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DEVELOPMENT OF HYBRID COMPOSITE BIPOLAR PLATES FOR PROTON  
EXCHANGE MEMBRANE FUEL CELLS

by

NATHANIEL JAMES RICHIE

A THESIS

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

2011

Approved by

Dr. K. Chandrashekhara, Advisor  
Dr. Frank Liou  
Dr. Thomas Schuman

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## ABSTRACT

Bipolar plates are one of the most expensive components of a PEM fuel cell and by far the heaviest. Bipolar plates are responsible for providing flow fields for reaction gases, acting as current collectors for electrons liberated during the chemical reaction inside the cell, and providing structural support for the fuel cell stack.

Current PEM fuel cell bipolar plate technology is built on the use of sintered graphite which is costly and requires time-consuming machining. Furthermore, due to the brittle nature of graphite, plates must be made relatively thick which adds significant weight and volume to larger stacks, such as those required for automobiles.

Hybrid composite bipolar plates were developed with the goal of providing an alternative material which offers sufficient conductivity, corrosion resistance, and mechanical strength. A conductive resin system using epoxy, polyaniline, carbon black, and milled carbon fibers was developed to serve as a matrix for continuous carbon fiber reinforcement which enhanced both strength and conductivity above what is possible to achieve through the use of chopped fibers.

The developed conductive resin system showed a high glass transition temperature (above 180 °C) and tensile strength greater than or equal to 41 MPa. The developed hybrid composite material showed conductivity greater than 100 S/cm and excellent tensile and flexural strength, far exceeding industry targets.

## ACKNOWLEDGEMENTS

I would to express my gratitude to my advisor, Dr. K. Chandrashekhara for his guidance, encouragement, and support throughout my M.S. studies. I would also like to thank Dr. Thomas Schuman for his help and support in the polymer chemistry aspects of the project. His advice made it possible to complete this work in a timely manner. I would also like to thank Dr. Frank Liou for serving on my committee and for chairing the weekly project meetings.

Funding for this project was provided by the Air Force Research Laboratory with additional support provided by the NASA-Missouri Space Grant Consortium. The support provided by the Chancellor's Fellowship is also gratefully acknowledged. The generous material contributions of Cytex Industries, AkzoNobel, Emerald Performance Materials, and King Industries are also appreciated.

I would also like to acknowledge my fellow graduate students who made time spent in the lab more enjoyable. In particular, I would like to thank Raju Vuppalapati, Rongpeng Wang, and Ram Butukuri who provided ideas and help in completing this work.

Finally, I would to thank my family, whose love and support have sustained me throughout my studies. Without you, none of this would have been possible.

## TABLE OF CONTENTS

	Page
ABSTRACT.....	iii
ACKNOWLEDGEMENTS.....	iv
LIST OF FIGURES .....	vii
LIST OF TABLES.....	viii
SECTION	
1. INTRODUCTION.....	1
PREFACE.....	1
1.1 FUEL CELLS .....	1
1.2 FUNCTION OF BIPOLAR PLATES .....	3
1.3 RESEARCH OBJECTIVES .....	5
2. BACKGROUND.....	7
PREFACE.....	7
2.1 REQUIREMENTS FOR BIPOLAR PLATES .....	7
2.2 BIPOLAR PLATE MATERIALS .....	8
2.2.1 Graphite Plates.....	8
2.2.2 Metallic Plates.....	9
2.2.3 Polymer Composite Plates.....	10
2.3 RESEARCH OBJECTIVES .....	14
3. DEVELOPMENT OF HYBRID COMPOSITE BIPOLAR PLATES.....	15
3.1 ABSTRACT.....	15
3.2 INTRODUCTION .....	15
3.3 MATERIAL SELECTION .....	18
3.3.1 Epoxy.....	18
3.3.2 Polyaniline.....	19
3.3.3 Carbon Black.....	20
3.3.4 Carbon Fiber.....	22
3.4 DEVELOPMENT OF CONDUCTIVE RESIN SYSTEM.....	23
3.5 COMPRESSION MOLDING.....	26
3.6 PERFORMANCE EVALUATION .....	27

3.6.1 Differential Scanning Calorimetry.....	27
3.6.2 Thermogravimetric Analysis. ....	28
3.6.3 Determination of Electrical Conductivity. ....	29
3.6.4 Measurement of Mechanical Properties.....	30
3.6.4.1 Tensile properties.....	30
3.6.4.2 Flexural properties. ....	31
3.6.5 Molding of Composite Bipolar Plates.....	32
4. RESULTS AND DISCUSSION .....	33
4.1 CONDUCTIVE RESIN SYSTEM PERFORMANCE.....	33
4.1.1 Differential Scanning Calorimetry.....	33
4.1.2 Thermogravimetric Analysis. ....	35
4.1.3 Electrical Conductivity. ....	36
4.1.4 Mechanical Performance. ....	39
4.2 HYBRID COMPOSITE PERFORMANCE .....	41
4.2.1 Electrical Conductivity. ....	42
4.2.2 Mechanical Performance. ....	42
4.3 MOLDING OF COMPOSITE BIPOLAR PLATES .....	43
5. CONCLUSIONS .....	44
BIBLIOGRAPHY .....	45
VITA.....	47

## LIST OF FIGURES

Figure	Page
1.1. PEM fuel cell diagram .....	2
1.2. Cost breakdowns for PEM fuel cell components.....	4
3.1. Percolation structure in resin .....	24
3.2. Comparison of wrinkled surface and surface obtained using perf ply.....	26
3.3 Four point probe system.....	30
3.4. Tensile testing fixture .....	31
3.5. Bipolar plate compression mold with parallel flow field.....	32
4.1. Dynamic DSC scans comparing the effect of polyaniline on behavior of the reaction behavior of Epon 826 .....	33
4.2 Effect of polyaniline on glass transition temperature .....	34
4.3. Thermal stability of Epon 826 and Epalloy 8240 .....	35
4.4. Conductivity of polyaniline filled Epon 826 .....	37
4.5 Conductivity of Ketjenblack EC600-JD filled Epon 826 .....	37
4.6. Conductivity of filled Epon 826 .....	38
4.7. Comparison of the effect of filler level on conductivity .....	40
4.8. Comparison of tensile strength of conductive resins .....	40
4.9. Comparison of tensile modulus of conductive resin systems .....	41
4.10. Compression molded hybrid composite bipolar plate .....	43



**LIST OF TABLES**

Table	Page
1.1 Bipolar plate property targets (* denotes Plug Power target) .....	4
2.1. Properties of metals used for bipolar plates compared to graphite [3] .....	9
3.1 Iodine numbers for various carbon blacks [12, 13] .....	21
3.2 Properties of various milled carbon fibers [14, 15] .....	22
4.1. Glass transition temperature of PANI filled epoxy.....	34
4.2 Conductivity values for various conductive resin systems .....	38
4.3. Tensile properties for the conductive resin system.....	39
4.4. Composition of hybrid composite material manufactured by compression molding.....	41
4.5. Mechanical properties of the developed hybrid composite bipolar plate material.....	42

# 1. INTRODUCTION

## PREFACE

The following section serves to introduce the proton exchange membrane (PEM) fuel cell, its operating principles, and components. Specifically, the role of the bipolar plate and its importance to the fuel cell's future as a source of alternative energy is explored.

## 1.1 FUEL CELLS

A fuel cell is a type of electrochemical cell which converts chemical to electrical energy. While related to electrical batteries, fuel cells differ in that they are supplied an external reactant as opposed to storing its electricity chemically in a closed system. A fuel cell is made of three major components: anode, cathode, and electrolyte. Different fuel cell types utilize various electrolyte chemistries and bipolar plate materials, but have the same general structure. Proton exchange membrane fuel cells are a class of fuel cell that utilizes a polymeric semipermeable membrane (most commonly DuPont Nafion) to conduct protons, while separating the reactant gases (hydrogen and oxygen).

A basic PEM fuel cell consists of an electrolyte membrane sandwiched between two bipolar plates as shown in Figure 1.1. Hydrogen gas is passed through flow fields in one bipolar plate where it diffuses through the gas diffusion layer (GDL). The hydrogen gas then encounters the membrane electrode assembly which consists of a catalyst which drives the reduction and oxidation reactions and the electrolyte membrane which allows the protons to pass from anode to cathode. The electrons liberated by the oxidation of hydrogen are passed through an external circuit by way of the conductive bipolar plates

and the protons are transported from anode to cathode through the electrolyte membrane. When the hydrogen protons reach the cathode, they react with oxygen and electrons which return from the external circuit to form water which is exhausted from the cell. The electrons passed through the external circuit are the electrical power which can be used for anything from powering a car to recharging a cellular phone. Each individual cell will produce approximately 0.7 V, making a set of cells in series or a “stack” necessary to obtain any significant amount of power.

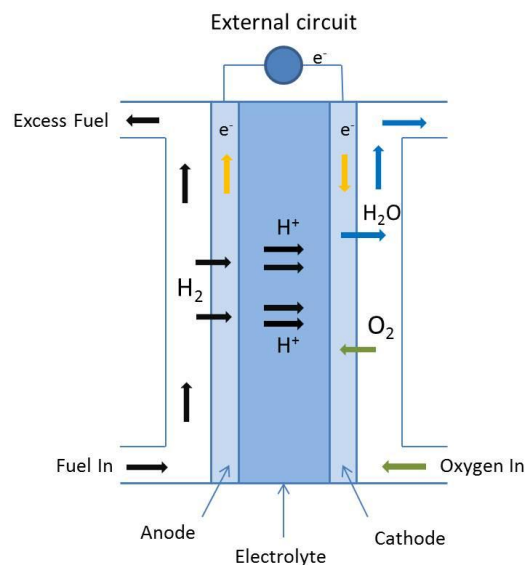


Figure 1.1. PEM fuel cell diagram

Fuel cells have demonstrated a great deal of potential for providing power since their use by NASA in the 1960's as portable power sources for astronauts. Hydrogen fuel cells demonstrate high operating efficiency and zero pollution emissions. They represent an efficient means of converting hydrogen into electrical energy and have the potential to

allow for a conversion to a “hydrogen economy”. If combined with other forms of alternative energy such as wind, solar, or hydrokinetic turbines, fuel cells offer a portable way to store excess power generated by these sources in remote areas such as rural villages or military forward operating bases.

