and strength are compared for different types of polymer composite bipolar plates. The in-plane conductivity for the wet-lay composite plates is larger than the vinyl ester and epoxy thermosets and also the PVDF. Through-plane conductivity compares well to the vinyl esters. The tensile and flexural strengths of the wet-lay composites are noticeably higher than those values for the other composites.

Table 2.3 - Properties of polymer composite bipolar plates

Manufacturer	Polymer	Graphite/glass or reinforcing fiber (wt/wt%)	Conductivity (S/cm)		Mechanical Strength	
			In-plane	Through-plane	Tensile (MPa)	Flexural (MPa)
GE[35]	PVDF	80	119	-	-	30.0
GE[34]	PVDF	64 + 16 CF	109	-	-	42.7
LANL[28]	Vinyl Ester	68	60	-	23.4	29.6
Premix[28]	Vinyl Ester	68	85	-	24.1	28.2
BMC[28]	Vinyl Ester	69	30	-	26.2	27.9
Commercial[28]	-	-	105	-	19.3	20.7
BMC 940[40]	Vinyl Ester	-	100	50	30.3	40.0
Plug Power[41]	Vinyl Ester	68	55	20	26.2	40.0
Commercial[25]	Epoxy	90	3	-	-	-
DuPont[41]	-	-	-	25-33	25.1	53.1
SGL[42]	-	-	100	20	-	40.0
Virginia Tech[1, 37]	PET	65 + 7 GF	230	18-25	36.5	53.0
Virginia Tech	PPS	70 + 6 CF	271	19	57.5	95.8

Although many polymers and different combinations of conductive fillers have been investigated, the wet-lay process using polymer fibers, reinforcing fibers and graphite powder has been shown to produce bipolar plates with the best balance of properties.[1, 37] Mechanical strength is higher than that of any other polymer composite bipolar plate. Bulk conductivity values not only are well above the DOE target, but are consistently over twice the bulk conductivity values of most other polymer composite materials while still being able to maintain high strength. Where the wet-lay bipolar plates are deficient is the through-plane conductivity. These values are lower than those of all other polymer composite plates from which through-plane conductivities have been reported. If through-plane conductivity can be increased by a factor of two or more, then wet-lay generated bipolar plates can potentially exhibit the best balance of conductivity and strength of all other polymer composite bipolar plate.

2.4 Molding technologies and their applications in the production of bipolar plates

Polymer composite materials have traditionally been formed or molded using compression molding. This is generally due to the poor flow nature of polymer composites containing high levels of conductive fillers, especially fibers. Injection molding is the ideal method for forming channels because it allows for injection of the resin into a cold mold followed by forming and ejection of part all in a relatively short amount of time. However, it is difficult to use this method with polymer composite with high levels of fillers. Injection molding has still been attempted with limited success with polymer resin, graphite powder, and even small weight percents of carbon fiber. The third method is injection/compression molding, incorporating the functions of the previous two methods. Although no reports have been made on the use of injection/compression molding for the production of bipolar plates, its background and potential for use should be discussed.

2.4.1 Injection molding

Injection molding (IM) is probably the most widely used process for manufacturing thermoplastic parts, converting thermoplastic pellets or powder to a large number of useful products.[43, 44] IM is a technique where a polymer or polymer composite is heated to a temperature where the compound will flow readily and then injected into a cold mold. In essence, what happens is that polymer pellets are plasticated in a single-screw extruder, and the melted polymer accumulates at the end of the screw. The polymer is pushed forward by the screw into a mold cavity. The melt enters the mold cavity and begins to cool and solidify as it touches the mold wall. Once solidification is complete, the mold plates open and the part is ejected.

A major advantage to using IM is the relative ease and speed at which parts can be developed. Injection molding is favored over compression molding or other competitive molding processes because of its rapid cycle time.

The major difficulty in using IM to manufacture bipolar plates is its inability to handle materials with poor flow characteristics. Wet-lay material consists of a large percentage of fibers and fillers that the viscosity is very low, therefore making it too difficult to extrude into a mold. Most IM applications deal with polymer pellets by themselves or mixed with other polymer particles or powders. The addition of carbon, glass, or other reinforcing fibers exhibits an inability for the material to readily flow even when heated.

Low-flow or poor flowing materials are not the only drawback to using injection molding. Warping and shrinkage of final parts are common outcomes with IM.[44] Colder molds create a greater tendency to warp in several ways. There is less opportunity for relaxation of orientation, and the more rapid cooling produces unwanted cooling stresses. Increasing packing pressure also creates more stresses and inhibits relaxation. Another disadvantage to injection molding is that there is always some scrap material that is wasted.

Although the production of polymer composite plates by means of injection molding can be troublesome, there has been success in producing plates, depending on the fillers and additives.[45] Standard composite mixtures consisting of thermoplastic polymer and a carbon compound mixture using an IM process have shown good results. Injection molded polymer composites using 50% wt. graphite as an additive, with no carbon fiber or other reinforcing fiber have shown bulk conductivities of 20 S/cm, much lower than the target. The thickness of the plates is 4 mm, which is 1mm thicker than the target of 2-3 mm.[46] The demonstrated cycle time for the IM process is 30-60 s, with the annual output in the range of several thousand plates, either blank or with a flow-field. The opportunity to increase the annual production rate is possible with other molding processes while maintaining electrical and mechanical properties.

Further accomplishments have been made with injection molding using a liquid crystalline polymer (LCP) as the polymer resin.[36] LCP's have orientational order but very little, if any, positional order. This allows them to flow like a liquid but have the mechanical stability (high tensile strength) of a solid. The LCP composite material also includes nickel-coated graphite fibers less than 2 cm in length in the weight percent of 5-

50%, with a non-liquid crystalline binder resin at 0.1-20% by weight. The resistivity is determined to be 0.01 Ω-cm, very comparable to graphite plates, with a thickness in the range of 1-3 mm.

2.4.2 Compression molding

Compression molding is primarily used to process thermosets or difficult-to-process thermoplastics.[37, 47-49] Examples of these thermoplastics would be fiber filled composites or elastomers. To accomplish compression molding, a certain mass of material is place in the mold whose volume is adequate to fill the mold when the plates are pushed together. The preliminary material may be in the form of a sheet, or stacks of sheets containing long continuous fibers. Initially the surface area of the plates may be completely or only partially covered by the material. However, when the mold is compressed and the plates are brought together, the material is forced to cover the rest of the mold surface. This applied pressure leads to shaping, compaction, and bonding of the sheets of material.

Compression molding is a simple and effective way to get channels formed into a polymer composite preform. Because polymer composite materials with high filler contents do not flow readily, compression molding can be used to stamp channels into a blank preform or raw wet-lay material. Although injection molding has been used successfully with polymer resins containing fibers up to 5-10 mm, generally fiber lengths greater than 10 mm require compression molding.[49] Fiber lengths used in wet-lay material are >10 mm.

The challenge in making compression molding the most efficient means of forming channels relies in minimizing heating and cooling times. Specifically, is it possible to get a heated part into the mold and compressed while the preform still retains enough heat to remain formable? The maximum processing temperature for most polymer resins in use are commonly about 20-40 ^{o}C above the melting temperature. This small temperature gap is problematic to ensure that convection and conductive losses are kept minimal while the hot preform is transferred from the heater into the mold and compressed. Experimentally this is difficult to test, but with the help of heat transfer models it can be estimated.

Polymer process modeling, design sensitivity, and numerical optimization are combined to design processes for the manufacture of plastic components via the compression molding process.[50] To compute the fill time and filling pattern, a moving boundary can be developed based on the volume-of-fluid (VOF) technique. The design sensitivities for the transient coupled pressure and volume fraction analyses are evaluated using the direct differentiation method. Molding and sensitivity analyses are combined with numerical optimization to design, not just analyze, the compression molding process. These types of models have been used to analyze the complex flow of a polymer melt in arbitrary geometries under various pressure conditions. This provides engineers with information on not only compression molding, but also injection molding.[51]

2.5 Heating technologies and their applications in the polymer processing

This section discusses the importance of heating performs quickly to prepare them for channel molding. Once heating is obtained, the goal is to insert a heated blank preform or wet-lay material into a cold mold that will allow the polymer to form and crystallize while cooling to a desired temperature. This is a key step in the design of a fast, efficient process that can be commercialized into a mass production process. In addition to heating, the cooling of the bipolar plate is of similar importance. This cooling time needs to be very fast also, much less than one minute. One of the major obstacles in the overall manufacturing scheme is designing a process where the raw material or a preform can be heated to a processing temperature just before the gas flow channels are compression molded into the part. There are several different types of possible heating methods, but the electrical properties of the plate may determine how well a particular heating method will work. For instance the plate may be too conductive to use a certain method, but not conductive enough for another one.

2.5.1 Resistance Heating

Resistance heating involves passing an electric current through a partially conductive material, which is the heating element.[52] This method usually involves the embedding of an electrode in the structure, or attaching an electrode on the structure. The materials of heating elements cannot be too low in electrical resistivity, as this would result in the resistance of the resistance to be too low. The resistivity cannot be too high either as this would result in the current in the heating element to be too low (unless the voltage is very high).

Carbon fiber composites can be heated or cured by ohmic heating resulting from passing an electrical current through the fibers. The power developed in the part is given by:

$$P = V\ I \quad \text{(Watts)} \tag{5}$$

where:

V = voltage induced (volts)

I = current induced (amps)

Because V = I R, the power can now be re-written as:

$$P = I^2 R \tag{6}$$

where R is the resistance of the material (Ohms)

Carbon fiber composites have shown to be an attractive heating element for resistance heating. Carbon fiber mats exhibiting an electrical resistance of 0.11 Ω cm have heated up to 134 ^{o}C in just over 200 seconds using a power supply of 6.5 W.[52] This time frame is much too long to be competitive. Increasing the power, thereby directly increasing the heating rate would resolve this issue so long as the power is not too high that it burns the sample. Materials with high thermal conductivities heat more rapidly with resistance heating. Thermal conductivities for polymer composite bipolar plates, even though electrically conductive, are generally low, around 4-5 W/m K. Therefore, even using high power supplies the heating time is large.

Electrical resistance heating is relatively simple and the capital is inexpensive, but it places restrictions on the process design. The major restriction is physical contact between the electrical source and sample. An ideal bipolar plate manufacturing process may include continuous movement of samples through a heater and into a mold. This is unattainable with electrical resistance heating and would add significant processing time to the overall manufacturing scheme. Another disadvantage is the non-uniformity of current passing through the sample. Electricity generally takes the shortest route through a conductor, creating an uneven distribution of heat when significantly large samples are concerned. A majority of the sample would then rely on heat by conduction to finalize the heat transfer. Furthermore, because of electricity's generation and transmission losses, this method is not an efficient means of heat transfer when compared to other heating technologies.

2.5.2 Microwave heating

In microwave processing, energy is supplied by an electromagnetic field directly to the material. This results in rapid heating throughout the material thickness with reduced thermal gradients. This effect is called volumetric heating and can reduce time and save energy. Both the microwave field and the dielectric properties of the plate govern its ability to absorb microwave energy. Knowledge of electromagnetic theory and dielectric response are essential to optimize the processing of materials with microwaves. In Fig. 2.4 is shown the electromagnetic spectrum displaying the frequency range of microwaves and other common waves.

The main mechanism of interaction between materials and microwaves are dipole interactions.[53] Dipole interactions occur with polar molecules. The polar ends of a molecule tend to align themselves and oscillate in step with the oscillating electric field. Collisions and friction between moving molecules result in heating. Generally the more polar a molecule is, the more effectively it will couple with the microwave field.

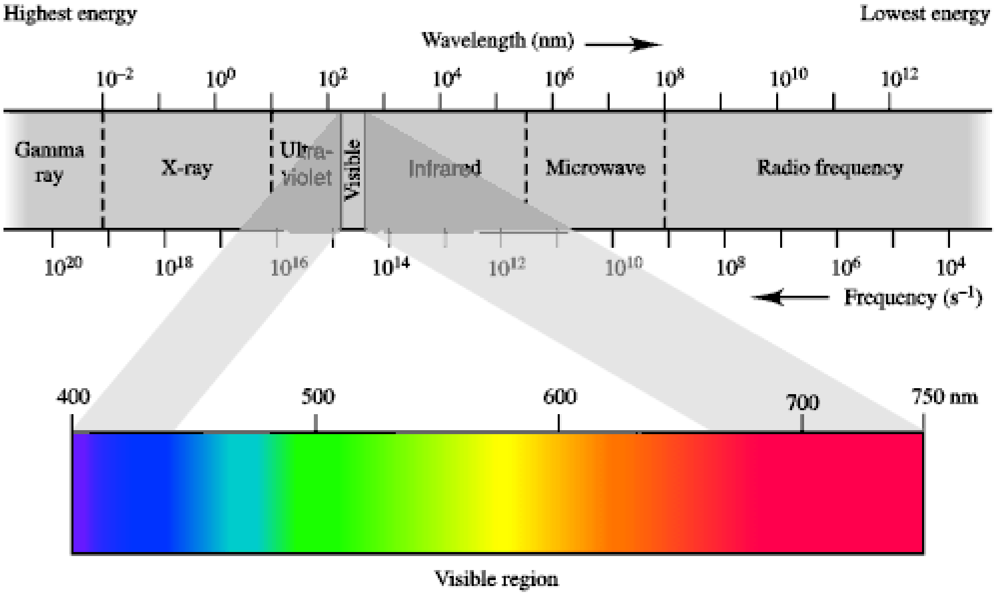

Figure 2.4 – Electromagnetic spectrum.[54]

Microwave processing has been pursued heavily in the rubber and food industry over the past few decades.[55] The electric field in industrial microwaves operates at about 2.45 GHz as opposed to the conventional microwave ovens that operate at 900-1000 MHz. Microwave energy is converted into heat by interactions between the microwave field and the conductivity or dielectric properties of the material. The average power per unit volume converted into heat is:

$$P = 2\pi f\, C\varepsilon' \tan\delta\, E^2 \tag{7}$$

where:

f - frequency of electrical field

C – capacitance of the material in picofarads

ε' - dielectric constant; a measure of resistance to an electric field

tan δ - loss tangent; ratio of reactance to resistance

E – electric field strength in V/cm

where:

$$\varepsilon'' = \varepsilon' \tan \delta \tag{8}$$

where ε" is the dielectric loss factor; indicates the ability of a material to store energy

The loss tangent is probably the most important parameter in microwave processing.[56, 57] This parameter characterizes the ability of the material to convert absorbed microwave power into heat. A "high loss" material (high tan δ and ε") is said to heat more effectively than a "low loss" material (low tan δ and ε").

Since the electric field penetrates and is generated within, power dissipation is independent of the heat flow through the material. This holds until the conduction and convection losses become important. Unlike conventional thermal heating methods, the thermal conductivity of a material does not directly affect the strength or power of the electric field. Instead the heating rate is based solely on the dielectric properties of the material. Orientation polarization due to the presence of permanent dipoles in a molecule is the major energy coupling mechanism available for heating.[58, 59] To evaluate the influence that structure-property relationships will have on microwave processability, it is important that the dielectric properties be thoroughly investigated and correlated with chemical and morphological conformation.

Materials can either absorb or reflect the energy from a microwave electric field. The chemical composition will affect how it behaves in a microwave field. In Fig. 2.5 is shown a general relationship between dielectric properties of a material and temperature. This figure shows that until the T_g of the polymer is reached, it is difficult to heat the material because the dielectric properties are so low. However, once the glass transition temperature is reached, the dielectric properties increase and the material will start to absorb microwaves and heat up.

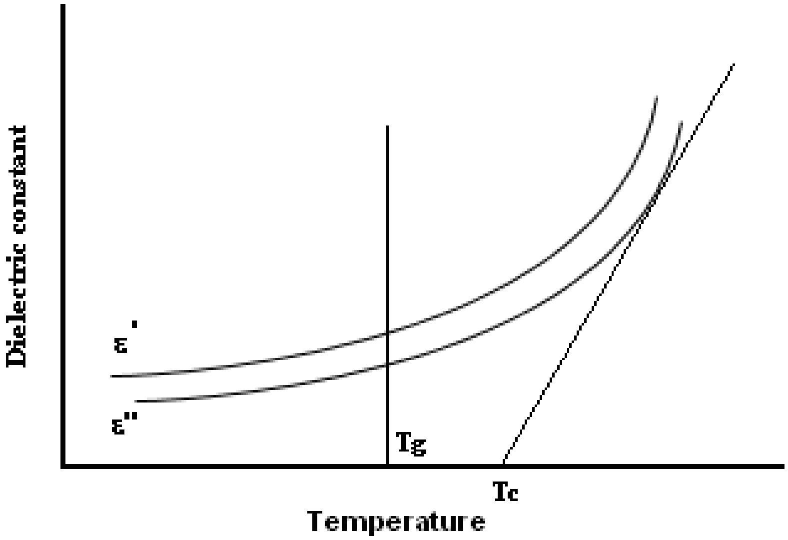

Figure 2.5 – Representation of the dielectric behavior of polar polymers in the microwave frequency range.[60]

Even though polar groups may be present in a long polymer chain, the dielectric loss factor is relatively low (polymers usually << 1.0 at room temperature and in the microwave frequency range) when compared to water (≈ 20.0) and can still be difficult to initiate heating with microwaves alone. Low dielectric loss factors and high glass transition temperatures may require an additional heating method to be incorporated to preheat polymers.

Microwave processing can be used over a broad range of polymers, including thermosets, thermoplastics, rubbers, and composites where crystallinity and conductivity are variant. With polymers, crystallinity affects the dielectric properties. Polymers with a degree of crystallinity above 45% are essentially transparent to microwaves due to the restriction of dipoles.[57] As the degree of crystallinity increases, the loss factor decreases. The addition of conductive fibers or fillers can strongly influence the overall dielectric loss. Microwaves selectively couple with the constituent materials of higher dielectric loss. To complicate matters, dielectric properties of composites are anisotropic, significantly affecting the penetration of microwaves. The presence of conductive fillers may inhibit microwave heating by decreasing the skin depth (also called penetration depth). The reason why foodstuffs containing water and other conductive particles like salt heat so well is that foodstuffs generally have a microwave impedance of the order of 100 ohms. Carbon fiber composites are typically of the order of 0.5 ohms. The microwave impedance of air is about 377 Ohms; thus microwaves in a microwave oven couple well with most foodstuffs. The very low impedance of carbon fiber composites cause the microwaves to be reflected from their surface so very little heating occurs.

Conductors modify the electric field pattern in and around the composite, potentially resulting in very different heating profiles than from the neat resin.[61, 62] The limitation in using conductive fillers and fibers is their high dielectric loss. Conductive particles reflect the microwaves so that efficient heating of a composite material is unattainable. Incorporating conductive fillers may result in the formation of local hot spots and electrical arcing. Arcing is caused by a jump in current from one piece of conducting material to another through an insulating medium. The results can be a spark, or as much as a fire, as may be seen by placing metal in a conventional microwave.

In graphite loaded bipolar plates, arcing can occur within the material from two adjacent, but non-connected particles of graphite. As discussed, graphite is very conductive, and the addition of carbon reinforcing fiber in some of our plates helps add to the conductivity. Because our plates are conductive, they appear electromagnetically similar to a metal plate, acting as a good reflector of microwaves. Although the number of candidates for microwave heating is numerous, typically, conductive polymers or the use of conductive fillers are not suitable for this application.

2.5.3 Dielectric heating

As discussed in the previous section, heat transfer to poor thermal conductors is difficult. Surface overheating or burning may occur. Dielectric heating may be a solution to this problem. The phenomenon known as dielectric heating occurs when an electrical insulator is placed in a high frequency field, similar to that of microwaves.[63] Because the electric field penetrates the material, heat is generated from within. The contrast to microwave heating is the lower frequency dielectric heating operates at, in the range of 2-100 MHz.

In general there are two types of matter (substances) in the universe that affect electromagnetic (EM) waves, conductors and insulators. These properties are determined by the atomic structure of the atoms and molecules. Insulators are called dielectrics by scientists. Most, but not all conductors are metals, such as copper, aluminum, silver and gold. Most, but not all dielectrics are non metals. Examples of dielectrics are paper, plastic, Teflon, glass, ceramic and wood. Very pure water is a good dielectric substance, but salt water is a rather poor conductor.

Most molecules are polarizable in an electric field as seen in Fig 2.6. The degree of polarization and the energy required to achieve it control the loss factor or dissipation factor of the material. In a high frequency electrical field, a considerable amount of energy is imparted to each molecule of the material, causing the molecules to oscillate as the field alternates with each cycle. The energy appears as heat. In a uniform electric field, and with a homogeneous material, the same amount of heat is imparted to each molecule. If the surfaces are being cooled, the temperature rise at the surface is much less than the interior because the heat is generated within. This effect is undesirable when heating polymer composite material because it is necessary to have the surfaces of preform plates to be heated in order to mold channels.

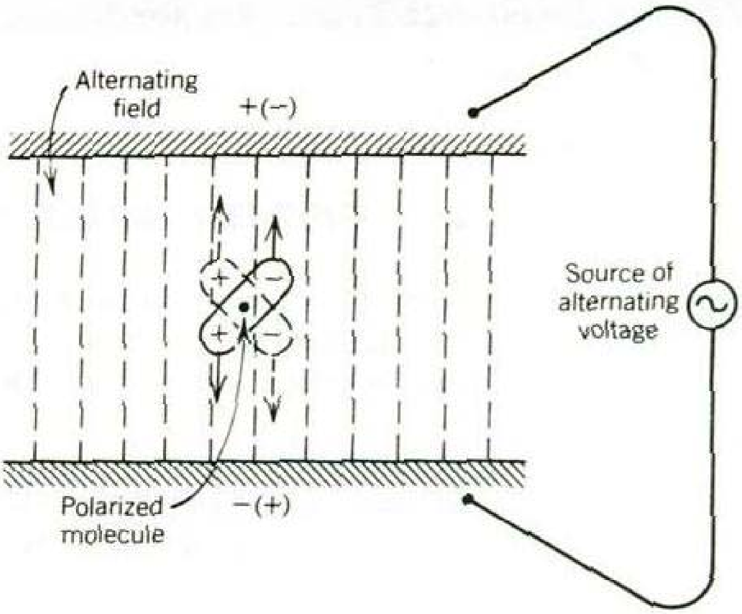

Figure 2.6 – Molecular dipole immersed in a high frequency field.[63]

Because dielectric heating requires an electric field, the materials must be poor conductors or non-conductors of electricity. A good conductor would act as a short circuit and the fields near the conductor would be very weak. The conductivity of conductive polymer composite preforms makes them an unlikely candidate for dielectric heating. Even if neighboring graphite particles are not touching, when placed in an electric field, current could jump or arc through the plate. This would also cause a short circuit effect as it would in a microwave frequency range. Dielectric heating is most useful in applications where the sample to be heated is an electrical insulator such as rubber, wood, and certain polymer resins.

2.5.4 Radiation heating

The process by which heat is transferred from one body by virtue of its temperature, without the aid of an intervening medium, is called thermal radiation. The physical mechanism is usually envisioned as transported electromagnetic waves or transported by photons. The temperature and the physical properties of a material will dictate the radiant efficiency and wavelengths emitted. Thermal radiation is often used to heat up preforms used in blow molding or plastic sheets used in thermoforming. The major property determining how well a material will absorb or reflect radiation waves is its emissivity. This is its relative emissivity based on a blackbody with a perfect emissivity of 1.0.

The emissive power is given by:

$$P = \varepsilon \sigma T^4 \quad (9)$$

where:

ε - emissivity of material

σ - Stefan-Boltzmann constant

T – Temperature in Kelvin

Further calculations can be done to estimate the time required for a material to heat up using radiation heating. Biot and Fourier relationships are dimensionless quantities allowing for these types of calculations to be estimated using the emissivity and thermal conductivity of the material.[64] It is sometimes assumed that all the radiation from the light source is absorbed at the surface. However this is not always the case as some materials transmit portions of the incident radiation of certain wavelengths rather than absorb them. Graphite composite plates are not a blackbody but considered to be a gray body. Typical emissivity values for graphite are 0.8-0.9.

To better approximate the quantity of heat transferred from a radiation source, it is common to view the system as a resistance network. The radiation surface, sample surface, and medium between the surfaces are represented by a resistor as shown in Fig 2.7.

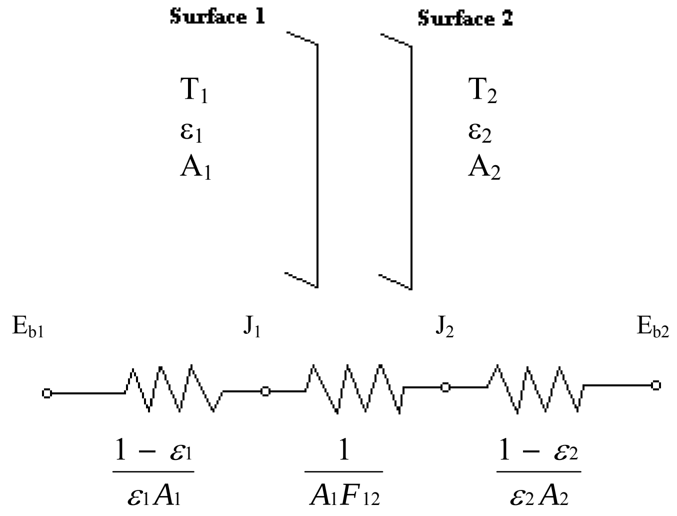

Figure 2.7 – Radiation network for blackbody radiation source and graybody sample.[65]

Where:

T = surface temperature

ε = emissivity

A = surface area

F_{12} = view factor

E_b represents the blackbody emittance

J_i represents the potential

The radiant heat transfer can be calculated as:

$$q = \frac{\Delta E_b}{\sum R} \tag{10}$$

Where R is the resistance in Ohms and q is the heat flux in Watts or BTU/hr.

Substituting in $E_b = \sigma T^4$, the net radiative heat transfer is:

$$q = \frac{\sigma (T_1^4 - T_2^4)}{\frac{1-\varepsilon_1}{\varepsilon_1 A1} + \frac{1}{A_1 F_{12}} + \frac{1-\varepsilon_2}{\varepsilon_2 A_2}} \tag{11}$$

Beer's law is also useful in determining the intensity of incident radiation as a function of depth. Mathematically, the absorbing of radiation is treated as a source term in the energy equation with units of energy per unit area per unit time. Beer's law is given by:

$$\frac{I_x(\lambda)}{I_s(\lambda)} = e^{-k(\lambda)x} \tag{12}$$

where:

I_s – Intensity of radiation at the surface

I_x – Intensity of radiation at depth, x k(λ) – absorption coefficient

After performing an energy balance to find energy per unit area per unit time, equation 12 becomes:

$$\dot{S} = I_s k(\lambda) e^{-k(\lambda)x} \tag{13}$$

Radiation heating is particularly valuable when just heating the surface. Once heat is absorbed on the surface, heat will then conduct inwards towards the center. Conduction up to several hundred degrees Celsius can be effective but relatively time consuming.

Radiation heating needs to be carefully evaluated for compatibility with the sample. As heat is conducting inwards towards the center, the surfaces of the sample continue to increase in temperature. It is possible to degrade the polymer on and near the surface while this occurs. The next subsection introduces a method to heat the entire part at once, eliminating non-uniform heating.

2.5.5 Induction heating

The basis for heating by induction was discovered by Michael Faraday in 1831. His experimental conclusions stated that an electric current can be produced by a changing magnetic field. These effects are used to design transformers by changing the level of voltage from one circuit to another. A byproduct of this transformation was heat generated in the magnetic core of the transformer. After general acceptance of induction for the melting of metal, the attention of scientists and engineers was turned in another direction. Because the depth of current penetration in a given metal varies with the material electrical resistivity, magnetic permeability, and frequency, it is possible to heat specific areas of a piece of metal without heating others.[66, 67] This leads to welding, spot heating, annealing, etc.

