HIGHLY CONDUCTIVE EPOXY/GRAPHITE POLYMER COMPOSITE BIPOLAR PLATES IN PROTON EXCHANGE MEMBRANE (PEM) FUEL CELLS

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ABSTRACT

In this work, highly conductive carbon-filled epoxy composites were developed for manufacturing bipolar plates in proton exchange membrane (PEM) fuel cells. These composites were prepared by solution intercalation mixing, followed by compression molding and curing. The in-plane and through-plane electrical conductivity, thermal and mechanical properties, gas barrier properties, and hygrothermal characteristics were determined as a function of carbon-filler type and content. For this purpose, expanded graphite and carbon black were used as a synergistic combination. Mixtures of aromatic and aliphatic epoxy resin were used as the polymer matrix to capitalize on the ductility of the aliphatic epoxy and chemical stability of the aromatic epoxy.

The composites showed high glass transition temperatures ($T_g \sim 180^\circ$C), high thermal degradation temperatures ($T_d \sim 415^\circ$C), and in-plane conductivity of 200-500 S/cm with carbon fillers as low as 50 wt%. These composites also showed strong mechanical properties, such as flexural modulus, flexural strength, and impact strength, which either met or exceeded the targets. In addition, these composites showed excellent thermal conductivity greater than 50 W/m$^2$K, small values of linear coefficient of thermal expansion, and dramatically reduced oxygen permeation rate.

The values of mechanical and thermal properties and electrical conductivity of the composites did not change upon exposure to boiling water, aqueous sulfuric acid solution...
and hydrogen peroxide solution, indicating that the composites provided long-term reliability and durability under PEM fuel cell operating conditions.

Experimental data show that the composites developed in this study are suitable for application as bipolar plates in PEM fuel cells.
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CHAPTER I

INTRODUCTION

1.1 Research Significance

Global energy consumption grew dramatically in the 20th century with the increase in world population, improvements in living standards, and rapid development in industries and transportation systems [1-5]. The existing energy system in the US and in the world is largely based on combustion of the finite resource of fossil fuels—petroleum, natural gas, and coal, which are non-renewable. Large consumption of fossil fuels caused environmental concerns, such as global warming which in turn reinforced the need to reduce carbon dioxide (CO₂) emission and environmental pollutants such as nitrogen oxides (NOₓ), sulfur oxides (SOₓ), volatile organic chemicals (VOCs), and particulates. In view of these issues, development and utilization of more efficient energy conversion devices are necessary to meet the energy demands at a reduced rate of energy consumption with corresponding reductions in pollutants and CO₂ emissions. This will slow down the consumption of limited global energy resources and enable sustainable development.

Fuel cells are fundamentally much more energy-efficient than conventional power sources, and can achieve as high as 80% system efficiency in integrated units with co-
generation of heat utilization [4]. In fuel cells, chemical energy of a fuel is converted directly into electricity and heat without going through combustion. Therefore, fuel cells are not limited by the maximum efficiency dictated by the Carnot cycle of heat engines or internal combustion engines.

Hydrogen is considered as an ideal fuel for fuel cells. The primary byproduct of a H$_2$/air fuel cell is water. No air pollutants such as NO$_x$, SO$_x$, CO or particulates are produced if pure hydrogen is used. Fuel cells emit 40-60% less CO$_2$ than conventional energy sources when hydrogen is reformed from carbon-based fuels [1,4]. Emissions of CO$_2$ can be completely eliminated when hydrogen is produced by using solar or wind power. Fuel cells are quiet due to no moving parts and represent a class of highly efficient and exceptionally clean power sources.

Among various types of fuel cells, proton exchange membrane (PEM) fuel cells are considered a promising candidate for a zero-emission power source required in environmentally friendly transportation and stationary applications. High efficiency and power density, low operating temperature, and quick startup make PEM fuel cells very attractive in applications requiring from a few watts to megawatts of power, e.g., portable equipment, automobiles, and military communication installations and stationary applications [4]. The PEM fuel cell is recognized by the U.S. Department of Energy (DOE) as the main candidate to replace the internal combustion engine in transportation applications.

The major technical challenges of PEM fuel cells are high cost, large weight, and large volume of the fuel cell stack. The bipolar plates, an integral part of PEM fuel cells,
perform as the current conductors between cells, provide conduits for flow of reactant gases (such as hydrogen and oxygen), and hence constitute the backbone of a power stack. Conventional graphite bipolar plates contribute to 45-60% of the stack cost, 80% of the weight, and almost all the volume of the PEM fuel cell stack [6-8]. The development of alternative bipolar plates with significantly lower weight, volume, and cost would facilitate the commercialization of the PEM fuel cells for a wide range of applications and especially for transportation applications where a cost target of bipolar plates for fuel cell vehicle is established at US $10/kW [5,9-10].

1.2 History of Fuel Cells

The first demonstration of a fuel cell was conducted by the Welsh scientist Sir William Robert Grove in 1839. Grove then developed the first fuel cell which he referred to as a “gas battery” in 1843 [4]. The chemists Ludwig Mond and Charles Langer coined the term “fuel cell” in 1889 as they attempted to build the first practical device using air and industrial coal gas. A British engineer, Dr. Francis Thomas Bacon wrote the next major chapter in the fuel cell story. In 1932, Bacon developed the first successful fuel cell. He used hydrogen, oxygen, an alkaline electrolyte, and nickel electrodes. This device, which he named the “Bacon Cell”, was in essence the first alkaline fuel cell (AFC). It was not until 1959 that Bacon successfully developed a 5 kW stationary alkali fuel cell and a practical 5 kW unit capable of powering a welding machine. Hary Karl Ihrig, an engineer for the Allis-Chalmers Manufacturing Company, was also intrigued with the fuel cell technology. His breakthrough came when he demonstrated a 20-horsepower
tractor powered by a 15 kW fuel cell stack in October of 1959. This was the first fuel cell-powered vehicle.

A large boost in fuel cell technology came from the Natural Aeronautics & Space Agency (NASA). In the late 1950s, NASA began to build a compact electricity generator for use on space missions. NASA soon came to fund hundreds of research contracts for fuel cell technology.

In 1955, W. Thomas Grubb, a chemist working for General Electric Company (GE), modified the original fuel cell design by using a sulphonated polystyrene ion-exchange membrane as the electrolyte. Three years later, another GE chemist, Leonard Niedrach, devised a way of depositing platinum onto the membrane, which served as the catalyst for the necessary hydrogen oxidation and oxygen reduction reactions. This became known as the Grubb-Niedrach fuel cell, also the first Proton Exchange Membrane (PEM) Fuel Cell. GE went on developing this technology together with NASA, which led to its use in the Gemini space project. This was the first commercial use of a fuel cell.

In the 1960s, aircraft engine manufacturer Pratt & Whitney licensed Bacon’s US patents on alkaline fuel cell (AFC) for use in Apollo spacecraft to supply electricity and drinking water. AFC has subsequently been used on most manned U.S. space missions, including those of the space shuttles. The successful application of fuel cells in the American manned space program, together with the policy to commercialize space technology led to substantial development programs in the US and Japan in the 1970s and 1980s, and later in Europe. At the beginning of 21st century, environmental concerns and
global energy limitations stimulated new and expanding interest in fuel cell technology. The use of fuel cells moved industries, transportation systems, and stationary power sources onto improved energy conversion efficiency, reduced CO₂ emission and air pollutants, and a more sustainable development.

The major efforts in fuel cell development are presently focused on developing stationary power units and power systems for transportation applications. The first bus powered by a fuel cell was completed in 1993, and several fuel cell-cars are currently being built in Europe and in the United States. Daimler Benz and Toyota launched prototype fuel cell-powered cars in 1997 [4].

Worldwide, different types of fuel cells have been developed for different applications. Fuel cell energy is now expected to replace traditional power sources in the very wide range of applications requiring a few watts up to megawatts.

1.3 Types of Fuel Cells

A fuel cell is an electrochemical energy conversion device, which converts the chemical energy of a fuel and an oxidant directly into electrical energy and heat by a process occurring at an electrode-electrolyte assembly system. Generally, the reactants flow in and the reaction products flow out while the electrolyte and electrodes remain inside the cell. Therefore, a fuel cell can run virtually continuously as long as the necessary flows are maintained.

Fuel cells are classified primarily by the kind of electrolyte they use. The type of electrolyte determines the kind of chemical reactions that take place in the cell, the
catalysts required, temperature range in which the cell operates, and the fuel required among other factors. These characteristics, in turn, affect the applications for which these cells are most suitable. There are several types of fuel cells currently under development, each with its own advantages, limitations, and potential applications. The most promising types include the following seven different systems:

1. Proton exchange membrane fuel cell (PEMFC)

Proton exchange membrane (PEM) fuel cell is also called a polymer electrolyte membrane fuel cell. The PEM fuel cell uses a solid polymer as the electrolyte and porous carbon electrodes containing a platinum catalyst. With a solid and immobile electrolyte, this type of cell is inherently very simple. PEM fuel cells operate at relatively low temperatures, around 80 °C. Low temperature operation allows them to start quickly and results in less wear on system components and thus better durability. The PEM fuel cells deliver high power density, favorable power-to-weight ratio, low sensitivity to orientation, and can vary their output very quickly to meet shifts in power demand, compared to other types of fuel cells. These characteristics make PEM fuel cells suitable for applications, such as automobile, where quick startup is required. PEM fuel cells are used primarily for transportation applications and some stationary applications.

However, PEM fuel cells require a noble metal catalyst (typically platinum) to facilitate the dissociation of hydrogen molecules into protons and electrons. Recent research work explored the use of sophisticated catalyst and electrode techniques, so that only a small amount of platinum is needed. Thus the cost of platinum catalyst is a small
part of the total price of PEM fuel cells. However, this platinum catalyst is extremely sensitive to carbon monoxide (CO) poisoning, as CO binds to the platinum catalyst at the anode, thereby decreasing the fuel cell efficiency. Therefore, hydrogen at high level of purity must be used. The problem of hydrogen supply is not really addressed, as shown in existing literature [1,4]. Another significant barrier for usage of PEM fuel cells in vehicles is hydrogen storage. Most fuel cell vehicles (FCVs) powered by pure hydrogen must store hydrogen onboard as a compressed gas in pressurized tanks. Due to the low energy density of hydrogen, it is difficult to store enough hydrogen onboard. Higher density liquid fuels such as alcohol or hydrocarbon fuel can be used instead, but the vehicles must have an onboard fuel processor to reform the alcohol or hydrocarbon fuel to hydrogen. This increases the costs and the maintenance requirements.

2. Phosphoric acid fuel cell (PAFC)

Phosphoric acid fuel cells (PAFCs) use liquid phosphoric acid as an electrolyte—the acid is contained in a Teflon-bonded silicon carbide matrix. A platinum catalyst contained in porous carbon electrodes and fairly high operating temperatures (~220 °C) are used to maintain the reaction rate at a reasonable level. The PAFC is more tolerant to impurities in the hydrogen fuels than PEM fuel cells. PAFC is extraordinarily reliable. It is known to run continuously for over one year without any maintenance requiring shutdown or human intervention [4]. The PAFC was the first to be produced in commercial quantity and enjoy widespread use. This type of fuel cells is typically used for stationary
power generation, but some PAFCs have been used to power large vehicles such as city buses. The PAFCs are typically large, heavy, and also expensive.

3. Direct methanol fuel cell (DMFC)

Direct methanol fuel cell (DMFC) is similar to the PEM fuel cell in that they both use a polymer membrane as electrolyte. DMFC, however, is powered by pure methanol, which is mixed with steam and is fed directly to the fuel cell anode. The anode catalyst itself derives the hydrogen from the liquid methanol, thus eliminating the need of a fuel reformer. Methanol has higher energy density than hydrogen, and is also easier to transport and supply to the public using the current infrastructure since it is a liquid, like gasoline.

The DMFC typically operate at a temperature between 50-80 ºC. The power density of DMFC is relatively low. It is usually used in tiny to mid-sized applications, to power cellular phones, laptops, and so on.

4. Alkaline fuel cell (AFC)

Alkaline fuel cell (AFC) uses a solution of potassium hydroxide in water as the electrolyte and can use a variety of non-precious metals as a catalyst at the anode and cathode. High temperature AFCs operate at temperatures between 100-250 ºC. More recent AFC designs operate at lower temperatures of roughly 23-70 ºC.

AFCs are high performance fuel cells due to the fast rate at which chemical reactions take place in the cell. The AFCs are also very efficient, and can achieve power
generating efficiency of up to 70%. They were used on the Apollo and Shuttle Orbiter crafts to provide both electricity and drinking water onboard [4].

A major disadvantage of AFC is that the fuel cell is easily poisoned by carbon dioxide (CO₂). In fact, even a small amount of CO₂ in air can affect the operation of the cell, making it necessary to purify both the hydrogen and oxygen used in the cell. This purification process is costly. Susceptibility to poisoning also affects the lifetime of the cells. This is possibly the most significant obstacle in commercializing the AFC technology.

5. Molten carbonate fuel cell (MCFC)

The molten carbonate fuel cell (MCFC) uses an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic lithium aluminum oxide (LiAlO₂) matrix, and operates at high temperatures—approximately 650 °C. Non-precious metals can be used as catalyst at the anode and cathode since the MCFC is used at extremely high temperatures. The MCFC can reach high efficiencies approaching 60%, considerably higher than the 37-42% efficiencies of a PAFC plant. If the waste heat is captured and used, the overall efficiencies can be as high as 85% [4].