## **1.2 FUNCTION OF BIPOLAR PLATES**

In a PEM fuel cell, the bipolar plates serve multiple functions such as providing flow fields for the reaction gases, acting as current collectors for the electrons liberated at the anode, and providing structural support to the fuel cell stack. Bipolar plates get their name from the fact that in a fuel cell stack, one side of a single plate will serve as the anode for one cell, while the other side will be the cathode for the adjacent cell.

Within a fuel cell stack, bipolar plates represent one of the most significant contributors to cost, weight, and volume [1]. Figure 1.2 shows the Department of energy cost estimate for each component of a fuel cell. The bipolar plate is the single most expensive component at 29% of the total stack cost. In order to reduce the cost of fuel cells, the DOE has established a target of \$35/kW for the automotive industry (current costs are estimated at \$200/kW) [2]. This results in an approximate cost target of \$10/kW for bipolar plates. Reduction in the cost of bipolar plates requires new materials and process to be developed.

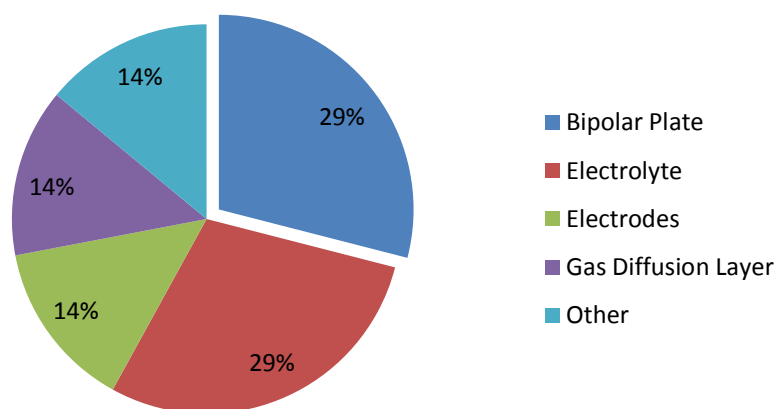


Figure 1.2. Cost breakdowns for PEM fuel cell components

To facilitate the development of new materials for bipolar plates, the DOE and members of the industry have established performance targets. Table 1.1 presents those targets which represent the minimum acceptable performance for current and near-future applications.

Table 1.1 Bipolar plate property targets (\* denotes Plug Power target)

Parameter	Target Value
Electrical Conductivity (In-Plane)	>100 S/cm
Corrosion Resistance	< 16 $\mu\text{A}/\text{cm}^2$
Good Mechanical Properties	41 MPa Tensile* 59 MPa Flexural* 40.5 J Impact Strength*
Thermal Conductivity	> 10 $\text{W}(\text{mK})^{-1}$ *

The most significant barrier to the development of new bipolar plate materials is the competing requirements of performance and cost which must contend with the reality that any developed material must lend itself to high volume production and processing. Research in this area has shown it to be very difficult to find a material which meets all of the performance and cost targets, while conforming to a processing and production scheme suitable for high volume manufacturing. Current and promising bipolar plate material technology is discussed in Section 2.2.

### **1.3 RESEARCH OBJECTIVES**

While in recent years there has been a great deal of interest in the development of polymer composite materials for bipolar plates, most of this work focuses on the exclusive use of particulate composites. These materials often meet conductivity requirements, but fail to provide sufficient mechanical strength and fall short of established performance targets.

Therefore, the primary goal of this work is to develop a polymer composite material that not only provides sufficient conductivity, but also retains sufficient mechanical strength to meet performance targets. To accomplish this, several steps must be completed. The first is to select a polymer resin suitable for the elevated operating temperature (80°C) and corrosive environment within a PEM fuel cell. The second step is to impart conductivity to the resin through the addition of particulate and short fiber reinforcements. The third step is to develop a hybrid composite material suitable for mass production which meets both conductivity and mechanical performance targets.

To overcome the challenge of imparting electrical conductivity to a polymer composite while maintaining mechanical performance, a hybrid composite approach is taken. A hybrid composite is a material which combines multiple types of reinforcement to achieve enhanced properties over those provided by a single reinforcement type. In this case, the developed material is a combination of particle, short fiber, and continuous fiber reinforcement. The addition of discontinuous fibers and particulate reinforcement serves to increase conductivity by creating a conductive network within the polymer matrix, while allowing for molding of flow channels. This reduces manufacturing time and cost by eliminating costly machining steps. The presence of continuous fiber reinforcement provides high mechanical strength and enhances electrical conductivity.

## 2. BACKGROUND

### PREFACE

This section provides a review of literature related to this project. This material covers bipolar plate requirements, materials in use and being researched for bipolar plates and their processing methods.

### 2.1 REQUIREMENTS FOR BIPOLAR PLATES

To select a material for use as a bipolar plate, a clear understanding of the performance requirements must be developed. The Department of Energy has established performance targets for electrical conductivity, cost, permeability, and other parameters presented below. These goals have also been supplemented by industry research organizations such as Plug Power who has established thermal conductivity, tensile, and flexural strength targets (also presented below).

Bipolar plate performance targets:

- Electrical conductivity ( $> 100 \text{ S/cm}$ )
- Low permeability ( $< 2 \times 10^{-6} \text{ cm}^3/(\text{cm}^2 \text{ s})$ )
- Corrosion resistant ( $< 16 \text{ mA/cm}^2$ )
- Tensile strength ( $> 41 \text{ MPa}$ )
- Flexural strength ( $> 59 \text{ MPa}$ )
- High thermal conductivity ( $> 10 \text{ W/m K}$ )



## 2.2 BIPOLAR PLATE MATERIALS

In order to meet the performance requirements established by the DOE a range of materials have been investigated. The commercial bipolar plate market is currently dominated by graphite plates, but metallic and polymer composite materials also have a market presence. The following subsections will provide an overview of each material technology and explore their respective advantages and shortcomings.

**2.2.1 Graphite Plates.** Graphite plates are the most commonly available commercial bipolar plates. Graphite offers good conductivity and low weight, but manufacturing costs are very high. The most significant drawbacks to graphite plates are the required thickness of the plates and the cost of manufacturing and processing.

Although graphite has a lower density than metal, its poor mechanical properties (brittleness and porosity) require greater thickness and therefore add weight and volume to fuel cell stacks. Typical graphite plates are limited to 4-6 mm in thickness while a thickness of 2-3 mm is desired for the next generation of bipolar plates.

Manufacturing of graphite plates is a time-consuming process. To start, raw graphite is formed into blocks by high-temperature sintering. The sintered graphite block is then cut into slabs which suffer from excessive porosity due to the sintering process. To reduce porosity the slabs are vacuum infused with resin and polished.

Another source of cost and time in production for graphite plates is the formation of gas flow channels. This is usually accomplished by machining which can take several hours and typically costs \$20-78/kW [3].

**2.2.2 Metallic Plates.** Metals are well known for good electrical and thermal conductivity and therefore are being considered for use in the manufacture of bipolar plates. Metals have electrical conductivities of two or three orders of magnitude greater than graphite and offer excellent mechanical properties, allowing for plates as thin as 1-2 mm. This is significantly thinner than graphite plates (approximately one third), greatly reducing the total volume of the fuel cell stack. Table 2.1 summarizes the key properties of metal bipolar plates.

Table 2.1. Properties of metals used for bipolar plates compared to graphite [3]

	Aluminum	Stainless Steel	Graphite
Conductivity (S/cm)	370,000	10,000	110-680
Density (g/cm <sup>3</sup> )	2.7	8.0	1.8-2
Thickness (mm)	1-2	1-2	5-6

Aluminum possesses a relatively low density, good strength, and higher thermal conductivity than stainless steel. Furthermore, aluminum bipolar plates can be manufactured by casting, machining, and etching. This leads to lower production time and costs when compared to graphite. However, aluminum suffers from the formation of an electrically insulating oxide layer which impedes bipolar plate performance.

Stainless steel has been shown to have the potential to meet all of the requirements for bipolar plates. It represents a relatively low cost material with high

electrical and thermal conductivity, good mechanical properties, and ease of machining. Stainless steel bipolar plates can be rapidly manufactured in large quantities by stamping, rolling, or even metal injection molding. Like aluminum, stainless steel also forms an oxide layer in the acidic environment within the fuel cell. However, unlike aluminum where the primary concern surrounding oxidation of the plate is performance loss, stainless steel forms  $\text{Cr}_2\text{O}_3$  which can contaminate the platinum catalyst through ion leaching [4].

In order to overcome the oxidation problem, coated stainless steel has been a significant focus of bipolar plate research. Anti-corrosion coatings represent a significant challenge to the adoption of metallic bipolar plates in that they add cost, processing time, and may inhibit performance by increasing interfacial resistance. Most conventional coatings have been demonstrated to be cost prohibitive and/or leave surface defects which result in accelerated local corrosion, damaging the fuel cell. The development of cost-effective coatings is the most significant research area in metallic bipolar plates.