Induction heating occurs when an electrically conductive material (magnetic or nonmagnetic) is exposed to an alternating magnetic field, eddy currents are induced and the material is heated due to resistive losses of the eddy currents (Fig. 2.8)[68]. Polymer composite bipolar plates can be induction heated because of the conductive graphite filler or carbon fiber reinforcements. Glass fiber reinforced composites can be induction heated by means of an additional electrical conductor. Again, graphite particles are acceptable as conductive fillers in these applications. Heat generation in thermoplastic composites due to induction heating occurs due to the induced eddy currents flowing along conductive loops in the composite. In each conductive loop, heating occurs wherever there is a voltage drop due to electrical resistance or impedance. The resultant heating is volumetric in nature, as it is an internal heat generation mechanism dependent on intrinsic properties of the composite. Induction heating generally follows Ohm's law (Eqs. 5 and 6 from section 2.6.1). The resistance of the material is the most important parameter when sizing a generator. Knowing the resistance of the material and either the induced voltage or current, power can be calculated using Ohm's law in order to size an induction heater. The induced voltage follows the equation:

$$\mathrm{V}_{\mathrm{ind}} = \mathrm{N}\frac{d\Theta}{dt} \tag{14}$$

where:

N – number of coil turns

$\frac{d\Theta}{dt}$ - is the rate at which the magnetic field is changing in lines per second

Equation 14 can be re-written as:

$$V_{ind} = 2\pi f \mu H A \tag{15}$$

where:

f – frequency of field

μ - magnetic permeability

H – magnetic field intensity

A – area enclosed by the conductive loop

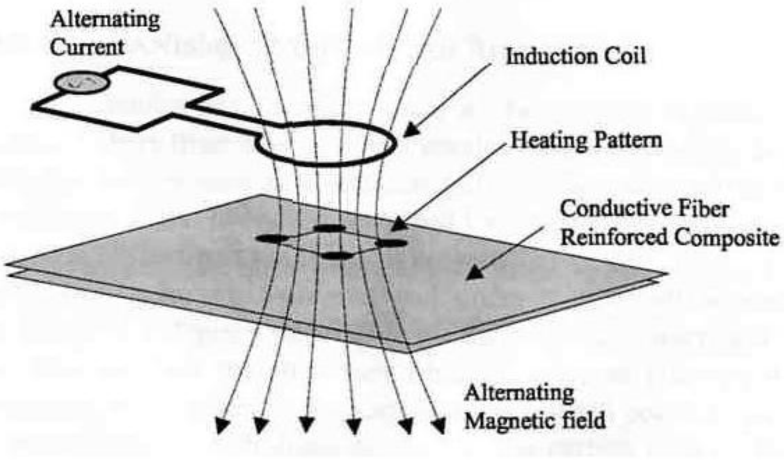

Figure 2.8 - Schematic of the induction heating process.

Although metals heat well and are the most widely used candidate for this method, it is not necessary that a magnetic metal be the only prospect for induction heating.[66, 69, 70] Magnetic materials are excellent candidates due to the hysteresis losses that occur in addition to the generated eddy currents. These losses are caused by friction between molecules when the material is magnetized first in one direction and then in another. The molecules can be regarded as small magnets which turn around with each reversal of direction of the magnetic field. Work is required to turn them around, and this energy is converted into additional heat. Hysteresis losses are not required for good induction heating allowing conductive thermoplastics such as polymer composite bipolar plates to be compatible with induction heating.

A representation of the overall process for bipolar plate production is shown in Fig 2.9.[71] Preforms can be placed on a conveyor belt, where they are transferred to a heater of some sort. The heater in this particular process is induction heating. It is very useful because of the ability to roll under the heating coils without any contact with the heating device at all. When the plate is heated to the desired temperature, it is then transferred to a mold where is may be compression molded. The heating process will be shown later in this section to take less than 10 seconds while the preform compression molding process has also shown to take less than 10 seconds.[47]

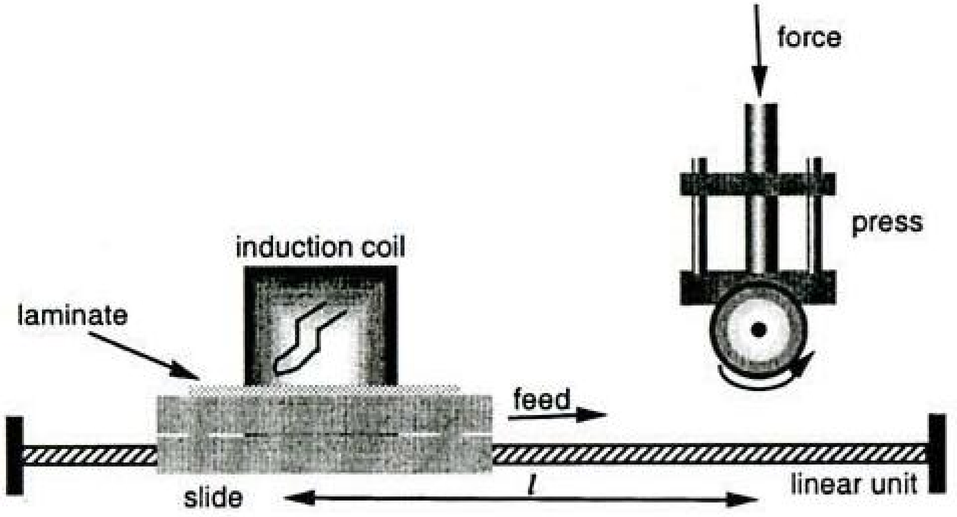

Figure 2.9 – Schematic of a continuous induction heating process.

The primary advantage to using induction heating is the high volumetric heating rates, leading faster production times compared to conventional heating methods. As stated earlier, faster production rates is an important goal towards the mass production of bipolar plates. Pinpoint accuracy can be obtained using induction heating.[72, 73] Good accuracy is a result of flexible and high-precision control of the process. The more traditional heating methods rely on conduction, convection, or radiation heat transfer through the thickness of the composite, requiring time to equilibrate at a desired processing temperature. As shown in Fig. 2.10, temperatures near the processing temperatures of PET and PPS can be reached in less than 10 seconds.[71] This is due to the eddy current generation within the entire part of the material and the high efficiency or high transferable heat (Fig. 2.11). These experiments were performed with a 650-1000 kHz, 5.2 kW induction generator. With a variable frequency generator, it is also possible to analyze how the frequency affected the heating rate. As expected, using a frequency of 1000 kHz the heating time to 300 ^oC took 6 seconds, while at 800 kHz it took 20 seconds. If the frequency was increased to 26 MHz, a heating time of 1 second was calculated. Experiments were also performed to find out how the distance between the coil and sample affected the heating rate. When the coil was 2 mm from the sample, it was able to heat up to 300 ^oC in 6 seconds. When the distance was increased to 10 mm, the heating time took 120 seconds. This shows the importance of making sure that the magnetic field surrounds the part to be heated or the eddy current generation will be weak.

Because induction heating has shown excellent results with conductive polymer composite, it may have the most potential in a cost effective and time limited process. The amount of transferable heat is greater than any other method, so it would be necessary to have a significant advantage in another method to choose it over induction heating.[71] The fact that the preform does not have to come into contact with any part of the heater is important. It may save time not to have clamps or nodes contact the preform. Using a cold mold, the heated plate can be formed, cooled, and crystallized all in a matter of seconds. When preforms are used as the heating component, preliminary heating of a blank preform coupled with compression molding has shown to take less than 10 seconds using a cold mold. Induction heating makes this process 100 times faster than conventional methods where the preform is normally required to heat by conduction, molded, and then cooled by conduction.

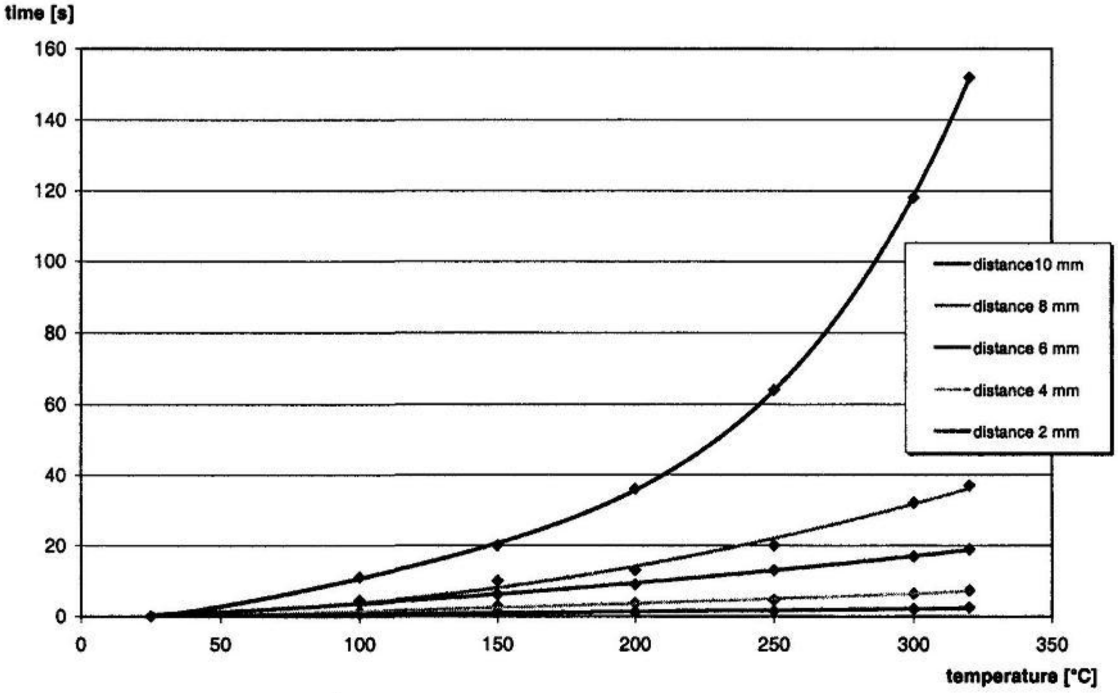

Figure 2.10 – Influence of the distance between induction coil and sample on the heating time. Sample is 3 mm thick.

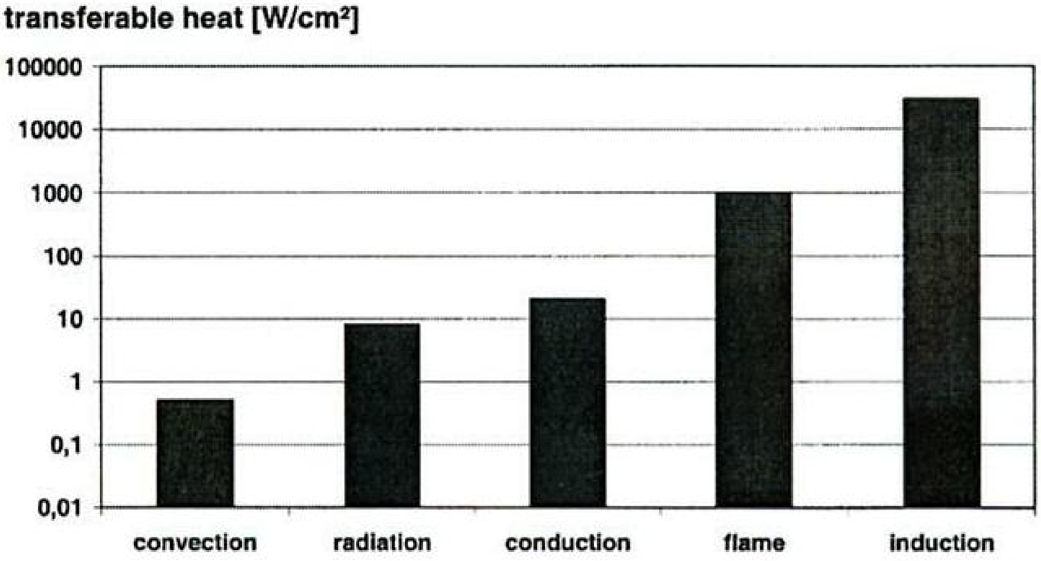

Figure 2.11 – Transferable heat with different heating mechanisms.

2.6 Research Objectives

Fuel cells have gained a large amount of interest in the last few years as a non-emission power supply in the automotive industry. With the bipolar plate representing about a third of the overall cost of a fuel cell stack, it is important to develop a cost effective bipolar plate comprising of low material costs coupled with low manufacturing costs. Low manufacturing costs are mainly dependent on the required processing time to heat a particular material and the subsequent ease of forming channels while cooling the material.

The use of polymer composites has moved to the forefront as a possible material from which bipolar plates are made. Metal, graphite, and carbon/carbon bipolar plates have all performed well when comparing to DOE target values but they continue to require expensive, complex, and costly machining steps which makes it highly unlikely that these types of materials can become commercialized. The material costs of polymer fibers, graphite particles, and carbon fiber are fairly inexpensive.[7] The material costs are generally about \$4/kW, with the total cost target for a bipolar plate at \$10/kW. It may be possible to reach the demanding cost targets if an automated process can be developed. The Institute of Gas Technology (IGT) and its subcontractors have built a pilot production line with a molding capacity of 5 plates/hour.[7] The pilot line addresses the key automation steps for preparation of the composite blend, transferring to the mold, forming of the plates, releasing from the molds, post-molding operations, and QA/QC operations.

The goal of my research project is to develop a processing method to manufacture polymer composite bipolar from wet-lay material in a time efficient manner. The process is initiated with the wet-lay process combining polymer fibers, reinforcing fibers, and graphite. From the wet-lay material there are two options which are going to be investigated. The first is the ability to insert stacks of wet-lay material into a mold to compression mold channels directly. The second option is to compression mold a blank preform which will have channels molded into it in a subsequent step. Both options will require heating the sheets or preform to a desired temperature. The best heating method will be determined using heat transfer models, calculations, and experimentations. Once the material is heated, channels will be formed into the part, where more design parameters will come into play. A challenging part of this project is a way to get the heated element into a mold quickly. Heat losses by convection and conduction are significant between processing steps so this is an important design area. To further complicate the automation of the process, polymer composites can become flimsy when heated above the melting point making them difficult to handle and drop into a mold. The mold used for producing channels will have to be at a temperature lower than the melt temperature of the resin to cool the material down through the crystallization temperature range of the polymer. This cooling rate should be fast enough to meet time constraints for the overall process but not too fast where the polymer is quenched and does not crystallize. At the end of the process a bipolar plate will be generated with channels molded into the surfaces. Tests will need to be done on the plates to ensure that they meet conductivity, mechanical strength, permeability, and other requirements set by DOE mentioned in previous sections.

Questions that will need to be addressed are: Is induction heating best for conductive polymer composite plates or is radiation heating sufficient? What is the optimum graphite percentage that yields satisfactory conductivity properties as well as mechanical properties? How can a heated part be transferred to a mold for compression molding? What is the optimum temperature of the mold when the preform is inserted? What is the desired temperature of the plate when it can be released from the mold? What is the cost of the process and what is the estimated rate of production?

2.7 References

1. Huang, J., Baird, Donald G., McGrath, James E., *Development of Fuel Cell Bipolar Plates From Graphite Filled Wet-lay Thermoplastic Composite Materials.* J. Power Sources, **150**, (2000), 110-119.
2. Bar-On, I., Kirchain, Randy, Roth, Richard, *Technical Cost Analysis of PEM Fuel Cells.* J. of Power Sources, **109**, (2002), 71-75.
3. Landis, L., Tucker, J. L., in R&D Magazine, (2002), 36-38.
4. *POCO Quote*.
5. Wind, J., LaCroix, A., Braeuninger, S., Hedrich, P., Heller, C., Schudy, M., *Metal Bipolar Plates and Coatings*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editors: H. Wang, M.A. Sweikart, J.A. Turner, (2003), 295-307.
6. Besmann, T., Klett, James Henry, Jr., Lara-curzio, Edgar, *Carbon/Carbon Composite Bipolar Plate for Proton Exchange Membrane Fuel Cells.* J. Electrochem. Soc., **147**(11), (2000), 4083-4086.
7. Onischak, M., Marianowski, Leonard G., Fan, Qinbai, Chervinko, Jeremy, *Development of a $10/kW Bipolar Plate Separator Plate*, in DOE/EPRI/GRI Technology Review Conference. Institute of Gas Technology: Chicago, Il., (1999), 1-5.
8. Mepsted, G.O., Moore, J.M., *Performance and Durability of Bipolar Plate Materials*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd., (2003), 286-293.

9. Pylkkanen, T., WO 02/071524 A1 (2002).

10. Ghouse, M., Abaoud, H., Al-Boeiz, A., Al-Zaharani, S., *Fabrication and Characterisation of the Graphite Bi-Polar Plates Used in a 0.25 kW PAFC Stack.* Int. J. Hydrogen Energy, **23**(8), (1998), 721-730.

11. Cho, E.A., Jeon, U.-S., Ha, H.Y., Hong, S.-A., Oh, I.-H., *Characteristics of Composite Bipolar Plates for Polymer Electrolyte Membrane Fuel Cells.* J. Power Sources, **125**, (2004), 178-182.

12. RoBberg, K., Trapp, V., *Graphite-Based Bipolar Plates*, in *Handbook of Fuel Cells-Fundamentals, Technology and Applications*, H.A.G. Wolf Vielstich, Arnold Lamm, Editors: John Wiley & Sons, Ltd., (2003), 308-314.

13. Scholta, J., Rohland, B., Trapp, V., Focken, U., *Investigations on Novel Low-Cost Graphite Composite Bipolar Plates.* J. Power Sources, **84**, (1999), 231-234.

14. Baird, D.G., Huang, Jianhua, McGrath, James E., *Polymer Electrolyte Membrane for Fuel Cells.* Plast. Eng., **59**(12), (2003), 46-55.

15. Wang, H., Sweikart, Mary Ann, Turner, John A., *Stainless Steel as Bipolar Plate Material for Polymer Electrolyte Membrane Fuel Cells.* J. Power Sources, **115**, (2003), 243-251.

16. Morita, Y., Kamoshita, S., Shimizu, T., Miyano, T., Izumi, K., Yatsugami, Y., Takanashi, T.., Kajikawa, Y., Kodama, K., JP 2003297380, (2003).

17. Hodgson, D.R., May, B., Adcock, P.L., Davies, D.P., *New Lightweight Bipolar Plate System for Polymer Electrolyte Membrane Fuel Cells.* J. of Power Sources, **96**, (2001), 233-235.

18. Brady, M.P., et al., *Assessment of Thermal Nitridation to Protect Metal Bipolar Plates in Polymer Electrolyte Membrane Fuel Cells.* Elect. Solid-State Letters, **5**(11), (2002), A245-A247.

19. Tian, R., Sun, Juncai, Wang, Liang, *Plasma-Nitrided Austenitic Stainless Steel 316L as Bipolar Plate for PEMFC.* Int. J. Hydrogen Energy, **31**, (2006), 1874-1878.

20. Tawfik, H., Hung, Y., Mahajan, D., *Metal Bipolar Plates for PEM Fuel Cell-A Review.* In Press, 2006.

21. Wang, Y., Northwood, Derek. O., *An Investigation into Polypyrrole Coated 316L Stainless Steel as a Bipolar Plate Material for PEM Fuel Cells.* In Press, 2006.

22. Joseph, Shine, McClure, J. C., Chianelli, R., Pich, P., Sebastian, P.J. *Conducting polymer coated stainless steel bipolar plates for proton exchange membrane fuel cells (PEMFC).* Int. J. Hyd. Energy, **30**(12), (2005), 1239-1344.

23. Emanuelson, R.C., Luoma, warren L., Taylor, William A., US 4,301,222, (1981).

24. Tang, Z., Qu, D., Xiong, J., Zou, Z., *Effects of Infiltration Conditions on the Desification Behavior of Carbon/Carbon Composites Prepared by Directional-Flow Thermal Gradient CVI Process.* Carbon, **41,** (2003), 2703-2710.

25. Pellegri, A., Spaziante, Placido M., US 4,197,178, (1980).

26. Busick, D.N., Wilson, S., *Development of Composite Materials for PEFC Bipolar Plates.* Mat. Res. Soc. Symp. Proc., **575**, (2000), 247-251.

27. Clulow, J.G., Zappitelli, F.E., Carlstrom, C.M., Zemsky, J.I.L., Busick, D.N., Wilson, M.S. *Development of Vinyl Ester/Graphite Composite Bipolar Plates.*

AIChE Spring National Meeting, March 10-14, New Orleans, LA., (2002), 417-425.

28. Wilson, M.S., Busick, Deanna N., US 6,248,467 (2001).
29. Busick, D.N., Wilson, S., *Low-Cost Composite Materials for PEFC Bipolar Plates*, Fuel Cells Bulletin, **2**(5) (1999), 6-8.
30. Landis, L., Tucker, Jonathan L., *Making Better Fuel Cells: Through-Plane resistivity Measurement of Graphite-Filled Bipolar Plates*, White Paper, Editor: Keithley Instruments, Inc. (2002).
31. Kuan, H.., Ma, C.M., Chen, K.H., Chen, S., *Prepearation, Electrical, Mechanical and Thermal Properties of Composite Bipolar Plate for a Fuel Cell.* J. Power Sources, **134**, (2004), 7-17.
32. Jousse, F., Salas, J.F., Giroud, F., Icard, B., Laurent, J.Y., Serre Combe, P., *Development of New Bi-Polar Plates Based on Electrically Conductive Polymers for PEMFC* Federation of European Materials Societies, Sept. 27-30, Munich, Germany, (1999), 181-186.
33. Mighri, F., Huneault, Michael A., Champagne, Michel F., *Electrically Conductive Thermoplastic Blends for Injection and Compression Molding of Bipolar Plates in the Fuel Cell Application.* Polym. Eng. Sci., **44**(9), (2004), 1755-1655.
34. Balko, E., N., Lawrance, Richard J., US 4,339,322 (1982).
35. Lawrance, R.J., US 4,214,969 (1980).
36. Bisaria, M.K., Andrin, Peter, Abdou, Mohamed, Cai, Yuqi, US 6,379,795 (2002).

37. Huang, J., Baird, Donald G., *Compression Molding of Highly Conductive Fuel Cell Bipolar Plates From a Thermoplastic Composite*, ANTEC Conference Proceedings, May 4-8, Nashville, TN. (2003), 2151-2155.

38. Tucker, K.W., Weeks, Gregory P., US 5,614,312 (1997).

39. *Arkema Quote*.

40. http://www.matweb.com/search/SpecificMaterial.asp?bassnum=PPTSM029.

41. http://www.dupont.com/fuelcells/pdf/plates.pdf.

42. http://sglcarbon.com/sgl_t/fuelcell/products/bma5.html.

43. Baird, D.G., Collias, Dimitris I., *Polymer Processing - Principles and Design*. 1st ed., Editor: John Wiley & Sons, (1998), 277-280.

44. Zheng, R., Kennedy, P., Phan-Thien, N., Fan, X-J., *Thermoviscoelastic Simulation of Thermally and Pressure-Induced Stress in Injection Molding for the Prediction of Shrinkage and Warpage for fibre-Reinforced Thermoplastics*. J. Non-Newtonian Fluid Mech., **84**, (1999), 159-190.

45. Heinzel, A., Mahlendrf, F., Niemzig, O., Kreuz, C., *Injection Moulded Low Cost Bipolar Plates for PEM Fuel Cells*. J. Power Sources, **131** (2004), 35-40.

46. Middleman, E., Kout, W., Vogelaar, B., Lenssen, J., de Waal, E., *Bipolar Plates for PEM Fuel Cells*. J. Power Sources, **118** (2003), 44-46.

47. Baird, D.G., Collias, Dimitris I., *Polymer Processing - Principles and Design*. 1st ed. Editor: John Wiley & Sons, (1998), 283-285.

48. Guan, R., Wang, Biqin, Lu, Deping, Fang, Quan, Xiang, Banglong, *Microcellular Thin PET Sheet Foam Preparation by Compression Molding*. Journal of Applied Polymer Science, **93**(4) (2004), 1698-1704.

49. Friedrich, K., Evstatiev, M., Fakirov, S., Evstatiev, O., Ishii, M., Harrass, M., *Microfibrillar Reinforced Composites from PET/PP Blends: Processing, Morphology and Mechnical Properties.* Composites Science & Technology, **65**(1), (2005), 107-116.

50. Smith, D.E., Tortorelli, Daniel A., Tucker III, Charles L., *Analysis and Sensitivity Analysis for Polymer Injection and Compression Molding.* Comput. Methods Appl. Mech. Engrg., **167** (1998), 325-344.

51. Pillai, K.M., Tucker, C.L., Phelan, F.R., *Numerical Simulation of Injection/Compression Liquid Composite Molding. Part 2: Preform Compression.* Composites Part A, (32), (2001), 207-220.

52. Chung, D.D.L., *Review: Electrical Applications of Carbon Materials.* J. Mater. Sci., **39**, (2004), 2645-2661.

53. Wei, J. and M.C. Hawley, *Utilization of Microwaves in Processing of Polymer Composites*. Polymeric Materials Science and Eng. 72, (1995), 10-12.

54. http://www.mhhe.com/physsci/chemistry/carey5e/Ch13/ch13-1.html.

55. Chen, M., Siochi, E.J., Ward, T.C., McGrath, J.E., *Basic Ideas of Microwave Processing of Polymers.* Polymer Engineering & Science, **33**(17), (1993), 1092-1109.

56. Stein, D.F., Edgar, Richard, H., Iskander, Magdy F., Johnson, D. Lynn, Jonhson, Sylvia M., Lob, Chester G., Shaw, Jane M., Stutton, Willard H., Tien, Ping K., *Microwave Processing of Materials*. Editor: National Academy Press. (1994), 1.-135.

57. Kreith, F., Bohn, Mark S., *Principles of Heat Transfer*, Editor: C. Robichaud., (1986), 17-20, 427-457.

58. Lind, A.C., Medgyesi, L.N., Kurz, J.E., McKinney, H.F., Wear, F.C. *Microwave Heating for Manufacturing Carbon-Fiber Thermoplastics*. Mat. Res. Soc. Symp. Proc. **189**, (1991), 461-467.

59. Adegbite, V., Fellows, L., Wei, J., Qiu, Y., Hawley, M. *Uniform Microwave Heating of Polymer Matrix Composites.* Ceramic Transactions, **59**, (1995), 149-157.

60. *Milestone: Microwave Synthesis -- Technical Details*. [cited; Available from: www.milestonesci.com (2004).

61. Chen, M., Hellgeth, J.W., Ward, T.C., McGrath, J.E., *Microwave Processing of Two-Phase Systems: Composites and Polymer Blends.* Polymer Engineering & Science, **35**(2) (1995), 144-150.

62. Thostenson, E.T., Chou, T.-W., *Microwave Processing: Fundamentals and Applications.* Composites, **30**(Part A) (1999), 1055-1071.

63. Rothstein, M., *Dielectric Heating*, Encyclopedia of Polymer Science, vol 5. Editor: Interscience Publishers. (1966), 1-23.

64. Baird, D.G., Collias, Dimitris I., *Polymer Processing - Principles and Design*. 1st ed., Editor: John Wiley & Sons. (1998), 111-118.

65. Watson, R.D., Chapman, Kirby S., *Radiant Heating & Cooling Handbook*. Editor: McGraw-Hill. (2002), 2.57-2.134.

66. Tudbury, C.A., *Basics of Induction Heating*. Vol. 1., Editor: John F. Rider. (1960), 1-132.

67. Rudnev, V., Loveless, Don, Cook, Raymond, Black, Micah, *Handbook of Induction Heating*. Editor: Marcel Dekker. (2003), 11-184.

68. Kim, H., Yarlagadda, Shridhar, Gillespie, John W., Jr., Shevchenko, Nicholas B., Fink, Bruce K., *A Study on the Induction Heating of Carbon Fiber Reinforced Thermoplastic Composites.* Adv. Composite Mater., **11**(1) (2002), 71-80.

69. Lawless, G.W., Reinhart, T.J., *A Study on the Induction Heating of Organic Composite*, 24th International SAMPE Technical Conference. **24**, (1992), T375-T384.

70. Lin, W., Buneman, Oscar, Miller, A.K., *Induction Heating Model for Graphite Fiber/thermoplastic Matrix Composites*, SAMPE Journal, **27**(6), (1991), 45-51.

71. Rudolf, R., Mitschang, P., Neitzel, M., *Induction Heating of Continuous Carbon-Fibre-Reinforced Thermoplastics.* Composites, **31**(Part A) (2000), 1191-1202.

72. Di Barba, P., Dughiero, f., Lupi, S., Savini, A., *Optimal Shape Design of Devices and Systems for Induction-Heating: Methodologies and Applications.* Compel, **22**(1) (2003), 111-122.

73. Gzhivachevskii, M., Vuitovich, M., Dikusar, V.V., *Optimal Control for Induction-Heating Processes Under Constraints of General Form.* J. Mathematical Sciences, **116**(6) (2003), 3753-3777.

3 Development of bipolar plates for fuel cells from graphite filled wet-lay material and a thermoplastic laminate skin layer

Preface

This chapter addresses a new approach in the development of compression moldable thermoplastic bipolar plates to satisfy the research objective associated with maintaining a sufficient balance of properties. Specifically, a laminate structure approach is used to improve on existing electrical properties, with observations on formability issues and potential commercialization. This chapter is organized in manuscript form and has been accepted for publication with the Journal of Power Sources.

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Development of bipolar plates for fuel cells from graphite filled wet-lay material and a thermoplastic laminate skin layer

Brent D. Cunningham[a,*], Jianhua Huang[a], Donald G. Baird[a]

[a]Chemical Engineering and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061

3.1 Abstract

In this paper a method with the potential to rapidly produce thermoplastic polymer composite bipolar plates with improved formability and through-plane conductivity is described. In our earlier work it was reported that composite bipolar plates made with graphite filled wet-lay materials exhibited excellent mechanical properties and in-plane electrical conductivity at ambient temperature. However, the through-plane conductivity and formability of the materials needed improvement. In this work laminate polymer composite plates consisting of a wet-lay based core and a fluoropolymer/graphite skin layer are manufactured in an effort to improve formability and through-plane conductivity. These plates are characterized by their through-plane and in-plane conductivity, half-cell resistance, and mechanical properties at ambient and elevated temperatures. The laminate plates with PPS based wet-lay core exhibited bulk conductivities of above 300 S/cm, tensile strength of up to 34 MPa, and flexural strength of up to 54 MPa at ambient temperature. Compared to the bipolar plates consisting of wet-lay material only, the bipolar plates with laminate structure exhibited an increase in through-plane conductivity of 25-35%, as well as a decrease in half-cell resistance by a

factor of up to 5 at ambient temperature. The laminate bipolar plates can be manufactured in several ways with two of them being discussed in detail in the paper.