Unlike AFC, PAFC, and PEMFC, the MCFC does not require an external reformer to convert energy-dense fuel to hydrogen. Due to the high temperatures at which they operate, these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming, which also reduces the cost.
The primary disadvantage of current MCFC technology is durability. The high temperatures at which the cell operates and the corrosive electrolyte used accelerate components breakdown and corrosion, thus decreasing the lifetime of the cell.

6. Solid oxide fuel cell (SOFC)

The solid oxide fuel cell (SOFC) uses a hard, non-porous ceramic compound as the electrolyte and operates at very high temperatures—around 1000 °C. Since the electrolyte is a solid, the cells do not have to be constructed in the plate-like configuration typical of other fuel cell types. The efficiency of SOFC is around 50-60% at converting fuel to electricity [1]. In applications designed to capture and utilize the heat of the system (co-generation), overall fuel use efficiencies could reach 80-85% [1]. The high temperature operation facilitates the use of non-precious metal catalysts, and also allows the SOFC to reform fuels internally, which enables the use of a variety of fuels and reduces the cost.

The main problem of the SOFC is the high temperature operation, which results in a slow startup and requires significant thermal shielding to retain heat and protect personnel. This may be acceptable for utility applications but not for transportation and small portable applications. The high operating temperatures also place stringent durability requirements on materials. The development of low-cost materials with high durability at fuel cell operating temperatures is the key technical challenge facing the SOFC technology.
7. Regenerative fuel cell

The regenerative (reversible) fuel cell is a close-loop form for power generation. Water is separated into hydrogen and oxygen by a solar-powered electrolyzer. The hydrogen and oxygen are fed into the fuel cell which generates electricity, heat, and water. The water is then recirculated back to the solar-powered electrolyzer and the process begins again. This is a comparatively new fuel cell technology being developed by NASA and others worldwide [4].

Table 1.1 Different types of fuel cells [4].

<table>
<thead>
<tr>
<th>Fuel Cell Type</th>
<th>Electrolyte</th>
<th>Operating T(ºC)</th>
<th>Fuel</th>
<th>Power (W)</th>
<th>Applications &amp; Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFC</td>
<td>KOH solution</td>
<td>50-200</td>
<td>H₂</td>
<td>1k-10k</td>
<td>Space Vehicles, e.g. Apollo, Shuttle</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High Efficiency, Aging, Expensive</td>
</tr>
<tr>
<td>PEMFC</td>
<td>Solid ion exchange membrane</td>
<td>60-120</td>
<td>H₂</td>
<td>1-1M</td>
<td>Automobiles, Portable Power</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H₂ Storage Questions</td>
</tr>
<tr>
<td>DMFC</td>
<td>Solid ion exchange membrane</td>
<td>50-140</td>
<td>CH₃OH</td>
<td>1-100</td>
<td>Portable Power, Military, Automobiles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Small, Light, Attractive Fuel Catalyst &amp; Membrane Issues</td>
</tr>
<tr>
<td>PAFC</td>
<td>Phosphoric acid</td>
<td>220</td>
<td>H₂</td>
<td>10k-1M</td>
<td>Stationary Applications</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Large Numbers of 200kw CHP in Use</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Large, Heavy &amp; High Capital Cost</td>
</tr>
<tr>
<td>MCFC</td>
<td>Li₂CO₃ &amp; K₂CO₃</td>
<td>650</td>
<td>H₂ or CH₄</td>
<td>100k-10M</td>
<td>Stationary Applications</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Medium to Large CHP System</td>
</tr>
<tr>
<td>SOFC</td>
<td>Ritttria stabilized Zirconia</td>
<td>950-1050</td>
<td>H₂ or CH₄</td>
<td>2 k-10 M</td>
<td>Stationary Applications</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>All Size of CHP Systems</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Too High Operating T</td>
</tr>
</tbody>
</table>
In summary, different fuel cell types are usually distinguished by the electrolyte materials. Basic information about the various fuel cell systems that are currently under development is summarized in Table 1.1.

The fuel cell system can also be distinguished by the operating temperatures. The low-temperature fuel cell systems include Alkaline Fuel cell (AFC), Polymer Electrolyte Membrane Fuel cell (PEMFC), Phosphoric Acid Fuel Cell (PAFC), and Direct Methanol Fuel Cell (DMFC). The high-temperature fuel cell systems are Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC).

Fuel cells are promising alternative energy devices that can convert chemical energy of a fuel and oxidant directly into electricity without combustion. Among these several fuel cells, PEM fuel cell is a low operating temperature fuel cell, typically at temperatures of 60-120 °C. Therefore, PEM fuel cells are unique from the other commercially viable types of fuel cells. Consequently, fast start-up times are achievable only with PEM fuel cells. Furthermore, the thin electrolyte membrane allows PEM fuel cells to produce relatively high power while occupying a minimal amount of volume. These characteristics of fast start-up time and high power density make PEM fuel cells the best candidate for application in portable devices, such as laptop computers, cell phones, and automobiles. Most vehicle manufactures recognize PEM fuel cells as a potential replacement for internal combustion engines.
1.4 Basic Principles of PEM Fuel Cells

The basic principle of PEM fuel cells is very simple. Hydrogen and oxygen react to generate water, and at the same time generate electricity and heat. The chemistry for a fuel cell is shown below:

Anode side: \[ 2H_2 \rightarrow 4H^+ + 4e^- \]

Cathode side: \[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]

Net reaction: \[ 2H_2 + O_2 \rightarrow 2H_2O \]

The pressurized hydrogen gas (H\textsubscript{2}) entering the fuel cell on the anode side. This gas is forced through the catalyst by pressure. A H\textsubscript{2} molecule splits into two H\textsuperscript{+} ions and two electrons (e\textsuperscript{-}) after it comes in contact with the platinum on the catalyst. The electrons are conducted through the anode, where they make their way through the external circuit, e.g., a turning motor, and return to the cathode side of the fuel cell. Meanwhile, on the cathode side of the fuel cell, oxygen gas (O\textsubscript{2}) is being forced through the catalyst, where it forms two oxygen atoms. Each of these atoms has one pair of electrons and attracts the two H\textsuperscript{+} ions through the membrane, where they combine with two of the electrons from the external circuit to form a water molecule (H\textsubscript{2}O). This reaction in a single fuel cell produces only about 0.7 volts of electric energy. To get this voltage up to a reasonable level, many separate fuel cells must be combined to form a fuel-cell stack.

PEMFCs operate at fairly low temperatures (~80°C), which means they warm up quickly and do not require expensive containment structures. Constant improvements in
the engineering and materials used in these cells have increased the power density to a level where a small size device can power a car.

1.5 Components of PEM Fuel Cell Stack

A typical PEM fuel cell consists of the four major components: (1) solid polymer electrolyte, (2) electro-catalytic anode electrode, (3) electro-catalytic cathode electrode, and (4) bipolar plates.

Solid polymer electrolyte used as membrane in PEM fuel cells needs to be good proton conductors. A very commonly used electrolyte in PEM fuel cell is the sulphonated fluoro polymers, usually fluoroethylene. The most well known and well established of these is Nafion (® DuPont).

The sulphonic acid group —SO₃H is ionized, and the end of the functional groups in side chain is actually SO₃⁻ ion. For this reason, the resulting structure is called an ionomer. A key property of sulphonic acid is that it is highly hydrophilic. In Nafion, hydrophilic regions are created within a generally hydrophobic substance. The hydrophilic regions lead to absorption of large quantities of water. Within the hydrated regions, the H⁺ ions are relatively weakly attracted to the SO₃⁻ groups, and are able to move. The Nafion membranes are highly chemically resistant, mechanically strong, acidic, and can absorb large quantities of water. If the membrane is well hydrated, the H⁺ ions can move freely within the material.

The membrane is sandwiched between electro-catalytic porous anode and cathode electrodes. The anode, the negative post of the fuel cell, conducts the electrons that are
ionized from the hydrogen atoms so that they can go through an external circuit. It has channels etched into it that disperse the hydrogen gas equally over the surface of the catalyst. The cathode, the positive post of the fuel cell, has channels etched into it that distribute the oxygen to the surface of the catalyst. It also conducts the electrons back from the external circuit to the catalyst, where they can recombine with the hydrogen ions and oxygen to form water.

The catalyst on the electrodes is a special material that facilitates the reaction between oxygen and hydrogen. It is usually made of platinum powder, very thinly coated onto carbon paper or cloth. The catalyst surface is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen. The platinum-coated side of the catalyst faces the PEM.

1.6 Current Issues in PEM Fuel Cell

PEM fuel cells have been recognized as the most promising energy converting devices due to low or zero emissions and high efficiency. It has been demonstrated that PEM fuel cells are able to meet transportation and stationary power requirements, which has driven further development of this technology towards commercialization. However, PEM fuel cells have several major technical obstacles to overcome before they can be commercialized: high cost and heavy weight, and low reliability and durability.

Currently, the main drawbacks of PEM fuel cells are the cost, weight and volume. It is known that the bipolar plates contribute the majority of the cost and weight of PEM fuel cell stack. As mentioned section 1.1, currently the bipolar plates account for 80% of
the total weight and 45% of the stack cost [6-8]. Therefore, lower cost, lighter weight, and smaller volume bipolar plates need to be developed in conjunction with mechanical robustness, low hydrogen permeability, high electrical and thermal conductivity, and electrochemical stability.

Second, the low reliability and durability of the PEM fuel cells is another issue. The durability of the PEM fuel cells is primarily dependent on the durability of the solid electrolyte membrane and the reliability of the platinum catalyst on the electrodes. The solid electrolyte membranes are very soft and have weak mechanical properties, which makes the membrane easy to crack under hygrothermal cycles and vibration. The catalyst on both electrodes is very sensitive to CO in the fuel because the PEM fuel cell is operated at low temperatures. The efficiency and life time of the platinum catalyst is one of the reliability issues.

The third issue is that the available hydrogen sources, hydrogen storage devices and the corresponding infrastructure must be developed.

Water management is another critical issue, which needs to be resolved in the design and operation of PEM fuel cells. There must be sufficient water content in the polymer electrolyte to conduct the protons. However, too much water can flood the electrodes, thus blocking the pores in the electrodes or gas diffusion layer. A balance of the water content is needed.
1.7 Functions of Bipolar Plates

As an integral part of PEM fuel cells, the role of bipolar plates can be summarized as follows [11-19]. (1) They connect and separate the individual fuel cells in series to form a fuel cell stack. (2) They distribute fuel gas and oxygen over the whole active surface area of the membrane-electrode assemblies. (3) They conduct electrical current from the anode of one cell to the cathode of the next and also carry current away from the cell. (4) They facilitate water management within the cell. (5) They enable heat transfer. (6) They support thin membrane and electrodes and clamping forces for the stack assembly.

1.8 Requirements of the Bipolar Plates

In order to perform the functions of the bipolar plates listed above, ideally the composite plates should meet the following requirements [11-29]:

1. High electrical conductivity (DOE target [28]: >100 S/cm);
2. Chemical stability in the presence of fuel, oxidant and product water, which is acidic (pH = 2-3) (DOE target [28]: Corrosion resistance (<16μA/cm²),
3. Chemical compatibility ( no emissions affecting the electrode performance, no plate surface degradations occur);
4. High thermal conductivity (PlugPower’s target [29]: >10W(mK)^{-1});
5. Low thermal expansion coefficient;
6. Low permeability to fuel and oxidant (DOE target [28]: H₂ permeability (<2x10^{-6}cm³/(cm²·s))
7. Good mechanical properties (PlugPower’s targets [29]: tensile strength > 41 MPa, flexural strength > 59 MPa, impact strength > 40.5 Jm.1 (0.75 ft-lb/in); DOE target [28]: crush strength > 4200 kPa);
8. Thermal stability at fuel cell operating temperature (-40 to 120°C for fuel cell driven vehicles);
9. Low volume, light weight, and low cost
10. Easy manufacturability and rapid processability.
11. Thickness (≤ 2 mm) for applications in automobile vehicles;

1.9 Types of Bipolar Plates

There are many materials and methods for manufacture of bipolar plates. The most promising types and manufacturing methods of bipolar plates are described below.

1. Electro-graphite Bipolar Plates

One of the most well-established methods of manufacturing bipolar plates is by machining of electro-graphite sheets. Graphite is electrically conductive, and reasonably easy to machine. It also has lower density than that of any metal that might be considered suitable. A method to provide the necessary cooling channels within the stack is to make the bipolar plate assembly from two halves, which are identical. The back of each piece has the cooling channels cut in it, and the front has flow channels for the reactant gas. Two such pieces are put back to back to make a complete bipolar plate. Fuel cell stacks made in this way have provided competitive power density. The advantages of such
bipolar plates are summarized as follows — good electrical conductivity, corrosion resistance and performance, low density, and machinability [4].

However the graphite bipolar plates have several disadvantages. The machining of the graphite sheet to form the flow channels is very expensive and time consuming. Graphite is brittle, quite porous, and lack mechanical properties. In order to meet the gas tightness and mechanical property requirement, and mechanically support the fuel cell stacks, the plates need to be a few mm thick. Thus the final bipolar plate is not particularly light although the graphite itself is of lower density than metals.