Despite the excellent physical properties and high-volume manufacturing processes available for metal bipolar plates, current technology places the estimated cost at \$60-100/kW or 6 to 10 times the current target for transportation.

**2.2.3 Polymer Composite Plates.** The present status of both graphite and metal bipolar plate technology has resulted in interest in alternative materials with the hope of reducing costs and manufacturing complexity. A successful alternative material would need to combine the advantages of both graphite (corrosion resistance) and metal (mechanical properties and manufacturing ease). Polymer composites offer the

possibility of accomplishing this as they offer corrosion resistance, high specific strength and stiffness, and excellent moldability, allowing for formation of flow channels in one step.

Composite materials are best described as a system of two or more materials which possesses enhanced properties over its constituents. Composite materials are most commonly composed of a high-strength, discontinuous phase called the reinforcement and a weaker, continuous phase called the matrix. The matrix serves to distribute load to the reinforcement. Reinforcement materials are generally fibers such as glass, carbon, or aramid. Matrix materials are commonly polymer, metal, or ceramic.

Polymer composites are a class of composite material which utilizes a polymer matrix. Polymers used in composite materials can be divided into two major categories, thermoplastic and thermosetting. Thermoplastic polymers are a type of polymer which melts to a fluid when heated and hardens to a glassy state when cooled. Thermoplastics are composed of high-molecular-weight polymer chains which associate through intermolecular forces such as Van der Waals force, hydrogen bonding, and dipole-dipole interaction. This enables thermoplastics to be remelted and remolded. This is in contrast to thermosetting polymers which irreversibly “cure” when processed.

Thermosetting polymers are composed of prepolymers which undergo a chemical reaction which “crosslinks” the monomers into a covalently bonded network or polymer. This is an irreversible process which generally requires multiple components and the application of heat, microwaves, or UV light. When heated, thermosetting polymers will

decompose before a melting point is reached, making it necessary for any shaping to be done prior to complete curing.

The development of polymer composite bipolar plates has seen a great deal of interest in recent years and many attempts have been made to find a combination of materials which meet conductivity and strength requirements established by the DOE.

Much of the work in the field has focused on particulate fillers such as graphite and to a lesser extent discontinuous fibers. This approach has been met with mixed results with many studies showing a significant tradeoff between electrical and mechanical performance.

Bipolar plates developed at the University of Akron consisting of graphite and carbon black filled epoxy showed in-plane conductivity of 200-500 S/cm, but failed to meet the 41 MPa tensile strength target established by the DOE [5]. Furthermore, these composite materials showed long curing times, requiring 4-6 hours under 4,000 psi molding pressure and a subsequent 2 hour post cure in an oven. This long curing time is not conducive to high production rates. This work however did provide valuable insight into the benefits of using multiple conductive fillers.

The results showed a synergistic interaction between the graphite and carbon black fillers which served to increase conductivity. This was found to be the result of carbon black agglomerates forming additional conductive pathways between the expanded graphite particles, thus reducing the resistance of the material.

A similar investigation of the effect of carbon fillers on conductivity and mechanical properties of composites was performed J.H. Lee, et al. [6]. The work

performed examined the effect of carbon black, carbon fiber, and carbon nanotubes on the conductivity and properties of graphite/epoxy composites. It was found that carbon black had a lower percolation threshold than carbon fiber and therefore began to effect conductivity at levels low enough to not compromise mechanical properties. The most significant benefits were provided by the addition of 2 vol.% carbon nanotubes, but the high cost of nanotubes make them undesirable for bipolar plate applications.

Since the use of continuous or chopped fibers provides higher strength than particulate reinforcement, but makes forming the fine features required for flow channels difficult, researchers at Virginia Tech have developed a “laminated bipolar plate” [7]. This material consists of a polyvinylidene fluoride/graphite-based laminate mixture and a chopped carbon fiber, graphite, and polyphenylene sulfide based wet-lay core. By using only particulate fillers in the outer lamina, the authors were able to increase the formability and in-plane conductivity. In-plane conductivity was measured as 230 S/cm. This material exhibited better mechanical properties than other composite plates using only particulate fillers, but still fell short of DOE targets with tensile and flexural strength not exceeding 36.5 and 53.0 MPa respectively (DOE targets are 41 and 59 MPa).

Though less common, some work has been done to investigate the use of continuous fiber reinforcement in composite bipolar plates with good results. Hwang, et al. compression molded carbon fiber prepreg to form bipolar plates [8]. The material was found to have an in-plane conductivity of 300 S/cm, tensile strength of 520 MPa, and flexural strength of 316 MPa. These properties are all well above the DOE targets. However, it is not clear that the method is practical for production of commercial bipolar

plates as the material was only pressed into a corrugated shape which is not the same as a bipolar plate with a network of flow channels.

### **2.3 RESEARCH OBJECTIVES**

Recent trends toward environmental awareness and the proliferation of portable electronic devices have generated significant interest in fuel cell technology as a clean and powerful energy source for both transportation and portable power applications. The need for affordable, lightweight, compact fuel cells has rendered current bipolar plate technology obsolete and left an unfilled need for high performance materials which can meet multiple competing performance targets.

Polymer composite materials appear to be very promising candidates for bipolar plates, but to-date research efforts have been met with little success due to the low strength inherent in particulate composites. To overcome this deficiency and further enhance electrical conductivity, this research focuses on the development of a hybrid composite material which utilizes continuous fibers, milled fibers, and particulates to achieve the necessary properties while preserving the ability to mold flow channels into the plate during forming.

The goal of the project is to develop a hybrid composite material utilizing various conductive reinforcements. First, a conductive resin system consisting of polymer and conductive fillers such as milled fibers, polyaniline, and/or carbon black will be developed. The developed resin system should have improved conductivity over the neat resin, but maintain sufficient processability to be used as a matrix for continuous carbon reinforcement. The conductive resin and continuous carbon fiber reinforcement will be

compression molded to form bipolar plate material. Testing of the hybrid composite will be done to determine if conductivity and mechanical strength are sufficient to meet DOE requirements.

### **3. DEVELOPMENT OF HYBRID COMPOSITE BIPOLAR PLATES**

#### **3.1 ABSTRACT**

Traditional PEM fuel cell technology uses graphite bipolar plates which are good conductors and corrosion resistant, but have poor mechanical properties. Minimum plate thickness is limited and manufacturing costs are high due to the challenges posed by the brittleness of graphite. To overcome the problems posed by graphite plates, a polymer composite material is developed as an alternative.

In the present work, a hybrid composite material is developed for use as bipolar plates in PEM fuel cells. A conductive resin system composed of DKD Thermalgraph milled carbon fibers, Ketjenblack EC600-JD Carbon Black, and Versicon Polyaniline dispersed into Epon 826 epoxy is developed. The effect of fillers on curing, conductivity and mechanical performance is considered. This conductive resin system is combined with continuous carbon fiber woven fabric reinforcement to form a hybrid composite material for use as bipolar plates in PEM fuel cells. The developed hybrid composite material is evaluated for electrical conductivity and mechanical performance.

#### **3.2 INTRODUCTION**

Proton exchange membrane (PEM) fuel cells are a potentially significant power source for transportation and portable electronics. However, before this technology can



be implemented on a large scale for these purposes several challenges must overcome. One of the most significant barriers to the adoption of PEM fuel cells is the high cost and weight of the current graphitic bipolar plate technology.

Sintered graphite bipolar plates offer good conductivity and corrosion resistance, but possess poor mechanical properties which necessitates thicker plates than is ideal. Furthermore, manufacturing costs for these plates is very high due to expensive and time-consuming machining and sealing processes which are necessary for forming reactant gas flow channels and reducing porosity. Alternative materials appear to be necessary to reduce the cost and weight of fuel cell stacks and open new markets for fuel cell technology. To this end, materials such as metals and polymer composites have been considered as potential solutions to the issues posed by graphite plates.

To guide the development of these alternative materials, the Department of Energy and industry research groups such as Plug Power have established some baseline properties for acceptable bipolar plate materials. These performance targets are [9]:

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

Given the requirement that bipolar plates be good conductors, metals have a certain appeal due to their inherent electrical, thermal, and mechanical properties. Metal plates can also be formed by a variety of efficient methods such as stamping, rolling, or metal injection molding. However, metal plates experience oxidation due to the acidic environment inside the fuel cell. This oxidation leads to the formation of a passivation layer which increase contact resistance, decreasing cell efficiency. In the case of stainless steels, the formation of  $\text{Cr}_2\text{O}_3$  can contaminate the platinum catalyst through ion leaching. Anti-corrosion coatings designed to protect metal plates have proven expensive and sometimes imperfect in their coverage.

Polymer composites are chemically stable and offer high specific strength and stiffness as well as several manufacturing methods suitable for low-cost, high-volume production. The challenge in developing a suitable polymer composite material is to impart sufficient conductivity to the material without sacrificing mechanical strength and ease of processing.

Most research in this area has focused on the use of particulate composites and has been met with limited success. While most developed materials have shown sufficient conductivity, they have fallen short of strength targets and in some cases have relied on processing methods that are likely too time-consuming and expensive to be commercialized.

In the present work, a hybrid composite material is developed for use as bipolar plates in PEM fuel cells. A conductive resin system is developed using epoxy and conductive carbon fillers. The developed resin system is used as a matrix for AS4-3K-

8HS carbon fabric to produce a hybrid composite material by compression molding. The resulting material is tested for electrical and mechanical properties and the results are compared to bipolar plate performance targets established by the Department of Energy.