3.2 Introduction

Polymer electrolyte membrane (PEM) fuel cells have drawn attention as alternative sources of energy for use in stationary and automotive applications. Bipolar plates are by weight, volume, and cost one of the most significant parts of a fuel cell stack. Bipolar plates must exhibit excellent electrical conductivity, adequate mechanical stability, corrosion resistance, and low gas permeability. Furthermore, bipolar plates must be amenable to a rapid, low cost processing methodology if they are to be widely used in the automotive industry.

The endeavor to develop a suitable material for bipolar plate production is based on the following requirements that must be met in the PEM fuel cell operating range of 60-120 ^{o}C:

- Electrical conductivity (> 100 S/cm)*
- Low permeability ($< 2 \times 10^{-6}$ cm^3/(cm^2 s))*
- Corrosion resistant (< 16 mA/cm^2)*
- Tensile strength (> 41 MPa)#
- Flexural strength (> 59 MPa)#
- High thermal conductivity (> 10 W/m K)#
- Chemical and electrochemical stability
- Low thermal expansion
- Resistance to compressive creep

- Efficient processability

*Department of Energy (DOE) & FreedomCAR specified targets at ambient temperature[1]
#Plug Power targets at ambient temperature[2]

Although the bipolar plate targets are specified at ambient temperature, the temperature dependency on the properties of thermoplastic polymer composite material should be considered. The electrical conductivity target is specified as bulk, or in-plane conductivity. Although no target has been specified for through-plane conductivity, it is thought to be an important measurement because the through-plane direction is the route that electrons travel in an operating fuel cell. Corrosion resistance is mainly a concern with metal plates and metal coated fibers, but it can also apply to polymer systems that may dissolve electrochemically in a fuel cell. The mechanical targets are specified for ambient temperature, while targets at elevated temperatures have not yet been specified. Efficient processability incorporates several factors, including material and production costs and the ability to be rapidly manufactured.

Traditional materials for producing bipolar plates are sintered graphite and metal.[3] Graphite plates have been used because they possess high electrical conductivity, corrosion resistance, and a lower density than that of metals. Problems with graphite plates include brittleness and the cost associated with machining channels into the surface. Because the material and machining cost of graphite plates are exorbitant, at least for the automotive industry, the development of a more suitable material has promoted extensive research. Metal bipolar plates such as stainless steel, aluminum, and titanium have gained attention for their high electrical conductivity, mechanical strength, and negligible gas permeability.[3-5] The main advantage with metal plates is that channels can be embossed or etched into the surface, relieving much time and cost associated with machining. However, because metals are subject to corrosion and leaching of ions, a coating must be applied to the surface to provide a protective layer. Unfortunately, the protective layer can be highly electrically insulating, drastically reducing the bulk conductivity of the plate. Additionally, metal plates contribute a significant amount of weight to the overall fuel cell stack. Therefore, it is desired to make the metal plates very thin.

In an effort to improve on sintered graphite, researchers at Oak Ridge National Laboratory (ORNL) have developed carbon/carbon composite bipolar plates by slurry molding carbon fiber and phenolic resin.[6] ORNL researchers claim that the plates have high electrical conductivity and adequate mechanical stability. However, the manufacturing step in the production of carbon/carbon plates is complex and expensive due to a chemical vapor infiltration (CVI) process. CVI operates at very high temperatures for extended times, sealing the carbon/phenolic resin preforms by depositing carbon onto the surface. Unfortunately, channels must still be machined into the surfaces of the carbon/carbon plates.

Graphite-based polymer composite bipolar plates have shown to potentially meet target requirements. They offer advantages such as lower cost, higher flexibility, and are lighter in weight when compared to metallic and graphite plates. The gas flow channels can be molded directly into the surfaces of the plate, eliminating the need for a costly machining step. Researchers at Los Alamos National Laboratory (LANL) have developed a bipolar plate based on a vinyl ester thermosetting polymer resin and graphite powder.[2, 7] Bulk conductivities were measured to be as high as 85 S/cm with tensile and flexural strength at 25 and 38 MPa, respectively when measured at ambient temperature which are still lower than the specified targets. A compression molding process was used for producing the bipolar plates in which channels were formed in less than 10 minutes.[8, 9] The advantage in using a thermosetting polymer is that when the polymer is heated and compression molded, the plate cures and does not require subsequent cooling. Therefore, the plate can be immediately released from the mold. However, a postcure may be necessary, and can take as long as one hour to complete.[8] Blunk and coworkers[10] have developed an epoxy based system using expandable graphite that has exhibited low resistances. However, the flexural strength of the plates did not reach the target value. Although the graphite filled epoxy system has shown potential for use in bipolar plate production, the generation of the epoxy bipolar plates requires a 20 minute curing time and the expandable graphite is anticipated to be expensive to manufacture. The epoxy-based bipolar plates also require the machining of channels. Poly(vinylidene fluoride) (PVDF), a thermoplastic fluoropolymer matrix, has been used with graphite particles and carbon fiber to produce bipolar plates.[11] Bulk conductivity values have reached 109 S/cm at ambient temperature, exceeding the DOE target. However, the flexural strength was only 42.7 MPa at ambient temperature, lower than the goal of 59 MPa. Liquid crystalline polymer/graphite mixtures have been considered for bipolar plate production because of their ability to be injection molded due to the low viscosity of the polymer.[12] The injection molding process allows for a relatively short cycle time of 30 seconds. Bulk conductivities have reached as high as 100 S/cm at ambient temperature, just reaching the minimum target, but no mechanical properties or through-plane conductivities were reported, and it is anticipated that the mechanical properties may not reach the targets.

Huang and coworkers[13, 14] reported the development of conductive polymer composite materials generated by means of a wet-lay process. The wet-lay materials were compression molded to form highly conductive and strong bipolar plates. Bulk conductivities (in-plane) and mechanical properties of the plates were higher than that of any other polymer composite plates when measured at ambient temperature (see Table 3.1). However, the through-plane conductivity, half-cell resistance, and formability of the plates needed further improvement. Considering that the half-cell resistances were previously measured on monopolar plates (i.e., single-sided plate), the values are expected to be even higher for the double-sided bipolar plates if no further improvements are made for the materials.

Table 3.1 – Comparison of conductive and mechanical properties measured at ambient temperature for polymer composite materials used in the production of bipolar plates.

Source	Polymer	Graphite/glass or carbon reinforcing fiber (wt/wt%)	Conductivity (S/cm)		Mechanical Strength (MPa)	
			In-plane	Through-plane	Tensile	Flexural
Target			>100[a]	-	41.0[b]	59.0[b]
GE[15]	PVDF	80/0	119	-	-	30.0
GE[[11]	PVDF	64/16 CF	109	-	-	42.7
LANL[8]	Vinyl Ester	68/0	60	-	23.4	29.6
BMC[16, 17]	Vinyl Ester	70/0	95	50	30.3	38.6
Plug Power[2]	Vinyl Ester	68/0	55	20	26.2	40.0
Patent[18]	Epoxy	90/0	3	-	-	-
DuPont[19]	-	-	-	25-33	25.1	53.1
Virginia Tech[13]	PET	65/7 GF	230	18-25	36.5	53.0
Virginia Tech	PPS	70/6 CF	271	19	57.5	95.8

[a] DOE target for conductivity at ambient temperature[1]
[b] Plug Power targets for mechanical strength at ambient temperature[2]

In this paper a laminate structure is proposed to improve the formability and through-plane conductivity of the bipolar plates. The bipolar plates with wet-lay material in the core and thermoplastic (e.g. PVDF)/graphite composite powders on the outer layers are generated by two methods. One is to put composite powders on the surfaces of the wet-lay sheet stacks and compression mold at a temperature to melt the polymer which is called the one-step molding method. The other is to generate a consolidated wet-lay composite plaque first, followed by the addition of composite powders on the surfaces of the flat plaque and compression mold the composite (at a temperature sufficient to melt the polymer in the surface only). This is called the two-step molding method. We will asses the bipolar plates made by the two different methods and discuss the advantages and disadvantages of the processes. The evaluation will be focused on the electrical conductivity and mechanical properties of the composites, as well as the half-cell resistance and appearance of the bipolar plates. Instead of single-sided bipolar plate as used previously, bipolar plates with gas follow channels on both sides will be generated and used in the evaluation. It turns out to be important to generate and evaluate bipolar plates under conditions as close as possible to those experienced by the bipolar plate under fuel cell operating conditions.

3.3 Experimental

3.3.1 Materials

The two thermoplastic fibers used were poly(ethylene terephthalate) (PET) (6 mm long) and poly(phenylene sulfide) (PPS) (6 mm long) at levels in the range of 13-40 wt%. Conoco carbon fibers (nominal length ½”) or E-glass fibers were used as reinforcing fibers in the range of 6-9 wt%. Timrex® KS-150 and Timcal™ TC-300 graphite particles were used as the conductive filler in the range of 50-80 wt%. Microglass (1 wt%) was also added to help particle retention. PVDF (Kynar 761 from Arkema Inc.) was used in combination with TC-300 graphite powder as the laminate material.

3.3.2 Production and molding of wet-lay composite sheet material

In Fig. 3.1 is shown the scheme for production of the wet-lay composite materials and bipolar plates. Wet-lay sheets containing a thermoplastic fiber, reinforcing fiber, conductive graphite particles, and microglass were generated with a slurry-making process on a Herty papermaking machine donated by DuPont. The slurry contained 1 wt% solids in water. First, the cut thermoplastic fibers were added to the water in a pulper and agitated for 10 minutes. Next, the cut reinforcing fibers, graphite particles, and microglass were added and mixed for 3-6 minutes. The slurry was then pumped into a head box containing a sieve screen, generating a sheet of porous material. The sheet was continuously rolled through an oven at the melting point of the polymer to continue drying and partially melt the thermoplastic fibers.

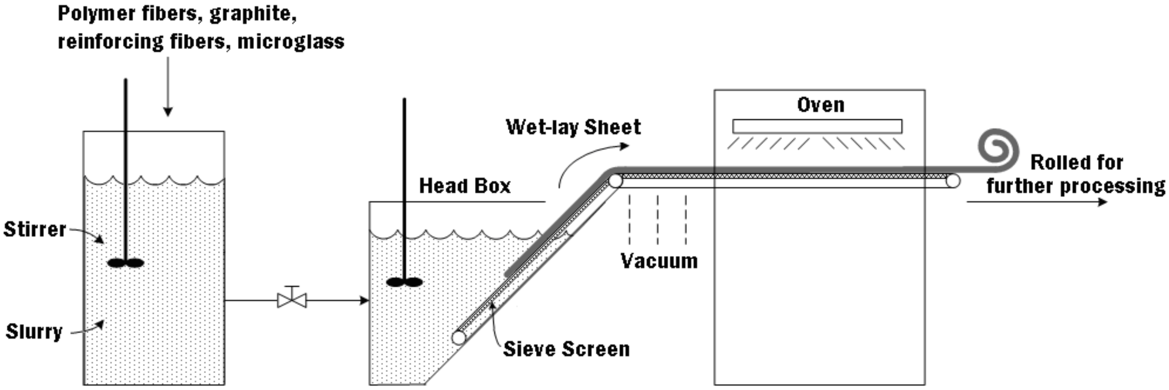

Figure 3.1 – The process to develop wet-lay polymer composite sheets.

The procedure carried out by Huang and coworkers[13, 14] for making a test sample or bipolar plate from wet-lay material was followed in this work. The material was cut to fit the shape of a mold and stacked to provide a desired thickness. The mold was then placed between platen heaters of a hydraulic press set at approximately 20 °C above the melting point of the thermoplastic fiber (277 °C for PET based composites, 305 °C for PPS based composites). The material was compression molded for 7-10 minutes at a constant compaction load of 10,000 pounds. The platen heaters were turned off and the mold was allowed to cool to 30 °C while still under pressure. The mold was then removed from the press and the flat plaque or bipolar plate was taken out of the mold.

Although a batch process was used in this work, a continuous process is envisioned in the future.

3.3.3 Novel laminate approach

In this paper are described two methods to produce laminate bipolar plates. The first, called the one-step method, was begun by covering the bottom surface of the mold with a desired amount of PVDF/graphite mixture and spreading it evenly over the surface. Next, a pre-determined number of wet-lay sheets were stacked on top of the PVDF/graphite mixture. Finally, another layer of PVDF/graphite (same amount as placed in the bottom of the mold) was spread evenly on top of the wet-lay sheets. The mold was closed and placed into a heated press for compression molding. The molding temperature for this method was based on the polymer with the higher processing temperature (i.e. using a PPS based wet-lay core this is about 300 ^{o}C). Note: Care should be taken to control the temperature at 300 ^{o}C because PVDF is known to release gaseous hydrofluoric acid at 315 ^{o}C. Upon compression molding, the PVDF/graphite powder penetrates into the porous wet-lay material (> 50% voids) to help bond the skin layer to the core material. The second process is called the two-step method. First, the wet-lay sheets by themselves were placed into a heated mold and compression molded to form a pre-consolidated flat plaque. After being removed from the mold, PVDF/graphite was added to the bottom surface of the mold and on top of the flat plaque similar to the one-step method. The mold was closed and placed into a heated press for compression molding. The molding temperature for this method was set at approximately 200 ^{o}C. A lower processing temperature was used because the wet-lay material was already consolidated, and only the PVDF required processing. In the two-step method the sole form of bonding between the skin layer and the wet-lay core was adhesion between the surfaces. The level of PVDF/graphite powder added to the surfaces of the wet-lay material was varied from 15-33 vol% (on each side) to evaluate how differences in the level of laminate layer would affect the composite properties. In Figure 3.2 is shown a picture of a compression molded laminate bipolar plate of dimensions 4.75 x 5.5 in with 0.8 x 0.8 mm parallel serpentine style channel design.

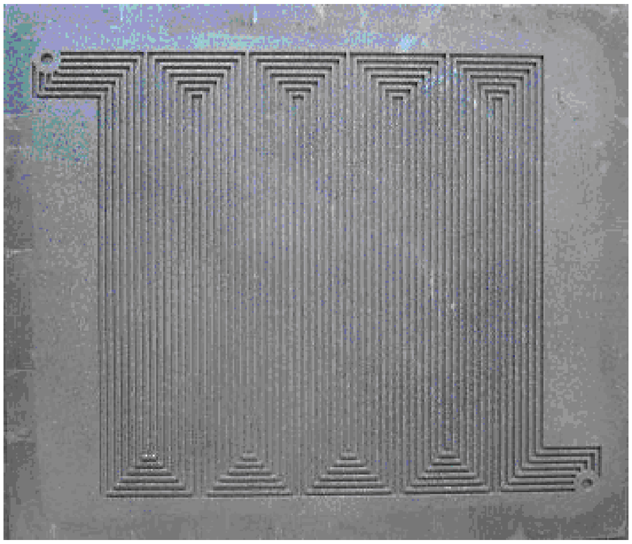

Figure 3.2 – One side of a laminate polymer composite bipolar plate showing the 7-channel parallel serpentine style design. Plate dimensions are 12 x 14 cm. Channel dimensions are 0.8 x 0.8 mm.

3.3.4 Measurement of mechanical properties

The tensile and flexural tests were performed on an Instron 4204 at room temperature in accordance with ASTM D638 and D790 standards, respectively. The mechanical tests were also performed at 80, 100 ^{o}C, and 120 ^{o}C to evaluate the strength in an environment that more accurately reflects that found in PEM fuel cells. The specimens sizes were approximately 76.2 mm x 8.5 mm x 3.0 mm (L x W x T) and were cut from a flat plaque.

3.3.5 Measurement of in-plane and through-plane conductivity

In-plane (bulk) conductivities were measured according to ASTM Standard F76-86. Current contacts were placed at the four corners of the plaque allowing for a constant current to pass through the specimen. The voltage drop was measured across the specimen with a Keithley 2000 digital multi-meter at ambient conditions. Two characteristic resistances, R_A and R_B were measured. The plaque resistance, R_S, is obtained by solving the Van der Pauw equation:

$$\exp(-\pi R_A/R_S) + \exp(-\pi R_B/R_S) = 1 \qquad (1)$$

The resistivity, ρ, is given by $\rho=R_S d$, where d is the thickness of specimen. The volume conductivity, σ_B, is defined as $1/\rho$.

Through-plane conductivities were measured based on a method proposed by Landis and Tucker.[20] A 76.2 mm x 76.2 mm plaque was placed between gold plated copper electrodes. Between the electrodes and sample was placed a piece of carbon paper (Toray TGP-H120) to improve electrical contact between the electrodes and sample. The system was placed under a compaction force of 2000 pounds (approximately 1000 psi) and the resistance was measured. The sample was removed, and the resistance of the test cell (including carbon paper) was measured again under the same conditions to obtain a “baseline” resistance. The sample resistance could then be calculated by subtracting the baseline resistance from the total resistance. The resistivity of the material was calculated by:

$$\rho = [(R_T - R_{baseline})A] / L \qquad (2)$$

where ρ is resistivity, A is cross-sectional area of sample, L is the thickness of sample, and R_T and $R_{baseline}$ are total resistance and baseline resistance, respectively. The through-plane conductivity, σ_T, was then calculated as $1/\rho$.

3.3.6 Measurement of half-cell resistance

To measure the half-cell resistance of a bipolar plate, an apparatus was set up similarly to the one used to measure through-plane conductivity. A bipolar plate having dimensions 12.2 x 14.0 x 0.3 cm and an active area of 100 cm^2 was placed between the gold plated copper electrodes. Carbon paper (Toray TGP-H-120) was placed on both sides of the bipolar plate, and hence, in between the sample and electrodes. The size of the carbon paper was 10 x 10 cm in order to completely cover the active area. The sample was placed under a compaction force of 2000 pounds (approximately 130 psi) while a constant current of 250 mA was passed through the sample. The potential was measured between the collectors and the half-cell resistance was calculated based on Ohm's law. The bipolar plate was removed, and the potential across the electrodes and carbon paper was measured to produce a baseline resistance. The baseline resistance, that is the resistance of the testing circuit excluding the bipolar plate but including carbon papers and electrodes, was measured after testing of the plate. This was done to ensure the stability of the baseline of the instrument and to evaluate the contribution of the bipolar plate to the total half-cell resistance.

3.4 Results and Discussion

3.4.1 Production of the wet-lay composite materials and bipolar plates

The initial idea to produce bipolar plates from wet-lay generated material was based on the desire to overcome the restriction on adding high levels of fillers (>50%) to a polymer matrix while allowing the material to flow and fill the cavity of a mold. When a slurry was produced with thermoplastic fibers, reinforcing fibers, and conductive graphite particles, filler loading levels >80% have been successfully reached while allowing the material to be compression molded.[13, 21]

PET was the initial thermoplastic fiber used for the development of wet-lay material. Because PET may not be the ideal polymer matrix for bipolar plates due to hydrolytic degradation, we turned our attention to the modification of the PET based material.

3.4.2 Production of laminate composite materials and bipolar plates

It was found that a mixture of chemical resistant polymer and graphite particles could be used to form a protective layer for the PET composite plate.[13, 22] The conductive polymer mixture that forms the skin layer should meet several requirements, including excellent chemical and electrochemical resistance, high electrical conductivity, and formation of a composite with good adhesion at the interfaces. PVDF (Kynar 761) meets these requirements, and also possesses a broad processing temperature range (from 175 to 300 ^{o}C) that overlaps with the molding temperature of PET.[23] Therefore, the outer layer consisted of a 20/80 wt% ratio of PVDF/graphite. The ratio was chosen in order to maintain a consistent level of filler concentration throughout the skin layer and wet-lay core.

While concerns still remain for using PET based material in a fuel cell environment, an alternative thermoplastic matrix was investigated. PPS is a semi-crystalline polymer with a melting temperature of 285 ^{o}C, glass transition temperature of approximately 88 ^{o}C, and a high degree of chemical resistance. The highly stable chemical bonds of its molecular structure impart a remarkable degree of molecular stability toward both thermal degradation and chemical reactivity, making it an improved matrix over PET.[24] It is regarded as second only to polytetrafluoroethylene (PTFE) in overall chemical resistance.[25] Furthermore, results have shown (Table 3.1) that PPS based wet-lay composites exhibit comparable conductivity and superior mechanial properties relative to PET based wet-lay composites when measured at ambient temperature.[13] Therefore, it was believed that using PPS based wet-lay material in the core of a bipolar plate could provide sufficient strength, while the PVDF in the laminate layer could be used to promote improved formability when compression molded and the possibility for a significant reduction in the heating/cooling cycle of the molding process.

The volume percent of laminate material for a given plate was varied to obtain a balance of conductivity, mechanical strength and complete formation of gas flow channels into the PVDF/graphite powder. Based on formability observations, 20 vol% PVDF/graphite on each surface was found to be the minimum level that still allowed for complete formation of channels into the PVDF/graphite powder using our specific channel design. Dropping below 20 vol% did not provide sufficient laminate material for channel formation with our channel design, while increasing the laminate content above

20 vol% had a negative effect on overall mechanical properties measured at ambient temperature as shown in Figs. 3.3 and 3.4. The wet-lay core material typically contained 70 - 80 wt% graphite particles. Therefore, for this paper a nomenclature of 20Lam80PPS designates that the entire laminate plate consists of 20 vol% of PVDF/graphite mixture on each surface, with the wet-lay core consisting of a PPS matrix with 80 wt% conductive graphite particles.

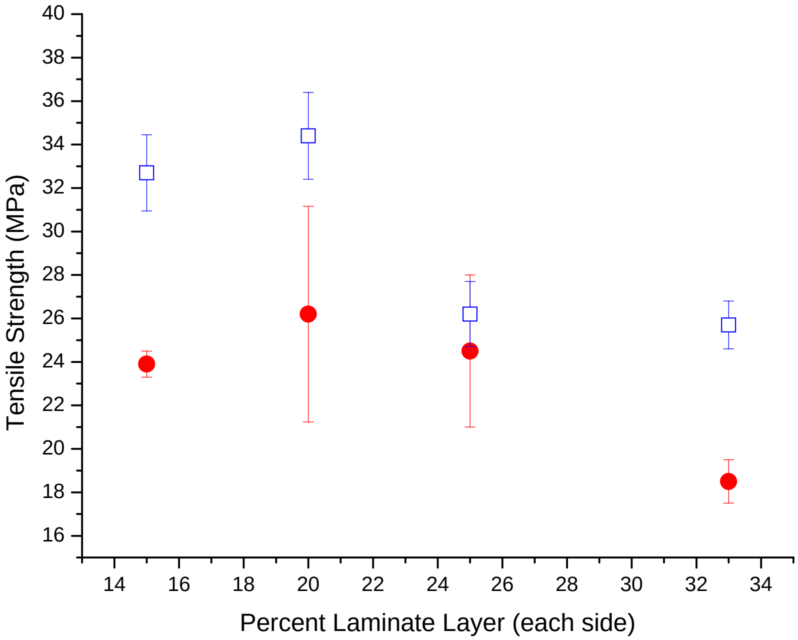

Figure 3.3 – Tensile strength measured at ambient temperature of various volume percents of skin-layer on the surfaces of a PPS-TC70 core material processed by the one-step (□) and two-step (●) methods. Error bars indicate one std. dev.

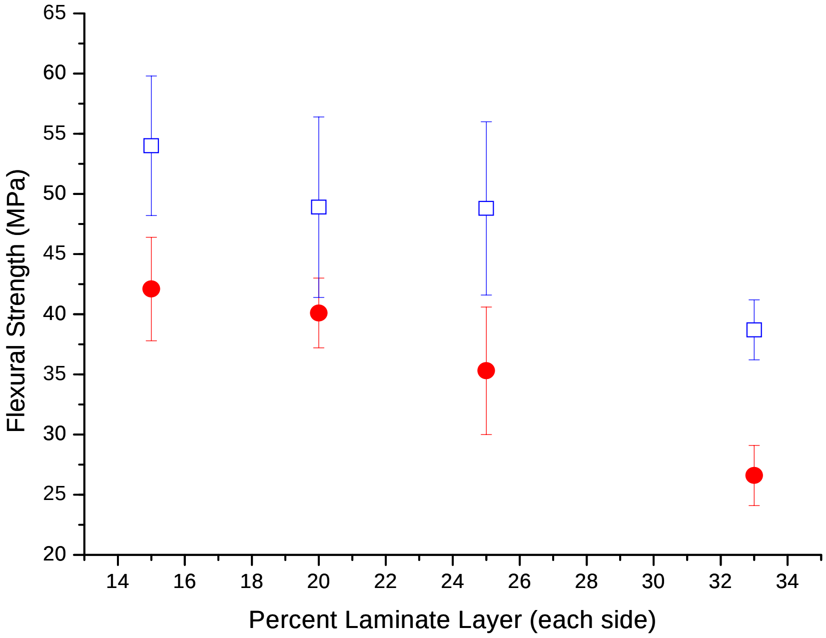

Figure 3.4 - Flexural strength measured at ambient temperature of various volume percents of skin-layer on the surfaces of a PPS-TC70 core material processed by the one-step (□) and two-step (●) methods. Error bars indicate one std. dev.

As stated in section 3.3.3, the laminate plates were produced by either the one-step or two-step molding method. Potentially there could be differences in the mechanical strengths of plates produced by the two methods because of differences in adhesion of the outer layer to the core composite material. Furthermore, processing schemes will be different because in the one-step method the entire part has to be heated, whereas in the two-step method only the surfaces have to be heated. In the one-step method, the laminate powder was added to the surfaces of sheets of porous wet-lay material. Unfortunately, the porous wet-lay material typically exhibited a significant amount of loft. When a number of wet-lay sheets were stacked, loft was further enhanced. It was difficult to manually spread the laminate powder evenly over a non-uniform surface such as the porous wet-lay sheets. The two-step method offered an advantage over the one-step method. It was found to be significantly easier to evenly spread the laminate powder over a solid, flat surface. Therefore, it may be possible to continuously manufacture bipolar plates by the two-step method as shown in Fig. 3.5. In this process, sheets of wet-lay material may be continuously rolled through a calendar creating a compacted blank plaque. The laminate powder can be metered onto the surface while being continuously rolled to other parts of the processing line. The potential disadvantage in this process is the possibility for de-lamination to occur due to poor adhesion of the laminate layer onto the pre-consolidated wet-lay core material.

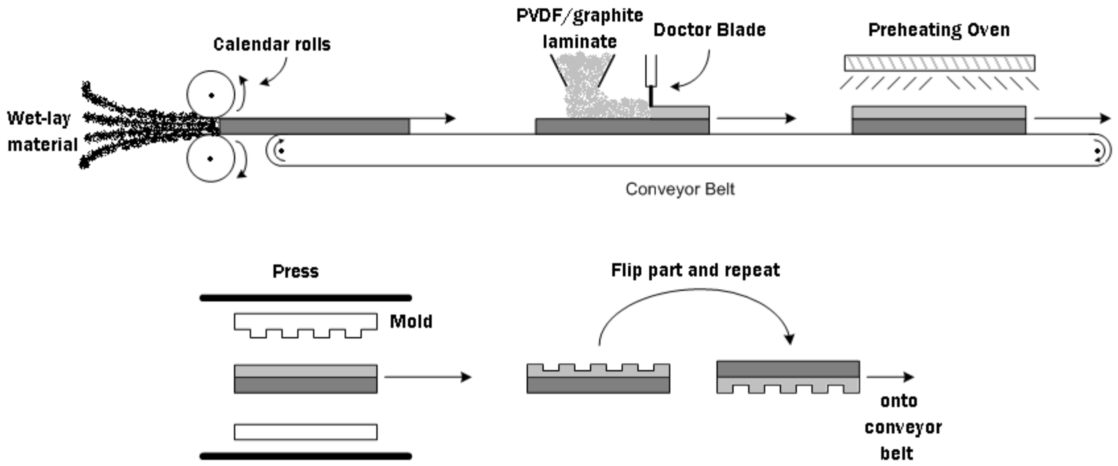

Figure 3.5 – Envisioned process for the continuous manufacturing of laminate polymer composite bipolar plates by pre-consolidating the wet-lay core material.

3.4.3 Electrical conductivity of laminate composite materials

Electrical conductivity is one of the most important properties of bipolar plates. Huang et al.[13] reported the electrical properties of wet-lay based composites compared to other polymer composite materials (see Table 3.1). PET and PPS based wet-lay composites have exhibited in-plane (bulk) conductivities higher than 200 S/cm, well exceeding the DOE target of 100 S/cm. These values were also higher than any other polymer composite material with similar graphite loadings.