2. Metal bipolar plates

The use of metal bipolar plates in PEMFC stacks offers a number of advantages, particularly for transportation applications, including low-cost mass-production via stamping, or embossing of sheet product; fabrication in very thin film (<200μm) to reduce weight and volume in the overall stack; impermeability to fuel, oxidant and water vapor; and in general, excellent thermal conduction properties and good mechanical robustness, even as a thin stamped foil. The primary challenge with metal bipolar plates is surface corrosion and dissolution because they are exposed to operating environment with a pH of 2-3 [30-32], and current drive to increase the operating temperature of the stack will only make this problem worse. Corrosion of the bipolar plate leads to a release of metal ions that can contaminate the electrolyte membrane and poison the electrode catalysts.
In addition, the formation of a passivating oxide or hydroxide layer on the surface of the metal will increase the contact resistance between the bipolar plate and the adjacent graphite electrode backing layer by many orders of magnitude. Both conditions can significantly degrade stack performance. A number of researchers have investigated various schemes for protecting metallic bipolar plates, most of which rely on a thin chemically inert yet electrically conductive coating. The greatest level of success that has been openly reported has been achieved with noble metal coatings such as gold and palladium. Unfortunately, commercial use of these materials, even as thin coatings, is cost-prohibitive.

3. Polymer Composite Bipolar Plates

Another promising alternative of graphite bipolar plates is polymer composite bipolar plates. The major advantages are that these are lower cost and lightweight, and are easily machined, with good corrosion resistance, relatively good mechanical properties, and good gas tightness. A major disadvantage is that polymers have extremely low electrical conductivity, so excessive conductive filler has to be incorporated. In this context, one needs to remember that it is difficult to get high conductivity and sufficient mechanical properties simultaneously.

Polymer composites are usually manufactured from a combination of graphite or carbon filler and a polymer resin with conventional polymer processing methods, such as compression molding and injection molding. The gas flow channels can be molded directly into the plates, thus eliminating the need for the costly machining step.
In this study, we focused on the development of the polymer composite bipolar plates. As will be seen later, these bipolar plates meet most of the requirements specified by US Department of Energy (DOE).

1.10 Conflicting Issues in Designing Polymer Composite Bipolar Plates

To achieve the DOE targets of strong mechanical properties and good gaseous tightness, the filler content should be small and the filler should be well-dispersed in the polymer matrix. However, in order to achieve high electrical and thermal conductivities of the composites, the intrinsically insulating polymer resin must be filled with high loadings of conductive particles such as carbon black and/or graphite. The global aggregates of network of the conductive particles are needed to form the electron conductive paths. These two requirements present conflicting scenarios as shown in Figure 1.1.

The electrical and thermal conductivities of the materials should be very high for application as bipolar plates in PEM fuel cells. Therefore, the conductive filler loadings greatly exceed percolation threshold concentrations, and approach or even surpass critical pigment volume concentrations (CPVC) of 50-70% in volume [6,33]. At the percolation threshold concentration, an interconnecting path of conductive graphite particles forms and extends throughout the entire sample thickness, thus enabling electrons to “percolate”. The electrical resistance decreases by many orders of magnitude as the material goes through an insulator–conductor transition. At higher graphite loadings such as that at the CPVC, there is no enough polymer binder to carry the graphite particles. Many more
percolation pathways form for enhanced conductivity, but the materials become to be porous and weak [33]. As a result, composite plate materials with high graphite content are extremely brittle, and have poor gas barrier properties. Note that above the CPVC, the material has insufficient carrier polymer and behaves like a solid; consequently, the material does not flow and fill the mold well during processing. Consequently, the filler loadings of the composites should be at graphite levels well beyond these percolation levels for conductivity but slightly below the CPVC to achieve adequate strength, flow, and gas impermeability.

![Layered Fillers](image1.png)

![Spherical Fillers](image2.png)

Figure 1.1 Conflicting scenarios in achieving both high electrical conductivity and strong mechanical properties when designing the polymer composite bipolar plates.
1.11 State of the Art of Bipolar Plates

Currently, the existing polymer composite bipolar plates have relatively low electrical and thermal conductivities and poor mechanical properties. Many of the commercial bipolar plates could not achieve the DOE targets yet. Properties of some of the representative bipolar plates are summarized in Table 1.2. Further work needs to be done to improve the overall performance of the bipolar plates to achieve the DOE targets.

Table 1.2 Properties of current polymer composite bipolar plates under development [10]. GP, CF, EG and CB represent respectively graphite particles, carbon fiber, expanded graphite and carbon black.

<table>
<thead>
<tr>
<th>Manufacturers/ Patents</th>
<th>Polymer</th>
<th>Filler (wt %)</th>
<th>σ (S/cm)</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>In-plane</td>
<td>Thru-lane</td>
</tr>
<tr>
<td>US 6,248,467 (LANL)</td>
<td>Vinyl Ester</td>
<td>68 GP</td>
<td>60</td>
<td>30</td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
<td>105</td>
<td>21</td>
</tr>
<tr>
<td>Premix Inc.</td>
<td>Vinyl Ester</td>
<td>68 GP</td>
<td>85</td>
<td>28</td>
</tr>
<tr>
<td>BMC 940</td>
<td>Vinyl Ester</td>
<td>100</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Plug Power</td>
<td>Vinyl Ester</td>
<td>68 GP</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>US 4,214,969(GE)</td>
<td>PVDF</td>
<td>74 GP</td>
<td>119</td>
<td>35-37</td>
</tr>
<tr>
<td>US 5,942,347 (GTI)</td>
<td>Phenolic</td>
<td>77.5 GP</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>US 6,171,720 (ORNL)</td>
<td>Phenolic</td>
<td>CF</td>
<td>200-300</td>
<td></td>
</tr>
<tr>
<td>DuPont</td>
<td></td>
<td></td>
<td>25-33</td>
<td>53</td>
</tr>
<tr>
<td>SGL</td>
<td></td>
<td></td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>H2 Economy</td>
<td></td>
<td></td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Virginia Tech</td>
<td>PPS</td>
<td>76GP&amp;CF</td>
<td>271</td>
<td>19</td>
</tr>
<tr>
<td>U Akron</td>
<td>Epoxy</td>
<td>50EG&amp;CB</td>
<td>300-500</td>
<td>77-79</td>
</tr>
<tr>
<td>DOE target Value</td>
<td></td>
<td></td>
<td>100</td>
<td>59</td>
</tr>
</tbody>
</table>
1.12 Specific Contribution of This Research

As mentioned in the section 1.10, the requirements of high electrical and thermal conductivities and good mechanical and gas barrier properties present conflicting scenarios in the production of good bipolar plates. In order to get high conductivities, high filler loadings and global aggregates of network of conductive particles are necessary. However, to achieve good mechanical and gas barrier properties, the filler loading should be low and well-dispersed. This contradiction was solved in the present work to obtain the objectives.

In this study, our main ideas were to develop a composite material to achieve high electrical and thermal conductivities, and good mechanical and gas barrier properties simultaneously. First, expanded graphite was chosen as the major conductive filler. The graphite particles have layered and network structures. The thickness of the layers is less than 20 nm, and the layers are in contact with each other to form a electrically conductive network. In this way, both good dispersion and electron conductive networks are achieved at the same time. Furthermore, small amount of electrically conductive carbon black particles are added in the formulation. The combination of expanded graphite and carbon black present a synergistic effect on electrical conductivity. Thus highly conductive composites are developed with a reduced level of total filler content. The layered expanded graphite particles also provide the composites desired barrier properties.

Second, a solution interaction mixing method involving low shear force was developed to prepare the compound used in molding of bipolar plate composites. Low viscous epoxy resins were chosen, which penetrate into the expanded graphite gallery
between layers. The layered and network structures of the expanded graphite are maintained in the composites after epoxy was cured. These layered and network structures form global electron conductive paths in the composites at relatively low filler loadings. There is enough polymer resin to fill the expanded graphite inter-layers and pores in the composites at much lower filler loadings than CPVC. Thus, the composites also offer strong mechanical properties and good gas barrier properties.

Furthermore, the expanded graphite used in this work is treated by concentrated sulphuric and nitric acids before expansion. Some reactive functional groups, such as carboxyl, hydroxyl, and epoxide groups are formed on the surface of the graphite surface, which react readily with the epoxy curing agent DDS. Strong interaction between polymer matrix and filler particles offered strong interfacial adhesion, and in turn deliver strong mechanical properties and gas barrier properties to the composites.

Another contribution of our work is the design of a hygrothermal test was designed to test the reliability and durability of the polymer composite bipolar plates in the severe PEM fuel cell service conditions of high temperatures, high humidity, and high acidic environment.
CHAPTER II

BACKGROUND

Bipolar plates are a major component of PEM fuel cells with multi-functionality. They also provide architecture and geometry, and contribute to large volume, mass and cost. They are responsible for the mechanical integration of PEM fuel cell stack. They distribute fuel and oxidant uniformly over the active areas, conduct electrical current from cell to cell, facilitate water and heat management, support the thin and soft membrane electrode assembly (MEA), and the clamping force of the stack, and prevent leakage of gases and coolant. Hence, vigorous research and development activities worldwide focus on bipolar plates for improvement of the performance of the current fuel cell stacks. Furthermore, bipolar plates must be made of inexpensive, lightweight materials, and must be easily manufactured.

There are three types of PEM fuel cell bipolar plates under study worldwide. The main materials studied to date include non-porous graphite (electro-graphite), metal, and polymer composite bipolar plates. Each has some advantages and limitations as well as unique manufacturing processes.
2.1 Electro-graphite Bipolar Plates

Traditionally, the most commonly used bipolar plate material is non-porous graphite because of its excellent chemical stability, and good electrical conductivities. The electrical conductivity of Poco® graphite bipolar plates (from Poco Inc.) is about 680 S/cm [34-35]. Furthermore, graphite is highly hydrophobic and also possesses very good thermal conductivity, which can facilitate heat and water management in the PEM fuel cell stack. Currently, non-porous graphite bipolar plates are considered the industrial standard in terms of stack performance. Other alternative bipolar plates are compared with the electro-graphite bipolar plates to evaluate the performance.

However, non-porous graphite is very brittle, lacks desired mechanical strength, and has high gas permeability. Consequently, the graphite bipolar plates need to be manufactured with a thickness of several millimeters, which makes the bipolar plates heavy and bulky. In addition, the channels for gas flow and coolant flow need to be machined on the surface of graphite. The cutting and machining of the flow channels is time consuming and costly. In view of all these factors, electro-graphite bipolar plates are considered not suitable for applications in portable devices and automobile vehicles.

Vigorous efforts are underway to develop alternative materials for bipolar plates so that the weight, volume, and cost can be reduced, while the stack performance is comparable to electro-graphite bipolar plates. Metal sheet bipolar plates are promising candidates due to their high electrical and thermal conductivities, strong mechanical properties, and good gas impermeability. Furthermore, metal bipolar plates can be
effectively mass produced as the flow channels can be easily shaped and stamped on the metal sheets.

2.2 Metal Bipolar Plates

Metal sheets are preferable in industry due to strong mechanical properties, high electrical and thermal conductivity, and easy manufacturability into desired shapes. Various types of non-coated metal, metal alloy, and metal foams have been investigated for possible replacement of electro-graphite bipolar plates. They include aluminum, stainless steel, titanium, nickel, copper, and their alloys [36-74].

However, bipolar plates are exposed to an operating environment with a pH of 2-3 [30-32] at temperatures around 80 ºC, and the metal plates undergo corrosion and dissolution. A passivation oxidation layer forms on the surface of the metal sheets after corrosion. This passivation layer protects metals from further corrosion to a certain extent. However, the passivation layer is usually porous and thicker corrosion layer forms due to long term exposure. This thick passivation layer increase the surface electrical resistance of the plates and hence the contact resistance between plates and the MEA assembly. Consequently, the overall power output of the PEM fuel cell stack decreases due to voltage loss between the plates and the MEA assembly.

In addition, the dissolved metal ions may lead to poisoning of PEM membrane and hence lowering the ionic conductivity. In the worst case, the protons in the membrane are exchanged with the metal ions, resulting in dramatic decrease of the proton conductivity of the membrane.
In light of these issues, protective coatings on metal plates are necessary to improve the corrosion resistance and to increase the surface electrical conductivity of the metal bipolar plates. A brief review of on non-coated and coated metal bipolar plates under active development is given as follows.

2.2.1 Non-coated Metal Bipolar Plates

Noble metal bipolar plates, such as gold and platinum, have excellent performance, which is comparable to or even better than that of electro-graphite bipolar plates [40]. However, gold and platinum are very expensive. Thus, it is not practical to make bipolar plates from these noble metals. The cost itself prohibits the commercialization of noble metal bipolar plates.

Inexpensive metals, such as stainless steel, aluminium, titanium, copper, and their alloys without protective coatings have been investigated. The corrosion rate and corrosion products, contact resistance, power output of the stack, and long-term durability are the major concerns for metal bipolar plates [14,44,54-55,58-59,62,66,68,70-72].

Different grades of uncoated stainless steels have received considerable attention due to their relatively high strength, high chemical stability, low gas permeability, wide range of alloy choice, and applicability to mass production and low cost [55,62,66-71]. Li et al. [66] studied electrochemical corrosion characteristics of uncoated stainless steel 316 (SS316). They reported that the SS316 are prone to corrosion and dissolution in acidic environment. A porous corrosion product layer formed on the surface. The corrosion
progressed with the increase of immersion time. They suggested that a protecting coating is necessary to enhance the corrosion resistance and electrical conductivity.