### **3.3 MATERIAL SELECTION**

The following sub-sections provide a description of the materials used, their properties, and pertinent findings from the literature.

**3.3.1 Epoxy.** An epoxy is a thermosetting polymer formed by the polymerization of epoxide (resin). Epoxy resin is most commonly obtained from the reaction epichlorohydrin and Bisphenol-A (or one of several other chemicals such as Bisphenol-F). Polymerization of epoxy resin is achieved by chemical reaction of the resin with a catalyst or “hardener”. The most common curing paradigms use anhydrides or amines, resulting in a copolymer of epoxide and hardener. An alternative method is to use a Lewis acid catalyst to achieve homopolymerization of the epoxy. The choice of curing agent can have significant effects on the curing time, heat required, and final material properties.

Amines are the most common curing agent for epoxy resins. An amine is an organic compound which contains a nitrogen atom with a lone pair. Primary and secondary amines are used as hardeners, while tertiary amines are used to accelerate the reaction. Amines are typically employed at ratios of approximately 50:50 amine to epoxide and reaction time is generally several hours. The reaction rate is strongly affected by the amount of hardener used, with high levels leading to faster curing times. This often leads to undesirable effects such as lower thermal stability.

An anhydride is an organic compound composed of two acyl groups bonded to a single oxygen atom. Anhydride cure is often used when high service temperatures are expected as it imparts good thermal resistance to the cured material. Anhydrides are typically used at levels of 0.5 to 0.9 equivalents of anhydride to equivalent of epoxy and typically require long post cure cycles to achieve full mechanical properties.

Cationic polymerization or homopolymerization is achieved through the use of Lewis acid catalysts such as  $\text{BF}_3$ . Instead of a copolymer of epoxide and amine or epoxide and anhydride, cationic curing results in an epoxide homopolymer. Lewis acids are highly reactive and are generally used in the form of a complex such as  $\text{BF}_3$ -MEA (Boron Trifluoride Mono-Ethylamine). Lewis acid complexes exhibit excellent stability at room temperature and allow for very long pot life once combined with epoxy resin. Lewis acid catalyst are very powerful and typically used in ratios of 1-10 wt.%. Curing usually takes place very rapidly (minutes) at temperatures of 100-180 °C and results in material with good thermal and chemical resistance.

In this research, Epon 826 (Bisphenol-A based epoxy) and Epalloy 8240 (Novolac epoxy) have been investigated for their suitability as matrix materials for composite bipolar plates. A  $\text{BF}_3$ -MEA Lewis acid catalyst driven cure has been selected for its resulting thermal and chemical resistance and its fast cure times which is important for the low cycle times required for high-volume production of bipolar plates.

**3.3.2 Polyaniline.** Polyaniline (PANI) is a member of a class of polymers known as intrinsically conducting polymers (ICP). While most polymers behave as electrical insulators, these have conductivities ranging from semi-conductor ( $10^{-8}$  to  $10^3$  S/cm) to

metallic (up to  $10^8$  S/cm). The key difference between ICPs and other polymers is the presence of conjugated double bonds along to the backbone of the polymer chain.

A conjugated polymer is one in which the bonds between carbon atoms are alternatively double and single bonded. While every bond contains strong localized sigma ( $\sigma$ ) bonding, each double bond contains a weaker pi ( $\pi$ ) bond. This is not enough to achieve conductivity though as all electron orbitals are filled, therefore doping is required. Doping improves charge mobility, allowing easier propagation along polymer chains and hopping between neighboring chains.

Polyaniline and other ICPs show poor processability in their pure form. Therefore, they are often blended with other polymers to form a more useable, but less conductive material. In this research, commercial doped polyaniline powder under the name Versicon (Allied-Signal) was blended with the aforementioned epoxy resins to form conductive blends. Versicon is a blend of p-TSA (p-toluene sulfonic acid) and DBSA (Dodecyl Alkylbenzene Sulfonic Acid) doped PANI.

The acid doping of Versicon and other polyaniline precludes the use of amine curing agents for the epoxy resin. The presence of a base such as an amine would negatively affect the doping the level of the PANI through acid-base interaction [10]. Avoiding this negative interaction was a factor in the selection of a Lewis acid curing agent.

**3.3.3 Carbon Black.** Carbon black is a form of amorphous carbon produced by the incomplete combustion of heavy petroleum products. Typical carbon blacks are pure carbon clusters with aciniform morphology. Aciniform is an adjective meaning “shaped

like a cluster of grapes”. This refers to the branched cluster-like grouping of spherical carbon particles, usually called agglomerates. With a high surface-area-to-volume ratio, carbon black offers high conductivity at low concentrations, making it an appealing component to a conductive resin system.

Conductivity of carbon black is dependent on particle size, structure, and porosity. Small particle size with high surface area leads to higher inter-aggregate forces, resulting in secondary conductive structures. This leads to high-conductivity, but can have an effect on mechanical properties. Typical conductivity values for carbon black ranges from 10-100 S/cm and the material demonstrates relatively low percolation thresholds.

Ketjenblack EC 600JD is a special type of highly conductive carbon black from AkzoNobel. EC 600JD exhibits extreme porosity, resulting in exceptionally high surface area. Surface area as measured by iodine adsorption for EC 600JD is 1000-1100 mg/g, whereas furnace blacks usually measure surface area below 130 mg/g [11]. This high surface area combined with a highly branched structure results in much higher than typical conductivity. Table 3.1 compares typical properties of some commonly used conductive carbon blacks.

Table 3.1 Iodine numbers for various carbon blacks [12, 13]

<b>Carbon Black Type</b>	<b>Iodine Number (mg/g)</b>
Ketjenblack EC600	1000-1100
Vulcan XC72	253
Furnace Black	80-130

Dispersion of carbon black is essential to achieving good conductivity. In the dry state, carbon black aggregates are attracted to one another and form large clusters which must be broken up to achieve uniform properties and efficient percolation. The use of high shear mixing to disperse carbon black, polyaniline, or other discontinuous fillers into a liquid resin is the best way to accomplish this. Melt compounding is used to disperse carbon black into thermoplastic matrices.

**3.3.4 Carbon Fiber.** Carbon fiber is extremely thin filaments (5-10  $\mu\text{m}$ ) composed of greater than 90% carbon. These fibers exhibit extremely high stiffness and strength as well as good electrical and thermal conductivity. There are several different precursors used to make carbon fibers and each affects the properties and diameter of the final product. The most common precursors from which carbon fibers are made are polyacrylonitrile (PAN), rayon, and petroleum pitch. Pitch based carbon fibers show higher thermal and electrical conductivity than PAN based fibers, making them appealing for bipolar plate applications. The properties of several types of carbon fibers are compared in Table 3.2.

Table 3.2 Properties of various milled carbon fibers [14, 15]

<b>Carbon Fiber</b>	<b>Electrical Resistivity (<math>\mu\Omega\text{-m}</math>)</b>	<b>Fiber Length (microns)</b>	<b>Thermal Conductivity (W/mK)</b>
DKD Thermalgraph	< 3.0	200	400-650
Panex 30	14.0	200	Not Provided
Tenax Milled	13.8	50-450	Not Provided

The highest composite material properties are achieved with the use of continuous fibers. That is, fibers which run continuously through the composite material. However, the high stiffness of the material makes it difficult or impossible for continuous fibers to conform to very fine mold features such as those of bipolar plate gas flow channels (typically 1-2mm square in cross section). Chopped fibers are available in lengths ranging from 0.25-2 in. and milled fibers are available in even shorter lengths of 50-500 microns. Though composite materials using discontinuous reinforcements will possess lower strength and stiffness, randomly dispersed fibers yield isotropic properties and have significantly greater formability than continuous fiber composites.

While beneficial in some applications, the orthotropic nature of most composite materials has some significant implications for composite bipolar plates. The longitudinal alignment of carbon fiber creates very high thermal and electrical conductivity in the longitudinal direction, but results in poor conductivity in the radial direction. Therefore, a composite bipolar plate using only continuous fiber reinforcement would exhibit good properties in the fiber direction, but would not conduct heat or electricity well in the through-plane direction or in-plane perpendicular to the fiber direction. To overcome this, the present work has made use of discontinuous fibers in the form of DKD Thermalgraph milled pitch based carbon fibers from Cytec Industries in addition to woven carbon fabric.

### **3.4 DEVELOPMENT OF CONDUCTIVE RESIN SYSTEM**

Due to the insulating nature of epoxies and other common polymers and orthotropic nature of carbon fiber, it is important to impart electrical conductivity to the resin by means of conductive fibers and particles. The resulting resin system will have



improved characteristics and will be used as the matrix for continuous carbon fiber reinforcement to manufacture bipolar plates.

The development of the conductive resin system is prefaced on an understanding of a phenomenon known as percolation. Percolation occurs when conductive fillers are at a sufficient volume concentration within the matrix to form an interconnected network. Figure 3.1 shows a graphical depiction of percolation. At this concentration the resistance of the material will undergo a several order of magnitude decrease. The use of multiple fillers with different geometries and particle sizes has been shown to enhance composite conductivity above what would be expected based solely on percolation [5]. Therefore, as discussed in Section 3.3.1, a number of materials (polyaniline, carbon black, and milled carbon fibers) are considered in the present work.