In Table 3.2 are shown electrical conductivity results for the laminate flat plaque test specimens. The laminate plaques exhibit improved in-plane and through-plane conductivities when compared to plaques generated from wet-lay material only. Laminate plaques exhibit bulk conductivities above 300 S/cm, with through-plane conductivities as high as 50 S/cm. Both of these values represent significant improvements achieved by the laminate structure. When materials of similar compositions differing only by processing method are compared, plates produced by the one-step method exhibit slightly higher conductivities, especially in the through-plane direction. This may be expected because when the material is compression molded via the one-step method, PVDF/graphite powder penetrates into the porous wet-lay material. Therefore, a more conductive network may be generated in the through-plane direction using the one-step molding method. When comparing the graphite type at the 70 wt% level, it appears that the TC-300 type graphite provides the composite material with higher in-plane and through-plane conductivity than those generated using KS-150 graphite. Unfortunately, no data has been obtained for composites generated with 80% TC-300 graphite particles in the wet-lay material.

Table 3.2 – Conductivity results measured at ambient temperature of laminate flat plaque test specimens consisting of an 80/20 ratio of graphite/PVDF laminate layer on each side, as a function of graphite type, graphite concentration, and processing method. Plaques consist of 20 vol% laminate layer on both sides.

Material designating the amount and type of graphite contained in the wet-lay core	Processing Method	In-plane conductivity (S/cm)	Through-plane conductivity (S/cm)
Laminate with 70% TC-300 graphite in core	One-step	209-325	17-32
Laminate with 70% TC-300 graphite in core	Two-step	203-350	14-24
Laminate with 70% KS-150 graphite in core	One-step	166-238	16-24
Laminate with 70% KS-150 graphite in core	Two-step	147-178	16-17
Laminate with 80% KS-150 graphite in core	One-step	164-226	18-26
Laminate with 80% KS-150 graphite in core	Two-step	186-251	15-23

It is important to realize that graphite filled polymer composite plates may have different properties and performances in different directions. It is apparent from Table 3.1 and 3.2 that the through-plane conductivities for all wet-lay and laminate based composites are significantly lower than the in-plane conductivities. This may be attributed to several possible factors. First, the graphite particles are not spherical, but rather elongated platelets that may orient in a plane perpendicular to the direction of the compaction force during molding. This plane is designated as the *X*-*Y* (in-plane) direction as shown in Fig. 3.6. Furthermore, when forming the wet-lay sheets, the thermoplastic and reinforcing fibers also align in the *X*-*Y* direction and may help induce the graphite particles to orient in the same direction. It is believed that for compression molded composite bipolar plates, the higher the aspect ratio of the graphite used, the greater the ratio of in-plane to through-plane conductivity. This might explain why composites generated from wet-lay and laminate material with TC-300 graphite (greater aspect ratio), have a higher ratio of in-plane to through-plane conductivities when compared to composites generated with KS-150 graphite (smaller aspect ratio) (see Table 3.2). Although the use of a more spherically shaped graphite particle reduces the in-plane to through-plane ratio, it might not necessarily improve the through-plane conductivity.

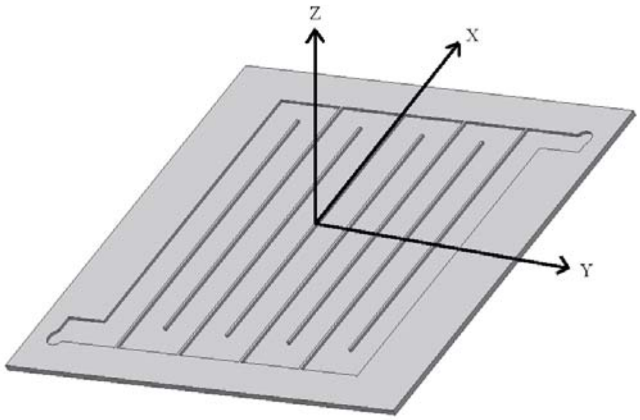

Figure 3.6 – Laminate plate representation showing the direction of the X-Y plane and Z plane.

3.4.4 Mechanical properties of wet-lay composite materials

In addition to electrical conductivity, the bipolar plates should also have adequate mechanical properties and resistance to creep to be used in fuel cell stacks where they would be subjected to a constant compressive load. However, for polymer composites doped with high levels of conductive particles and/or fibers, it is difficult to obtain high conductivity and sufficient mechanical properties simultaneously. As a result the mechanical properties of most composite materials used to produce bipolar plates are still lower than the target values with the exception being the PPS based wet-lay composites when measured at ambient temperature (see Table 3.1).

Laminate plates produced using a PPS based wet-lay core have potential to meet electrical and mechanical properties simultaneously. In Figs. 3.4 and 3.5 are shown the flexural and tensile strengths of laminate plates at various vol% of PVDF/graphite using a PPS based wet-lay core and their dependency on the production method. The laminate plates exhibit lower strength than wet-lay composite material as reported in Table 3.1. A decrease in mechanical properties is expected with the laminate plates because the surfaces are comprised of the relatively weaker PVDF matrix. However, due to the presence of wet-lay in the core, the mechanical strengths of the laminate plates still compared well to the vinyl ester and PVDF based polymer composite materials, even at high loading levels of the laminate layer (33 vol% on each side). Composite materials generated by the one-step method generally show a 30 - 40% increase in flexural and tensile strengths. This increase may be attributed to the penetration of the outer skin layer into the porous wet-lay sheets when compression molded, thus creating a stronger network throughout the entire plate than those generated by the two-step method in which the outer layer contains only PVDF and graphite.

In Table 3.3 are shown the tensile and flexural strengths and moduli of various compositions of laminate plates using the one-step and two-step methods tested at different temperatures. Mechanical properties are evaluated at elevated temperatures typical of fuel cell operation (80, 100, and 120 ^{o}C). The moduli show a significant decrease when temperature is elevated. The decrease in modulus is expected, especially because the testing temperatures are near or above the T_g's of PPS (~88 ^{o}C) and PVDF (~ -30 ^{o}C). The flexural and tensile strengths exhibit a significant dependency on the processing method at ambient temperature. However, at elevated temperatures there appears to be less dependency on the processing method, but the flexural and tensile strengths are still below the target value even at low loading levels of laminate layer. Additionally, because PEM fuel cell operation temperatures are above the T_g's of both PPS and PVDF, the compressive creep of the laminate material should be evaluated even though both PPS and PVDF possess high degrees of crystallinity.

Table 3.3 – Comparisons of mechanical properties measure at ambient temperature of laminate flat plaque test specimens consisting of a PPS based wet-lay core containing 70 and 80% graphite, and compression molded using the one-step and two-step methods.

Material	Testing Temp. (^oC)	Processing Method	Flexural Modulus (GPa)	Flexural Strength at Break (MPa)	Tensile Modulus (GPa)	Tensile Strength at Break (MPa)
20Lam70PPS	20	One-step	7.238	48.9	15.765	34.4
	80		3.571	36.9	14.023	25.7
	100		3.416	37.7	14.231	27.7
	120		2.659	34.3	7.817	25.4
20Lam70PPS	20	Two-step	6.090	40.1	14.037	26.2
	80		3.400	41.2	14.165	27.8
	100		2.890	40.1	9.506	30.4
	120		2.605	35.5	7.416	25.0
20Lam80PPS	20	One-step	6.630	30.6	10.855	25.0
	80		3.940	28.2	8.401	17.8
	100		3.394	32.2	9.447	14.2
	120		2.922	34.8	8.132	18.5
20Lam80PPS	20	Two-step	5.530	29.9	11.624	15.2
	80		3.432	27.7	6.601	16.7
	100		2.863	31.6	9.105	15.0
	120		2.471	27.2	5.885	18.1
15Lam70PPS	20	One-step	8.089	54.0	16.048	32.7
15Lam70PPS	120	One-step	2.900	44.7	9.561	29.1
25Lam70PPS	20	One-step	8.156	48.8	16.228	26.2
25Lam70PPS	120	One-step	2.950	34.1	10.083	23.2

3.4.5 Half-cell resistance of wet-lay composite plates

Although electrical conductivity of the materials used to produce bipolar plates is important, the performance of the bipolar plate in a fuel cell is the defining characteristic. A bipolar plate may have electrical properties that drastically differ from flat plaque test specimens because of the molded gas flow channels in the surfaces. Additionally, interfacial resistance between bipolar plates and the membrane electrode assembly, gas diffusion layer, etc. also contribute to the total resistance. To evaluate their contribution to the electrical properties of the bipolar plates, half-cell resistance tests were conducted at ambient temperature. In addition to measuring the resistance of the entire assembly, the resistance of the electrodes and carbon paper was measured to produce a baseline resistance. The measurement of a baseline was found to be important because the contact resistance between current collectors and carbon paper could differ dramatically depending on the specific collectors used.

Half-cell resistances measured on bipolar plates can exhibit significant differences than those measured on monopolar plates of similar compositions. Half-cell resistances for wet-lay based bipolar plates are measured to be 0.11-0.19 Ω cm^2 (see Fig.3.7). Huang et al.[13] reported half-cell resistances for wet-lay based monopolar plates less than 0.03 Ω cm^2. It is expected that the half-cell resistance for wet-lay based bipolar plates would measure twice as high as monopolar plates of the same composition because of reduced contact area. However, the half-cell resistances of wet-lay based bipolar plates exhibit a 4-6 fold increase over that of wet-lay based monopolar plates of the same composition. This may be due to several factors. First, when the wet-lay material is compression molded into a monopolar plate, the material exhibits poor flowability in the rib area of the mold. The situation may be worse when using a double-sided mold instead of a single-sided mold. Second, due to the anisotropy of the wet-lay material there may not be uniform pressure over the plate when compression molding. Because monopolar plates typically had a thickness of 2.4 mm while the bipolar plates had a thickness of 3.6-3.8 mm, there may be a larger number of voids present in the bipolar plate. Last, the active areas for measuring the half-cell resistance of a monopolar plate was 100 cm^2 (channel side) and 168.5 cm^2 (flat side), whereas the active areas for measuring the half-cell resistance of a bipolar plate was 100 cm^2 on both sides. Because a smaller total active area was used for the bipolar plates, and that bipolar plates contain double-sided features, they are likely to exhibit a higher half-cell resistance than that of monopolar plates.

In Fig. 3.7 are presented comparisons of the through-plane conductivities for wet-lay material and laminate composite materials, as well as their respective half-cell resistance of a bipolar plate generated from material of similar compositions. The through-plane conductivities increase with the addition of PVDF/graphite on the surfaces by 25-35%. Furthermore, the laminate plates exhibit a decrease in half-cell resistance by a factor of up to 5. An increase in through-plane conductivity is expected for the laminate plates, but it is surprising to see a greater change in the half-cell resistance. The dramatic decrease in half-cell resistance using the laminate structure is believed to be due to several factors. First, bipolar plates generated by wet-lay material do not have surfaces as smooth as that of laminate bipolar plates as suggested in Fig. 3.8. As a result, the wet-lay based plates have higher contact resistance between the plate and carbon papers and, thus, higher half-cell resistances. Second, the difference of through-plane conductivities for wet-lay and laminate bipolar plates may be greater than that of flat samples used in the conductivity test. While poor formability of wet-lay sheets may not influence the formation of flat samples, it can have a great impact on the formation of double-sided bipolar plates and lead to lower through-plane conductivity (due to uneven compaction pressures of the materials) in comparison with the flat samples. For laminate bipolar plates, there is no such difference due to improved material formability. Third, when compressed with a bipolar plate mold, the graphite particles in the PVDF matrix (outer layers of laminate bipolar plate) in the rib area may align more in the *Z* direction compared to that in the wet-lay sheets, resulting in higher through-plane conductivity of the laminate plates.

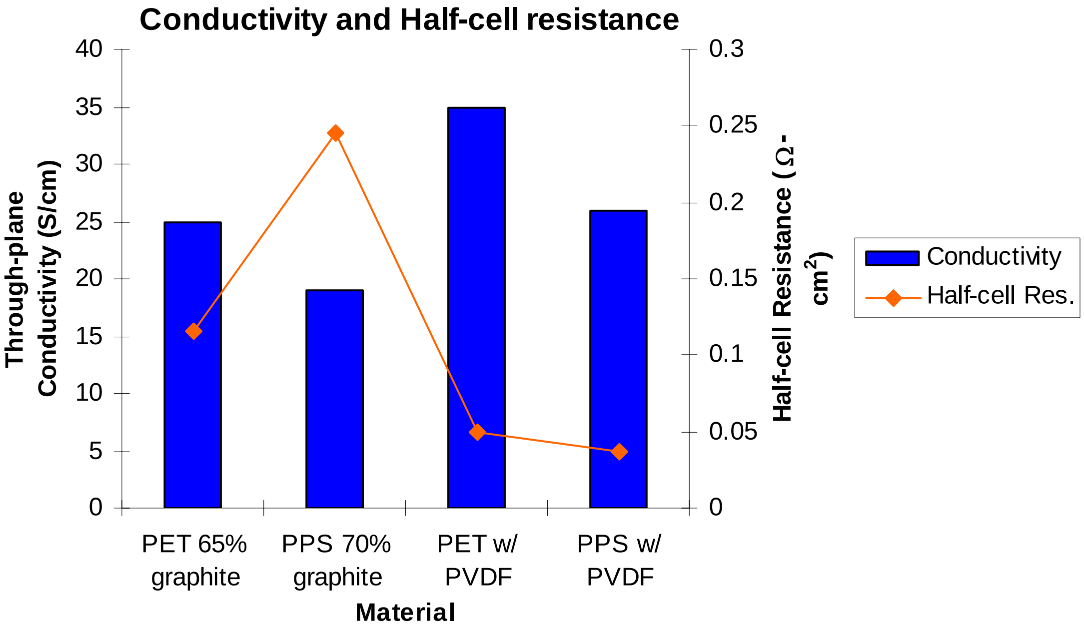

Figure 3.7 – Through-plane conductivity and half-cell resistance comparisons for compression molded wet-lay material and laminate plates measured at ambient temperature.

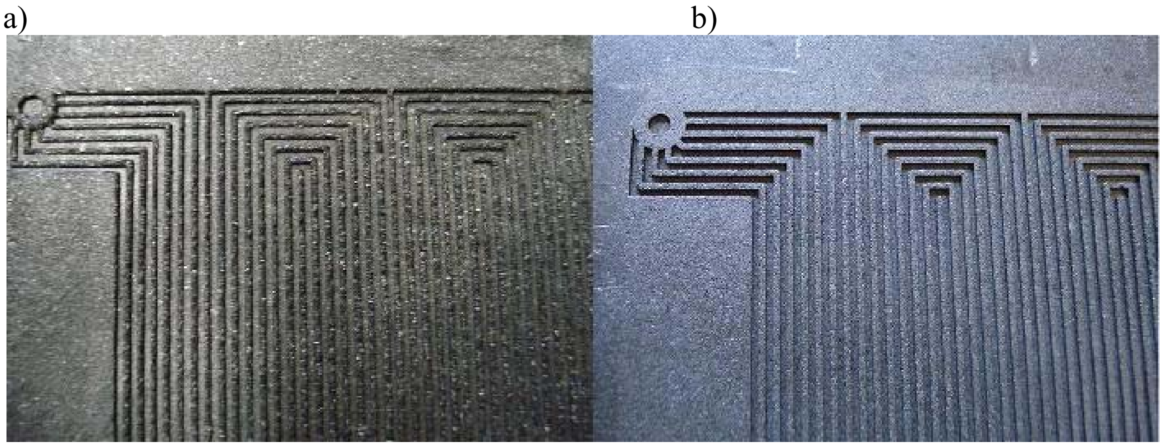

Figure 3.8 – a) Expanded view of a bipolar plate generated by wet-lay material and b) expanded view of a laminate bipolar plate showing improved channel formation.

3.5 Conclusions

A new method has been developed to produce cost-effective bipolar plates with high electrical conductivity, good mechanical properties and potential rapid manufacturability. Composite sheets consisting of graphite particles, PPS or PET fibers and carbon fibers were first generated by means of a wet-lay process. The porous sheets were then stacked and covered with fluoropolymer/graphite particles and compression molded to form layered composite bipolar plates with gas flow channels. Compared to the bipolar plates consisting of wet-lay composite materials only, the bipolar plates with laminate structure have improved formability, higher in-plane and through-plane conductivities and significantly lower half-cell resistance. The shape and definition of the gas flow channels have also been improved by the laminate structure. Although the mechanical properties of the laminate plates are not as high as that of the wet-lay based plates, they are still higher than that of other polymer composite bipolar plates due to the presence of a strong wet-lay material in the core. While the one-step method is good for batch production of laminate bipolar plates with desired mechanical and electrical properties, the two-step method may be chosen for continuous mass production of the plates. It has been shown that the mechanical properties of the laminate plates decrease with temperature. However, it is believed that because PPS and PVDF both possess relatively high degrees of crystallinity, the laminate bipolar plates may still be able to perform well in a fuel cell stack. Nevertheless, compressive creep analysis should be performed on the laminate material. The mechanical properties of the laminate bipolar plates may be improved further by using a thermoplastic with higher strength (such as PPS instead of PVDF) in the skin layer. It is also believed that reducing the channel depth could provide improvements by allowing for a thinner plate to be made and potentially lowering the half-cell resistance of the bipolar plate.

3.6 Acknowledgements

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3.7 References

1. RoBberg, K., Trapp, V., *Graphite-Based Bipolar Plates*, in *Handbook of Fuel Cells-Fundamentals, Technology and Applications*, Editor: John Wiley & Sons, Ltd., (2003), 308-314.
2. Clulow, J.G., Zappitelli, F.E., Carlstrom, C.M., Zemsky, J.I.L., Busick, D.N., Wilson, M.S. *Development of Vinyl Ester/Graphite Composite Bipolar Plates*. AIChE Spring National Meeting., March 10-14, New Orleans, LA (2002), 417-425.
3. Mepsted, G.O., Moore, J.M., *Performance and Durability of Bipolar Plate Materials*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd., (2003), 286-293.
4. Wind, J., LaCroix, A., Braeuninger, S., Hedrich, P., Heller, C., Schudy, M., *Metal Bipolar Plates and Coatings*, in *Handbook of Fuel Cells-Fundamentals, Technology and Applications*, Editor: John Wiley & Sons, Ltd., (2003), 295-307.
5. Wang, H., Sweikart, Mary Ann, Turner, John A., *Stainless Steel as Bipolar Plate Material for Polymer Electrolyte Membrane Fuel Cells.* J. Power Sources, **115**, (2003), 243-251.
6. Besmann, T., Klett, James Henry, Jr., Lara-curzio, Edgar, *Carbon/Carbon Composite Bipolar Plate for Proton Exchange Membrane Fuel Cells.* J. Electrochem. Soc., **147**(11), (2000), 4083-4086.
7. Busick, D.N., Wilson, S., *Development of Composite Materials for PEFC Bipolar Plates.* Mat. Res. Soc. Symp. Proc., **575** (2000), 247-251.

8. Wilson, M.S., Busick, Deanna N., US 6,248,467 (2001).

9. Busick, D.N., Wilson, S., *Low-Cost Composite Materials for PEFC Bipolar Plates*, Fuel Cells Bulletin. **2**(5), (1999), 6-8.

10. Blunk, Richard, Elhamid, Abd, Hassan, Mahmoud, Lisi, Daniel, Mikhail, Youssef, *Polymeric Composite Bipolar Plates for Vehicular Applications.* J. Power Sources, **156**(2) (2006), 151-157.

11. Balko, E., N., Lawrance, Richard J., US 4,339,322 (1982).

12. Bisaria, M.K., Andrin, Peter, Abdou, Mohamed, Cai, Yuqi, US 6,379,795 (2002).

13. Huang, J., Baird, Donald G., McGrath, James E., *Development of Fuel Cell Bipolar Plates From Graphite Filled Wet-lay Thermoplastic Composite Materials.* J. Power Sources, **150** (2005), 110-119.

14. Cunningham, B.D., Baird, Donald G., *Review of Materials and Processing Methods in the Production of Bipolar Plates for Fuel Cells.* Int. Materials Reviews, **52**(1), (2007).

15. Lawrance, R.J., US 4.214.969 (1980).

16. http://www.matweb.com/search/SpecificMaterial.asp?bassnum=PPTSM029.

17. BMC Inc. Briefs, Editor: Grapevine Marketing, **13**(2) (2001), 2-4.

18. Pellegri, A., Spaziante, Placido M., US 4,197,178 (1980).

19. http://www.dupont.com/fuelcells/pdf/plates.pdf.

20. Landis, L., Tucker, Jonathan L., *Bipolar Plate Components Move to the Forefront*, R&D Magazine, (2002), 36-38.

21. Tucker, K.W., Weeks, Gregory P., US 5,614,312 (1997).

22. Baird, D.G., Huang, Jianhua, McGrath, J.,US APPL 2004-779,804 (2005).

23. *Kynar and Kynar Flex PVDF Technical Brochure, Elf Atochem North American Inc.*

24. http://www.cpchem.com/enu/ryton_pps_p_what_is_pps.asp.

25. Gardner, J.W., Boeke, P.J., *Handbook of Plastic Materials and Technology*, ed. I.I., Editor: Rubin. (1990), 423.

4 Development of bipolar plates for fuel cells from graphite filled wet-lay material and a compatible thermoplastic laminate skin layer

Preface

The work presented in this chapter is further progress on the previous chapter. Specifically, it aims at improvements in mechanical strength and dimensional stability by using a matching polymer structure throughout the bipolar plate. The work also quantitatively addresses surface roughness and its role in bipolar plate performance. This chapter is organized as a manuscript for future publication.

Development of bipolar plates for fuel cells from graphite filled wet-lay material and a compatible thermoplastic laminate skin layer

Brent D. Cunningham[a,*], Donald G. Baird[a]

[a]Chemical Engineering and Macromolecules and Interfaces Institute, Virginia Tech, Blacksburg, VA 24061

4.1 Abstract

In this paper a method with the potential to lead to the rapid production of thermoplastic polymer composite bipolar plates with improved mechanical properties, formability, and half-cell resistance is described. In our previous work it was reported that laminate structure composite bipolar plates made with a polyphenylene sulfide (PPS) based wet-lay material as the core and a polyvinylidene fluoride (PVDF)/graphite mixture as the laminate exhibited improved formability, through-plane conductivity, and half-cell resistance over that of wet-lay based bipolar plates. However, the mechanical strength of the laminate plates needed improvement. In this work laminate polymer composite plates consisting of a PPS/graphite based laminate mixture and a PPS based wet-lay core are manufactured in an effort to improve mechanical strength. Additionally, our existing channel design has been altered to reduce the channel depth from 0.8 mm to 0.5 mm in an effort to improve the half-cell resistance by reducing the total plate thickness. The plates are characterized by their half-cell resistance and mechanical properties at ambient and elevated temperatures. The PPS based laminate plates

exhibited half-cell resistances as low as 0.018 Ω-cm^2, tensile strength of up to 37 MPa, and flexural strength of up to 60 MPa at ambient temperature. The laminate bipolar plates can be manufactured in several ways with two of them being discussed in detail in the paper.

4.2 Introduction

Bipolar plates are by weight, volume, and cost one of the most significant parts of a fuel cell stack. Bipolar plates must exhibit excellent electrical conductivity, adequate mechanical stability, corrosion resistance (for metal plates/metal coated fillers), and low gas permeability. Furthermore, bipolar plates must be amenable to a rapid, low cost processing methodology if they are to be widely used in the automotive industry.

The endeavor to develop a suitable material for bipolar plate production is based on the following requirements to be met in the PEM fuel cell operating temperature range of 60-120 ^{o}C:

- Electrical conductivity (> 100 S cm^{-1})*
- Low permeability (< 2 x 10^{-6} cm^3 (cm^2 s)$^{-1}$)*
- Corrosion resistant (< 16 mA/cm^2)*
- Tensile strength (> 41 MPa)$^{\#}$
- Flexural strength (> 59 MPa)$^{\#}$
- High thermal conductivity (> 10 W (m K)$^{-1}$)$^{\#}$
- Chemical and electrochemical stability
- Low thermal expansion
- Resistance to compressive creep

- Efficient processability

*Department of Energy (DOE) and FreedomCAR specified targets at ambient temperature[1]
#Plug Power targets at ambient temperature[2]

Although the bipolar plate targets are specified at ambient temperature, the temperature dependency on the properties of thermoplastic polymer composite material should be considered. The electrical conductivity target is specified as bulk, or in-plane conductivity. Although no target has been specified for through-plane conductivity, it is thought to be an important measurement because the through-plane direction is the route that electrons travel in an operating fuel cell. Corrosion resistance is mainly a concern with metal plates and metal coated fibers, but it can also apply to polymer systems that may dissolve electrochemically in a fuel cell. The mechanical targets are specified for ambient temperature, while targets at elevated temperatures have not yet been specified. Efficient processability incorporates several factors, including material and production costs and the ability for rapid, continuous manufacturing.

Traditional materials for producing bipolar plates are sintered graphite and metal. Graphite plates have been used because they possess high electrical conductivity, corrosion resistance, and a lower density than that of metals.[3] Problems with graphite plates include brittleness and the cost associated with machining channels into the surface. Because the material and machining cost of graphite plates are exorbitant, at least for the automotive industry, the development of a more suitable material has drawn extensive research. Metal bipolar plates such as stainless steel, aluminum, and titanium have gained attention for their high electrical conductivity, mechanical strength, and negligible gas permeability[3-5]. The main advantage with metal plates is that channels can be embossed or etched into the surface, eliminating or reducing considerable time and cost associated with machining. However, because metals are subject to corrosion and leaching of ions, a coating must be applied to the surface to provide a protective layer. Unfortunately, the protective coating is highly electrically insulating and drastically increases the interfacial resistance of the metal bipolar plates. Many materials have been investigated to coat metal plates such as polypyrrole[6] and nitrides[7, 8], but it has been shown to be difficult to apply a protective layer thin enough to maintain low interfacial resistance while avoiding the existence of pinholes or defects in the surface, ultimately leading to bipolar plate failure.

In an effort to improve on sintered graphite, researchers at Oak Ridge National Laboratory (ORNL) have developed carbon/carbon composite bipolar plates by slurry molding carbon fiber and phenolic resin[9]. ORNL researchers claim that the plates have high electrical conductivity and adequate mechanical stability. However, the manufacturing step in the production of carbon/carbon plates is complex and expensive due to a chemical vapor infiltration (CVI) process. CVI operates at very high temperatures for extended times, sealing the carbon/phenolic resin preforms by depositing carbon onto the surface. Unfortunately, channels must still be machined into the surfaces of the carbon/carbon plates.

Graphite-based polymer composite bipolar plates have shown to potentially meet target requirements. They offer advantages such as lower cost, higher flexibility, and are lighter in weight when compared to metallic and graphite plates. The gas flow channels can be molded directly into the surfaces of the plate, eliminating the need for a costly machining step. Researchers at Los Alamos National Laboratory (LANL) have developed a bipolar plate based on a vinyl ester thermosetting polymer resin and graphite powder[2, 10]. Bulk conductivities were measured to be as high as 85 S/cm, with tensile and flexural strength at 25 and 38 MPa, respectively, when measured at ambient temperature which are still lower than the specified targets. A compression molding process was used for producing the bipolar plates in which channels were formed in less than 10 minutes[11, 12]. The advantage in using a thermosetting polymer is that when the polymer is heated and compression molded, the plate cures and does not require subsequent cooling. Therefore, the plate can be immediately released from the mold. However, a postcure may be necessary, and can take as long as one hour to complete[11]. Blunk and coworkers[13] have developed an epoxy based system using expandable graphite that has exhibited low resistances. However, the flexural strength of the plates did not reach the target value. Although the graphite filled epoxy system has shown potential for use in bipolar plate production, the generation of the epoxy bipolar plates requires a 20 minute curing time and the expandable graphite is anticipated to be expensive to manufacture. The epoxy-based bipolar plates also require machining of channels. Polyvinylidene fluoride (PVDF), a thermoplastic fluoropolymer matrix, has been used with graphite particles and carbon fiber to produce bipolar plates[14]. Bulk conductivity values have reached 109 S/cm at ambient temperature, exceeding the DOE target. However, the flexural strength was only 42.7 MPa, lower than the goal of 59 MPa at ambient temperature. Liquid crystalline polymer/graphite mixtures have been considered for bipolar plate production because of their ability to be injection molded due to the low viscosity of the polymer[15]. The injection molding process allows for a relatively short cycle time of 30 seconds. Bulk conductivities have reached values as high as 100 S/cm at ambient temperature, just reaching the minimum target, but no mechanical properties or through-plane conductivities were reported, and it is anticipated that the mechanical properties may not reach the targets.

Huang and coworkers[16-18] have reported the development of conductive polymer composite materials generated by means of a wet-lay process. The wet-lay materials were compression molded to form highly conductive and strong bipolar plates. Bulk conductivities (in-plane) and mechanical properties of the plates were higher than that of any other polymer composite plates measured at ambient temperature (see Table 4.1). However, the through-plane conductivity, half-cell resistance, and formability of the plates needed further improvement.