Davies et al. [70-71] investigated the performance of uncoated stainless steel 310, 316 and 904L and titanium bipolar plates. They concluded that the interfacial resistance losses decreased in the order of 316 > Ti > 310 > 904L as the passive film thickness decreased also in the same order. The fuel cell performance was observed to follow the order of 904L > 310 >316. This was explained as follows: As the thickness of passive films increases, the contact resistance increases, resulting in high voltage losses and less fuel cell power output. During the 3000 hours of endurance test, the surface resistance of the stainless steel alloys remained the same, which is different from other passivating metals such as titanium, whose electrical resistivity increased with respect to time, thus causing the cell to fail due to passivation layer formation. No evidence of corrosion was observed for stainless steel alloys. The cell performance degraded only slightly, which was slightly lower than that of graphite plate fuel cells.

Jayaraj et al. [58] compared the performance of iron-based amorphous alloys with stainless steel SS316L, and found that the Fe_{50}Cr_{18}Mo_{8}Al_{2}Y_{2}C_{14}B_{6} amorphous alloy provided significantly higher corrosion resistance than that of SS316L due to a more stable passive layer formed on the alloy surface. Both Davies and Jayaraj [58,70-71] suggested that uncoated metals or metal alloys can be used as bipolar plates if the chemical composition of the alloys are optimized.

Vaibhav et al. [59] evaluated if C-17200 copper-beryllium alloy can be used as bipolar plates in PEM fuel cells. They observed good corrosion resistance of the copper
alloy bipolar plates and found that single cell maintained its performance for 100 hours at a constant load of 1 A. These authors also suggested that better cell performance can be obtained using highly corrosion resistant surface treatment of the alloy.

Matsuura et al. [58] studied the pressure tolerance of the PEM fuel cells based on metal bipolar plates. It was found that sufficient contact between bipolar plate and its neighboring components can be achieved by applying a high compressive pressure, but large compressive load also induces serious damage to fuel cell systems.

Wang et al. [14,72] studied both austenitic (349™) and ferritic (AISI446) SS with high Cr content and reported that these materials showed good corrosion resistance.

Although large amounts of research work focused on uncoated metal bipolar plates, long-term performance of fuel cells remained unexplored. The surface oxide layer forms a passive layer on the metal surface if metals such as Al, Ti, Ni, etc. are used. The passive layers show fair corrosion resistance but poor surface contact resistance. As bipolar plates are used at high temperatures, high humidity, and under acidic environment, metal dissolution is imperative. Accordingly, power output deteriorates with time as the passive layers grow thicker. Moreover, the metal ions and oxides resulting from corrosion might foul the electrolyte and block the pores of the catalyst on electrodes. The dissolved metal ions also can diffuse into the membrane and exchange protons in the membrane. This results in dramatic decrease of ionic conductivity [40]. Therefore, the coating materials should also have high electrical conductivity on top of strong chemically corrosion resistance. In addition, the coating materials should have strong adhesion with the metal substrate. A brief review is presented next on coated metal bipolar plates.
2.1.2 Coated Metal Bipolar Plates

Aluminum, stainless steel, titanium and nickel are considered as alternative materials for bipolar plates in PEM fuel cells and coated by protective coating layers. These coatings should adhere well to the metal substrates, be electrically conductive, and show chemically inertness. The coefficient of thermal expansion of metals and the coatings should be close to each other to eliminate the formation of micro-pores and micro-cracks in the coating layers due to unequal thermal expansion. Two types of coatings, carbon-based and metal-based coatings have been investigated. Carbon-based coatings include graphite coating, diamond-like coating, and coatings of conductive polymer and organic self-assembled mono-layers. Noble metals, metal nitrides, and metal carbides are some of the metal-based coatings [36-39,41-43].

Show et al. [47-48] studied titanium bipolar plates with electrically conductive amorphous carbon (a-C) coating. The a-C film was deposited on Ti bipolar plates by using radio frequency plasma chemical vapor deposition (RF-plasma CVD) method at different temperatures. At low film growth temperature, the a-C film gave rise to high resistivity, and thus high contact resistance between the interface of bipolar plates and MEA assembly. As a result, the fuel cell output power decreases. At high film growth temperature up to 600 ºC, a film with low electrical resistivity is formed which reduces the contact resistance between the interface of bipolar plates and MEA assembly. Show et al. [47-48] also observed that the power output of the fuel cell increased from 1.3 W for uncoated Ti bipolar plates to 1.8 W with a-C coated Ti bipolar plates. However, these authors did not address the long time durability aspect of the coated bipolar plates.
Fukutsuka et al. [46] examined carbon-coated SUS304 stainless steel bipolar plates. The carbon coating was prepared by plasma-assisted chemical vapor deposition (CVD). It was found by Raman spectroscopy that carbon-coating mainly consisted of $sp^2$-type carbon (conductive carbonaceous materials). The carbon-coated SUS304 showed higher electrical conductivity than uncoated SUS304, indicating no passive film between carbon coating and SUS304 metal. It was found that the corrosion resistance of carbon-coated SUS304 depended on the polishing process of SUS304.

Lee et al. [67] investigated the diamond-like film coated 5052 aluminum alloy bipolar plates, where the coating was deposited by physical vapor deposition (PVD) process. This coated aluminum bipolar plate had better cell performance than graphite bipolar plate at low operating voltages, although fuel cell performance was examined only for a short time.

Conductive polymer coated stainless steel bipolar plates were widely investigated [36,53,56,64]. Joseph et al. [64] coated SS304 electrochemically with conductive polymers derived from polyaniline (PANI) and polypyrrole (PPY) and obtained improved corrosion resistance. However, the contact resistance was found to be relatively high and was attributed to moderate electrical conductivity of the polymer coatings. Lucio Garcia et al. [53] also studied the effects of PPY-coating on SS304 bipolar plates. They found that coating by PPY decreased the corrosion rate by several orders in magnitude within a short period of time. However the protective property of the PPY was found to be lost at longer immersion times.
Wang et al. [36,56] investigated PPY-coated SS316L bipolar plates, and PPY-gold dual layer coated SS316L bipolar plates. Both coatings decreased the corrosion rate of the bipolar plates, although better cell performance was obtained with PPY-gold dual layer coated bipolar plates. The metal ion concentration in solution was found to be less than 10 ppm after 5000h fuel cell operation when PPY-gold dual layer coated SS316L bipolar plates were used.

Much more effort has been directed to metal-based coatings [37-39,41-45,52,54,57,60,63,68-69]. Wind et al. [68] compared the cell performance of uncoated, Au-coated, and low cost material coated SS316L bipolar plates. Results revealed that the SS316L bipolar plates covered with a thin layer of coating gave good cell performance, comparable to that of graphite bipolar plates. It was also found that the layers were stable for at least 1000h.

Wang et al. [43] investigated bipolar plates fabricated from austenite stainless steels (316L, 317L, and 349™). These SS bipolar plates were coated with a thin layer of SnO2-F by low pressure CVD. For 316L and 317L bipolar plates, a SnO2-F coating reduced the interfacial contact resistance, while, for 349™, the coating increased the interfacial contact resistance. Coated 316L showed a steady increase of anodic current in PEM fuel cell environment, indicating this coating is not suitable for 316L. Coated 317L exhibited a stable current, indicating that SnO2-F coated 317L bipolar plates are suitable for PEM fuel cell.

Yang et al. [45] studied the effect of protective Cr-nitride (CrN and CrN2) surface layer by nitridation of Fe-based stainless steel alloys bipolar plates. The Cr-nitride
surface layers exhibited excellent corrosion resistance and low interfacial contact resistance under simulated PEM fuel cell environments.

Cho et al. [63] coated AISI 316 stainless steel bipolar plates with TiN and found that the electrical contact resistance and water contact angle of TiN-coated SS316 were comparable to those of graphite. In addition, the TiN-coated SS316 bipolar plates showed improved initial cell performance. Nitride-coated stainless steel bipolar plates were also developed by Siva et al. [54] and Tian et al. [57]. It was found that nitride-coated stainless steel bipolar plates exhibited low interfacial contact resistance and good corrosion resistance. Brady et al. [74] developed a preferential thermal nitridation process to form pinhole free CrN/Cr$_2$N coating on a model Ni-Cr alloy, which showed excellent corrosion resistance and good contact resistance.

2.2.3 Metal Foam Bipolar plates

As described in the above two sections, metal bipolar plates can be machined or stamped to the desired shape to accommodate the flow channels. However, machining flow channels on the surface of metals is time-consuming and costly. In the case of stamping, the stamping force tolerance is another concern. A better approach to form flow channels in the metals is to use perforated or foamed metals. Usually the foamed materials have up to 50 vol\% voids [4]. The bipolar plate is manufactured by putting two foamed materials, with a thin layer of solid metal between. The pores or voids in the foamed structure form the diffusion paths for gas. The solid thin layer in between two foamed metal pieces separates the fuel and oxidant effectively. One advantage of this
type of bipolar plates is that the metal foam sheets are readily available materials in market [fuel cell systems explained].

Kumar et al. [11,73] investigated three foamed materials, Ni-Cr metal foam (50 PPI), SS316 metal foam (20PPI), and carbon cloth. They found that carbon cloth was not feasible due to high contact pressures which in turn resulted in blockage of the pores, and consequently reduced fuel cell performance. In general, metal foam bipolar plates performed better than conventional metal bipolar plates with machined channel flow field. The Ni-Cr metal foam gave the best fuel cell performance. However, corrosion and corrosion related problems are big issues that need to be addressed for metal foam bipolar plates.

From the brief review presented above, we can see that metal bipolar plates—coated and non-coated—possess the advantages originating from low volume and light weight, good mechanical strength and flexibility of manufacturing. However, the long-term fuel cell performance of metal bipolar plates suffers from corrosion and corrosion related problems. Protective coatings on metallic bipolar plates improve the corrosion resistance and reduce the interfacial contact resistance, and thus to enhance the power output of the fuel cell. However, the coating processes are usually tedious and complicated and increase the cost of the metal bipolar plates significantly. Furthermore, coatings have not been always successful and viable due to occasional pinhole defects. Despite all development activities on metal bipolar plates for vehicle applications, no commercial product is available yet.
Another alternative candidate, polymer composite bipolar plate is under vigorous development and shows great promise for application in PEM fuel cells.

2.3 Polymer Composite Bipolar Plates

Polymer composites offer a more economic alternative route for manufacturing of bipolar plates. First, polymer composites are lightweight and chemically stable to acidic corrosive environment. Second, they can be molded into any shape and size by an array of polymer processing techniques. These attributes led to large scale research activities on polymer composite bipolar plates to replace electro-graphite bipolar plates, especially in PEM fuel cells for portable devices and automobiles.

Despite cost savings and easier manufacturability, polymer composites also have some obstacles to overcome. As is well-known, polymers are insulators. Therefore, high loadings of conductive fillers are necessary to obtain desired electrical conductivity, e.g., to reach the DOE target of 100 S/cm. The loadings are usually much higher than the percolation threshold concentration, and in some cases even approach and surpass the critical pigment volume concentration (CPVC). Such high filler loadings result in poor mechanical properties and poor gas barrier properties due to generation of voids at such high filler loadings. Consequently, the requirements of high electrical conductivity, good gas barrier properties, and strong mechanical properties for bipolar plates contradict each other. Many research groups have followed specific strategies to solve this contradiction. A brief review on the development of polymer composite bipolar plates is presented below.
Polymer composites that offer desired electrical conductivity can be categorized as metal-based and carbon-based composites, depending on the types of filler particles used. A majority of research activities in this area was focused on carbon-based polymer composites as carbon fillers provide lower density, are available in large varieties, and can be tailored to obtain desired particle size and morphology. On the contrary, the metal particles themselves offer higher electrical conductivities than carbon fillers, but they have higher density, and are prone to corrosion in highly acidic environment in PEM fuel cells. Corrosion, in turn, reduces the electrical conductivity. In view of this, the interface between metal particles and polymer matrix should be strong to prevent penetration of acid solution to the interface between polymer and metal particles. Such penetration of acid solution causes corrosion of metal particles and results in a drop of electrical conductivity.

2.3.1 Metal-based Polymer Composite Bipolar Plates

In this section, several studies on metal-based polymer composite bipolar plates are briefly described first. Researchers at Los Alamos National Laboratory (LANL) [71] developed a polymer composite bipolar plate based on porous graphite, polycarbonate, and stainless steel. In this case, graphite and stainless steel particles provided high electrical conductivity while good gas impermeability was derived from the stainless steel and polycarbonate. Furthermore, stainless steel provided rigidity to the structure while the graphite resisted corrosion. The polycarbonate contributed to chemical resistance and easy and rapid manufacturability.
Zhu et al. [75] reported a metal-based polymer composite bipolar plate using polyvinylidene fluoride (PVDF) as the matrix and titanium silicon carbide (Ti$_3$SiC$_2$) as the conductive filler. These authors obtained electrical conductivity of 29 S/cm with 80 wt% filler content, and a flexural strength of 25 MPa. Although these properties did not meet the DOE targets, they were comparable to some commercial polymer composite bipolar plates.

Kuo et al. [76] developed nylon 6—SS316L fiber composite bipolar plates using injection molding process. Their results showed that these bipolar plates are chemically and electrochemically stable.