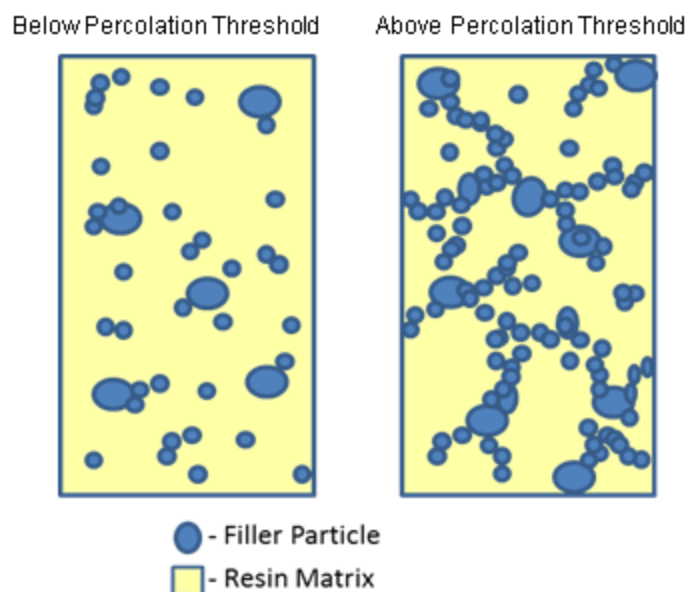


Figure 3.1. Percolation structure in resin

Resin samples were manufactured for conductivity and mechanical testing. Neat resin and conductive resin samples of various compositions were produced and evaluated to determine the appropriate conductive material loadings for the application.

The various conductive materials and Lewis acid catalyst were measured according to the desired levels and added to liquid epoxy resin and dispersed by high shear mixing for 10 minutes. Due to the high heat generated during mixing, the 10 minute total was broken in to two five minute spans with the resin being allowed to cool between each mixing period. The resin was then degassed in a vacuum oven at 50 °C for 30 minutes to remove air bubbles.

The resin was then poured into a prepared mold and cured in an oven at 150 °C for 1 hour and post cured at 180 °C for 1 hour. Parts were then demolded and flash was removed prior to testing.

Due to a surface wrinkling phenomenon caused by the  $\text{BF}_3$  Lewis acid catalyst used it was necessary to cover the samples with a perforated peel ply (perf ply) to obtain an acceptable surface finish from the open face mold used. Figure 3.2 shows the wrinkled surface and the surface obtained by the use of the perf ply. This surface wrinkling behavior has been investigated by researchers at the University of Minnesota. It is theorized that the formation of a mechanical skin on surface of the epoxy during cure leads to a compressive stress caused by diffusion of oligomers into the crosslinking skin, swelling it [16].

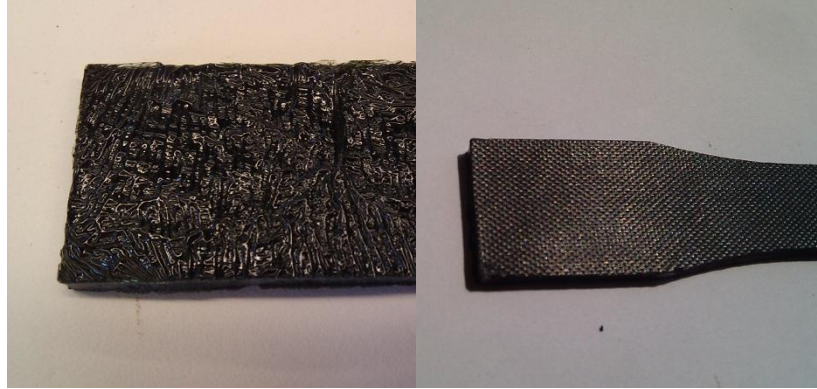


Figure 3.2. Comparison of wrinkled surface and surface obtained using perf ply

### 3.5 COMPRESSION MOLDING

Composite plaques were manufactured by means of compression molding, a composite manufacturing method which is suitable to high production rates and involves moderate capital investment.

In compression molding, a heated, two sided mold is filled with a preform and closed to apply heat and high pressure to the part causing it to fill the mold cavity and cure. Compression molding can be performed with a molding compound or laminate. Molding compound is a mixture of resin, chopped fibers, and fillers which is available in sheet form (sheet molding compound, SMC) or as a bulk, putty like material known as bulk molding compound (BMC). Alternatively, continuous fiber laminates may be made by stacking prepregs or placing a hand lay-up preform in the mold.

The manufacture of composite specimens for conductivity and mechanical testing was carried out by compression molding. Plaques of continuous carbon fiber reinforced

composite fabric in a conductive resin matrix were produced using the procedure outlined below.

Carbon fabric was cut to 10 x 10 in. squares and wetted out by hand with the conductive resin. Fabric was wetted on both sides to ensure proper distribution of the conductive particles and fibers. The wetted fabric was then stacked into a preform which was placed on a prepared mold which had been preheated to 150°C. The mold was placed on the heated platens of a Dake 75 ton capacity press. The mold was closed and the platens brought together to apply 100 psi of pressure to the plaque. The part was allowed to cure for 20 minutes at which time the mold was removed from the press and allowed to cool. The part was removed from the mold and post cured in an oven at 180°C for 1 hour.

### **3.6 PERFORMANCE EVALUATION**

The manufactured specimens of conductive resin and composite material were tested for the purpose of evaluating properties such as resin curing behavior, material mechanical properties, and electrical conductivity. The methods of testing and evaluation are described in the following sub-sections.

**3.6.1 Differential Scanning Calorimetry.** Differential scanning calorimetry (DSC) is a testing method which measures the difference in heat required to raise the temperature of a sample and reference. Changes in heat flow are measured as a function of temperature and testing is generally carried out at a constant ramp rate over a range of temperatures from -40 to 700°C.

For polymers, DSC testing can be used to evaluate curing behavior by measuring exothermic behavior at various temperatures. Additionally, cured polymer samples may be analyzed to measure thermal behavior by determining the glass transition temperature ( $T_g$ ). Glass transition temperature is the point at which a polymer undergoes phase change from a glassy to rubbery state in amorphous polymers. This transition has important implications for the mechanical properties of a polymer and a high  $T_g$  is very important for elevated service temperature applications as is the case for bipolar plates.

A TA Instruments Q1000 DSC was used in this work. Samples of approximately 5 mg in mass were analyzed under both ramp and isothermal temperature cycles. For analyzing cure, samples of uncured resin were run from 25-300°C at a ramp rate of 10°C/min. Additional samples were then run under isothermal conditions at selected temperatures obtained from the exothermic curve produced by the ramp cycle. These isothermal runs provide valuable information about the time required for the chemical reaction that cures the epoxy. Finally, cured samples were run to determine their  $T_g$ . These samples were run under a heat-cool-heat cycle to relax any residual thermal stress in the sample resulting from curing. Samples were run at a ramp rate of 10°C/min to provide accurate determination of the transition temperature.

**3.6.2 Thermogravimetric Analysis.** Thermogravimetric analysis (TGA) is a method for determining thermal stability of materials by measuring changes in weight relative to changes in temperature. It is valuable for determining thermal stability of polymers as well as volatile content and absorbed moisture.

A TGA analyzer consists of a high-precision balance with a platinum or ceramic pan on which a sample is placed. Sample sizes are in the milligram range and the size required depends on the percent of weight change that will occur as the balance is limited in its ability to accurately measure signal changes. The sample pan sits in an electrically heated furnace which is purged with either inert gas such as nitrogen or oxidizing gas such as pure oxygen or compressed air. Analysis is performed over a range of temperature (usually up to 1000°C) during which the mass of the sample is monitored and logged. Selection of temperature ramp rate is important because high ramp rates are known to reduce accuracy due to a phenomenon known as thermal lag. This is a delay between changes in furnace temperature and response of the polymer sample which has a relatively low thermal conductivity. This means that the recorded temperature and the sample temperature may be quite different under high ramp rate conditions. Such an error will cause weight loss to appear at higher temperatures than really is occurring. The recorded changes in mass can provide information about volatile content or thermal degradation of a material.

In this work, a TA Instrument Q50 TGA analysis instrument with a platinum pan was used. Samples of 10 mg were analyzed from 25 – 1000°C at a ramp rate of 10°C/min.

**3.6.3 Determination of Electrical Conductivity.** Measurement of in-plane conductivity was carried out by means of the four-point probe method in accordance with ASTM F374. The four-point probe method is a technique for measuring electrical resistance that uses separate current-carrying and voltage-sensing terminals to make highly accurate measurements. Unlike two-terminal sensing, the four-point technique is

not sensitive to the resistance of the probe wires or contact resistance between the sample and probe tips. A diagram of the system is provided in Figure 3.3.

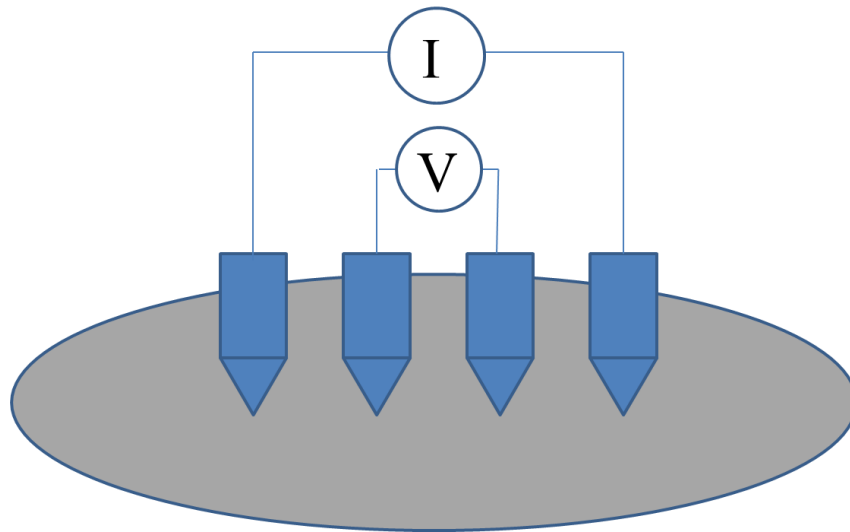


Figure 3.3 Four point probe system

An Alessi four point probe (C4S-44/5S, 1.25mm probe spacing) was used to measure the in-plane conductivity of resin and composite samples measuring 25 x 25 x 2 mm in this work.