Cunningham and coworkers[19] have improved on the through-plane conductivity, half-cell resistance, and formability of the wet-lay based bipolar plates by using a laminate approach. A PVDF/graphite mixture in powder form was applied to the surfaces of a polyphenylene sulfide (PPS) based wet-lay core material. The PVDF based laminate plates exhibited bulk conductivities greater than 300 S/cm at ambient temperature, well above the DOE target. Compared to the bipolar plates consisting of wet-lay material only, the laminate bipolar plates exhibited an increase in through-plane conductivity of 25-35%, as well as a decrease in half-cell resistance by a factor of up to 5. The tensile and flexural strengths were measured to be 34 MPa and 54 MPa, respectively, at ambient temperature both falling short of the target value but higher than those of any other polymer composite material used for the production of bipolar plates.

In this paper a PPS based laminate structure is investigated as a way to improve the mechanical properties over those of PVDF based laminate plates while maintaining sufficient formability and half-cell resistance of the bipolar plates. The laminate bipolar plates are generated by two methods. One is to put laminate mixture (in powder form) on the surfaces of the wet-lay sheet stacks and compression mold at a temperature to melt the polymer which is called the one-step molding method. The other is to generate a consolidated wet-lay composite plaque first and then add composite powders to the surfaces of the flat plaque followed by compression molding the composite to impart the channels. This is called the two-step molding method. We will asses the properties of the bipolar plates made by the two different methods and discuss the advantages and disadvantages of the processes. The evaluation will be focused on the mechanical properties of the composites, as well as the half-cell resistance and surface appearance of the bipolar plates.

4.3 Experimental

4.3.1 Materials

For generating the wet-lay material, a thermoplastic polymer used in the form of fibers was PPS (6 mm long) at levels in the range of 13-40 wt%. Conoco carbon fibers (nominal length ½”) were used as reinforcing fibers in the range of 6-9 wt%. Timrex® KS-150 and Timcal™ TC-300 graphite particles were used as the conductive filler in the range of 50-80 wt%. Microglass (1 wt%) was also added to help particle retention in the wet-lay preforms. PVDF (Kynar 761 from Arkema) was used with TC-300 graphite particles as the first type of laminate mixture. PPS powder (Primef® from Solvay) was used with TC-300 graphite particles as the second type of laminate mixture.

4.3.2 Production and molding of wet-lay composite sheet material

In Fig. 4.1 is shown the scheme for production of the wet-lay composite materials and bipolar plates. Wet-lay sheets containing a thermoplastic fiber, reinforcing fiber, conductive graphite particles, and microglass were generated with a slurry-making process on a Herty papermaking machine donated by DuPont. The slurry contained 1 wt% solids in water. First, the cut thermoplastic fibers were added to the water in a pulper and agitated for 10 minutes. Next, the cut reinforcing fibers, graphite particles, and microglass were added and mixed for 3-6 minutes. The slurry was then pumped into a head box containing a sieve screen, generating a sheet of porous material. The sheet was continuously rolled through an oven at the melting point of the polymer to continue drying and partially melt the thermoplastic fibers.

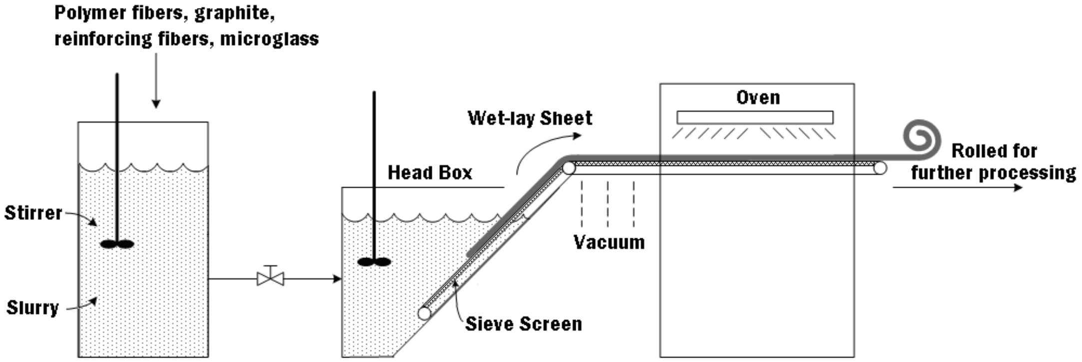

Figure 4.1 – The process to develop wet-lay polymer composite sheets.

The procedure carried out by Huang and coworkers[16, 17] for making a test sample or bipolar plate from wet-lay material was followed in this work. The material was cut to fit the shape of a mold and stacked to provide a desired thickness. The mold was then placed between platen heaters of a hydraulic press set at approximately 20 ^{o}C above the melting point of the thermoplastic fiber (300 ^{o}C for PPS based composites). The material was compression molded for 7-10 minutes at a constant applied pressure of 1,000 psi. The platen heaters were turned off and the mold was allowed to cool to 30 ^{o}C while still under pressure. The mold was then removed from the press and the flat plaque or bipolar plate was taken out of the mold. Although a batch process was used in this work, a continuous process is envisioned in the future.

4.3.3 Novel laminate approach

In this paper two methods to produce bipolar plates are described. The first, called the one-step method, consisted of initially covering the bottom surface of the mold with a desired amount of laminate mixture and spreading it evenly over the surface. Next, a pre-determined number of wet-lay sheets were stacked on top of the laminate mixture. Finally, another layer of laminate (same amount as placed in the bottom of the mold) was spread evenly on top of the wet-lay sheets. The mold was closed and placed into a heated press set at 300 ^{o}C for compression molding. Upon compression molding, the laminate powder penetrated into the porous wet-lay material (> 50% voids) to help construct a well bonded polymer network throughout the entire plate. The second process is called the two-step method. First, the wet-lay sheets by themselves were placed into a heated mold and compression molded to form a pre-consolidated flat plaque. After being removed from the mold, laminate powder was added to the bottom surface of the mold and on top of the flat plaque similar to the one-step method. The mold was closed and placed into a heated press for compression molding. The molding temperature for this method was set at approximately 20 ^{o}C above the melting point of the polymer in the laminate mixture (200 °C for PVDF, 300 °C for PPS). In the two-step method, the sole form of bonding between the skin layer and the wet-lay core was adhesion between the surfaces. The level of laminate powder added to the surfaces of the wet-lay material was varied from 15-25 vol% (on each side) to evaluate how differences in the level of laminate layer would affect the composite properties. Two channel designs of 0.8 mm wide x 0.8 mm deep and 0.8 mm wide x 0.5 mm deep were used to evaluate the dependency of half-cell resistance on channel depth of plates of similar compositions. In Fig. 4.2 is shown a picture of a compression molded laminate bipolar plate of dimensions 120 x 140 mm with 0.8 x 0.5 mm and a parallel serpentine style channel design.

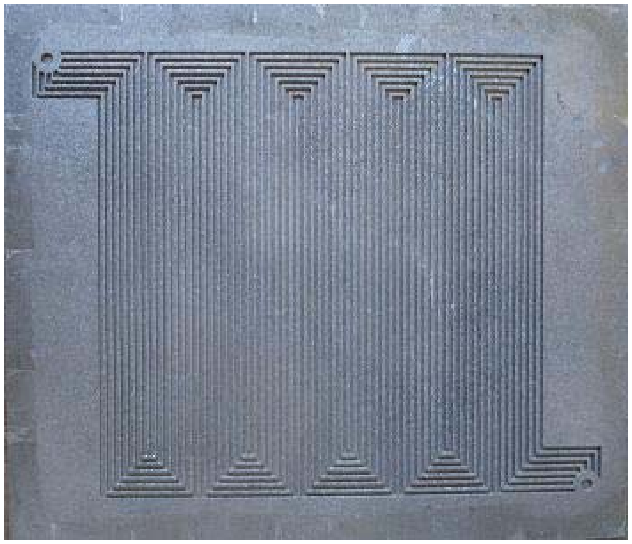

Figure 4.2 – One side of a PPS based laminate polymer composite bipolar plate showing the 7-channel parallel serpentine style design. Plate dimensions are 140 x 120 mm. Channel dimensions are 0.8 x 0.8 mm.

4.3.4 Measurement of mechanical properties

Tensile and flexural tests were performed on an Instron 4204 in accordance with ASTM D638 and D790 standards, respectively. Flexural tests were also performed on the PPS based laminates at 80 °C, 100 °C, and 120 °C to evaluate the strength in an environment that more accurately reflects that found in PEM fuel cells. The test specimen size was approximately 76.2 mm x 8.5 mm x 3.0 mm (L x W x T) and was cut from a flat plaque.

4.3.5 Measurement of in-plane and through-plane conductivity

In-plane (bulk) conductivity was measured according to ASTM Standard F76-86. Current contacts were placed at the four corners of the plaque allowing for a constant current to pass through the specimen. The voltage drop was measured across the specimen with a Keithley 2000 digital multi-meter at ambient conditions. Two characteristic resistances, R_A and R_B were measured. The plaque resistance, R_S, is obtained by solving the Van der Pauw equation:

$$\exp(-\pi R_A/R_S) + \exp(-\pi R_B/R_S) = 1 \tag{1}$$

The resistivity, ρ, is given by $\rho = R_S d$, where d is the thickness of specimen. The volume conductivity, σ_B, is defined as $1/\rho$.

Through-plane conductivities were measured based on a method proposed by Landis and Tucker[20]. A 76.2 mm x 76.2 mm plaque was placed between gold plated copper electrodes. Between the electrodes and sample was placed a piece of carbon paper (Toray TGP-H120) to improve electrical contact between the electrodes and sample. The system was placed under an applied pressure of approximately 220 psi and the resistance was measured. The sample was removed, and the resistance of the test cell (including carbon paper) was measured again under the same conditions to obtain a "baseline" resistance. The sample resistance could then be calculated by subtracting the baseline resistance from the total resistance. The resistivity of the material was calculated by:

$$\rho = [(R_T - R_{baseline})A] / L \qquad (2)$$

where ρ is resistivity, A is cross-sectional area of sample, L is the thickness of sample, and R_T and $R_{baseline}$ are total resistance and baseline resistance, respectively. The through-plane conductivity, σ_T, was then calculated as $1/\rho$.

4.3.6 Measurement of half-cell resistance

To measure the half-cell resistance of a bipolar plate, an apparatus was set up similarly to the one used to measure through-plane conductivity. A bipolar plate having length and width dimensions of 120 x 140 mm and an active area of 100 cm^2 was placed between the gold plated copper electrodes. Carbon paper (Toray TGP-H-120) was placed on both sides of the bipolar plate, and hence, in between the sample and electrodes. The size of the carbon paper was 100 x 100 mm in order to completely cover the active area. The sample was placed under an applied pressure of approximately 220 psi while a constant current of 250 mA was passed through the sample. It was acknowledged that in an operating fuel cell stack, the bipolar plates will be placed under 250 psi of pressure. However, due to the limitations of our apparatus, 220 psi was the maximum pressure applied to the bipolar plates. The potential was measured between the collectors and the half-cell resistance was calculated based on Ohm's law. The bipolar plate was removed, and the potential across the electrodes and carbon paper was measured to produce a baseline resistance. The baseline resistance, that is the resistance of the testing circuit excluding the bipolar plate but including carbon papers and electrodes, was measured after testing of the plate. This was done to ensure the stability of the baseline of the instrument and to evaluate the contribution of the bipolar plate to the total half-cell resistance.

4.3.7 Optical measurement of surface roughness

Surface roughness of bipolar plates was quantitatively measured using a TOPO 2-D Topography Analysis machine. The optical sensor measured the roughness along a 2 mm span of a channel that was compression molded into the surface. The optical sensor detected changes in the topography of the channel section in terms of peaks and valleys that emerged from a calculated centerline.

4.4 Results and Discussion

4.4.1 Production of laminate composite materials and bipolar plates

It was found that the addition of a PVDF/graphite skin layer that covers PPS based wet-lay material improved through-plane conductivity, half-cell resistance, and the formability of channels into the surfaces[19]. However, the mechanical strengths of the PVDF based laminate plates at ambient and elevated temperatures did not quite meet the target values. Furthermore, there were concerns about compatibility and hence, adhesion of PVDF to the PPS based wet-lay. Therefore, it was believed that using PPS instead of PVDF in the laminate powder mixture could provide a plate with sufficient strength due to the matching polymer structure and crystallization temperature range All laminate bipolar plates or flat plaques discussed in this paper contained a PPS based wet-lay core with 70 wt% TC-300 graphite particles and 6 wt% carbon fibers.

4.4.2 Electrical conductivity of laminate composite materials

Electrical conductivity is one of the most important properties of bipolar plates. Huang et al.[16] have reported the electrical properties of wet-lay based composites compared to other polymer composite materials measured at ambient temperature (see Table 4.1). PPS based wet-lay composites have exhibited in-plane (bulk) conductivities higher than 200 S/cm at ambient temperature, well exceeding the DOE target of 100 S/cm. These values were also higher than any other polymer composite material with similar graphite loadings. PVDF based laminate composites have exhibited bulk conductivity values above 200 S/cm at ambient temperature and improved through-plane conductivity values when compared to those of the wet-lay based composites[19]. PPS based laminate composites have also exhibited excellent in-plane conductivity values and through-plane conductivity values at ambient temperature comparable to those of the PVDF based laminate composites as shown in Table 4.2. When materials of similar compositions differing only by processing method are compared, the laminate plates produced by the one-step method exhibit slightly higher conductivities, especially in the through-plane direction. This may be expected because when the material is compression molded via the one-step method, the laminate powder penetrates into the porous wet-lay material. Therefore, a more conductive network may be generated in the through-plane direction using the one-step molding method.

Table 4.1 – Comparison of conductive and mechanical properties measured at ambient temperature for several polymer composite materials used in the production of bipolar plates.

Source	Polymer	Graphite/glass or carbon reinforcing fiber (wt/wt%)	Conductivity (S/cm)		Mechanical Strength (MPa)	
			In-plane	Through-plane	Tensile	Flexural
Target			>100[a]	-	41.0[b]	59.0[b]
GE[14]	PVDF	64/16 CF	109	-	-	42.7
LANL[11]	Vinyl Ester	68/0	60	-	23.4	29.6
Plug Power[2]	Vinyl Ester	68/0	55	20	26.2	40.0
DuPont[21]	-	-	-	25-33	25.1	53.1
Virginia Tech[16]	PET	65/7 GF	230	18-25	36.5	53.0
Virginia Tech	PPS	70/6 CF	271	19	57.5	95.8
Virginia Tech[19]	15% PVDF Laminate	70/6 CF	350	14-32	32.7	54.4
Virginia Tech	20% PVDF Laminate	80/6 CF	251	15-26	25.0	30.6

[a] DOE target for conductivity at the operating temperature of PEM fuel cells[1]
[b] Plug Power targets for mechanical strength at the operating temperature of PEM fuel cells[2]

Table 4.2 – Comparison of in-pane and through-plane conductivities at ambient temperature for PPS and PVDF based laminate composites generated by the one-step and two-step methods.

Material designating the amount and type of graphite contained in the wet-lay core	Processing Method	In-plane conductivity (S/cm)	Through-plane conductivity (S/cm)
20 vol% PPS laminate with 70% TC-300 graphite in core	One-step	209-325	13-30
20 vol% PPS laminate with 70% TC-300 graphite in core	Two-step	164-226	13-29
20 vol% PVDF laminate with 70% TC-300 graphite in core	One-step	181-292	17-32
20 vol% PVDF laminate with 70% TC-300 graphite in core	Two-step	203-350	14-24

It is important to realize that graphite filled polymer composite plates may have different properties and performances in different directions. It is apparent from Tables 4.1 and 4.2 that the through-plane conductivities for the wet-lay based and laminate composites are significantly lower than the in-plane conductivities. This may be attributed to several possible factors. First, the graphite particles are not spherical, but rather elongated platelets that may orient in a plane perpendicular to the direction of the compaction force during molding. This plane is designated as the *X*-*Y* (in-plane) direction as shown in Fig. 4.3. Furthermore, when forming the wet-lay sheets, the thermoplastic and reinforcing fibers also align in the *X*-*Y* direction and may help induce the graphite particles to orient in the same direction. It is believed that for compression molded composite bipolar plates, the higher the aspect ratio of the graphite used, the greater the ratio of in-plane to through-plane conductivity.

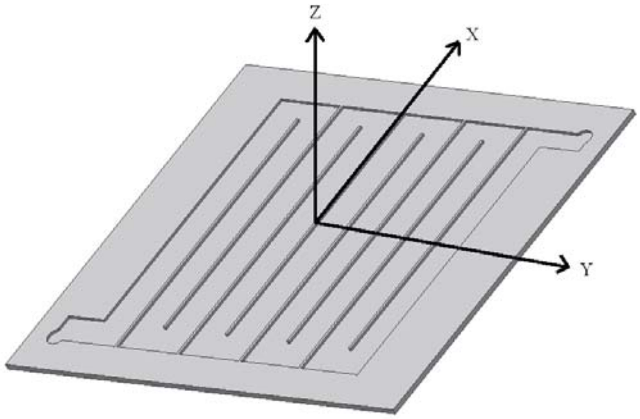

Figure 4.3 – Laminate bipolar plate representation showing the direction of the X-Y-Z planes.

4.4.3 Mechanical properties of wet-lay composite materials

In addition to electrical conductivity, the bipolar plates should also have adequate mechanical properties to be used in fuel cell stacks where they would be subjected to a constant compressive load. However, for polymer composites doped with high levels of conductive particles and/or fibers, it was difficult to obtain high conductivity and sufficient mechanical properties simultaneously. As a result the mechanical properties of most composite materials used to produce bipolar plates were still lower than the target values with the exception being the PPS based wet-lay composites (see Table 4.1). The PVDF based laminate material exhibited lower strength than wet-lay composite material. A decrease in mechanical properties is expected with the laminate plates because the surfaces are generated from a powder form of polymer and are not reinforced with carbon fiber. However, due to the presence of wet-lay in the core, the mechanical strengths of the laminate plates still compared well to the vinyl ester and PVDF based polymer composite materials.

As stated in section 4.3.3, the laminate plates were produced by either the one-step or two-step molding method. Potentially there could be differences in the mechanical strengths of plates produced by the two methods because of differences in adhesion of the outer layer to the core composite material. In Figs. 4.4 and 4.5 are shown the flexural and tensile strength of PPS based laminate flat plaque test specimens at various vol% of laminate layer and their dependency on processing method at ambient temperature. The strengths exhibited an increase with decreasing vol% of laminate material. This was expected because a lower vol% of laminate material resulted in a higher vol% of the stronger wet-lay in the core. The PPS based laminate flat plaque test specimens generally exhibited higher strength (about 20% higher flexural strength) than that of PVDF based laminate plaques measured at ambient temperature reported by Cunningham et al.[19]. However, the tensile strength of the15 vol% PPS based laminate material still did not quite reach the target of 41 MPa. The flexural strength of the 15 vol% PPS based laminate material had several data points that met the target of 59 MPa even when produced by the 2-step molding method. Overall there did not appear to be as large of a dependency on the processing method using the PPS based laminate plates as was exhibited by the PVDF based laminate plates. This may be due to the higher T_g of PPS (~ 88 ^oC and ~ -30 ^oC for PVDF) and the compatibility of the polymer in both the laminate and wet-lay material when using PPS throughout the plate. Whereas in the PVDF based laminate plates, there may not have been adequate adhesion between the laminate layer and the PPS based wet-lay core, especially in the 2-step molding method. It is also believed that de-lamination could occur using a PVDF based laminate layer and a PPS based wet-lay core.

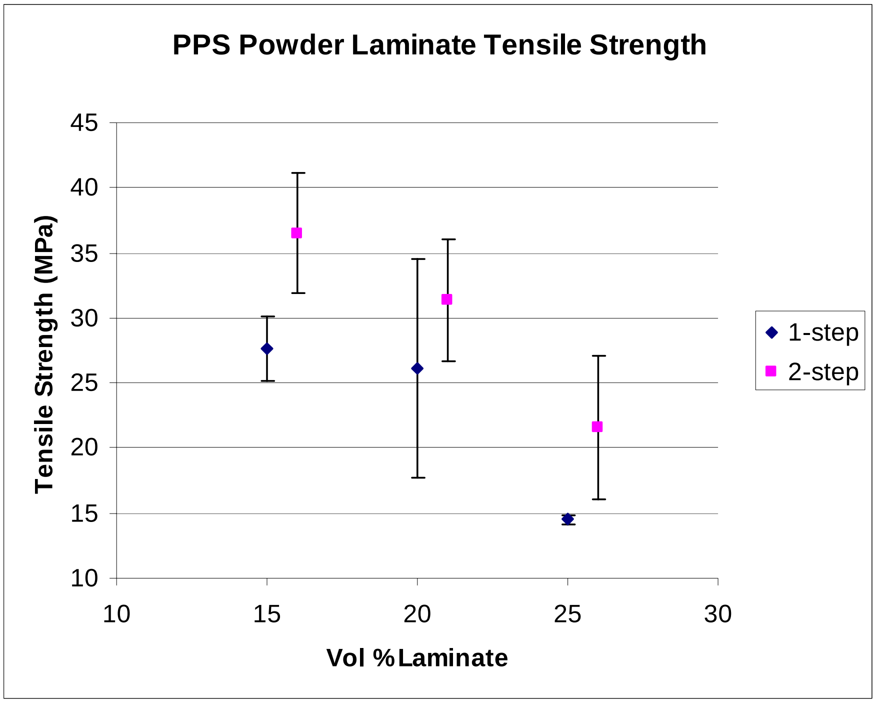

Figure 4.4 - Tensile strength at ambient temperature of various volume percents of PPS based laminate layer on the surfaces of a PPS based, 70% TC-300 wet-lay core material processed by the one-step (◆) and two-step (■) methods. Error bars indicate one std. dev.

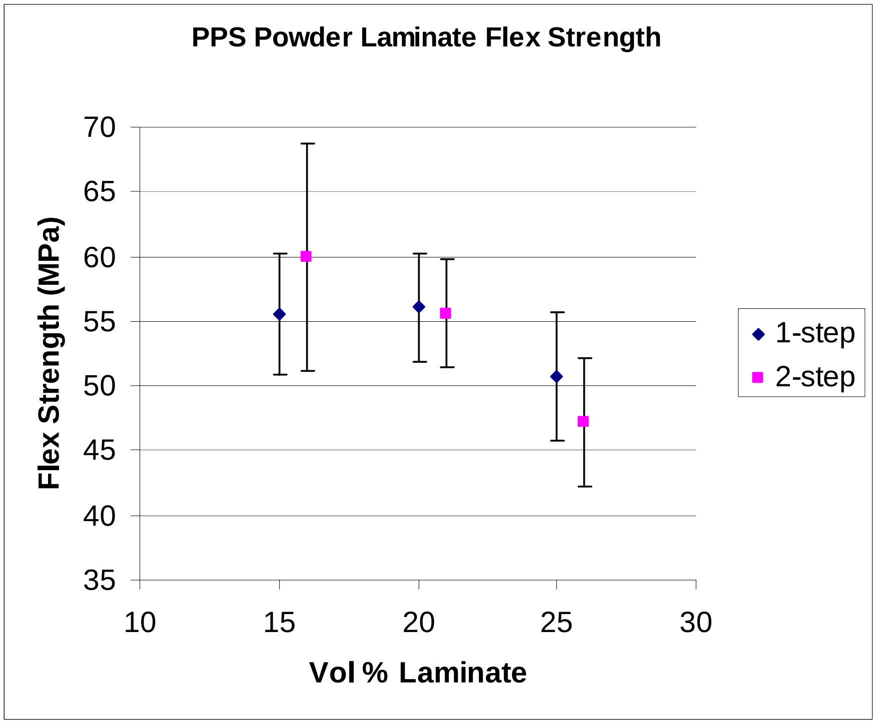

Figure 4.5 - Flexural strength at ambient temperature of various volume percents of PPS based laminate layer on the surfaces of a PPS based, 70% TC-300 wet-lay core material processed by the one-step (◆) and two-step (■) methods. Error bars indicate one std. dev.

In Table 4.3 is shown the flexural strength and modulus of PPS based laminate flat plaques at various temperatures. Because fuel cells operate at approximately 100 °C, the properties are reported over a range of temperatures of fuel cell operation. The flexural modulus generally decreased as temperature was increased due to the relatively low T_g of PPS. However, the flexural strength was maintained fairly well throughout the temperature testing range, measuring approximately 60 MPa, just above the DOE target value. The flexural modulus also exhibited higher values at elevated temperatures for the PPS based laminate material than that of PVDF based laminate material by approximately 30%. Therefore, in an operating fuel cell it is believed that the PPS based laminate bipolar plates will provide improved strength and stiffness over those of PVDF based laminate bipolar plates.

Table 4.3 – Comparison of flexural strength and modulus of PPS based laminate composites at various temperatures.

Material	Temperature (°C)	Flexural Strength (MPa)	Standard Deviation	Flexural Modulus (GPa)	Standard Deviation
15 vol% PPS Laminate	23	60.0	8.7	12.0	0.7
	80	63.1	6.8	13.4	0.4
	100	60.0	7.1	7.2	2.0
	120	57.6	5.2	6.9	0.4

4.4.4 Half-cell resistance of wet-lay composite plates

Although electrical conductivity of the materials used to produce bipolar plates is important, the performance of the bipolar plate in a fuel cell is the defining characteristic. A bipolar plate may have electrical properties that drastically differ from flat plaque test specimens because of the molded gas flow channels in the surfaces. To evaluate the electrical properties of the bipolar plates, half-cell resistance tests were conducted at ambient temperature as well as an optical analysis of the surface roughness of the bipolar plates to quantify the roughness.

In Fig. 4.6 are shown comparisons of half-cell resistances for 15 and 33 vol% laminate composite materials and thicknesses at an applied pressure of 220 psi. The half-cell resistances of the laminate bipolar plates with 0.5 mm deep channels were lower than those with 0.8 mm deep channels. Although the active area (surface area of bipolar plate contacting carbon paper) was not changed using shallower channels, the thickness of the bipolar plate was reduced by approximately 0.6 mm. PPS based laminate bipolar plates of 15 vol% with 0.5 mm deep channels exhibited half-cell resistance values of 0.025 Ω-cm^2, about 20% less than that of PVDF based laminate bipolar plates with 0.5 mm deep channels. It is believed that reducing the channel depth below 0.5 mm will allow for the total plate thickness to be further reduced, potentially lowering the half-cell resistance even more. This is demonstrated with the 33 vol% PPS based laminate bipolar plate of thickness 2.2 mm and 0.5 mm channel depth, which exhibited a half-cell resistance of 0.018 Ω-cm^2. Although 33 vol% laminate layer was not the ideal loading level for balancing electrical and mechanical properties, the dependency of half-cell resistance on the total plate thickness was established. Although half-cell resistance measurements were carried out under an applied pressure of 220 psi, it is acknowledged that an operating fuel cell stack may require bipolar plates to be placed under 250 psi applied pressure. Because the interfacial contact between carbon paper and bipolar plate is critical in the evaluation of half-cell resistance, and that higher pressure may improve interfacial contact, it is believed that taking measurements at 250 psi compaction pressure will show a further decrease in half-cell resistance.

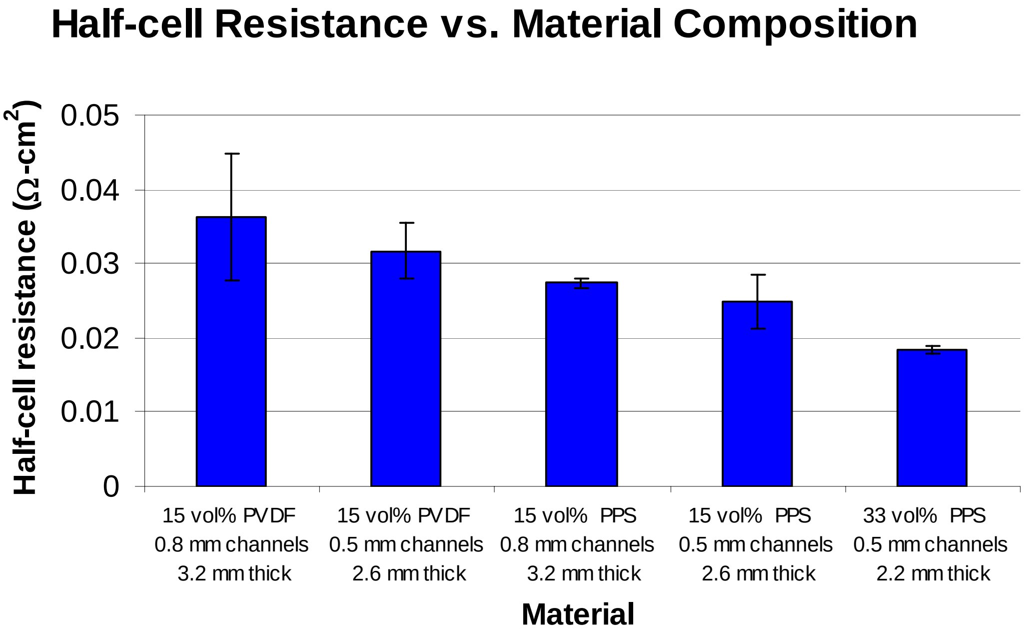

Figure 4.6 – Half-cell resistances of various compositions and thicknesses of laminate bipolar plates.