2.3.2 Carbon-based Polymer Composite Bipolar Plates

Carbon-based composite bipolar plates have been more extensively studied in conjunction with both thermoplastic and thermosetting resins with or without continuous fiber reinforcement. Thermoplastic resins including polypropylene (PP), polyethylene (PE), poly(vinylidene fluoride) (PVDF), poly(phenyl sulphone) (PPS), nylon 6 (PA6), polyethylene terephthalate (PET), PET /PVDF blend, poly(arylene disulfide), polyether sulphone (PES), and liquid crystalline polymers, have been studied [6,34,78-86]. Thermosetting resins such as phenolic resins, epoxy resins, and vinyl esters have been considered [78-89]. An array of conductive fillers has been used, e.g., expanded graphite, natural graphite, synthetic graphite, carbon black, carbon nanotube and nanofiber, and meso-carbon microbeads [75-89].
2.3.2.1 Carbon/Carbon Composite Bipolar Plates

Carbon/carbon composite bipolar plate technology has been developed by Oak Ridge National Laboratory (ORNL) [82,89], whereby composite parts were made from carbon and a graphitizable phenolic resin by injection molding. The graphitization process was achieved by heating the part to over 2500 ºC. However, non-uniform heating may cause warpage and dimensional non-uniformity, obviating plates with thickness less than a few mm. First, preforms of carbon fiber/phenolic resin composite bipolar plate were slurry molded for PEMFC. Second, composites were compression molded into the desired shape after filtering and drying the slurry. Third, the resin was graphitized by pyrolysis. The phenolic resin burnt during graphitization and resulted porous and brittle composite structures. A chemical vapor infiltration process was used to deposit a layer of carbon on the surface of the composites to fill the voids and to improve the gas barrier properties of the composites.

This technology has been scaled up by Porvair Fuel Cell Technology [89]. The performance characteristics of the carbon/carbon composite bipolar plates manufactured by Porvair Fuel Cell Technology posses high electrical conductivity of 200-300 S/cm, low density (~ 0.96g/cm³), good corrosion resistance, high temperature performance, and strong mechanical properties with biaxial flexural strength of 175 MPa. Although carbon/carbon composite bipolar plates have many advantages, the manufacturing procedure is complicated and costly.
2.3.2.2 Injection Molded Polymer Composite Bipolar Plates

The injection molding method has been successful for production of carbon-filled polymer composites. A composite compound or blend is prepared in a kneader, internal mixer, or an extruder. Second, bipolar plates from injection molding are fabricated directly from the blend with integrated gas and cooling channels molded simultaneously or further machined. Heinzel et al. [21] developed low cost carbon-based thermoplastic bipolar plates by injection molding. The conductivities of these composites ranged from 5-150 S/cm. Mighri et al. [6] also used injection molding method to prepare composite bipolar plates from PP and PPS filled with up to 60 wt% of graphite, carbon black, and carbon fiber. The highest conductivity of these composites was approximately 17 S/cm. Chen et al. [78] developed PA6/CB composite bipolar plates by injection molding process with conductivity of 12 S/cm with CB loading of 35 wt%. They found that the conductivity decreased dramatically when the composites were heated and the materials turned into an insulator at the temperatures of 80-90 ºC. However, typical PEM fuel cell operating temperatures are also 80-90 ºC. Wu et al. [34] developed a triple-continuous structure by injection molding of CNT filled PET/PVDF blend composites. The electrical conductivity was less than 1 S/cm with 6 wt% CNT, but strong mechanical properties were obtained for these composites.

In summary, we see that the injection molding process has its advantages, such as automated production, short cycle time, and accurate size. However, it also has obvious disadvantages, such as excessive mold wear for the high viscosity of the materials, limited flow ability, and poor electrical conductivity of the composites due to flow
induced orientation of the continuous fillers. Even the best of these bipolar plates offer low electrical conductivity and the scope of their applications in fuel cells is likely to be limited.

2.3.2.3 Compression Molded Polymer Composite Bipolar Plates

A commonly used and relatively successful method for mass-production of polymer composite bipolar plates is compression molding. Most of the compression molding processes used in literature starts with a powder compound or blend prepared in a kneader or an extruder at proper temperatures from a polymer binder resin and conductive filler particles. This powder is then fed into a heated mold in which the compound is allowed to flow, fill the mold cavity, and then compression molded directly into bipolar plates with gas channels stamped or further machined. If the binder is a thermosetting resin, sufficient chemical conversion of the binder must occur before the plate can be removed from the mold, which in turn dictates the molding time. In case of thermoplastic binder, the mold has to be cooled to a temperature below the melting temperature of the binder before the plate can be removed. Typical cycle times of 15-20 minutes for thermoplastic compounds have been reported.

One of the advantages of the compression molding process is that the powder compounds do not need to be very fluid. This allows much higher carbon-based filler loading in the composites. Consequently, adequate conductivity can be achieved. The shapes produced may not be very intricate. For example the cooling channels in the plates may not be made easily in one piece. However, these problems can be solved by
making the plate in two pieces. The reactant gas flow channels are molded on the front, while the cooling air channels are molded on the back. A complete bipolar plate is then made by stacking the two pieces back to back.

Various thermoplastic and thermosetting resins are used to prepare polymer composite bipolar plates by compression molding process, filled with different types and grades of conductive carbon fillers. Among these bipolar plates, expanded graphite filled polymer composites hold the great promise for commercial applications as bipolar plates in PEM fuel cells. A brief review of polymer composite bipolar plates developed for PEM fuel cells is described below.

Blunk et al. [27] developed a series of PP/graphite/CF and PVE/graphite/CF composite bipolar plates by a compression molding process. The carbon fiber alignment and conductive-tie layer technique were used to achieve high electrical conductivity in in-plane and through-plane directions, and also to reduce the contact resistance and interfacial area specific resistance. The highest in-plane electrical conductivity of ~250 S/cm was obtained for compression molded PVE/CF (15/85) composites, and 6 S/cm through-plane conductivity. The area specific resistance of the plate was 3.4 mΩ·cm². Although a significant improvement in electrical conductivity and reduction in interfacial area specific resistance were realized, very high filler loadings were still needed to meet conductivity targets.

Wolf et al. [83] developed a liquid crystal polymer composite bipolar plate by compression molding. The conductive fillers were a combination of carbon blacks and carbon fibers, and the loading level in the composite was below 40 vol.%. However,
conductivity less than 6 S/cm was achieved although the bipolar plate had excellent gas barrier properties and mechanical properties. Dweiri et al. [84] studied PP/graphite/CB composite bipolar plates by compression molding process. The electrical conductivity obtained was only around 7 S/cm even at graphite loading as high as 80 wt%. Similar work was also done by Yin et al. [85]. Very high loading of 85 wt% graphite power was required to reach DOE target of 100 S/cm.

From the above literature review, we can see that composites filled with either carbon black, carbon fiber, unexpanded graphite or their combinations, have conductivity still much lower than the DOE target of 100 S/cm at filler loading levels which can deliver good mechanical and gas barrier properties to the composites. Alternative conductive fillers or filler combinations need to be found to obtain high electrical conductivity and at the same time achieve good mechanical and gas barrier properties. Expanded graphite is a great choice. Recent literature shows significant progress in graphite-based composite bipolar plates with useful contributions of light-weight and low cost with desired properties [71]. Polymer composite bipolar plates are now commercially available from such suppliers as DuPont, H2 Economy, ICM Plastics, NedStack, to name a few. This shows that the technology of polymer composite bipolar plates is maturing [71].

Huang et al. [82] developed polyester/graphite/glass fiber polymer composite bipolar plates by compression molding process with a conductive-tie layer (CTL) on top of the plate surface. This plate achieved high bulk electrical conductivity larger than 200 S/cm at 65 wt% graphite loading level. The plate also possessed strong mechanical
properties. They suggested that the composites were suitable for bipolar plate application in PEM fuel cell.

Heo et al. [86] developed expanded graphite filled phenolic resin composite bipolar plates by compression molding process. High electrical conductivity of 250 S/cm was achieved, and at the same time high flexural strength of 50 MPa was obtained. Both of them met the DOE targets.

Xiao et al. [35] studied poly(arylene disulfide)/graphite nanosheet composites prepared by in-situ ring opening polymerization of cyclic arylene disulfide oligomers with dispersed nano-graphite (NanoG). As a comparison, they also investigated the corresponding expanded graphite (EG) composites. Results revealed that both EG and NanoG composites achieved high electrical conductivity, higher than 100 S/cm at the filler loadings as low as 50 wt%. The contact resistance was fairly low for both EG and NanoG composites.

Hentall et al. [87] selected exfoliated graphite Grafoil™ as bipolar plates for PEM fuel cells. They revealed that Grafoil™ offered significant cell performance gains over standard graphitic materials, probably because of its compressibility which enabled it to form an intimate contact with the electrodes, thus minimizing the interfacial contact resistance.

Barbir et al. [9] in Energy Partners (EP) developed molded graphite composite bipolar plates with the model NG2000 comprising a ~ 300 cm² flow field. The in-plane and through-plane electrical conductivities, and contact resistance were measured by a 4-point probe method. The characterization procedures were given in detail in this paper.
Their epoxy/graphite composite bipolar plates achieved bulk electrical conductivity of ~345 S/cm. The contact resistance was extremely low, about 0.87 mΩ·cm², comparable to 0.42 mΩ·cm² of electro-graphite bipolar plates. The cell performance was fairly good. The manufacture cost was about $145/kW, although the cost of the material was only $8.5/kW. Development of a manufacturing process for mass production was necessary to target manufacturing cost of $10/kW.

These data showed that expanded graphite nanocomposites are promising candidate for application as bipolar plates in PEM fuel cells. Currently, this type of polymer composite bipolar plates brings considerable advantages over other types of bipolar plates. Analysis of literature data shows expanded graphite composites have achieved fairly good electrical, mechanical and gas barrier properties. Easy and rapid manufacturing technology of expanded graphite is readily available in industry, such as injection molding process, in-situ polymerization process, and more promisingly compression molding processes. Lightweight, low volume and low cost can be achieved once this technology is scaled up to mass production stage. The technology of development of expanded graphite polymer composite bipolar plates is really maturing. Commercial expanded graphite composite bipolar plates beginning to appear in market and are mass manufactured in industry. However, more research is required to further improve the material properties, and thus the cell performance, such as thermal conductivity, chemical and thermal stability. Long-term reliability and durability of the composites in PEM fuel cell service conditions are needed to be investigated. Careful
characterization methods are needed before confidently claiming that the expanded graphite polymer composites can be used as bipolar plates in PEM fuel cells.

2.3.3 Improvement of Electrical Properties

There are several techniques developed by different authors to improve the electrical conductivity.

1. Rectification of the bipolar plate surface

The injection and compression molding methods alter the surface electrical conductivity. In view of this, several methods have been used in literature for post-molding rectification of the bipolar plates. Blunk et al. [27] and Huneault et al. [19] removed any insulating polymer-rich layer or polymer skin at the plate surface to expose the conductive filler. Most composite plates require a machining process to remove the insulating polymer skin. Huneault et al. [19] used 120-grit silicon carbide to remove the insulating polymer layer. This surface texturing is especially necessary for injection molded polymer composite bipolar plates.

For compression molded expanded graphite polymer composite bipolar plates, the composition of the surface and the bulk material is relatively uniform. The electrical conductivity is already high enough when proper preparation procedures. Therefore surface rectification is not needed.
2. Use of Conductive-tie Layer (CTL)

In the PEM fuel cell, bipolar plates are assembled together with MEA to form an integrated stack. In this assembly, the bipolar plates contact with a gas diffusion layer. It is known that electrons need to pass from the anode to the cathode of the stack through the bipolar plates, MEA, and gas diffusion layers. Thus the interfacial contact resistance (CR) should be low to avoid the voltage losses. Usually, the interfacial contact resistance between the bipolar plates and the gas diffusion layers is significantly high and contribute more to the total plate resistance compared to that of the bulk resistance of the materials, especially at low compression pressures. The origin of contact resistance is explained in Figure 2.1. It depends on many factors, such as bulk conductivity, plate flatness and roughness, assembly pressure, and surface composition of the materials. One way to reduce the contact resistance is to put a highly conductive-tie layer (CTL) on the surface of the plates to change the surface composition, surface flatness, and roughness.

![Figure 2.1 Schematic explanation of contact resistance.](image)

The CTL can be a noble metal such as silver, gold, and nickel, or a graphite layer. Usually, the silver layer is applied by using a physical vapor deposition process. Gold is preferred since it is stable under PEM fuel cell operating conditions. The graphite layer is
applied by using a high pressure 400-550 kPa blasting or impingement process in which graphite are sprayed at high velocities and embedded onto the plate surface.

Oh et al. [79] developed a polymer composite bipolar plate by injection molding process, followed by electroplating of noble metals such as Ni and /or Pd-Ni on the surface of the plates. This plate showed extremely high bulk electrical conductivity of $4.4 \times 10^3$ S/cm. The interfacial surface area resistance was $1.87 \text{ m}\Omega\cdot\text{cm}^2$. This result was very doubtful because CTL technique can only increase the surface electrical conductivity, and the contact resistance. It is not expected to enhance the through-plane conductivity of the composites because of the lack of conductive networks in the bulk of the materials.

Cunningham et al. [80-81] developed graphite filled bipolar plates. A laminate of PVDF/graphite composite with high filler loading was added onto composite with lower filler loading plate to reduce the surface resistance and the contact resistance. The plate with lower filler loading in the middle contributed to good gas barrier properties and mechanical properties.