**3.6.4 Measurement of Mechanical Properties.** Mechanical testing was conducted on both resin and composite specimens to determine the strength of the developed material.

**3.6.4.1 Tensile properties.** The tensile properties of neat resin and conductive resin were determined by testing according to ASTM D638 using Type I specimens.

Tensile and flexural properties of the composite material were measured according to ASTM D3039. For tensile testing, composite specimens of 250 x 25 x 2 mm were cut from compression molded plaques. Testing was carried out on an Instron 4469 testing machine using the setup shown in Figure 3.4.

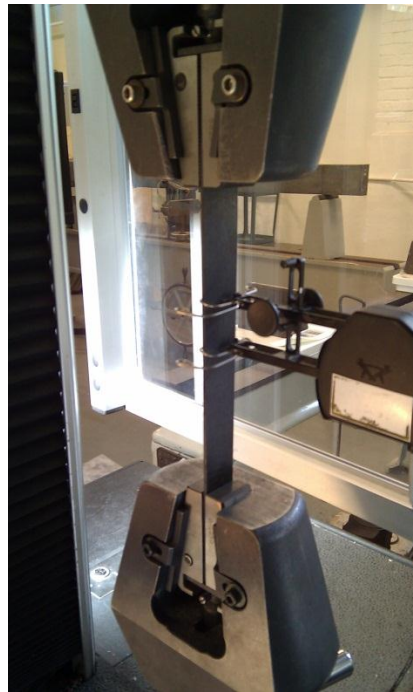


Figure 3.4. Tensile testing fixture

**3.6.4.2 Flexural properties.** Flexural testing of composite specimens was carried under the guidance of ASTM D790. Flexural specimens measuring 150 x 12.7 x 2 mm were cut from compression molded plaques. Each sample was tested using an Instron 4469 testing machine with a three-point loading fixture with a 1.6 in. support span and a crosshead speed of 0.5 in/min.



**3.6.5 Molding of Composite Bipolar Plates.** Composite bipolar plates were prototyped using the developed hybrid composite material and compression molding process. Figure 3.5 shows the compression mold with a parallel flow field design. Plates measuring 150 x 150 x 3 mm with 2 x 2 mm integral flow channels were molded using this tool and the same procedure described for the hybrid composite plaques with additional resin added for forming the flow channels.



Figure 3.5. Bipolar plate compression mold with parallel flow field

## 4. RESULTS AND DISCUSSION

### 4.1 CONDUCTIVE RESIN SYSTEM PERFORMANCE

**4.1.1 Differential Scanning Calorimetry.** DSC analysis was performed to establish a cure cycle and to test the glass transition temperature of the cured epoxy. Figure 4.1 shows the results of a dynamic DSC scan on Epon 826 with 3 wt.%  $\text{BF}_3$  catalyst and compares it with Epon 826 filled with 10 vol.% PANI (dashed and solid lines, respectively). The figure shows a clear effect of polyaniline on the curing reaction. The presence of PANI shifted the exotherm to much higher temperatures which resulted in slower curing at cure cycle temperatures established for the unfilled epoxy.

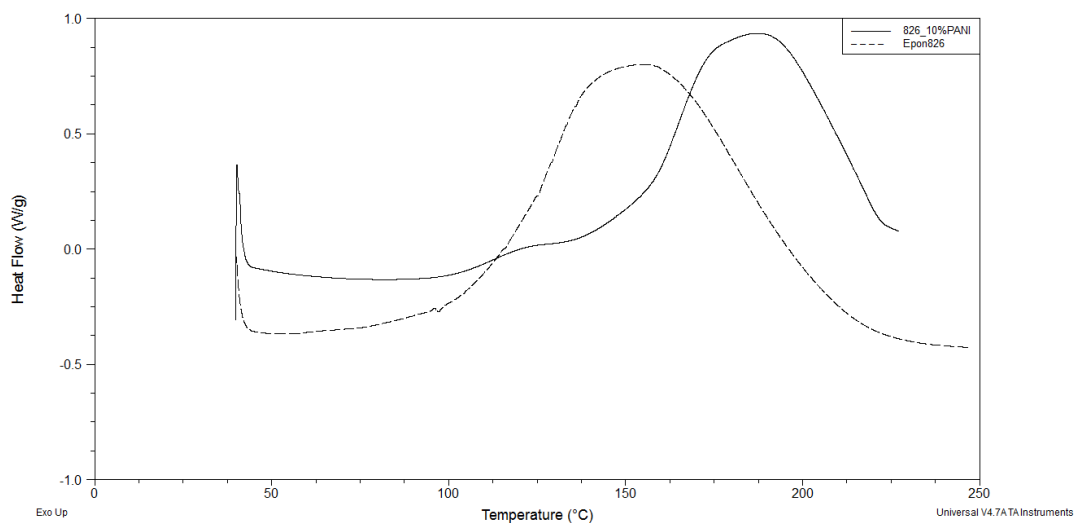


Figure 4.1. Dynamic DSC scans comparing the effect of polyaniline on the reaction behavior of Epon 826

The presence of polyaniline was also found to have a significant effect on glass transition temperature as shown in Figure 4.2 and Table 4.1 which details the values of  $T_g$  obtained. Samples of PANI filled Epon 826 and Epalloy 8240 were studied at PANI levels of 0, 10, and 20 vol.%. The results show that increasing PANI content is associated with a significant depression the  $T_g$  of the cured epoxy.

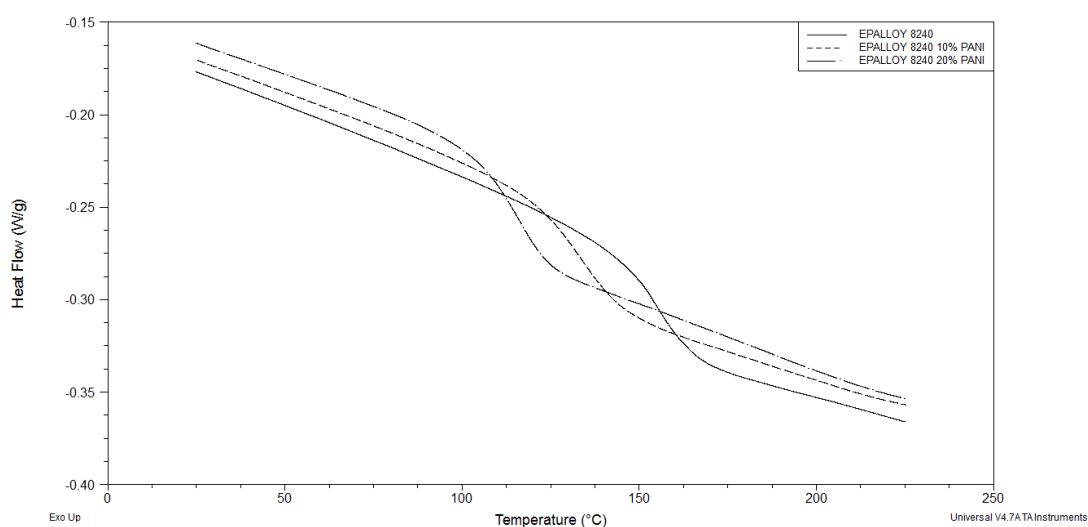


Figure 4.2 Effect of polyaniline on glass transition temperature

Table 4.1. Glass transition temperature of PANI filled epoxy

PANI Content (vol.%)	Glass Transition Temperature (°C)	
	Epon 826	Epalloy 8240
0	185.21	154.95
10	142.1	133.49
20	99.4	116.25

DSC analysis of carbon filled composites showed no such impact on the epoxy glass transition temperature. It has been proposed by some researchers that this phenomenon is the result of polyaniline acting as a plasticizer by reducing crosslinking density [17]. The observed effect of polyaniline on the properties and inhibition of the epoxy cure make it less appealing as a conductive resin system component. Additionally, the high glass transition temperature of Epon 826 makes it a better candidate than Epalloy 8240, especially when consideration is given to the desire to move to PEM fuel cells with membranes other than Nafion which would permit higher operating temperatures ( $> 100^{\circ}\text{C}$ ) and greater efficiency [18].

**4.1.2 Thermogravimetric Analysis.** The thermal stability of the epoxies was studied by TGA analysis. Figure 4.3 presents a comparison of the TGA results obtained from testing Epon 826 and Epalloy 8240 at  $10^{\circ}\text{C}/\text{min}$  across a temperature range from  $25 - 1000^{\circ}\text{C}$ . Both epoxies show nearly identical thermal stability with the onset of degradation occurring just above  $300^{\circ}\text{C}$ .