4.4.5 Surface Roughness of Compression Molded Bipolar Plates

Surface roughness is believed to significantly contribute to the half-cell resistance and performance of a bipolar plate in an operating fuel cell. Although the bipolar plate may possess good conductivity, the surface contact between the bipolar plate and the membrane electrode assembly (MEA), gas diffusion layer, etc. is important in the performance of the bipolar plate. In Fig. 4.7 is shown a two-dimensional surface profile of a wet-lay based bipolar plate and a PPS and PVDF based laminate bipolar plate. The PPS and PVDF based laminate bipolar plates exhibited values for peaks and valleys to reach a maximum of ± 3 µm. The wet-lay based bipolar plate exhibited values for peaks and valleys reaching as high as ± 12 µm. Both laminate bipolar plates exhibited significantly smoother surfaces than the wet-lay based bipolar plate. Therefore, the interfacial contact between the laminate bipolar plate and MEA should be drastically improved over that of the wet-lay based bipolar plate in an operating fuel cell. Because the surface roughness of the PVDF and PPS laminate plates were comparable, it was expected that they would provide similar interfacial contact with the MEA in an operating fuel cell.

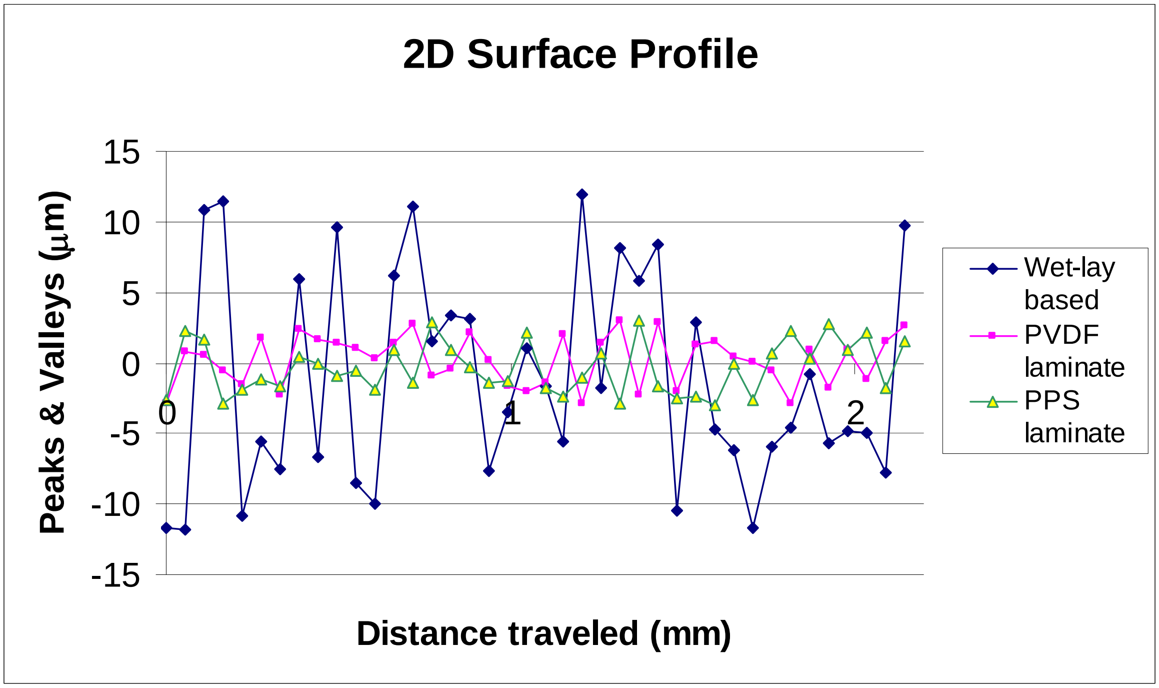

Figure 4.7 – Two-dimensional surface roughness profile of a wet-lay (♦), PVDF laminate (■), and PPS laminate (▲) based bipolar plates.

4.4.6 Potential for rapid, continuous manufacturing of bipolar plates

Although different production methods of PPS based laminate composites have not shown a significant influence on the mechanical or electrical properties, they can considerably influence the potential for continuous manufacturing. In the one-step method, the laminate powder was added to the surfaces of porous, lofty wet-lay sheets. When a number of sheets were stacked, loft was further enhanced. It was found to be difficult to spread the laminate powder evenly over a non-uniform surface created by the wet-lay sheets. The two-step method offered an advantage over the one-step method. It was found to be significantly easier to evenly spread the laminate powder over a solid, flat surface. Therefore, it may be possible to continuously manufacture bipolar plates using the two-step method by continuously consolidating wet-lay sheets through calendar rolls as shown in Fig. 4.8. The solid, consolidated wet-lay core can continue down the processing line where laminate powder would be metered on and doctor bladed to a desired thickness. The material would continue to pass underneath a heating source. Once heated, the material would be transferred underneath a mold for forming. Because the laminate powder can only be added to one side of the pre-consolidated wet-lay material at a time, it will be necessary to repeat most of the process for each bipolar plate in order to get laminate powder on the opposite side.

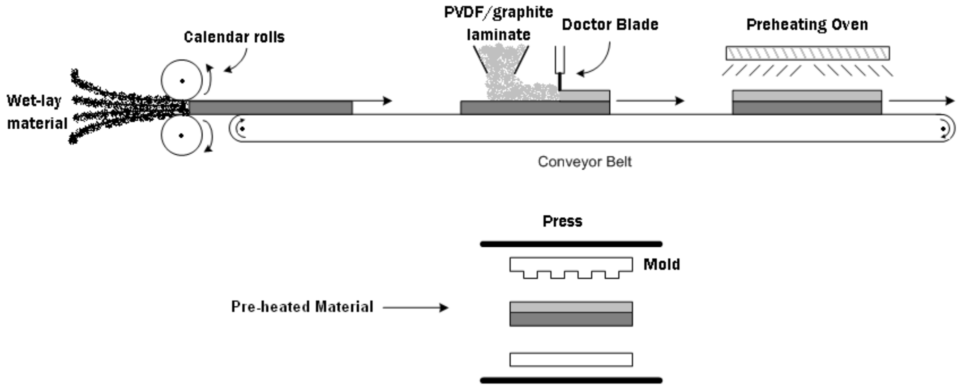

Figure 4.8 – Envisioned continuous process for the production of PPS based laminate bipolar plates.

4.5 Conclusions

A new method has been developed to produce potentially cost-effective bipolar plates with high electrical conductivity, good mechanical properties and potential rapid manufacturability. Composite sheets consisting of graphite particles, PPS fibers, carbon fibers, and microglass were first generated by means of a wet-lay process. The porous sheets were then stacked and covered with PPS/graphite particles and compression molded to form layered composite bipolar plates with gas flow channels. Compared to PVDF based laminate plates, the PPS based laminate plates exhibit higher mechanical strength, lower half-cell resistance, comparable formability, and the potential to avoid adhesion and de-lamination issues. Reducing the channel depth from 0.8 mm to 0.5 mm has also shown to significantly decrease the half-cell resistance. It is believed that reducing the channel depth further will allow for improvements in half-cell resistance, and require less laminate layer which may help increase the overall strength of the plate. Although the mechanical properties of the laminate plates are not as high as that of the wet-lay based plates, they are still higher than that of other polymer composite bipolar plates due to the presence of a strong wet-lay material in the core. While the one-step method is good for batch production of PPS based laminate bipolar plates, the two-step method may be chosen for continuous mass production of the bipolar plates without compromising mechanical or electrical properties. It is also believed that increasing the carbon fiber content in the wet-lay material may help provide more strength in the core.

4.6. Acknowledgements

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4.7 References

1. RoBberg, K., Trapp, V., *Graphite-Based Bipolar Plates*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd. (2003), 308-314.
2. Clulow, J.G., Zappitelli, F.E., Carlstrom, C.M., Zemsky, J.I.L., Busick, D.N., Wilson, M.S. *Development of Vinyl Ester/Graphite Composite Bipolar Plates*. AIChE Spring National Meeting, March 10-14, New Orleans, LA. (2002), 417-425.
3. Mepsted, G.O., Moore, J.M., *Performance and Durability of Bipolar Plate Materials*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd. (2003), 286-293.
4. Wind, J., LaCroix, A., Braeuninger, S., Hedrich, P., Heller, C., Schudy, M., *Metal Bipolar Plates and Coatings*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd. (2003), 295-307.
5. Wang, H., Sweikart, Mary Ann, Turner, John A., *Stainless Steel as Bipolar Plate Material for Polymer Electrolyte Membrane Fuel Cells.* J. Power Sources, **115** (2003), 243-251.
6. Wang, Y., Northwood D.O., *An Investigation into Polypyrrole Coated 316L Stainless Steel as a Bipolar Plate Material for PEM Fuel Cells*. (2006), In Press.
7. Tian, R., J. Sun, and L. Wang, *Plasma-nitrided Austentic Stainless Steel 316L as Bipolar Plate for PEMFC.* Int. J. Hyd. Energy, **31** (2006), 1874-1878.

8. Brady, M.P., Weisbrod, K., Zawodzinski, C., Pailauskas, I., Buchanan, R.A., *Assessment of Thermal Nitridation to Protect Metal Bipolar Plates in Polymer Electrolyte Membrane Fuel Cells*, Electrochemical and Solid-State Letters, 5(11) (2002) A245-A246.

9. Besmann, T., Klett, James Henry, Jr., Lara-curzio, Edgar, *Carbon/Carbon Composite Bipolar Plate for Proton Exchange Membrane Fuel Cells.* J. Electrochem. Soc., **147**(11) (2002), 4083-4086.

10. Busick, D.N., Wilson, S., *Development of Composite Materials for PEFC Bipolar Plates.* Mat. Res. Soc. Symp. Proc., **575** (2000), 247-251.

11. Wilson, M.S., Busick, Deanna N., US 6,248,467 (2001).

12. Busick, D.N., Wilson, S., *Low-Cost Composite Materials for PEFC Bipolar Plates*, Fuel Cells Bulletin, **2**(5) (1999), 6-8.

13. Blunk, R., Elhamid, M.H.A., Lisi, D., Mikhail, Y., *Polymeric Composite Bipolar Plates for Vehicular Applications.* J. Power Sources, **156**(2) (2006), 151-157.

14. Balko, E., N., Lawrance, Richard J., US 4,339,322 (1982).

15. Bisaria, M.K., Andrin, Peter, Abdou, Mohamed, Cai, Yuqi, US 6,379,795 (2002).

16. Huang, J., Baird, Donald G., McGrath, James E., *Development of Fuel Cell Bipolar Plates From Graphite Filled Wet-lay Thermoplastic Composite Materials.* J. Power Sources, **150** (2005), 110-119.

17. Cunningham, B.D., Baird, Donald G., *Review of Materials and Processing Methods in the Production of Bipolar Plates for Fuel Cells.* Int. Materials Reviews, **52**(1), 2007.

18. Cunningham, B., J. Huang, and D.G. Baird, *The Development of Economical Bipolar Plates for Fuel Cells.* J. Mater. Chem., **16**(45) (2006), 4385-4388.
19. Cunningham, B.D., J. Huang, and D.G. Baird, *Development of bipolar plates for fuel cells from graphite filled wet-lay material and a thermoplastic laminate skin layer*, J. Power Sources. (2007), In Press, doi:10.1016/j.jpowsour.2006.12.035.
20. Landis, L., Tucker, Jonathan L., *Bipolar Plate Components Move to the Forefront*, R&D Magazine, (2002), 36-38.
21. http://www.dupont.com/fuelcells/pdf/plates.pdf.

5 Modeling of a Continuous Process Mechanism for the Production of Laminate Structure Polymer Composite Bipolar Plates for Fuel Cells

Preface

This section focuses on the modeling and design of a rapid continuous processing scheme for commercialization of laminate polymer composite bipolar plates for fuel cells. This section is written in manuscript form for potential publication.

Modeling of a Continuous Process Mechanism for the Production of Laminate Structure Polymer Composite Bipolar Plates for Fuel Cells

Brent D. Cunningham[*,a] and Donald G. Baird[a]

Chemical Engineering and Macromolecules and Interfaces Institute
Virginia Tech, Blacksburg, VA 24061

5.1 Abstract

In this paper, the design and modeling of a rapid continuous process for the production of laminate polymer composite bipolar plates is described. It has been shown that polyphenylene sulfide (PPS) based laminate material has the potential to reach a sufficient balance of electrical and mechanical properties and may be amenable to a rapid continuous processing scheme. PPS based polymer composite material generated by means of a wet-lay process establishes the core of the bipolar plate and can be continuously consolidated. To generate a bipolar plate, PPS based laminate/graphite powder is applied to the surface of the solid core. It is possible to reach processing cycle times under 2 minutes using the laminate approach, thus meeting the bipolar plate cost target of $10/kW.

5.2 Introduction

The design of a rapid, continuous, low-cost process for the manufacturing of polymer composite bipolar plates is believed to be the major obstacle that must be overcome for their commercialization and requires the consideration of several factors.

First, the development of a conductive polymeric based material that maintains sufficient properties must be met. Second, the material must have the capability to be handled in a continuous processing scheme where the formation of channels can be molded directly into the surfaces in a timely manner. Third, the total cycle time for the formation of a bipolar plate should reach a time frame of 2-3 minutes in order to meet a cost target of $10/kW. The cycle time includes heating the material above the melting point of the polymer, transferring the part underneath a press, and stamping the channels into the surfaces while cooling the part.

The design of an economical manufacturing process for the production of polymer composite bipolar plates will depend on many factors, with the main one being the heating and cooling stages of the process. Because we are limited to using compression molding due to the high level of fillers, it is desired to heat the preform material externally from the press and insert the heated preform underneath a press. This will allow for faster heating rates when compared to conventional compression molding techniques of heating by conduction.

Heat transfer is important in the processing of polymeric materials. Polymers usually start out as solids and then are heated to temperatures above T_g and/or T_m before being shaped or molded. Radiation heat transfer is frequently used to heat polymers up rapidly before applying molding operations such as thermoforming or blow molding. However, it is believed that radiation heat transfer can be applied to preheat polymer composite material prior to compression molding. It is especially beneficial for the laminate structure design if the wet-lay core material is pre-consolidated because it is desired to only heat the surface, or just inside the surface of the material. As shown in

Fig. 5.1, a material can absorb, reflect, or transmit radiation energy depending on the emissivity of the material.[1-3] Because the laminate polymer composite material is mainly graphite particles, and that graphite has a high emissivity near that of a blackbody, it is assumed the all the radiation energy is absorbed on the surface and then conducts inwards based on Kirchoff's Law. Convective heat transfer modeling is performed to estimate the cooling of the preheated material during transfer to the mold. Conductive heat transfer modeling is used to estimate the cooling rate of the bipolar plate once the plate is compression molded using a cold mold.

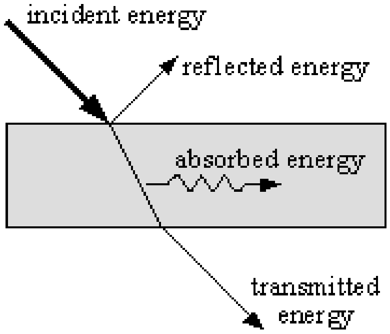

Figure 5.1 – Diagram of a material subjected to incident infrared radiation energy.

Radiation heating and heat transfer by conduction of the laminate structure material can be described by the one-dimensional heat transfer equation[4]:

$$\rho Cp \frac{\partial T}{\partial t} = k \frac{\partial^2 T}{\partial x^2} \qquad 1)$$

In Fig. 5.2 is shown the one-dimensional heat transfer in the laminate slab. Because the wet-lay core is pre-consolidated, and that it is desired to only heat the laminate powder, the centerline is taken to be the inner limit of laminate powder. The thickness, b, is taken as the thickness of laminate powder on either side of the core material. Therefore, the boundary conditions for the polymer composite laminate slab shown in Fig. 5.2 are:

B.C.1	at $x = b$	$q_x = -k\frac{\partial T}{\partial t} = h_r(T_1 - T_2)$
B.C.2	at $x = 0$	$q_x = 0$
I.C.	at $t = 0$	$T = T_0$

where, k is thermal conductivity, h_r is the heat transfer coefficient, T_1 is the slab temperature, T_2 is the radiation source temperature, T_0 is the initial temperature, b is the thickness of the laminate powder on each side, and q_x is the heat flux in the x-direction.

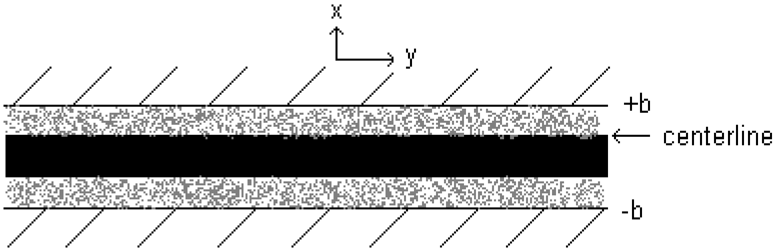

Figure 5.2 – One-dimensional heat transfer in the laminate slab with a heat flux in the x-direction.

It may be assumed that $T_2 >> T_1$, in which case:

$$h_r = F\sigma T_2^3 \qquad 2)$$

where F is the shape factor, and σ is the Stefan-Boltzmann constant.

We now introduce the following dimensionless variables:

$$\xi = x/b \qquad \Theta = \frac{T - T_1}{T_0 - T_1}$$

Equation 1 becomes:

$$\frac{\partial\Theta}{\partial t} = \frac{k}{\rho C_p b^2}\frac{\partial^2\Theta}{\partial\xi^2} \tag{3)}$$

where ρ and C_p are the density and specific heat capacity of the material, respectively.

The procedure for converting Eq. 3 to a system of ordinary differential equations is as follows. The region $0 \leq x \leq 1$ is divided up into N nodes or spatial points. In the case of the laminate slab, the node at the centerline is taken as 0, and the node at the wall is numbered NEQ + 1 = N. Using a central difference approximation, the differential equation (Eq. 3) at the interior nodes becomes:

$$\frac{d\Theta_i}{dt} = \alpha'\left[\frac{\Theta_{i-1} - 2\Theta_i + \Theta_{i+1}}{\Delta\xi^2}\right] \tag{4)}$$

where $\alpha' = k/\rho C_p b^2$ and $\Delta\xi$ is the distance between the nodes and i which runs from 2 to NEQ-1. At node 1, applying the forward difference approximation and B.C. 2 we find that:

$$\frac{\partial\Theta}{\partial x} = 0 = \frac{-3\Theta_0 + 4\Theta_1 - \Theta_2}{2\Delta\xi} \tag{5)}$$

or

$$\Theta_0 = \frac{1}{3}\left(4\Theta_1 - \Theta_2\right) \tag{6)}$$

At the mold wall we can express the backward difference approximation:

$$\frac{\partial\Theta}{\partial x} = \frac{3\Theta_i - 4\Theta_{i-1} + \Theta_{i-2}}{2\Delta\xi} \tag{7)}$$

to give:

$$\Theta_{NEQ+1} = \frac{4\Theta_{NEQ} - \Theta_{NEQ-1}}{3 + \left(2\Delta\xi hb\right) / k} \qquad 8)$$

The partial differential equation at node 1 becomes:

$$\frac{d\Theta_1}{dt} = \left(\frac{\alpha'}{\Delta\xi^2}\right)\left(-\frac{2}{3}\Theta_1 + \frac{2}{3}\Theta_2\right) \qquad 9)$$

And that at node NEQ is:

$$\frac{d\Theta_{NEQ}}{dt} = \left(\frac{\alpha'}{\Delta\xi^2}\right)\left[\Theta_{NEQ-1} - 2\Theta_{NEQ} + \frac{4\Theta_{NEQ} - \Theta_{NEQ-1}}{3 + \left(2\Delta\xi hb\right) / k}\right] \qquad 10)$$

The temperature at each boundary node is calculated at each time step using algebraic expressions in Eqs. 6 and 8. To solve Eq. 3 the laminate region of the composite slab is broken up into 10 segments. Because it is desirable to heat only the laminate region (surface powder layer), the centerline of the laminate slab is actually represented by x = 0 as shown in Fig. 5.2. The node at the centerline is numbered 0 and that at the surface is numbered 10. The differential equation at node 1 is given by Eq. 9 while that at node 9 is given by:

$$\frac{d\Theta_9}{dt} = \left(\frac{\alpha'}{\Delta\xi^2}\right)\left[\Theta_8 - 2\Theta_9 + \frac{4\Theta_9 - \Theta_8}{3 + \left(2\Delta\xi hb\right) / k}\right] \qquad 11)$$

The differential equations for the remaining nodes 2-8 are given by Eq. 4. The values of Θ at the boundaries, Θ_0 and Θ_{10}, are calculated after each time step using Eg. 6 for Θ_0 and the following equation for Θ_{10}:

$$\Theta_{10} = \frac{4\Theta_9 - \Theta_8}{3 + \left(2\Delta\xi hb\right) / k} \qquad 12)$$

The IMSL subroutine shown in Appendix D. is used to solve the system of ordinary differential equations.

Convective heat transfer takes place between a material and a surrounding fluid, in this case air. In our process the most important area of convective heat transfer occurs between the heating and cooling (forming) stage of the process. Once the polymer composite is heated by radiation, the material must be transferred underneath the mold. The physical transfer of the part from the heat source to the mold takes enough time to be critical in the overall heat transfer calculations. The heated polymer composite material may lose a substantial amount of heat before channels can be molded into the surface. Therefore, it is important to determine the time frame for the polymer composite material to be transferred from heat source to the molding step before the temperature of the polymer composite material drops below its processing temperature. The convective heat transfer coefficient is given in terms of the Prandtl number, Pr, and local Reynolds number, Re, as:

$$\frac{hx}{k} = 0.332 \ \mathrm{Pr}^{1/3} \ \mathrm{Re}^{1/2} \qquad \text{Eq. 13}$$

In this paper a continuous manufacturing scheme to produce thermoplastic polymer composite bipolar plates generated using a laminate structure is modeled and discussed. The laminate bipolar plates are composed of a polyphenylene sulfide (PPS) based wet-lay core containing PPS fibers, reinforcing carbon fibers, and conductive graphite particles and a PPS/graphite powder surface. PVDF and PPS have been considered as the thermoplastic polymer in the laminate material, but the PPS based laminate material has shown higher strengths and comparable conductivities to that of PVDF based laminate material.(see Chapter 4) There are various ways to generate laminate bipolar plates, with two methods being discussed in detail in this paper. The methods will be compared on a basis of heating/cooling cycle time and the potential that each method has for continuous manufacturing of bipolar plates. The heating/cooling cycle times are estimated by method of lines approach using the IMSL subroutine DIVPAG.

5.3 Experimental

5.3.1 Modeling of Ordinary Differential Equations

The modeling of a continuous process for the production of laminate polymer composite bipolar plates was performed using the DIVPAG IMSL subroutine. DIVPAG is a subroutine that solves a system of ordinary partial differential equations. In Table 1 of Appendix D. is shown the computer program to model the radiation heat transfer of the laminate region of the material. Similar programs are used to solve convective and conductive heat transfer differing mainly in the values of the heat transfer coefficient, H.

5.4 Results and Discussion

It is believed the most plausible way to develop the laminate polymer composite bipolar plates will be based on pre-consolidating the wet-lay material. This will provide a solid, flat surface so that laminate powder can be more easily metered on and leveled. In order to pre-consolidate the wet-lay material, a pre-determined number of wet-lay sheets can be continuously rolled through calendar rolls as shown in Fig. 5.3. The solid, consolidated wet-lay core can continue down the processing line where laminate powder would be metered on and doctor bladed to a desired thickness. The material would continue to pass underneath a heating source. Once heated, the material would be transferred underneath a mold for forming. Because the laminate powder can only be added to one side of the pre-consolidated wet-lay material at a time, it will be necessary to repeat most of the process for each bipolar plate in order to get laminate powder on the opposite side.

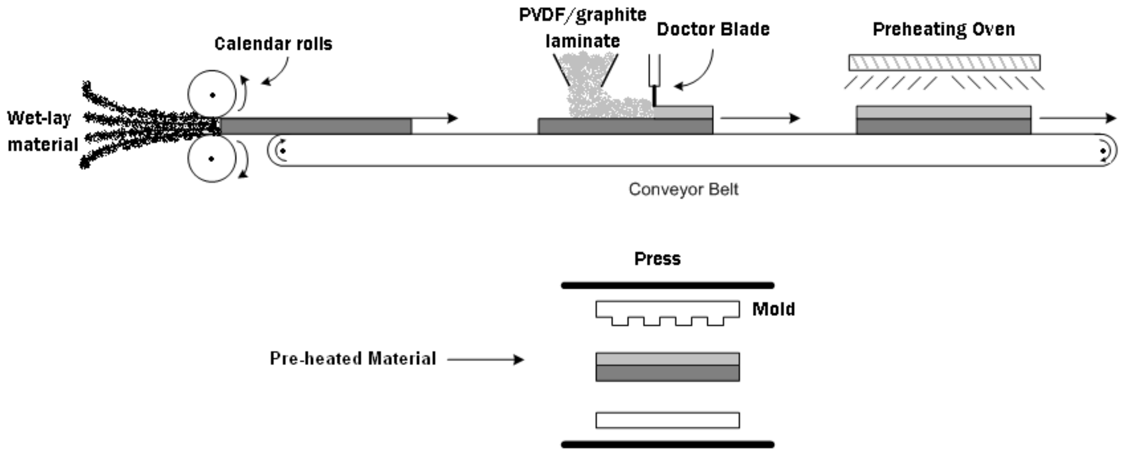

Figure 5.3 – Diagram of the continuous production of laminate bipolar plates.

In Fig. 5.4 is shown the first proposed method to produce laminate bipolar plates. In this method, two halves of the preform are processed simultaneously. Once laminate powder is doctor bladed onto the surfaces, radiation heating is used to heat the laminate powder. The two halves are transferred underneath a press and channels are molded into the material. The second heating step actually heats the exposed wet-lay surfaces which will become the center of the bipolar plate. Heating the underside of the “monopolar” plates is possible because the parts do not readily release from the mold. Once the wet-lay surfaces are heated, the two halves are fused together to form a bipolar plate. This final step requires rotation of the molds by 90° which may be difficult to accomplish.

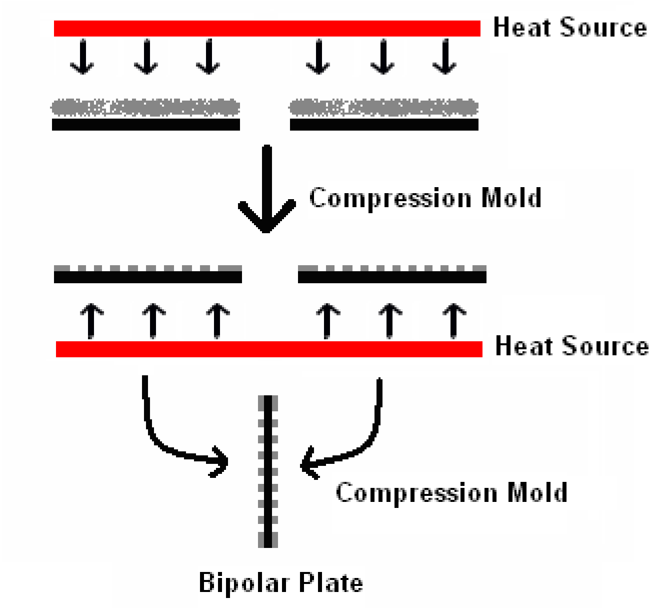

Figure 5.4 – First proposed method for the continuous processing of laminate bipolar plates.

In Fig. 5.5 is shown the second proposed method for the production of laminate polymer composite bipolar plates. In this method, one side of the preform is molded at a time. Similar to the first method, radiation is used to heat the laminate powder once it has been metered on and doctor bladed. The material rolls underneath a press and channels are molded into the surface producing a “monopolar” plate. The monopolar plate is then flipped over and the process is repeated to produce a bipolar plate.

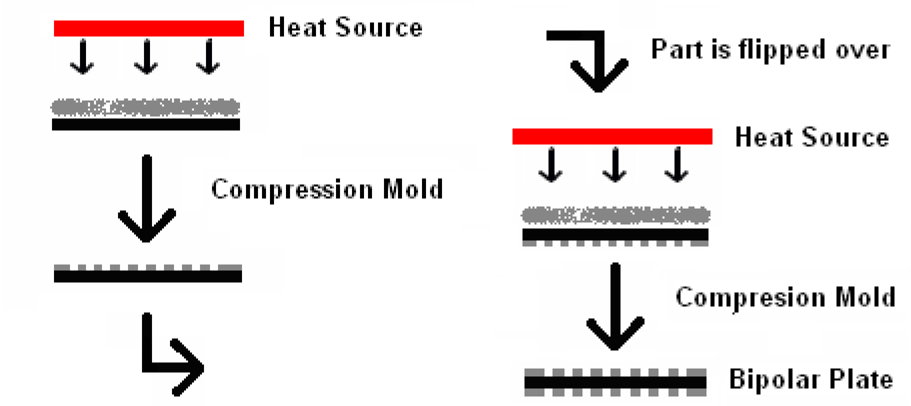

Figure 5.5 – Second proposed method for the continuous processing of laminate bipolar plates.