In summary, the CTL technique is an effective way to improve surface electrical conductivity and to reduce contact resistance. CTL can also rectify the surface flatness and roughness of the polymer composite bipolar plates, resulting in better contact and sealing of the PEM fuel cell stack. However, the CTL technique can not improve the bulk electrical conductivity and the through-plane conductivity. It also can not reduce the interfacial surface area resistance due to lack of conductive networks in the bulk of the composites.
3. Orientation of the conductive fibers to improve through-plane conductivity

In order to maximize the through-plane electrical conductivity of the plate, it is important to optimize filler micro-morphology and dispersion in the polymer matrix, and plate geometries. Blunk et al. [27] used a mold in injection molding to get a significant degree of alignment of the conductive carbon fiber at the top and the bottom land regions of the plate, especially where high conductivity is needed.

2.4 Summary of the Literature Review of Bipolar Plates

Recent literature shows some interesting progress in graphite-polymer composites. Middelman et al. [26] reported the development of conductive composite material with excellent properties and a process for large scale production of bipolar plates. Cho et al. [13] have developed carbon composite bipolar plates with long term performances comparable to graphite. Injection molding of low cost bipolar plates based on a thermoplastic and a carbon compound was reported by Heinzel et al. [21]. Kuan et al. [20] have developed vinyl ester-graphite composite bipolar plates by a bulk-molding process with properties similar to graphite plates.

Polymer-graphite composite bipolar plates are now available in the market and sold by companies, such as DuPont, H2Economy, ICM Plastics, NedStack, etc, which shows that the technology is rapidly maturing [71]. However, the electrical conductivities of these composites are still below the DOE target of 100 S/cm. For example, Middelman et al. [26] reported about 20 S/cm. T8 series bipolar plates of DuPont have a bulk
conductivity of 25-33 S/cm. Recent interest has been on low-cost production of bipolar plates with consistent and acceptable physical and chemical properties.

There is significant ongoing research on both coated metal bipolar plates and polymer-graphite composite bipolar plates. Even though there has been significant progress in both materials, they have yet to attain the long-term reliability and power density comparable to those of non-porous graphite. Expanded graphite composites hold the great promise for application as bipolar plates in PEM fuel cells. Economies, manufacturability, and long-term reliability will ultimately decide the fate of the materials.

2.5 Intrinsic Electrical Conductive Polymers and Polymer Composites

For conductive polymer composites, in order to obtain high conductivity, high loading level of conductive fillers is necessary to achieve the DOE targets. High filler loading level achieves excellent electrical properties and thermal conductivity. However, high filler loading level also results in poor mechanical properties and gas barrier properties. Intrinsic conductive polymers have high electrical conductivity when doped, and strong mechanical and good gas barrier properties. The possibility of intrinsic conductive polymers as bipolar plates was evaluated by researchers. A brief analysis of the properties of the existing intrinsic conductive polymers and possibility of being manufactured as bipolar plates is described below.
2.5.1 Intrinsic Conductive Polymers

In 1977, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa [90] discovered that polyacetylene (PA), a conjugated organic polymer, could obtain high levels of electrical conductivity when oxidized by halogen, so-called “doping”. The “doped” form of PA had a conductivity of $10^5$ S/m, which was higher than that of any previously known polymer. As a comparison, Teflon has a conductivity of $10^{-16}$ S/m and silver and copper $10^8$ S/m.

A key property of PA is the presence of conjugated double bonds along the backbone of the polymer chain. In conjugation, the bonds between the carbon atoms are alternately single and double. Every bond contains a localised “sigma” ($\sigma$) bond which forms a strong chemical bond. Every double bond contains a less strongly localised “pi” ($\pi$) bond which is weaker. However, conjugation is not enough to make the polymer conductive because orbitals are filled—no conduction because no “holes”. Therefore, doping of the conjugated polymers is necessary to gain conductivity.

Charge transport in doped conductive polymers is believed to occur through a combination of two primary mechanisms, propagation of charge along the polymer chain, and hopping between neighboring chains. High level of doping is necessary for high charge carrier mobility. Consequently, charge carrier can hop between different polymer chains, named an intermolecular charge transfer reaction. Because the interchain electron transfer interactions of conjugated polymers are relatively strong compared with the Van der waals and hydrogen bonding interchain interactions typical of saturated polymers,
Conductive polymers tend to be insoluble and infusible. Thus the processability of conductive polymers is proven to be a difficult problem.

Currently, the conductive polymer family was quickly broadened because of a significant research thrust initiated by the discovery of conductive PA. Conductive polymers include a number of conjugated hydrocarbon and aromatic heterocyclic polymers, such as poly(p-phenylene) PPP), poly((p-phenylene vinylene) (PPV), poly((p-phenylene sulfide) (PPS), polyaniline (PANI), polypyrrole (PPy), polythiophene (PT), and so on. Today conductive plastics are being developed for many uses, such as in corrosion inhibitors, compact capacitors, antistatic coating, electromagnetic shielding, and in “smart” windows, electroluminescent walls, and so on.

As is known, bipolar plates are exposed to high humidity, high temperatures, low pH environment with hydrogen and oxygen flow through them. Conductive polymers must demonstrate good solution or melt processability, environmental stability, mechanical integrity, in addition to high conductivity, for them to be used as bipolar plates in PEM fuel cells. Despite significant progress in the development of conductive polymers, none of them possess these desired properties. Most conductive polymers are insoluble and infusible. The processability is very poor. It is very difficult to manipulate conductive polymers to the desired shape of bipolar plates. Conductive polymers are environmental unstable and very reactive, even sensitive to moisture and air, because the dopants are very sensitive to oxidants and reductants. The conductivity changes significantly when exposed to different environments. In PEM fuel cell service conditions, the conductivity will be lost. Usually, the mechanical properties of conductive polymers
are also poor due to their rigidity and brittleness. In addition, they are prone to thermal degradation and are very costly.

Rao et al. [91] synthesized doped polyaniline (PANI)–poly(vinyl alcohol) (PVA) blends of different compositions (10, 30, 50, and 70 w/w). The blends showed relatively improved mechanical strengths but had lower degradation temperatures than the PANI salt and displayed conductivities as high as $10^{-2}$ to $10^{-1}$ S/cm.

Minto et al. [92] developed doped PANI/poly(methyl methacrylate) (PMMA) blends. The blend showed conductivity less than 10 S/cm with 20 wt% of PANI.

Banerjee et al. [93] developed polyaniline (PANI) nanoparticle filled poly(vinyl alcohol) (PVA) composites with low percolation threshold concentration of about 1 wt% of PANI. Electrical conductivity of about 1 S/cm was obtained for PVA/PANI blends with 9 wt% of PANI. Other polymers could also be used as matrix such as conventional polymers, poly(vinyl chloride) (PVC), polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(vinyl acetate) (PVAc).

Nano-sized polyaniline (PANI) particles dispersed in aqueous solution were prepared by Cho et al. [94] using both poly(vinyl alcohol) (PVA) and poly(styrene sulfonic acid) (PSSA) as polymeric stabilizers. The blends were cast into films. The conductivity was less than 0.1 S/cm.

Annala et al. [95] developed polyethylene/polyaniline (PE/PANI) blends. Plasticized PANI/camphorsulfonic acid (CSA) complexes and and –OH functionalized polyethylene (PE) were used. The hydrogen bonds between the PANI complex and the functionalized metallocene PE used as compatibilizer compensated the unfavorable
viscosities of the components. Mechanical properties of PE/PANI blends were improved, and electrical conductivity of the blends is less than 1 S/cm.

Some researchers investigated the conductive polymer powder filled polymer composites or polymer blends [91-95] as shown above. These materials are expensive, and have very low electrical conductivity, poor mechanical properties and low glass transition temperatures. From the analysis of the properties of the conductive polymers and their derived polymer blends or composites, we can conclude that the current existed conductive polymers are not suitable for application as bipolar plates in PEM fuel cells.

2.5.2 Conductive Polymer Composites

Compared to intrinsic conductive polymers, electrical conductive polymer composites is a rather easy way to obtain electrical conductive polymeric materials. Proper conductive filler in the form of power, flakes, fibers, or layered and network structures is incorporated in a polymer matrix through melting or solution mixing. The dispersed materials are then molded to different parts by using readily available processing methods, such as injection molding, compression molding, extrusion, and so on. Electrical conductive polymer composites served as an inexpensive approach to obtain conductive materials for applications where metals are not suitable. The conductivity and mechanical properties can be easily tailored by incorporation of different types, grades, amount of conductive fillers. The choices of conductive fillers are very wide, such as metal particles, carbon black, carbon fiber, carbon nanotube, and graphite. The undeniable benefits of conductive composites over intrinsic conductive
polymers boost a significant research thrust in development of different conductive composites. Conductive polymer composites are widely used for a large range of applications.

2.6 Graphite-related Conductive Fillers

In order to understand the basic structure and properties of graphite, let us first review the structure and properties of the various forms of carbon family. Carbon is the lightest element in Group IV in the periodic table with some unique properties. At ambient conditions, $sp^2$ bonded graphite (Fig. 2.2 a) [96] is the ground state phase of carbon At higher temperatures and pressures, $sp^3$ bonded cubic diamond (Fig.2.2 b) [96] is a stable form, while other regions show stability ranges for hexagonal diamond, hexagonal carbines, and liquid carbon. In addition to the bulk phases featured in the carbon phase, much attention has recently been focused on the small carbon clusters, since the discovery of fullerenes in 1985 by Kroto et al. [96] and of carbon nanotubes in 1991 by Iijima [96]. The physical reason these nanostructures form is that a graphene layer—defined as a single layer of 3D graphite—of finite size has many edge atoms with dangling bonds, and these dangling bonds correspond to high energy states. Therefore, the total energy of a small number (30-100) of carbon atoms is reduced by eliminating the dangling bonds, even at the expense of increasing the strain energy, thereby promoting the formation of closed cage fullerene molecules, the most stable being $C_{60}$ (Fig 2.2 c). Under slightly different growth conditions, carbon nanotubes (Fig 2.2 d) are found. The structure of a variety of forms of carbon is shown in Fig 2.2 [96].
a. Graphite                                           b. Diamond

c. Fullerene C\textsubscript{60}                 Schematic model for a fullerene dimer
d. A model for a carbon nanotube.       e. Schematic model for the microstructure of activated carbon fibers

f. Schematic presentation of the turbostratic stacking of graphene planes in carbons

Figure 2.2 Schematic representation of graphite-related materials [96].
A carbon nanotube (CNT) can be seen as a cylinder rolled from a graphene sheet, capped at both ends by hemispheres of fullerenes. The high curvature of the graphene sheets increases the total energy of the tubules per carbon atom, but this is more stable due to lowering the energy as dangling bonds at the edge of the graphene sheet are eliminated. Interest in graphitic nanostructures and the new capabilities of producing thin graphite films have stimulated the study of the electronic structure of graphene ribbons. Carbon nanotube research is probably the most active current research field in carbon science. The fundamental carbon nanotube is a single wall structure which has three basic geometries of edge states as shown in Figure.2.3 [96]—graphene ribbons terminated by armchair edges (Fig.2.3 a), by zigzag edges (Fig.2.3 b) and by chiral edges (Fig 2.3 c).

Figure 2.3 Schematic models for (a) armchair; (b) zigzag, and (c) chiral single-wall carbon nanotubes [96].
Carbon fibers (CF) (Fig. 2.2 e) represent an important class of graphite-related materials. There are several precursors that can be used to synthesize carbon fibers, but each produces fibers with different cross-sectional morphologies. The preferred orientation of the fiber axes for all carbon fibers is close to an in-plane direction of a graphene layer. This fact accounts for the high mechanical strength of these fibers. Most commercial carbon fibers exploit the great strength of carbon materials under tension, which is achieved when the carbon fibers are prepared from a polymer precursor, such as polyacrylonitrile (PAN), while fibers prepared from a mesophase pitch liquid crystal precursor are used for high modulus (stiffness) application.

Many commercial carbon materials, such as carbon fibers and glassy carbon, contain carbon networks that can be approximated by graphene ribbons. Studies of edge states might help the tailoring of commercial carbons to possess certain desired properties, such as the properties of porous carbons which have a very high density of edge states. Graphite edge sites are more reactive than the bulk sites because of the availability of dangling bonds. Thus, carbon clusters have been investigated in terms of their potential for the uptake of active species which could be of interest for many applications such as carbon batteries.

The pure graphite structure shown in Figure 2.4 consists of hexagonal net planes of carbon stacked along the c-axis in a staggered array usually denoted as ABAB… [97]. While this is the normal graphite stacking, ABCA… or ABAC…, etc. are possible sequences and the commonly observed stacking faults in graphite are a reflection of these
discrete stacking alternatives. For single crystals, there are natural graphite crystals and synthetic graphite crystals of various degrees of perfection.

![Graphite lattice showing the ABAB stacking of carbon layers](image)

Figure 2.4 Graphite lattice showing the ABAB stacking of carbon layers [97].