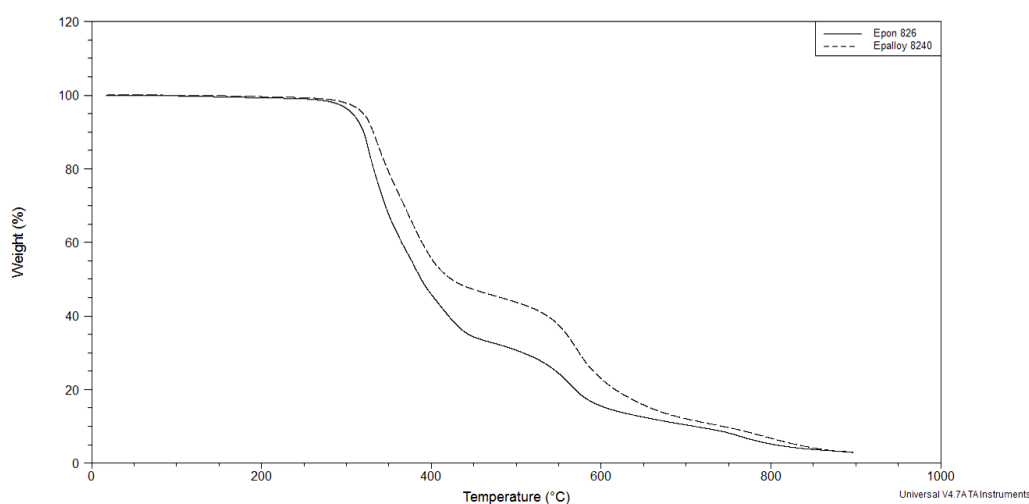


Figure 4.3. Thermal stability of Epon 826 and Epalloy 8240

**4.1.3 Electrical Conductivity.** The electrical conductivity of filled epoxy was explored with single fillers as well as multiple fillers. Single filler analysis was important to determine the percolation threshold of each conductive material as well as their efficiency in imparting conductivity to the epoxy.

Figure 4.4 presents the results of conductivity testing of polyaniline filled epoxy over a range of volume fractions. This data was obtained using a two-point probe system and conductive silver paint to reduce the effects of contact resistance. Based on this data, the percolation threshold was determined to be greater than 25 vol.% for PANI in Epon 826 and greater than 30% for PANI in Epalloy 8240.

Figure 4.5 shows conductivity data for Ketjenblack EC600 carbon black filled Epon 826. The results show Ketjenblack EC600 to be highly effective at increasing conductivity at low concentrations. The percolation threshold was determined to be around 5 vol.% for Ketjenblack EC600-JD which was important to determine for achieving the desired conductivity while maintaining processability.

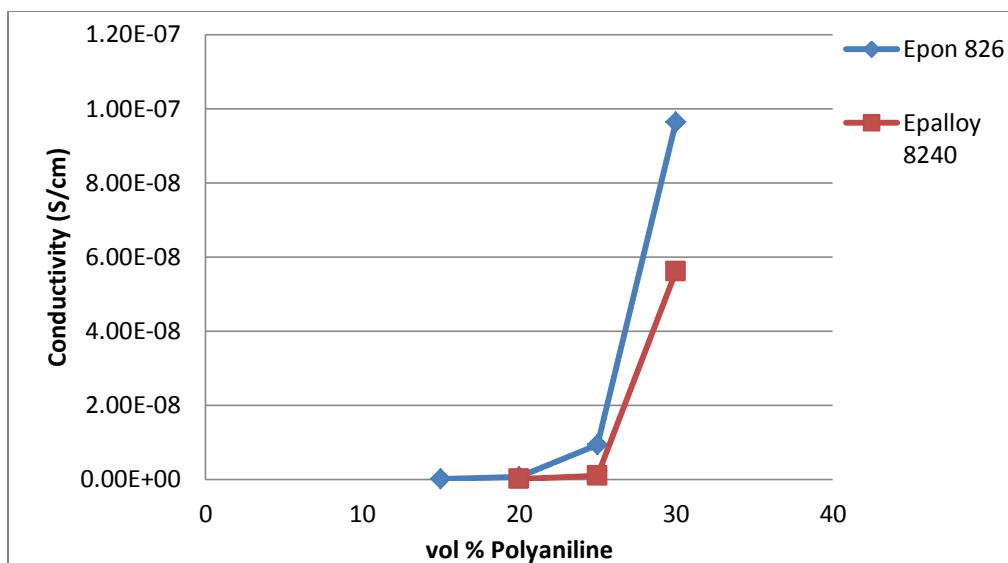


Figure 4.4. Conductivity of polyaniline filled Epon 826

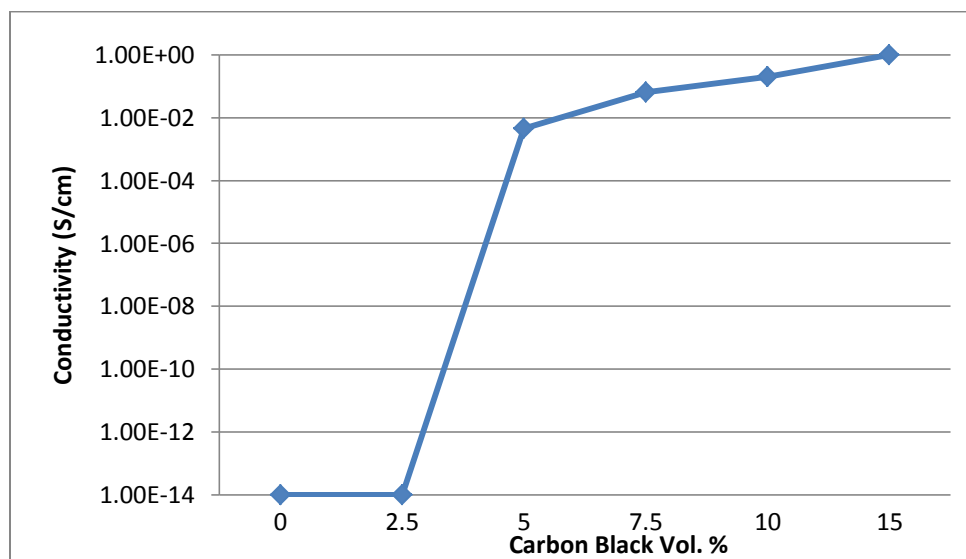


Figure 4.5 Conductivity of Ketjenblack EC600-JD filled Epon 826

To achieve the desired conductivity, the effect of combinations of Ketjenblack EC600 ( and DKD Thermalgraph fillers was explored. The conductivity data gathered is presented in Table 4.2, Figure 4.6, and Figure 4.7 (sample names correspond to those in Table 4.3) and show an enhancement in conductivity above that of single filler systems.

Table 4.2 Conductivity values for various conductive resin systems

DKD Thermalgraph (wt.%)	Ketjenblack EC600-JD (vol.%)	Conductivity (S/cm)
10	5	1.64E-4
15	5	4.83E-4
20	5	7.53E-3
10	7.5	3.20E-3
15	7.5	6.71E-3
20	7.5	8.24E-2
20	10	7.89E-1

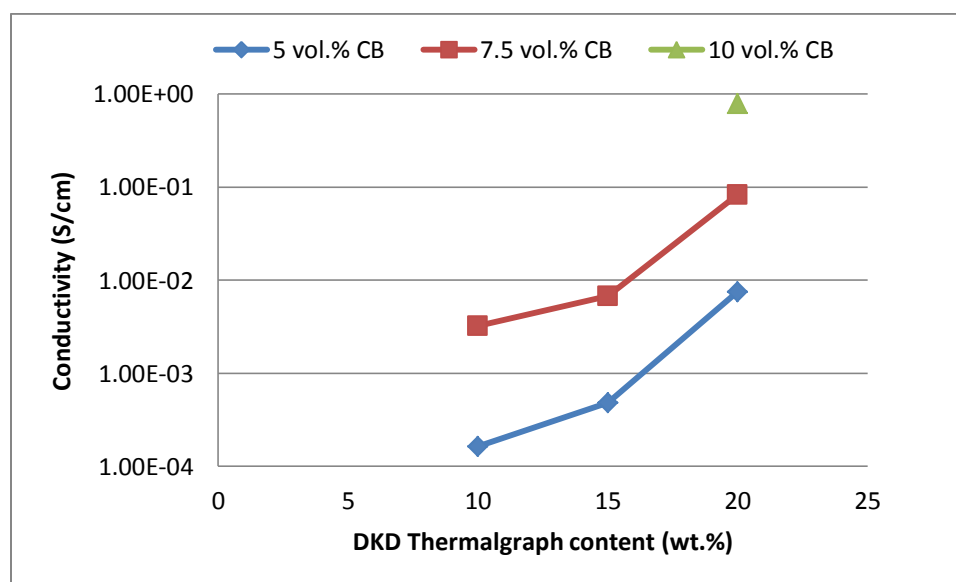


Figure 4.6. Conductivity of filled Epon 826

**4.1.4 Mechanical Performance.** Tensile testing of neat epoxy and conductive resin (filled epoxy) showed mechanical strength equal to or greater than the DOE target for tensile strength of the bipolar plate material. Table 4.3 shows a summary of the average tensile strengths obtained from testing.