The methods are similar by means of requiring two heating stages and two molding stages. Each method will be compared on total processing time and the logical determination on the ability to automate the process.

It is important to consider that before the laminate powder is heated, the mixture contains significant amount of voids. Therefore, the actual thickness of laminate powder to be heated will always be greater than the end thickness of the laminate layer after compression molding. The compression ratio of the laminate powder before and after molding is estimated to be approximately 3:1. Therefore, in the radiation heating program the thickness value, B, is set at 0.0015 m (1.5 mm) for molding 0.5 mm deep channels into the laminate material.

In Table 5.1 is shown the program output at various radiation source temperatures and the corresponding time to heat the center and surface of the laminate material. The nodal values for dimensionless temperature are given at each time step in the output. A PPS processing temperature above 300 ^{o}C can be reached in less than 30 seconds using a radiation source temperature above 1000 ^{o}C without degrading the polymer on the surface. Increasing the radiation source temperature to 1200 ^{o}C can heat the laminate power above the PPS processing temperature in about 13 seconds without degrading the polymer on the surface. Because both possible production methods require two heating stages (one for molding each side), the total radiation heating cycle time is estimated to be approximately 26 seconds using a radiation source temperature of 1200 °C.

Table 5.1 – Program output at various radiation source temperatures and the corresponding time for heating the center and surface of the laminate material.

Source Temp (°C) →		800		900		1000		1200	
Heating time (s) ↓		Θ	T (°C)	Θ	T (°C)	Θ	T (°C)	Θ	T (°C)
center	10	.934	76	.908	106	.876	146	.795	266
	20	.872	123	.822	181	.765	254	.631	459
	30	.813	170	.745	248	.669	348	-	-
surface	10	.931	78	.903	110	.870	152	.787	275
	20	.869	127	.819	183	.760	259	.624	467
	30	.811	172	.742	251	.664	353	-	-

The free convective heat transfer coefficient using ambient air is estimated to be approximately 13 W/mK. The laminate preform is also assumed to be at a temperature of 320 °C immediately after radiation heating. In Table 5.2 is shown convective cooling results after numerical modeling. Because the inner material will always be slightly hotter than the surface, it is more important to ensure that the surface retains enough heat for forming. After 16 seconds of convective cooling, the part will still be hot enough for the forming of channels (> 290 °C). Again, the total time contribution is doubled to 32 seconds because this phase takes place twice in the overall process. However, in an automated process, it is believed that the preheated laminate preform can be transferred from heat source to press in less than 16 seconds. It is also possible to use hot air to slow the convective cooling process if necessary.

Table 5.2 – Natural convection heat transfer results at ambient air temperature and a heated laminate preform at 320 ^{o}C.

Air Temp (^{o}C) →		25	
Cooling time (s) ↓		Θ	T (^{o}C)
surface	2	.986	316
	4	.973	312
	6	.961	308
	8	.948	305
	10	.936	301
	12	.924	298
	14	.912	295
	16	.900	292

Heat transfer by conduction for the production of polymer composite bipolar plates takes places once a mold contacts the pre-heated material. The mold temperature will be set at a temperature lower than the melting point of the polymer in the composite material that will allow for solidification and crystallization of the polymer to occur. It is assumed that there will be perfect thermal contact between the mold and the molten polymer. Therefore, we can use the same boundary conditions and initial conditions as used with radiation heat transfer, and the modeling equations (Eqs 4-12) are also the same. In Table 5.3 is shown the program output at various mold temperatures and the corresponding time to cool the center and surface of the laminate material using a heat transfer coefficient between the mold and plate to be 25 W/mK. The initial temperature of the material is assumed to be approximately 290 ^{o}C after assuming the full time span of convective cooling has taken place. This is considered to be the minimum temperature at which the plate must be at in order to retain enough heat to be formed. The desired end temperature (for release of part from mold) is based on the crystallization range of PPS. From DSC analysis (see Appendix A.), the crystallization range for PPS is about 240-255 ^{o}C. Therefore, it is desired to set the mold at a temperature that will quickly cool the bipolar plate below 240 °C. As shown in Table 5.3, using a mold temperature of 80 °C will cool the center of the bipolar plate to 240 °C in about 13 seconds.

Table 5.3 – Program output at various mold temperatures and the corresponding time for cooling the center and surface of the laminate material.

Mold Temp (°C) →			140	120	100	80
Heating time (s) ↓		Θ	T (°C)	T (°C)	T (°C)	T (°C)
center	0	1.000	290	290	290	290
	10	.820	263	259	256	252
	20	.672	241	234	228	221
	30	.551	223	214	205	196
	40	.452	208	197	186	175
	50	.370	196	183	170	158
	60	.304	186	172	158	144
	70	.249	177	162	147	132

The total heating/cooling cycle for a laminate bipolar plate has shown to be approximately 85 seconds. Even though the cycle time meets are target of within 2-3 minutes, it should be noted that the 85 second time span may even be a slight overestimation. It is believed that the transfer of the part from heating unit to mold can take as little as just a few seconds instead of a full 16 seconds. Also, it is possible to improve the radiation heat transfer by increasing the temperature of the radiative heat source. Additionally, using a colder mold will reduce the time for conductive cooling during molding. Considering these factors, a heating/cooling cycle time of less than 1 minute is possible.

Total processing time includes the heating/cooling cycle as well as part preparation and transfers. The metering and leveling of the powder requires a certain amount of time. Because the addition of the powder occurs just prior to the radiation heating step, it is assumed that the metering step can only take place as fast as the radiation heating step. Therefore, an additional 26 seconds will be required for the metering of laminate powder. Another step unaccounted for in the initial time estimate is the flipping of part. However, it is believed that this can be done without substantial time lapse. Considering these factors, a total processing cycle time of about one and a half minutes is possible.

Although the two proposed production methods in Fig. 5.4 and 5.5 are comparable from a heating/cooling cycle standpoint, the logistics behind their continuous automation are quite different. Process automation is a critical issue as it will make the process more competitive with other compression molding processes and injection molding. Use of devices to load, unload, and/or transfer the part, along with cutting and placement of the part will allow the process to handle the material in bulk and for high-volume production. In the first proposed method (Fig. 5.4), the main area for concern arises during the second heating step, where the two "monopolar" plates are fused together by heating the exposed wet-lay surfaces. After many small-scale batch experimentations, it has been observed that the composite material does not release freely from the mold after forming, allowing for the design of rotating the mold prior to the second compression molding step. However, rotating the halves 90^o so that they are parallel to each other may be problematic for flawless operation. In the second proposed method (Fig. 5.5), the only problematic step arises when the "monopolar" plate requires flipping after the first molding step. This problem may, however, be easier to approach and construct on a large scale rather than the 90^o rotation of two presses. There are numerous ways to flip a part over robotically, physically, or mechanically. Therefore, it is believed that the second proposed processing method has the potential for being developed into an automated and continuous commercialization operation.

Because the goal of a 2-3 minute cycle time is possible, the manufacturing cost of bipolar plates should be below the target of $10/kW. The material cost of PPS based laminate bipolar plates is about $3.20/lb, or $2-4/kW. Assuming that a technician is paid to monitor the process for one hour a day, the manual labor cost is estimated to be $1.60/kW. The capital cost of a hydraulic press capable of compression molding several bipolar plates simultaneously is approximately $30,000. Assuming that the press operates for five years, its contribution to the manufacturing cost is $0.10/kW. An overhead cost of 50% is estimated to be $1.85/kW. Therefore, the total molded bipolar plate cost is estimated to be $5-8/kW, under the goal of $10/kW. The total annual production of bipolar plates is estimated to be 250,000 based on a 24 hour, 260 work day year. It is desired to produce at least 500,000 plates a year. Therefore, a hydraulic press with multiple cavities will be beneficial in manufacturing a higher rate of bipolar plates without significant contribution to production costs.

5.5 Conclusions

The modeling of the continuous production of laminate bipolar plates shows the ability to meet a heating/cooling cycle target of 2-3 minutes. It is believed that the inner wet-lay core must be pre-consolidated in order to provide a solid, flat surface for the addition of laminate powder. Because only the surface (powder) requires heating, radiation heating is chosen to preheat the laminate material prior to compression molding. Molding channels into both sides of the laminate material actually requires the preform to go through each processing step twice, once for each side. Nevertheless, it is still anticipated to meet the processing time constraints. Taking into account material, operational, and overhead costs, the total molded bipolar plate cost should be under the goal of $10/kW. The total annual production of bipolar plates is estimated to be 250,000 based on a 24 hour, 260 work day year. The annual production can be improved upon using a two cavity mold, or even a four cavity mold allowing for several bipolar plates to be processed simultaneously.

5.6 Acknowledgements

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5.7 References

1. Cunningham, B.D. and D.G. Baird, *Review of Materials and Processing Methods in the Production of Bipolar Plates for Fuel Cells.* Int. J. Materials Review, **52**(1), (2007).
2. Chen, M., Hellgeth, J.W., Ward, T.C., McGrath, J.E., *Microwave Processing of Two-Phase Systems: Composites and Polymer Blends.* Polymer Engineering & Science, **35**(2) (1995), 144-150.
3. Thostenson, E.T., Chou, T.-W., *Microwave Processing: Fundamentals and Applications.* Composites, **30**(Part A) (1999), 1055-1071.
4. Baird, D.G., Collias, Dimitris I., *Polymer Processing - Principles and Design*. 1st ed., Editor: John Wiley & Sons, (1998), 111-118.

6 Conclusions

A new method has been developed to produce cost-effective bipolar plates with high electrical conductivity, good mechanical properties and the potential for rapid, continuous manufacturing. It has been shown that using wet-lay material provides a better balance of electrical and mechanical properties than any other polymer composite currently being researched for the production of bipolar plates. PVDF and PPS based bipolar plates generated by the laminate approach have shown to maintain good conductivity and satisfactory mechanical properties to that of wet-lay material while being much more amenable to a rapid, continuous production scheme. Compared to the PVDF based laminate plates, the PPS laminate plates exhibited higher mechanical strength, lower half-cell resistance, comparable formability, and the potential to avoid adhesion and de-lamination issues. At elevated temperature up to 100 ^{o}C, the laminate bipolar plates have shown to maintain sufficient flexural strength to be used in an operating fuel cell. Laminate bipolar plates generated as thin as 2.2 mm thick has shown to reach the half-cell resistance target of 0.02 W-cm2. It is anticipated that bipolar plates as thin as 1.0 mm are desired for commercial fuel cells in vehicular applications, thus further reducing the half-cell resistance. While the one-step molding method is good for batch production of PPS based laminate bipolar plates, the two-step method may be chosen for continuous operation without compromising mechanical or electrical properties. Using the two step production method, the laminate bipolar plates offer processing cycle times within the 2-3 minute goal and a total cost of approximately \$5-8/kW, under the cost target of \$10/kW. Assuming a 24 hour work day and 260 work days/year, the annual output is about 250,000 plates. Although it is desired to manufacture bipolar plates at a larger annual volume than 250,000 parts, there is certainly room for improvement in annual production in the shortening of the heating and cooling cycle and the availability to simultaneously mold several bipolar plates, potentially attaining over 1,000,000 plates/year.

7 Recommendations and Future Work

It is recommended to perform several alterations to the composite material to help further improve mechanical strength. Increasing the carbon fiber content may provide more reinforcement in the composite. Even though additional carbon fibers would likely replace graphite particles, the fibers are conductive and it is believed that high conductivity will still be maintained. It has been shown that reinforcing a polymer with nanoclays will significantly increase the modulus of the system. The nanoclay reinforced polymer has shown to increase the modulus of a polymer system by 100% when loaded as low as 4.7 wt%. The nanoclays have also shown to increase the heat distortion temperature and improve gas barrier properties. The use of such materials that may drastically improve mechanical properties without compromising electrical conductivity may provide processing improvements to be made. The wet-lay material which provides much of the strength in the laminate bipolar plates may become obsolete if nanoclays could help provide a polymer/graphite system with sufficient strength. Therefore, the wet-lay pre-consolidation stage could be eliminated, as well as potentially processing a bipolar plate in one step instead of two repeating steps, more than doubling the annual output.

There are many ideas and concerns that should be addressed in the future to evaluate the long-term effects of bipolar plates in fuel cells. Because bipolar plates will be under a constant compaction force when placed in an operating fuel cell, extensive evaluations of the compressive creep of thermoplastic composite plates should be performed. The life span target of a fuel cell stack is estimated to be five years. Therefore, it may be necessary to carry out compressive creep analysis at elevated temperatures in order to perform time-temperature superposition of the data to evaluate the long-term effects. Fatigue testing is also believed to be important for the laminate bipolar plates. This can be done using a flexural type apparatus applying an oscillatory stress on the material. The main reason to perform fatigue tests is to determine if de-lamination will pose a problem with the laminate material, even if compatible polymers are used throughout the material. Impact strength and compressive strength should also be measured on the bipolar plates to evaluate the integrity of the thin channels molded into the surfaces. Constructing a fuel cell with the laminate bipolar plates should be carried out to evaluate their performance and for comparisons with commercially manufactured plates such as graphite or metal. Analysis on the crystallization kinetics should be approached to determine the degree of crystallinity that the laminate plates can reach when cooled while molding. Experimentation, DSC analysis, and Avrami's equation can be used to help predict the degree of crystallization and the crystallization growth rate.

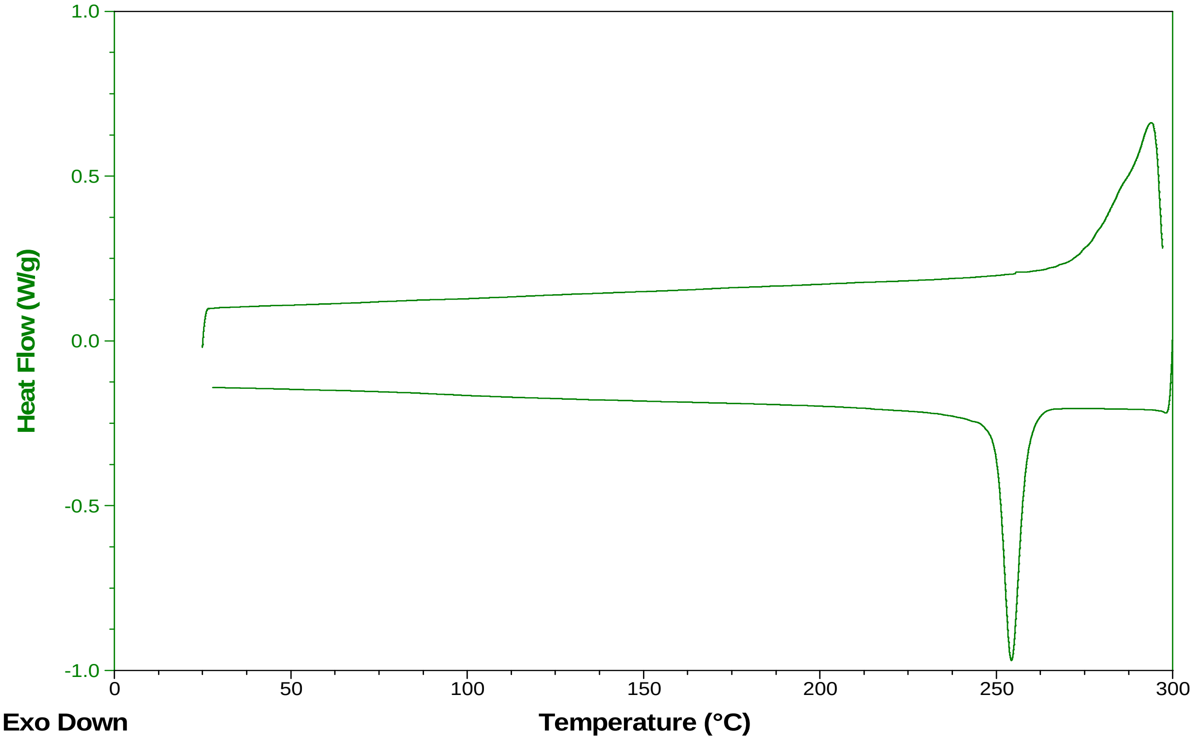
Appendix A. DSC Analysis of PPS Powder.

Preface

The PPS powder is grade T-1G from Solvay. This particular grade of PPS powder is used in the laminate region of the bipolar plates.

Sample: PPS T-1G
Size: 7.6000 mg
Method: Ramp

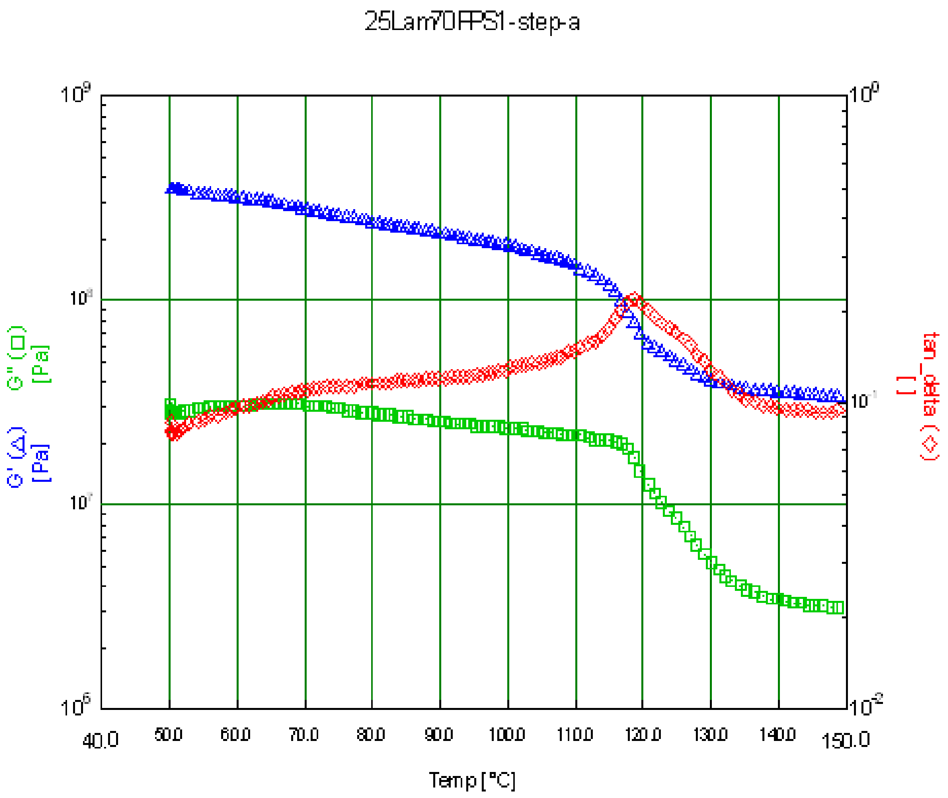
Operator: LB
Run Date: 2006-06-06 09:11

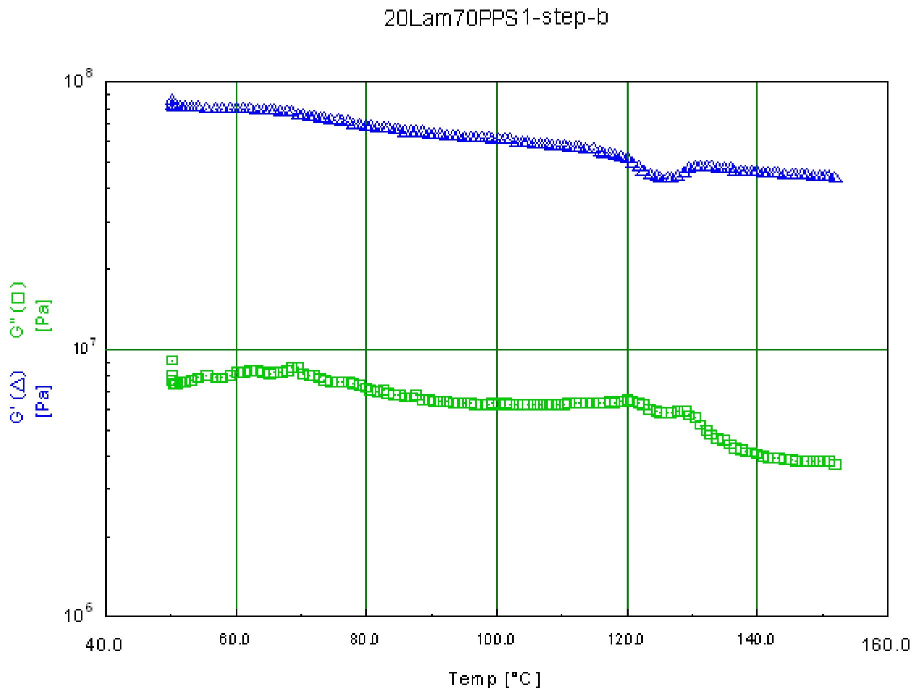


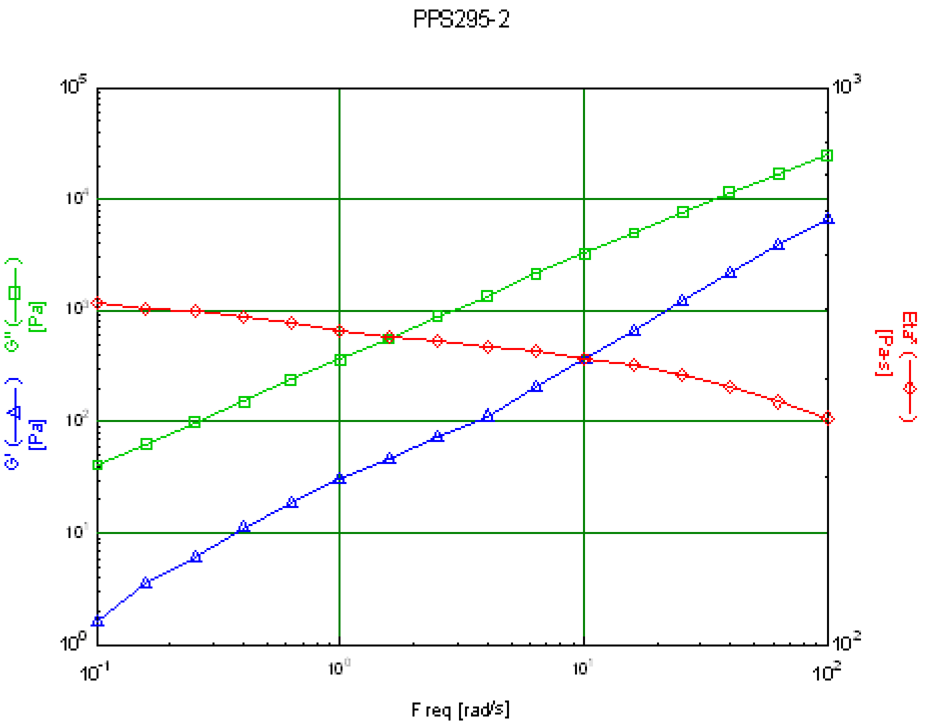
Appendix B. Rheology of PVDF and PPS Based Laminate Plates.

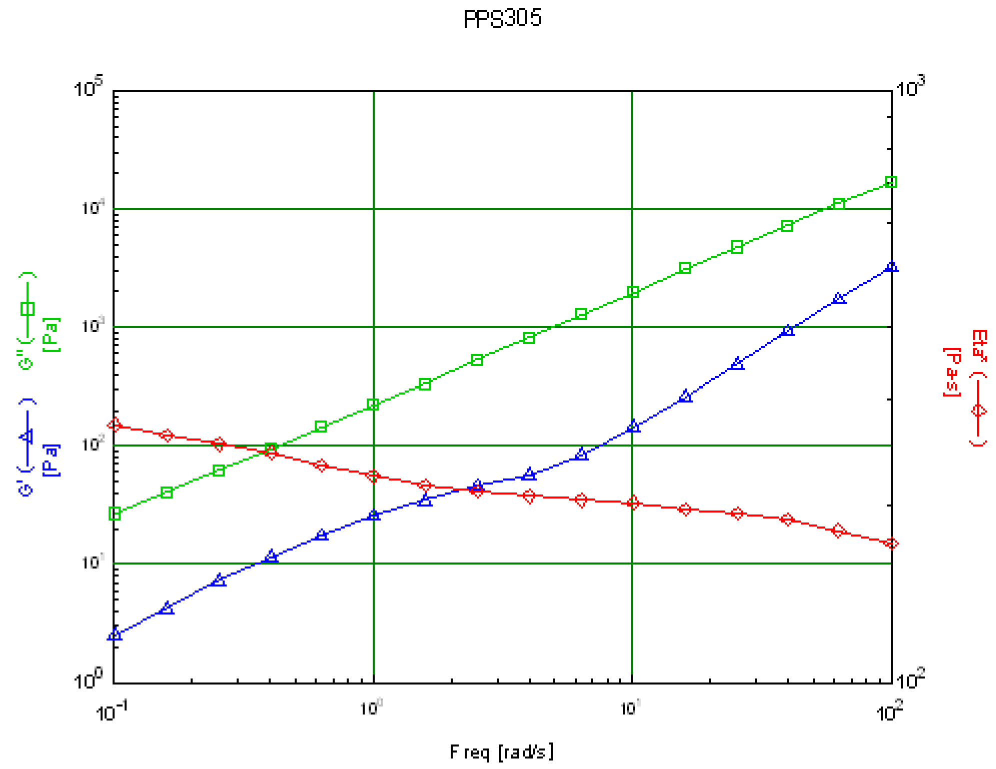
Preface

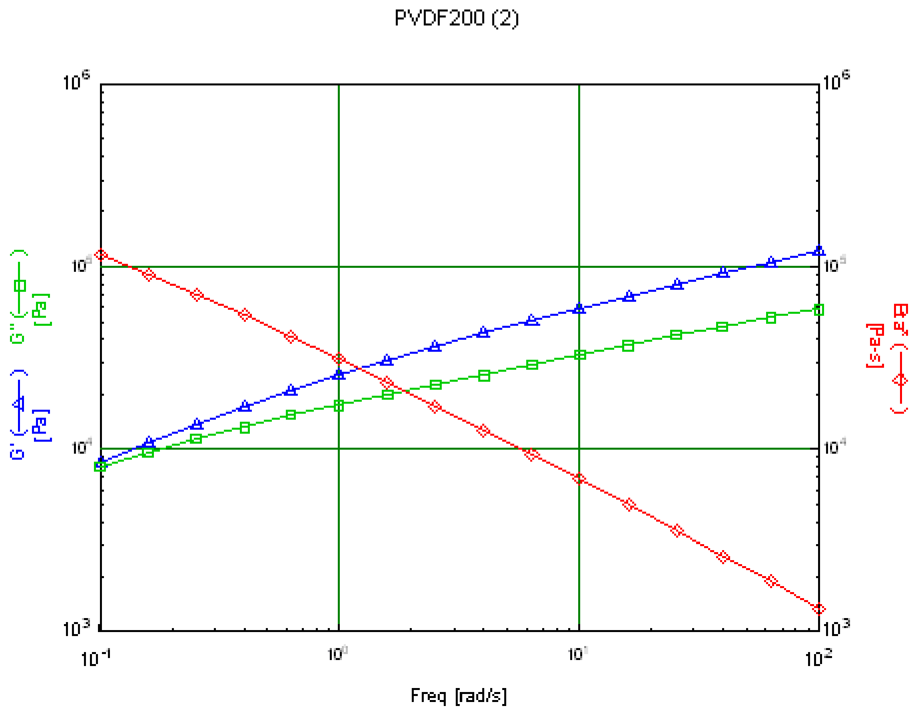
DMTA analysis was performed to determine G’ and G” for the polymer composite material. Frequency sweeps were also performed to determine the linear region of stress vs. strain.