Typical carbon blacks are composed of nearly pure carbon in colloidal entities of aciniform morphology. The term aciniform, meaning “clustered like grapes”, refers to the characteristic appearance of the colloidal entities composed of spheroidal particles fused together in clusters of branched, irregular shape as presented in Figure 2.6 [98-99]. The entities are generally called aggregates. Within each aggregate, the carbon atoms are arranged in imperfect graphite layers. The arrangement of carbon atoms and layers is referred to as microstructure. The layers are arranged more or less concentrically within each particle or growth center, with a fair degree of parallelism between adjacent layers in small regions or crystallites. The layers are continuous from one particle to the next within the aggregate.
A special grade of highly conductive carbon black, Ketjenblack EC300J and EC600JD are composed of aggregates exhibiting extreme porosity. Surface area of Ketjenblack EC measured by adsorption of nitrogen is 929 m$^2$/g, much higher than most grades of furnace blacks of surface area below about 130 m$^2$/g [98]. The specific surface areas are shown in Table 2.1. Ketjenblack EC also owes its ultrahigh conductivity to the highly branched and fibrillous structures. The distribution of particle and aggregate size is exceptionally broad, which may also contribute to strong network formation and thus to high conductivity. The primary particle size is less than 30 µm, and the size of the aggregate is about 100-300 nm [98].

Table 2.1 Specific surface area of typical conductive carbon blacks [98].

<table>
<thead>
<tr>
<th>Carbon Black</th>
<th>Surface area (m$^2$/g)</th>
<th>DBPA (cm$^2$/100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$N_2$</td>
<td>CTAB</td>
</tr>
<tr>
<td>Vulcan XC-72</td>
<td>180</td>
<td>86</td>
</tr>
<tr>
<td>Acetylene</td>
<td>70</td>
<td>78</td>
</tr>
<tr>
<td>Ketjenblack EC</td>
<td>929</td>
<td>480</td>
</tr>
</tbody>
</table>

Proper dispersion is essential because in the dry state, carbon black aggregates are always agglomerated or reversibly associated with many other aggregates. It is essential to separate the individual aggregates from each other without fracturing them.

The melt mixing process customarily used to produce good dispersion of carbon black in a polymer matrix generally leads to some fracture of carbon black aggregates so that the aggregates existing in the composite are smaller than in the dry states before
mixing. In composites exhibiting high electrical conductivity such as reinforced rubber, the aggregates are in extensive contact (or near contact) with each other. The breakdown of carbon black aggregates occurs mainly at the start of the mixing, and is nearly completed long before the black is well dispersed as judged by disappearance of agglomerates.

2.7 Introduction of Epoxy Resins

Epoxy resins have been the most important class of thermosetting resins in industry with applications as coating, composite matrix, potting compounds, encapsulants, structural adhesives, and many others. The versatility of applications are attributed to processability, low cost, high resistance to corrosion, excellent mechanical and thermal properties, low shrinkage on curing.

Nevertheless, the most commonly used epoxy resins, such as diglycidyl ether of bisphenol A (DGEBA) and their modified forms after curing with conventional curatives offer inadequate dimensional stability, high water uptake, and unacceptable dielectric properties for many advanced material applications. The development of specialty curatives such as aromatic diamines contributes positively to the improvement of the performance of epoxy resins [100].

The glycidyl groups in an aromatic epoxy resin are flexible segments that reduce the viscosity of the resin and enhance the processability. Unfortunately, they also decrease the heat resistance of the cured epoxy resin. The aliphatic linkages in glycidyl groups are the source for early thermal and thermooxidative degradation of a cured epoxy.
system. Multiple functionality and low molecular weight of epoxy to promote high cross-linking density and rigid structures between two glycidyl groups are key solutions to the improvement of thermal and mechanical properties of the cured epoxy resins. Undesirably, the rigid structures also drastically reduce the processability of a resin due to solubility reduction in common solvent and viscosity increases.

Epoxy resins contain strained three-membered epoxide rings and are quite reactive towards various reactants and cross-linking agents. The properties of the final thermoset depend not only on the structure of the epoxy resins but also on the type and the amount of the curing agents. The curing speed of an epoxy system is controlled by the curing process, the type and concentration of catalyst, and the chemistry of polymerization. The position of the epoxide rings is an additional important factor in the determination of epoxy reactivity.

Basically the epoxy group can be homo-polymerized to produce polyether linkages by three different mechanisms: anionic (Lewis base catalyzed), cationic (Lewis acid catalyzed), and coordination polymerizations. The third actually is a combined feature of the first two, since it involves coordination of the oxygen atom in monomer at a Lewis acid catalyst site, followed by attack on the thus-activated monomer by an alkoxide already present in the molecule. The polymerizations involve three steps: initiation, propagation, and termination. The organic bases, such as tertiary amines, are typical Lewis bases suitable for curing of epoxy resins. The most popular Lewis acids for curing by cationic mechanism of epoxy resins are BF₃ complexes. Metallic alkoxides are useful to cure epoxy resins through coordination mechanisms [100].
In addition to chain polymerization initiated by acid, base, and coordinating compounds, stepwise-addition polymerizations of epoxy resins by primary and secondary polyamines, polythiols, polycarboxylic acids, carboxylic anhydrides, and polyphenols are useful in developing epoxy formulations for various applications. These reactions can also be catalyzed by the addition of an acidic or a basic catalyst. The ratio of the curing agent to the epoxy resin becomes a very important factor in deciding the final material performance.

2.8 Current Work on Expanded Graphite Composites

Conductive polymer composites have attracted much attention mainly because of their numerous applications as antistatic materials, electromagnetic shielding materials, conductive films, conductive coatings, and phase-transfer catalysis material. The fillers usually used are metal powder, carbon black, carbon nanotube and nanofiber, and graphite. Many factors contribute to the conductivity of the composites, such as the characteristics of fillers and polymers, diameter and structure of fillers, concentration of fillers, states of dispersion, processing methods, processing temperature, and processing pressure. The conductive composites are characterized by a percolation threshold or a critical value at which the conductivity starts to increase as a function of filler content. However, the mechanical properties decrease drastically at high filler contents, typically at greater than 15 wt %. Therefore, much attention has been centered on the preparation of conducting composites with the objective of achieving a low percolation threshold [30-42].
Expanded graphite (EG) is more efficient than carbon blacks in producing electrically conductive polymer composites. EG has a large specific surface area, a unique layered nano-structure, high adsorption capacity, and large occluded volume. The naturally occurring graphite has strong affinity for non-polar molecules. During the oxidation process, however, the surface becomes polar as such functional groups, -OH and -COOH are formed at the surface of the graphite. Consequently, EG can also adsorb polar molecules. Moreover, it has excellent thermal conductivity of about 600 W/m/k and relatively high electrical conductivity of the order of $10^5$ S/cm at room temperature [101-103].

The design and manufacture of lightweight polymer composites with high electrical conductivity have been a research focus in recent years. Zheng et al. [104] investigated expanded graphite/polymer composites prepared by in situ polymerization. Poly(styrene-co-acrylonitrile)/expanded graphite composite sheets with very low in-plane resistivity $\sim 8.5 \times 10^{-3} \ \Omega \cdot \text{cm}$ and through-plane resistivity $\sim 1.2 \times 10^{-2} \ \Omega \cdot \text{cm}$ have been prepared. The expanded graphite was made by oxidation of the natural graphite flakes, followed by thermal expansion at 600 ºC. A closer inspection of the optical microscopy (OM) images of PSAN/EG composites was conducted by Zheng et al. [104] at higher magnification. The OM images show that all the graphite layers are well-connected. They observed that EG formed a network throughout the entire composite, in other words, the composite has a graphite-interpenetrating network structure. To confirm the network structure established with the OM investigations, a polished surface was examined by SEM after THF etching to remove the PSAN to expose the graphite phase. They
observed that the honeycomb structure of graphite was clearly remained and the diamond shaped pores are preserved. Thus the network structure of the composites is confirmed. A lightweight, highly conductive polymer composite based on PSAN and 11 wt% EG has been successfully made [104]. The oxidation and expansion conditions for EG manufacture are critical, and must be carefully controlled in order to avoid excessive oxidation. An EG with low expansion ratio (~30) and a honeycomb structure was produced. The in situ polymerization of the styrene and acrylonitrile monomers inside the diamond-shape pores of the EG produced a PSAN/EG composite with a well connected graphite network throughout the entire PSAN matrix. XRD and TEM results show that the graphite network possesses the same crystal structure as that of NG. Both the in-plane and through-thickness electrical conductivities of the PSAN/EG composite are very high. Especially, the through-thickness electrical conductivity of the composite is even slightly better than that of the natural graphite (NG), as shown in Table 2.2. The excellent electrical conductivity of the composite is attributed to the graphite network throughout the entire composite.

Table 2.2 Resistivities of NG, compressed EG and PSAN/EG composites at room temperatures [104].

<table>
<thead>
<tr>
<th>Directions</th>
<th>NG (Ω·cm)</th>
<th>EG (Ω·cm)</th>
<th>Composites (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Through-plane</td>
<td>$1.2 \times 10^{-1}$</td>
<td>$1.1 \times 10^{-1}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>In-plane</td>
<td>$4.0 \times 10^{-5}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$8.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Wang et al. [105] prepared and characterized polystyrene (PS)/graphite composite prepared by cationic grafting polymerization. The electrical conductivity increased from $10^{-16}$ S/cm for unfilled PS to $10^{-2}$ S/cm of PS/EG composite at graphite content of 13.4 wt%. The percolation threshold concentration was about 2.6 wt% of EG. The conductivity of PS/EG composite was found to be better than that of the NG powder/polymer composite at the same graphite content of 13.4 wt%. Poor electrical conductivity of NG filled composites was attributed to dense structures and poor dispersion of NG.

High performance antistatic and/or electrically conductive materials, used for casting and coating applications, are usually designed by combining the thermosetting resins and efficient electrically conductive fillers. A few basic polymeric matrices have been used for casting—acrylics, polyesters, polyurethanes (PU), and epoxies. Graphite is frequently used as electrically conductive filler due to its moderate cost and good conductivity. It also offers improvements in mechanical properties, as well as thermal and dimensional stability. Novak et al. [102] studied electrical conductivity of epoxy resins filled with two grades of synthetic graphite. They found that the composites became electrically conductive when filled with 22 vol% of the filler, which means the percolation threshold concentration, $\Phi_c$ equal to 22 vol%. However, the impact strength and the strength of adhesive joint decreased with the incorporation of synthetic graphite.

Ramirez-Garcia et al. [103] carried out research on charge percolation and electroanalytical performance from carbon composite microelectrodes. They found that the percolation threshold for synthetic graphite filled epoxy is 52 vol% and the composite
exhibited a bulk conductivity of 0.15 S/cm. The electrical conductivity increased dramatically to 96 S/cm when the synthetic graphite loading reached 67 vol%.

Chen et al. [106] investigated electrically conductive PP/EG nanocomposites. They prepared maleic anhydride grafted polypropylene (g-PP)/EG nanocomposites via solution intercalation. The results indicated that during solution intercalation, the g-PP molecules disentangled in the solution, and infiltrated into the micropores and interplanar spaces of EG through physical adsorption and solvation because of the porous feature of EG and polar interaction between the MAH group of g-PP and the –OH, –COOH groups on the graphite layers. It was argued that g-PP macromolecules supported and fixed the EG/g-PP compound networks and maintained the high aspect ratio of the graphite sheets in the nanocomposites. Thus, a conductive network spanning the entire specimen could be formed at a very low EG concentration of about 0.67 vol%, causing the system to “percolate.”

Qu et al. [107] investigated the piezoresistive behavior of expanded graphite reinforced maleated PP composites. The percolation threshold appeared to be very low ~ 0.4 wt%, and the conductivity increased to $10^{-8}$ S/cm. They applied pressure on the PP/EG composite with filler loading of 7.5 wt%. They found that the electrical resistivity decreased dramatically. An interesting piezoresistive phenomenon was tested and validated for the studied polymer nanocomposite system. The resistivity decreased rapidly with compressive stress of less than 10 MPa and reached a plateau value at a higher compressive stress from 10 MPa to 30 MPa. The resistivity increased slightly when the compressive stress increased beyond 30 MPa. They believed that the observed
piezoresistive phenomenon is caused by the formation of conductive paths and the
degeneration of such a network sequentially, which arises from the reorientation of the
graphite platelets in the matrix and their rupture due to the significant shear forces
generated from the large compressive stress, respectively. The studied materials also
exhibited a time-dependent piezoresistivity primarily caused by creep of polymer matrix.
The piezoresistive property can be utilized as passive sensing materials for micro-electro-
mechanical systems.

2.9 Graphene-based Polymer Composites

Graphene sheets—one-atom-thick two-dimensional layers of $sp^2$-bonded carbon—are predicted to have a range of unusual properties. Their thermal conductivity and mechanical stiffness may rival the remarkable in-plane values for graphite (3000 W/m/K and 1060 GPa, respectively); their fracture strength should be comparable to that of carbon nanotubes for similar types of defects; and recent studies have shown that individual graphene sheets have extraordinary electronic transport properties [108].

One possible route to harnessing these properties for applications would be to incorporate graphene sheets in a composite material. The manufacturing of such composites requires not only that graphene sheets should be produced on a sufficient scale but that they also be incorporated, and homogeneously distributed, into various matrices. Graphite, inexpensive and available in large quantity, unfortunately does not readily exfoliate to yield individual graphene sheets. A general approach for the preparation of graphene-polymer composites is via complete exfoliation of graphite and
molecular-level dispersion of individual, chemically modified graphene sheets within polymer hosts.