Table 4.3. Tensile properties for the conductive resin system

Sample Name	Filler Content* (Epon 826 resin used for all systems)	Tensile Strength ksi (MPa)	Young's Modulus ksi (MPa)
1	Neat Resin	$5.12 \pm 0.75$ ( $35.3 \pm 5.20$ )	$447.2 \pm 34.1$ ( $3083 \pm 235$ )
2	10 wt.% CF 7.5 vol.% CB	$6.56 \pm 0.90$ ( $45.3 \pm 6.19$ )	$796.5 \pm 120.5$ ( $5491 \pm 831$ )
3	15 wt.% CF 7.5 vol.% CB	$6.73 \pm 1.15$ ( $46.4 \pm 7.93$ )	$998.8 \pm 162.6$ ( $6886 \pm 1121$ )
4	20 wt.% CF 7.5 vol.% CB	$6.0 \pm 0.93$ ( $41.3 \pm 6.41$ )	$2766.3 \pm 537.8$ ( $19072 \pm 3708$ )
5	20 wt.% CF 10 vol.% CB	$6.13 \pm 1.09$ ( $42.2 \pm 7.54$ )	$3502.5 \pm 689.9$ ( $24148 \pm 4756$ )

\*CF = DKD Thermalgraph milled carbon fiber, CB = Ketjenblack EC600-JD



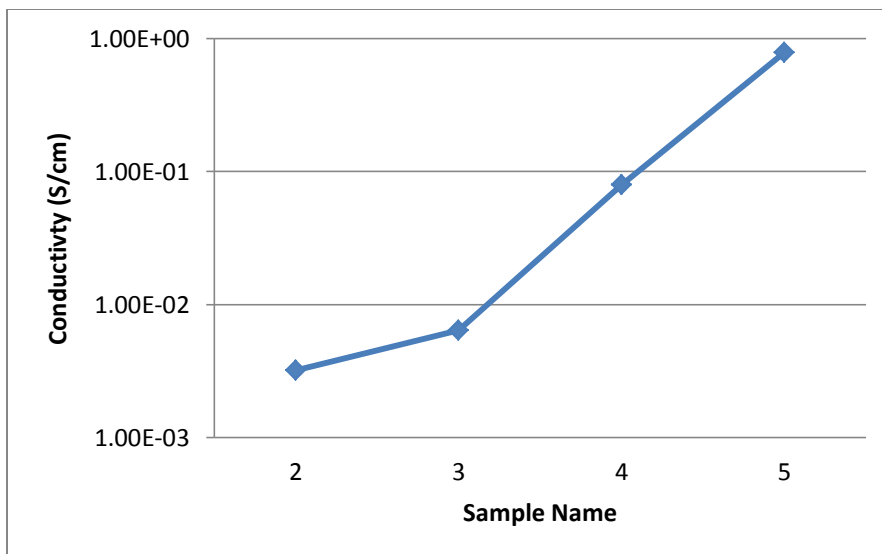


Figure 4.7. Comparison of the effect of filler level on conductivity

Graphical depictions of the effect of filler content on tensile strength and modulus are provided in Figure 4.8 and Figure 4.9, respectively. Sample names correspond to the names and compositions provided in Table 4.2.

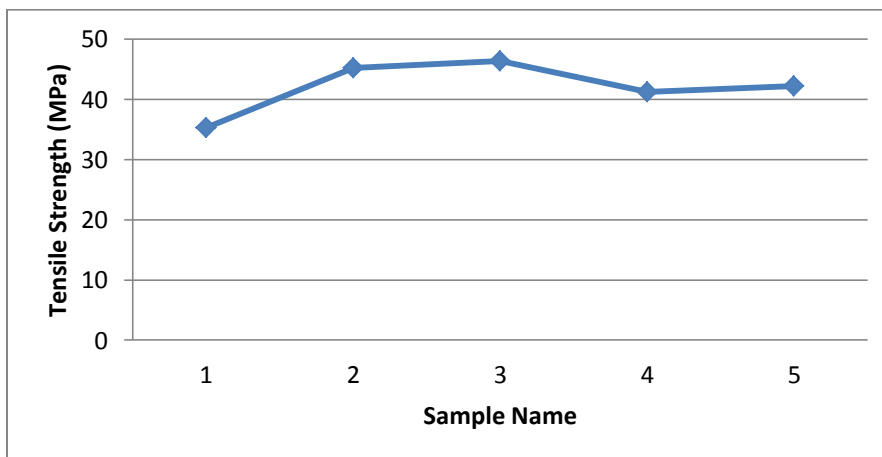


Figure 4.8. Comparison of tensile strength of conductive resins

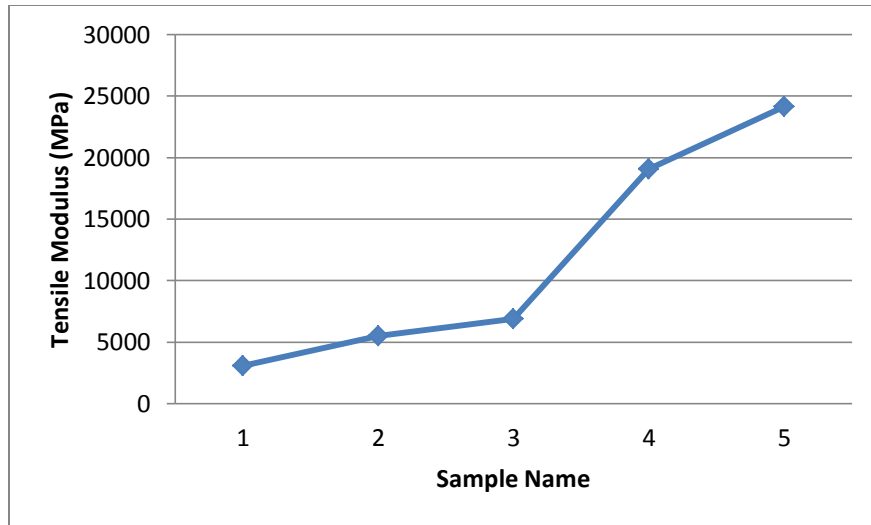


Figure 4.9. Comparison of tensile modulus of conductive resin systems

## 4.2 HYBRID COMPOSITE PERFORMANCE

Hybrid composite material with the compositions described in Table 4.4 was manufactured using the described compression molding process. The manufactured plaques were then used to evaluate electrical and mechanical performance.

Table 4.4. Composition of hybrid composite material manufactured by compression molding

Sample Designation	Carbon Fabric	Conductive Resin
C1	AS4-3K-8HS 4 layers [0 90] <sub>s</sub>	10 wt% DKD Thermalgraph and 7.5 vol.% Ketjenblack EC600 in Epon 826
C2	AS4-3K-8HS 4 layers [0 90] <sub>s</sub>	15 wt% DKD Thermalgraph and 7.5 vol.% Ketjenblack in Epon 826

**4.2.1 Electrical Conductivity.** Samples were cut from compression molded composite plaques and tested using the four-point probe method. In-plane conductivity for the hybrid composite material using conductive resin composed of 10 wt.% DKD Thermalgraph (CF) and 7.5 vol.% Ketjenblack EC600-JD(CB) in Epon 826 showed conductivity of 67.4 S/cm. The use of the conductive resin system composed of 15 wt.% CF and 7.5 vol.% CB in Epon 826 was found to increase the conductivity to 170 S/cm. Finally, hybrid composite composed of 20 wt.% CF and 7.5 vol.% CB was tested and showed conductivity of 203 S/cm. The DOE target for in-plane conductivity is 100 S/cm and both the 15 wt.% CF and 20 wt.% CF resin system produced properties that meet this requirement.

**4.2.2 Mechanical Performance.** Tensile testing of the hybrid composite material was conducted for composite specimens described in Table 4.4. The average tensile and flexural strengths are given in Table 4.5 and show far material strength well above the DOE targets of 41 and 59 MPa respectively.

Table 4.5. Mechanical properties of the developed hybrid composite bipolar plate material

<b>Composition (Sample Designation)</b>	<b>Tensile Strength ksi (MPa)</b>	<b>Flexural Strength ksi (MPa)</b>
C1	49.02 ± 6.9 (338 ± 47.6)	77.14 ± 3.29 (532 ± 22.6)
C2	48.03 ± 5.8 ( 331 ± 40.0)	91.33 ± 8.17 (630 ± 56.3)

### 4.3 MOLDING OF COMPOSITE BIPOLAR PLATES

Composite bipolar plates with integral flow channels were manufactured by compression molding. Plates measuring 150 x 150 x 3 mm with 2 x 2 mm flow parallel flow channels were formed using the developed 15 wt% CF and 7.5 vol% CB resin system and 3 layers of carbon fiber fabric with a more highly loaded resin (20 wt.% DKD Thermalgraph and 10 vol.% Ketjenblack EC600-JD) used on the top layer to enhance performance while allowing for flow channel molding. Figure 4.10 shows the molded plate with flow channels. The mold design needs improvement as releasing of the part was difficult and led to some chipping along the flow channels.



Figure 4.10. Compression molded hybrid composite bipolar plate

## 5. CONCLUSIONS

Hybrid composite material was developed for use in manufacturing bipolar plates. The material showed sufficient electrical conductivity, tensile, and flexural strength to meet Department of Energy and industry targets. The novel use of a conductive resin system with continuous carbon fiber reinforcement allowed the necessary conductivity levels to be achieved while maintaining high strength.

In developing the conductive resin system, Ketjenblack EC600-JD carbon black showed high performance at low filler levels which is important for processability. The discovered effect of polyaniline on the glass transition temperature of the epoxy resin made it unsuitable for this application and its use was discontinued after this was discovered.

The developed material demonstrated the ability to be formed with flow channels in a one-step molding process. Further refinement of the mold design should lead to a more acceptable surface finish and reduce the frequency of chipping of the lands and grooves of the flow channels during demolding.

The hybrid composite material with continuous fiber reinforcement showed excellent strength and good conductivity, with both well above Department of Energy and industry performance targets. This material represents a potential alternative to graphite bipolar plates.

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## **VITA**

Nathaniel James Richie was born and grew up in Bangor, Maine. He graduated with a B.S. in Mechanical Engineering from the University of Maine in May, 2009. He joined the Mechanical Engineering M.S. program at the Missouri University of Science and Technology in the fall of 2009. He received his Master's degree in December of 2011.