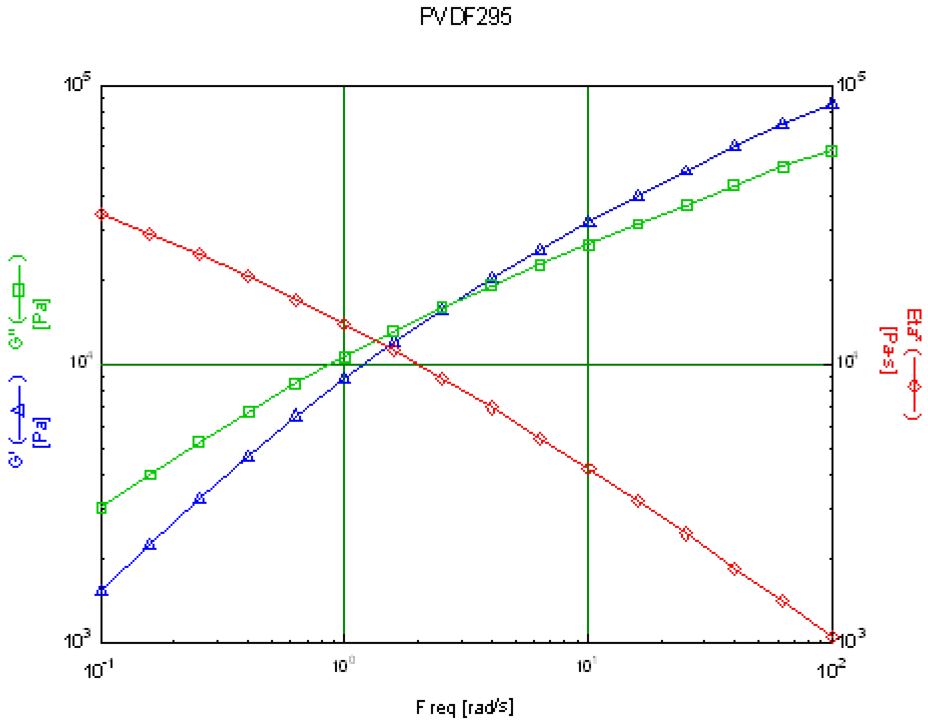

25Lam70PPS1-step-a
10^9
10^8
10^7
10^6
10^0
10^-1
10^-2
G' (Δ) [Pa]
G'' (□) [Pa]
tan_delta (◇) [ ]
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
Temp [°C]


20Lam70PPS1-step-b
10^8
10^7
10^6
G' (Δ) [Pa]
G'' (□) [Pa]
40.0
60.0
80.0
100.0
120.0
140.0
160.0
Temp [°C]


PPS295-2
10^5
10^4
10^3
10^2
10^1
10^0
10^3
10^2
10^-1
10^0
10^1
10^2
G' ( ) [Pa]
G'' ( ) [Pa]
Eta* ( ) [Pa-s]
Freq [rad/s]


PPS305
10^5
10^4
10^3
10^2
10^1
10^0
10^3
10^2
10^-1
10^0
10^1
10^2
G' ( ) [Pa]
G'' ( ) [Pa]
Eta* ( ) [Pa-s]
Freq [rad/s]

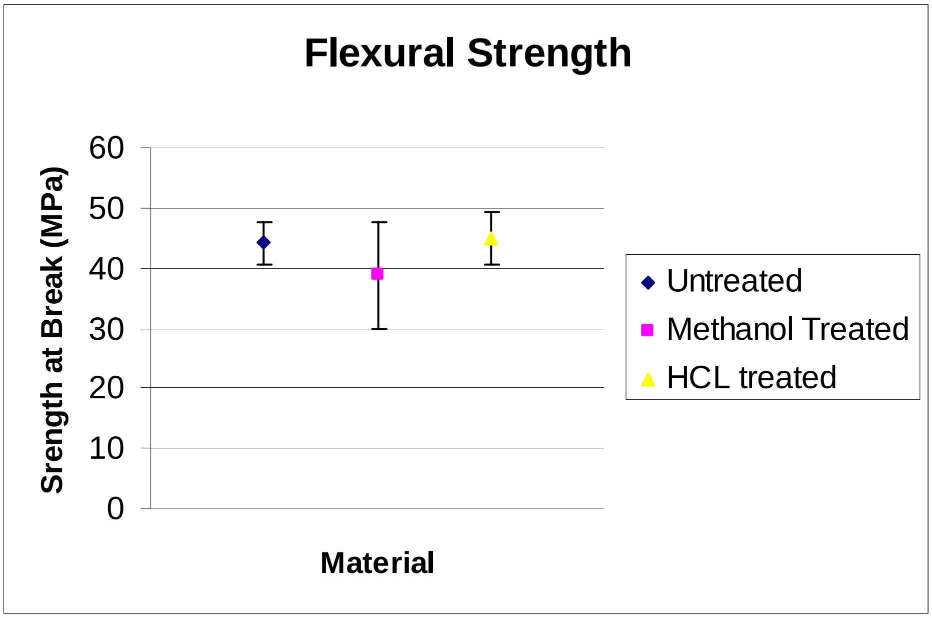

PVDF200 (2)
G' (—△—) [Pa]
G'' (—□—) [Pa]
Eta* (—◇—) [Pa-s]
10^6
10^5
10^4
10^3
10^-1
10^0
10^1
10^2
Freq [rad/s]


PVDF295
G' (—△—) [Pa]
G'' (—□—) [Pa]
Eta* (—◇—) [Pa-s]
10^5
10^4
10^3
10^-1
10^0
10^1
10^2
Freq [rad/s]

Appendix C. Chemical Resistance of PVDF Based Laminate Material.

Preface

Chemical resistance tests were performed to compare flexural strength of untreated material and material exposed to hydrochloric acid (HCl) and methanol. The tests were run according to ASTM D543-06. Methanol was selected to evaluate the chemical resistance of the material for use in direct methanol fuel cells, the next most popular fuel cell next to PEMFC's. HCl was chosen to evaluate the chemical resistance in the presence of a strong acid.


Flexural Strength
Srength at Break (MPa)
60
50
40
30
20
10
0
Material
Untreated
Methanol Treated
HCL treated

Appendix D. DIVPAG IMSL Subroutine Used for Modeling.

Table 1 - Program to solve ordinary differential equations using the IMSL subroutine DIVPAG.

```
     INTEGER NEQ, NPARAM, IDO, IEND, IMETH, INORM
      PARAMETER (NEQ=9, NPARAM=50)
      DOUBLE PRECISION A(1,1), FCN, FCNJ, HINIT, PARAM(NPARAM),
     & TOL, X, XEND, Y(NEQ),T,DX,H,RHO,CP,AL,B,T0,T10,K,DELTAT,
     & F,SIG,TSOURCE
      EXTERNAL DIVPAG, SSET, UMACH, FCN, FCNJ
C INITIALIZE
      HINIT = 1.0E-5
      INORM = 2
      IMETH = 2
      CALL SSET (NPARAM, 0.0, PARAM, 1)
      IDO = 1
      PARAM(1) = HINIT
      PARAM(10) = INORM
      PARAM(12) = IMETH
      PARAM(4) = 100000
      TOL = 1.0E-4
C SPECIFICATION OF INITIAL CONDITIONS
      DO 1 II=1,9
        Y(II)=1.0
    1 CONTINUE
      T0 = 1.0
      T10 = 1.0
C MATERIAL PROPERTIES
      K = 4
      RHO = 1.86E6
      CP = 0.9
      AL = K/(RHO*CP)
      F = 0.6
      SIG = 5.67E-8
      TSOURCE = 1000
      H = F*SIG*TSOURCE**3
      DX = 0.1
      B = 0.0015
      DELTAT = 10.0
C T=TIME(SEC)
      T = 0.0
      DO 10 IEND = 1,11
        WRITE(6,20)T,(N,N=0,NEQ+1),T0,(Y(I),I=1,9),T10
   20   FORMAT (25X,'THE SOLUTION AT TIME t = ',F5.1,
     &    /,11I6,/,11F6.3,//)
      T=T+DELTAT
      XEND = T
```

```
      CALL DIVPAG (IDO, NEQ, FCN, FCNJ, A, X, XEND, TOL,
     &    PARAM, Y)
      T0 = (1.0/3.0)*(4.0*Y(1)-Y(2))
      T10 = -(Y(8)-4.0*Y(9))/((2.0*DX*B*H)/K+3.0)
   10 CONTINUE
      IDO=3
      CALL DIVPAG (IDO, NEQ, FCN, FCNJ, A, X, XEND, TOL,
     &    PARAM, Y)
      STOP
      END
C CALCULATE TIME DERIVATIVES
      SUBROUTINE FCN (NEQ, X, Y, YPRIME)
      INTEGER NEQ, JJ
      DOUBLE PRECISION X,Y(NEQ),YPRIME(NEQ),K,DX,H,AL,B,
     & F,SIG,TSOURCE
      K = 4
      RHO = 1.86E6
      CP = 0.9
      AL = K/(RHO*CP)
      F = 0.6
      SIG = 5.67E-8
      TSOURCE = 1000
      H = F*SIG*TSOURCE**3
      DX = 0.1
      B = 0.0015
      DO 2 JJ=1,7
      YPRIME(JJ+1)=(AL/DX**2/B**2)*(Y(JJ)-2.0*Y(JJ+1)+Y(JJ+2))
    2  CONTINUE
C Y(PRIME) FOR NODAL POINTS (1)-ZERO ENERGY FLUX, (9)-FINITE FLUX
      YPRIME(1)=(AL/DX**2/B**2)*((-(2.0/3.0)*Y(1)+(2.0/3.0)*Y(2)))
      YPRIME(9)=(AL/DX**2/B**2)*(Y(8)-2.0*Y(9)+(4.0*Y(9)-Y(8))
     &   /(3.0+(2.0*DX*B*H)/K))
      RETURN
      END
C  DUMMY ROUTINE
      SUBROUTINE FCNJ (NEQ, X, Y, DYPDY)
      INTEGER NEQ
      DOUBLE PRECISION X, Y(NEQ), DYPDY(*)
      RETURN
      END
```

APPENDIX E. Flexural and Tensile Strength and Modulus of Various Laminate Material at Elevated Temperatures.

Preface

The flexural and tensile strength and modulus were tested at temperatures of 20, 80,100, and 120 °C to better evaluate the mechanical properties of the material in an operating fuel cell.

Table 1 – Flexural strength and modulus of various materials at various temperatures.

Material	Temperature (^{o}C)	Flexural Strength (MPa)	Std. dev.	Flexural Modulus (GPa)	Std. dev.
20% PVDF Laminate	20	48.9	4.8	7.2	0.2
	80	36.9	2.6	3.6	0.1
	100	37.7	3.8	3.4	0.1
	120	34.3	5.0	2.7	0.2
15% PVDF Laminate	20	51.0	5.8	8.1	0.3
	120	44.7	5.6	2.9	0.3
20% PVDF Laminate	20	60.0	8.7	12.0	0.7
	80	63.1	6.8	13.4	0.4
	100	60.0	7.1	7.2	2.0
	120	57.6	5.2	6.9	0.4

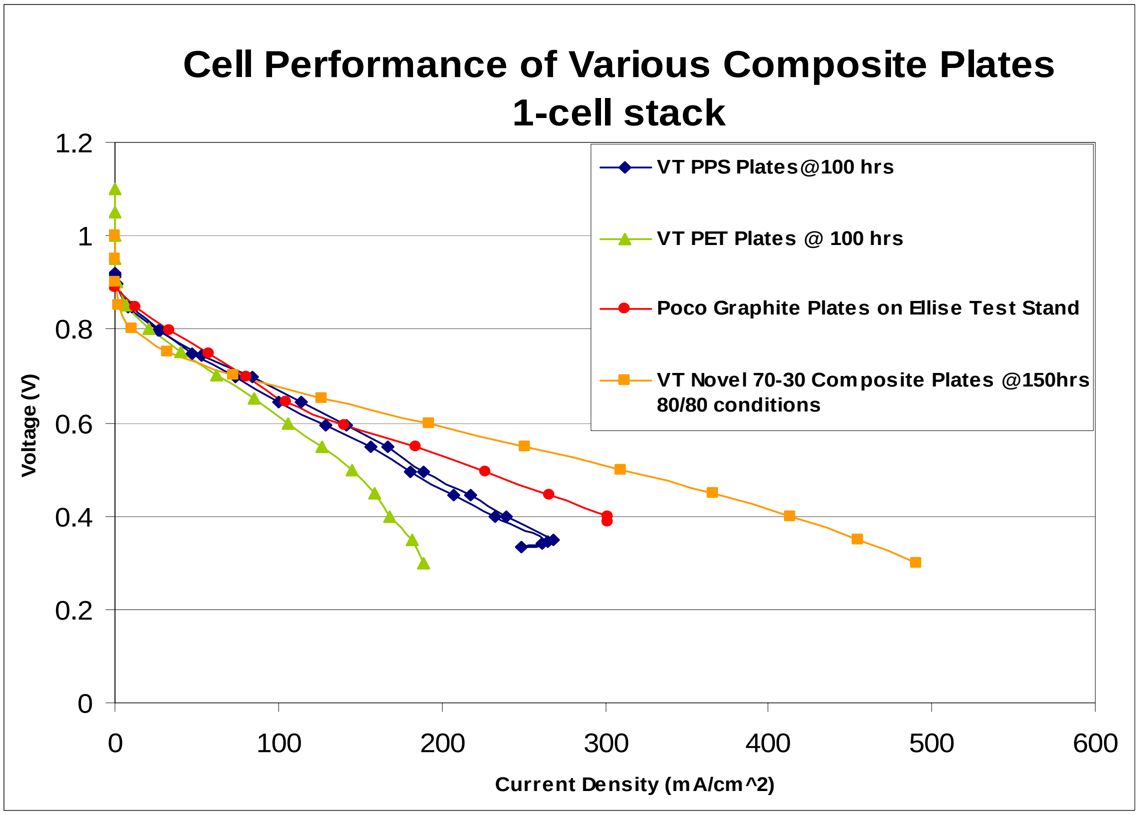
Table 2 –Tensile strength and modulus of various materials at various temperatures.

Material	Temperature (^{o}C)	Tensile Strength (MPa)	Std. dev.	Tensile Modulus (GPa)	Std. dev.
20% PVDF Laminate	20	33.7	5.7	14.2	0.3
	80	24.7	4.1	15.3	5.8
	100	25.2	0.3	15.0	6.7
	120	25.4	3.5	7.8	4.8
15% PVDF Laminate	20	28.3	5.2	15.9	4.6
	120	29.1	2.6	9.6	4.8
20% PVDF Laminate	20	36.5	4.6	16.1	2.0
	80	33.1	3.3	8.6	5.7
	100	25.6	2.9	11.9	4.5
	120	23.3	4.1	10.6	4.6

Appendix F. Performance Curve of Various Monopolar Plates.

Preface

The performance of a PET based wet-lay, PPS based wet-lay, PVDF based laminate, and POCO® graphite plate was monitored in a 1-cell fuel cell assembly.


Cell Performance of Various Composite Plates
1-cell stack
Voltage (V)
1.2
1
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
Current Density (mA/cm^2)
VT PPS Plates@100 hrs
VT PET Plates @ 100 hrs
Poco Graphite Plates on Ellise Test Stand
VT Novel 70-30 Composite Plates @150hrs 80/80 conditions

Appendix G. The Development of Economical Bipolar Plates for Fuel Cells

Preface

Appendix A. is a short highlight article published with the Journal of Materials Chemistry focusing on the current research of bipolar plates and the main issues that need to be overcome in order to make them more economical to manufacture commercially. This section is in its published form.

The Development of Economical Bipolar Plates for Fuel Cells

Brent Cunningham[*a] and Donald G. Baird[a]

[a]*Department of Chemical Engineering and Macromolecules and Interfaces Institute, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA.*

One of the major challenges in the production of economical polymer electrolyte membrane (PEM) fuel cells for automotive applications is the development of materials for the generation of bipolar plates which meet all the property requirements and can be readily manufactured to impart fine channels for transporting hydrogen and oxygen. Bipolar plates can be made from various materials with the most common being graphite, metal, carbon/carbon, and polymer composites. Each type of material has its strengths and weaknesses. Materials for polymer composites are relatively inexpensive and channels can be formed by means of compression or injection molding. The key is to develop a balance between sufficient electrical conductivity and mechanical properties while allowing for rapid, continuous manufacturing.

Biography:

After receiving his B.S. degree from Purdue University in chemical engineering in 2000, Brent Cunningham entered the polymer processing research area. He is currently working on his PhD degree form Virginia Polytechnic Institute and State University in Macromolecular Science and Engineering, concentrating on polymer composite bipolar plates for fuel cells.

D. G. Baird received his B.S. and M.S. degrees from Michigan State University and his PhD from the University of Wisconsin-Madison. In 1978 he joined the faculty of Virginia Tech where he his presently the Harry C. Wyatt Professor of Chemical Engineering. He has won several awards including the International Award for Education (2002) and the International Award for Research (2003) from the Society of Plastics Engineers. He is the primary author of a textbook entitled *Polymer Processing: Principles and Design* (John Wiley and Sons).

Bipolar plates (an example of which is shown in Fig. 1) are by weight, volume, and cost one of the most significant parts of a fuel cell stack.[1, 2] Bipolar plates represent about a third of the overall cost of a fuel cell. Present cost estimates for a working fuel cell are about $200/kW, which leaves the cost of a bipolar plate at $60-

70/kW. With the DOE cost target for a fuel cell set at \$35/kW for the automotive industry, the cost target for bipolar plates is \$10/kW.

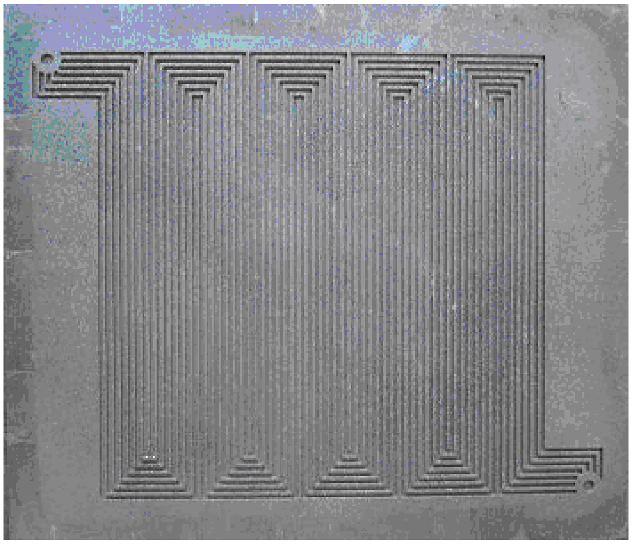


Figure 1 – One side of a bipolar plate showing a 7-channel parallel serpentine style design. Plate dimensions are 12 x 14 x 0.3 cm thick. Channel dimensions are 0.08 x 0.08 cm.

The bipolar plate has three main functions: uniform distribution of gases over the whole area of the membrane electrode assembly (MEA); separation of the fuel (e.g. H_2) and O_2 and the prevention of gas leakage; and collecting the current produced by the electrochemical reactions.[3-5] Furthermore, the bipolar plate carries the clamping force required to hold the fuel cell stack together. A set of specified targets and requirements for bipolar plates are summarized below:

- Bulk (in-plane) electric conductivity (>100 S/cm)*
- H_2 Permeability ($< 2\times10^{-6}$ cm^3/cm^2-sec)*
- Corrosion rate (<16 $\mu A/cm^2$)*
- Flexural strength >59 MPa$^{\#}$
- Tensile strength > 41 MPa$^{\#}$

- Thermal conductivity >10 W/mK[#]
- Thermal stability up to 120 °C
- Chemical stability in the presence of fuel, oxidant, water, and acidic conditions
- Rapid and inexpensive manufacturing

* DOE and FreedomCAR targets[6]
[#] Plug Power targets[7]

Graphite has been the standard material used in the production of bipolar plates due to its high conductivity. Unfortunately, graphite is brittle and has poor mechanical properties.[6] The main difficulty in using graphite to produce bipolar plates is that the production of channels in the surfaces requires machining, a very costly and time consuming step. In addition, post processing (such as resin impregnation) is needed to make graphite plates impermeable to gases.[8]

Because of the costly machining step associated with graphite, a variety of metals have been investigated for the production of bipolar plates. Metals such as stainless steel, aluminum, and titanium have been considered with the most promising being stainless steel.[6, 9] Metallic plates typically have high bulk electrical conductivity, thermal conductivity, negligible gas permeability, and excellent mechanical properties. Techniques such as etching and batch stamping have been developed for producing channels into metallic plates representing significant improvements over machining. However, due to poor corrosion resistance of metal plates and the possibility for metal ions to leach into the MEA, a coating must be applied to the surfaces of the plates to form a protective layer. The protective coating leads to enhanced electrical resistance at the interface, the magnitude of which has not been reported in the open literature.

Researchers at Oak Ridge National Laboratory developed carbon/carbon bipolar plates. They claimed that the plates exhibited high electrical characteristics along with excellent mechanical properties.[10] The manufacturing process consisted of multiple steps, including the production of carbon fiber/phenolic resin preforms by a slurry-molding technique followed by densification by chemical vapor infiltration (CVI). The CVI process is likely to be too complicated and costly to be used for bipolar plates for automotive applications.

Because material and machining costs for graphite and carbon/carbon plates are prohibitive at least for the automotive industry, and metal plates must be uniformly covered with a protective coating which has shown to be difficult to accomplish[9], extensive efforts have been made to develop alternative materials for bipolar plate production. Polymer composites have been considered for bipolar plate production because of their potential to be processed rapidly. Molding techniques for polymer composites have shown the greatest potential in reducing bipolar plate manufacturing time and cost over machining or etching. Thermoplastic composite materials can be heated above the melting temperature of the polymer allowing for channels to be molded directly into the surfaces. It has been shown that the cost of molding a polymer composite bipolar plate is 10-20 times less expensive than that of machining.[7] Molding techniques can also reduce production times to several minutes. Researchers at Los Alamos National Laboratories (LANL) have developed compression moldable bipolar plates based on a vinyl ester thermosetting polymer matrix filled with graphite that can be compression molded in about 10 minutes[11]. The advantage in using a thermosetting polymer is that when the polymer is heated and compression molded, the plate cures and does not require subsequent cooling. Therefore, the plate can be immediately released from the mold. However, a postcure may be necessary, and can take as long as one hour to complete.[12] Furthermore, the mechanical properties do not meet the targets (see Table 1). Poly(vinylidene fluoride) (PVDF), a thermoplastic fluoropolymer matrix, has been used with graphite particles and carbon fiber to produce bipolar plates.[3] Bulk conductivity values have reached 109 S/cm, exceeding the DOE target. However, the flexural strength was only 42.7 MPa, lower than the goal of 59 MPa. Liquid crystalline polymer/graphite mixtures have been considered for bipolar plate production because of their ability to be used with injection molding due to the low viscosity of the polymer.[13] The injection molding process allows for a relatively short cycle time of 30 seconds. Bulk conductivities have reached as high as 100 S/cm, just reaching the minimum target, but no mechanical properties or through-plane conductivities were reported and it is anticipated that the properties may not reach the targets.

Table 1 – Comparison of electrical and mechanical properties at ambient temperature for polymer composite material used for the production of bipolar plates.

Source	Polymer	Graphite/glass or carbon reinforcing fiber (wt/wt%)	Conductivity (S/cm)		Mechanical Strength	
			In-plane	Through-plane	Tensile (MPa)	Flexural (MPa)
Target			>100[a]	-	41.0[b]	59.0[b]
LANL[12]	Vinyl Ester	68/0	60	-	23.4	29.6
GE[3]	PVDF	64/16 CF	109	-	-	42.7
Virginia Tech[8]	PET	65/7 GF	230	18-25	36.5	53.0
Virginia Tech	PPS	70/6 CF	271	19	57.5	95.8
Virginia Tech[14]	PPS core PVDF skin	70/6 CF core 80/0 laminate	147-350	14-32	34.4	48.9

[a] DOE target for conductivity[6]

[b] Plug Power targets for mechanical strength[7]

Huang and coworkers[8] have reported the development of conductive polymer composite materials generated by means of a wet-lay process. The wet-lay process was chosen because of its potential to create conductive, strong composite plaques when compression molded.[8, 16] Poly(phenylene sulfide) (PPS) based wet-lay generated composites exhibited bulk conductivities and mechanical properties that meet the targets and are higher than those of any other polymer composite material used to produce bipolar plates as shown in Table 1. An area that needs improvement for the wet-lay based material is through-plane conductivity and formability of channels into the surfaces.

In an effort to address the through-plane conductivity and formability of the wet-lay based material, Huang and coworkers[8, 14, 17] have developed a laminate approach to produce compression moldable polymer composite materials using a combination of wet-lay based material and a fluoropolymer/graphite mixture. PVDF was used as the polymer in the laminate layer to create a surface much more amenable for molding, while wet-lay material was used to produce a solid, strong core material. The laminate approach offered several significant advantages. First, the laminate structure was shown to increase through-plane conductivity by 25-35%. Second, PVDF had a much lower melting temperature than PPS (about 100 ^{o}C lower) offering a shorter heating and subsequent cooling cycle. Third, when channels were compression molded into the PVDF/graphite powder, significant improvements in channel formation were observed. The smoother surfaces were due to the absence of fibers in the laminate layer. It was believed that smoother surfaces would reduce the contact resistance between the bipolar plate and MEA. The half-cell resistance of the laminate bipolar plates showed a significant reduction over that of wet-lay based bipolar plates. Thus, the performance of laminate bipolar plates in a functioning fuel cell was enhanced over that of wet-lay based bipolar plates.

The main drawback in using polymer composite materials is their relatively low conductivity when compared to graphite and metal plates. While mechanical strength exceeds that of graphite plates, polymer composite plates exhibit a much lower strength than that of metal plates. There are also concerns about whether thermoplastic polymer composite bipolar plates will perform well in a fuel cell because at operating temperatures there may be some loss of mechanical strength and stiffness depending on the choice of thermoplastic.

It is believed that the defining factor in developing economical bipolar plates relies in the design of a rapid, continuous molding scheme. Bipolar plates based on the laminate approach can potentially be continuously manufactured. It is possible to pre-consolidate sheets of wet-lay material by continuously rolling the material through calendar or embossing rolls. The laminate powder can be metered onto the consolidated plaque, where the laminate surfaces are heated to prepare for the final molding step. Because the powder layer is thin and has a high thermal conductivity due to the high concentration of graphite particles, the time associated with molding has been estimated to take less than 10 seconds. Furthermore, it has been estimated that the part can be heated to its processing temperature by means of radiation in well under 60 seconds. Therefore, there is potential for the development of laminate polymer composite bipolar plates to be commercially manufactured.

In summary, the major challenge is the generation of composite materials which can be processed rapidly to produce bipolar plates with adequate electrical conductivity and mechanical properties. Significant progress has been made, but there is still room for improvement.

Acknowledgements

We are very grateful for funding provided by the Department of Energy (grant #DE-FG02-05ER86254) through a STTR grant to Nanosonic, Inc.

References

1. Bar-On, I., Kirchain, Randy, Roth, Richard, *Technical Cost Analysis of PEM Fuel Cells.* J. of Power Sources, **109** (2002), 71-75.
2. Middleman, E., Kout, W., Vogelaar, B., Lenssen, J., de Waal, E., *Bipolar Plates for PEM Fuel Cells.* J. Power Sources, **118** (2003), 44-46.
3. Balko, E., N., Lawrance, Richard J., US 4,339,322 (1982).
4. Lawrance, R.J., US 4,214,969 (1980).
5. Thring, R.H., *Fuel Cells for Automotive Applications*, Editor: R. H. Thring, (2004), 6-9.
6. Mepsted, G.O., Moore, J.M., *Performance and Durability of Bipolar Plate Materials*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd. (2003), 286-293.
7. Clulow, J.G., Zappitelli, F.E., Carlstrom, C.M., Zemsky, J.I.L., Busick, D.N., Wilson, M.S. *Development of Vinyl Ester/Graphite Composite Bipolar Plates*. *AIChE Spring National Meeting*. March 10-14, New Orleans, LA. (2002), 417-425.
8. Huang, J., Baird, Donald G., McGrath, James E., *Development of Fuel Cell Bipolar Plates From Graphite Filled Wet-lay Thermoplastic Composite Materials.* J. Power Sources, **150** (2005), 110-119.
9. Wind, J., LaCroix, A., Braeuninger, S., Hedrich, P., Heller, C., Schudy, M., *Metal Bipolar Plates and Coatings*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd. (2003), 295-307.

10. Besmann, T., Klett, James Henry, Jr., Lara-curzio, Edgar, *Carbon/Carbon Composite Bipolar Plate for Proton Exchange Membrane Fuel Cells.* J. Electrochem. Soc., **147**(11) (2000), 4083-4086.
11. Busick, D.N., Wilson, S., *Low-Cost Composite Materials for PEFC Bipolar Plates*, Fuel Cells Bulletin, **2**(5) (1999), 6-8.
12. Wilson, M.S., Busick, Deanna N., US 6,248,467 (2001).
13. Bisaria, M.K., Andrin, Peter, Abdou, Mohamed, Cai, Yuqi, US 6,379,795 (2002).
14. Baird, D.G., Huang, Jianhua, McGrath, J., US APPL 2004-779,804 (2005).
15. RoBberg, K., Trapp, V., *Graphite-Based Bipolar Plates*, Handbook of Fuel Cells-Fundamentals, Technology and Applications, Editor: John Wiley & Sons, Ltd., (2003), 308-314.
16. Tucker, K.W., Weeks, Gregory P., US 5,614,312 (1997).
17. Cunningham, B.D., Baird, Donald G., *Review of Materials and Processing Methods in the Production of Bipolar Plates for Fuel Cells.* Int. Materials Reviews, **52**(1) (2007).

Vita

The author was born in Roanoke, Virginia on May 6, 1978, where he lived in Michigan, Florida, and Georgia before returning to his mothers' hometown of Christiansburg, Virginia in 1986. After graduating from Christiansburg High School in 1996, he attended Purdue University to pursue a Bachelor of Science degree in Chemical Engineering. His undergraduate education and experience were enhanced by studying abroad at the University College London, in London, England. Upon graduation, the author began his career in industry for 2 years in Indiana, working for Heritage Environmental Services, LLC. and Flowserve, Inc. In 2003, the author returned to school at Virginia Polytechnic Institute and State University. Presently, he is a candidate for a Doctor of Philosophy degree in Macromolecular Science and Engineering under the direction of Donald G. Baird.

Brent Cunningham