Stankovich et al. [108] successfully developed fully exfoliated graphite oxide nanoplatelets. A number of chemically modified graphite oxides were prepared by treating graphite oxide with organic isocyanates. The isocyanate treatment reduces the hydrophilic character of graphene oxide sheets by forming amide and carbamate ester bonds to the carboxyl and hydroxyl groups of graphite oxide, respectively. As a result, such isocyanate-derivatized graphite oxides readily form stable dispersions in polar aprotic solvents such as N,N-dimethylformamide (DMF), consisting of completely exfoliated, functionalized individual graphene oxide sheets with thickness ~1 nm as determined by atomic force microscopy (AFM). These dispersions of isocyanate-derivatized graphite oxide allow graphene oxide sheets to be intimately mixed with many organic polymers, facilitating synthesis of graphene–polymer composites. Coupled with the possibility that graphite oxide can be chemically reduced, nanocomposites of polymer and isocyanate-derivatized graphite oxide were expected to be electrically conductive.

Schniepp et al. [109] used thermal exfoliation to produce graphene sheets. The dried graphite oxide is rapidly heated (>2000 °C/min) to 1050 °C, and then split into individual sheets through evolution of CO₂.

Stankovich et al. [110] developed electrically conductive graphene–polymer nanocomposites by solution phase mixing of the exfoliated phenyl isocyanate-treated graphite oxide sheets [108] with polystyrene (PS), followed by chemical reduction of graphite oxide. These composites feature individual graphene sheets well dispersed
throughout the polymer matrix. The presence of the polymer in solution during the reduction step was the key to preventing the agglomeration of the graphene sheets. As the reduction proceeds, the sheets become coated with the polymer and remain individually dispersed. This PS/graphene composite exhibits a percolation threshold of 0.1 vol% for room-temperature electrical conductivity, the lowest reported value for any carbon-based composite except for those involving carbon nanotubes; at only 1 vol%, this composite has a conductivity of 0.1 S/cm, which is sufficient for many electrical applications.

This bottom-up chemical approach of tuning the graphene sheet properties provides a path to a broad new class of graphene based materials and their use in a variety of applications.

2.10 Characterization of Thermal Conductivity

Fukushima et al. [111] investigated the thermal conductivity of exfoliated graphite filled composites. In this paper, Three methods were used to determine the thermal conductivity of the nanocomposites, including DSC method, modified hot-wire method, and halogen flash lamp method. The details used by the author were summarized below.

2.10.1 DSC method

Differential scanning calorimeters have been used to measure the thermal conductivity of various materials. In practice, a quartz disk 6 mm in diameter and 1 mm
thick was used as a reference sample. The composite samples were also prepared using the same geometry. Approximately 15 mg of gallium ($T_m = 29.8^\circ$C) was placed on the top surface of a quartz sample, set in the DSC cell, and heated from 20 to 40°C at 0.1°C/min ramp rate. This gallium melt was performed twice to ensure intimate contact of the gallium with the sample, and to induce quasi-static thermal equilibrium. The data from the second melt was used for calculations. Since the melting rate of gallium depends on the heat flow through the quartz disk, the slope of the heat flow vs. temperature ($q$) profile through the melt is indicative of the thermal conductivity ($K_x$) of the object sample. Because the same quantity of gallium was used for all measurements, and all samples were similar in size, the thermal conductivity of the composite samples may be calculated by the following Equation 2.1.

$$K_x = \frac{q_x^2}{q_q^2} \cdot \frac{d_x}{d_r} \cdot K_q$$  \hspace{1cm} (2.1)

where $K_x$ – thermal conductivity of object sample (W/m/k); $K_q$ – thermal conductivity of quartz (W/m/k)=1.37; $q_x$ – heat flow through object sample (W/g/k); $q_q$ – heat flow through quartz sample (W/g/k); $d_x$ – thickness of object sample (mm) and $d_r$ – thickness of object sample (mm).

The slope of heat flow through quartz was measured for two quartz (as unknown) samples, and averaged to determine $q_q$. The $K_x$ values were calculated using two samples per composite formulation.
2.10.2 Modified hot-wire method

This method is a transient technique that determines the rate of heat flow from one material to another. In practice, a heating element, supported on a backing, is placed in contact with the material to be evaluated. The temperature of the heating element is monitored, and the rate of temperature increase in at the sensor surface is inversely proportional to the ability of the sample to transfer heat. Using this approach, the thermal conductivity of the specimen can be quickly and non-destructively determined. Measurements were collected by Mathis Instruments Ltd. (Fredericton, NB, Canada) personnel using their TC-30 unit.

2.10.3 Flash method

A halogen flash lamp fires a pulse at the sample’s lower surface while the temperature of the reverse surface is measured by infrared detectors. Specific heat is measured by comparing the temperature rise of the sample to the temperature rise of a reference sample of known specific heat. By knowing the density of the sample the thermal conductivity can be calculated. Measurements were collected by the personnel of Netzsch Instruments, Inc. (Burlington, MA, USA) using their LFA 447 unit.

Three different methods for measuring thermal conductivity were compared. The DSC method gave good results up to 1.5 W/m/k but diverged from the pulsed lamp method above 1.5 W/m/k. The DSC method should be limited to use for materials having thermal conductivities less than about 1 W/m/k. However, the halogen pulsed lamp method and the modified hot-wire method showed good agreement up to 1.5 W/m/k. The
halogen lamp flash method revealed that exfoliated graphite nanoplatelet composites with up to 20 vol% exfoliated graphite exhibited thermal conductivities of more than 4 W/m/k which is significantly higher than the control polymer matrix. Thus, exfoliated graphite nanocomposites offered great promise in applications where thermal management is a priority in performance.

The addition of small amounts of exfoliated graphite flakes showed a marked improvement in thermal and electrical conductivity of the composites.

2.11 Surface Characterization of GO and EG

For polymer composites, one important factor that determines the final properties of the composites is the adhesion between the interface of filler and the polymer matrix. Therefore knowing the surface chemistry of the filler phase and the polymer phase is very important.

As is well known, there are large amount of functional groups such as –COOH, -OH, carbonyl, epoxide, and ether groups, on the surface of the graphite oxide (GO), also called graphite intercalated compound (GIC). After thermal shock of the GO at very high temperature, graphite material expands and most of the functional groups degrade. Literature data analysis shows that there are still small amounts of functional groups on the surface. The surface characterization methods used in the literature include FT-IR, XPS, NMR, and so on. Some of the literature characterization methods and results are described below.
An NMR study result described by Schniepp et al. [109] has shown that GO as used in the thermal exfoliation process contains aromatic regions randomly interspersed with oxidized aliphatic six-membered rings. The oxidized rings contain C-O-C (epoxide) and C-OH groups, while the sheets terminate with C-OH and -COOH groups. Some of these functional groups are retained in the thermally exfoliated nanoplates of graphene stacks. Thus, when used as a nanofiller in a polymer (poly(methyl methacrylate)) matrix, these functionalized graphene stacks offer comparable or better thermal, mechanical, and electrical property enhancements than SWCNTs. In contrast to pristine graphite, the graphene derived sheets in graphite oxide (graphene oxide sheets) are heavily oxidized, bearing hydroxyl and epoxide functional groups on their basal planes, in addition to carbonyl and carboxyl groups located at the sheet edges. The presence of these functional groups makes graphene oxide sheets strongly hydrophilic, which allows graphite oxide to readily swell and disperse in water. A mild ultrasonic treatment of graphite oxide in water results in its exfoliation to form stable aqueous dispersions that consist almost entirely of 1-nm-thick sheets. In fact, at present, exfoliation of graphite oxide is the only way to produce stable suspensions of quasi-two-dimensional carbon sheets, making this a strategic starting point for large-scale synthesis of graphene sheets. As such, graphite oxide has recently attracted attention as filler for polymer nanocomposites.

2.12 Hygrothermal Effect on Properties of Composites

As low temperature PEM fuel cells are operated in high acidic environment with high temperature of around 80°C and high humidity, bipolar plates should be of great
resistance to chemical and electrochemical corrosion or degradation. Thus, it is important to evaluate the effects of these conditions on the electrical conductivity, mechanical and thermal properties, and especially on hydrolytic and chemical stability.

Hygrothermal effect is the change in properties due to moisture absorption and temperature change. In this study, this hygrothermal effect on the properties of the composites will be investigated by using water reflux, hydrogen peroxide reflux and acid reflux experiments at water boiling temperature for periods up to five weeks.

The hygrothermal effects on epoxy resins and composites have been studied by many research groups. Knowledge of the bonding character of water molecules in epoxy resins is important and fundamental for understanding of hygrothermal effects. Even though considerable research has focused on hygrothermal effects, water diffusion mode and related mechanisms in epoxy resin are still not fully understood. This is because in part to the reality that the hygrothermal effects in epoxy are quite complex. Two mechanistic approaches have emerged that generally characterize the nature of water in epoxy. One is the free volume approach which presumes that water diffuses into epoxy resin and resides in the free volume of the material. For this approach bonding between water molecule and epoxy resin network is deemed insignificant [112-114]. The other approach is the interaction concept that suggests water molecules couple strongly with certain hydrophilic functional groups such as hydroxyl or amine in epoxy resin [112-114].

Zhou et al. [112-114] assessed the nature of sorbed water and the related hygrothermal effects in epoxy resins. They also studied the hygrothermal effects on the thermal properties of epoxy resins. In their experiments, three epoxy systems (DGEBA +
mPDA, TGDDM + DDS, and Fiberite 934TM) were used. Water sorption was achieved by immersing the materials in distilled water at constant temperatures for 1530 hours. Water absorption and desorption profiles were analyzed to determine the diffusion parameters.

The study by Zhou et al. [112-114] also showed that water molecules bonded with epoxy resins through hydrogen bonding. Two types of bound water were found in epoxy resins. The binding types were classified as Type I or Type II bonding, depending on difference in the bond complex and activation energy. The activation energy of Type I and Type II bound water was ~ 10 and ~ 15 kcal/mol, respectively, as shown in Figure 2.5-2.7. Type I bonding corresponded to a water molecule which forms a single hydrogen bond with the epoxy resin network. This water molecule possessed lower activation energy and was easier to remove from the resin. Type II bonding was as a result of a water molecule forming multiple hydrogen bonds with the resin network. This water molecule, therefore, possessed higher activation energy and was correspondingly harder to remove. Type I bound water was the dominant form of the total amount of sorbed water. The amount of Type II bound water depended strongly on the exposure temperature and time. Higher immersion temperature and longer exposure time resulted in a greater amount of Type II bound water.
Figure 2.5 Schematic drawing of water desorption process [112].

Figure 2.6 Activation energy of TGDDM + DDS system [112].

$Q_{\text{type I}}$ was obtained by desorption of saturated specimens at 45°C, 60°C, 75°C and 90°C.

$Q_{\text{type II}}$ was obtained by desorption of semi-dried specimens at 115°C, 130°C, 145°C and 160°C. For comparison absorption activation energy is also shown [112].
Figure 2.7 Possible bound water complexes in epoxy network: (a) water molecules form one hydrogen bond with resin network and have lower activation energy, and (b) water molecules form multiple hydrogen bonds with resin network and have higher activation energy [112].

Zhou et al. [113] also investigated hygrothermal effects on physical properties such as $T_g$ in epoxy resins. They contend that $T_g$ value was influenced by a dual-mechanism process. That is, Type I bound water causes a steep drop in $T_g$ owing to breakage of interchain bonds and Type II bound water lessens the drop in $T_g$ via secondary crosslinking resulting from water-resin network interaction.

When Type I bound water was removed under conditions where the desorption temperature was comparable to the absorption temperature, Type II bound water was still retained in the resin and the $T_g$ was completely recovered. This observation indicated the
dominance of Type I bound water on influencing $T_g$ depression. The removal of Type I bound water in turn restored inter-chain Van der Waals bonding and $T_g$ quickly recovers. The secondary crosslink effect on $T_g$ was relatively weak and masked by the recovery of inter-chain bonding. An increase in $T_g$ induced by Type II bound water has been observed at the semi-dried desorption stage. This behavior is shown in Table 2.3.

Table 2.3 Comparison of experimental and calculated $T_g$ of epoxy resins [113].

<table>
<thead>
<tr>
<th></th>
<th>TGDDM+DDS</th>
<th>DGEBA+mPDA</th>
<th>Fiberite 934</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C) (dry, as prepared)</td>
<td>251</td>
<td>173</td>
<td>218</td>
</tr>
<tr>
<td>$T_g$ (°C) (wet, calculated)</td>
<td>144</td>
<td>120</td>
<td>133</td>
</tr>
<tr>
<td>$T_g$ (°C) (wet, experimental)</td>
<td>81-132</td>
<td>80-124</td>
<td>87-127</td>
</tr>
</tbody>
</table>

(Calculation data was based on the polymer-diluent model. Experiment results were tested by TMA and varied from different immersion temperatures and exposure time.)

And they also explained that the variation in $T_g$ of epoxy exposed to a hygrothermal environment was rationalized as follows: i) change in $T_g$ does not depend solely on the water content alone in epoxy resins, ii) $T_g$ is influenced by the hygrothermal history of the materials, iii) for a given epoxy system longer time and higher exposure temperature result in higher value of $T_g$, and iv) Type I and Type II bound water influences on $T_g$ variation by quite different mechanisms and in opposing ways. Type I bound water breaks the initial inter-chain Van der Waals force and hydrogen bonds resulting in the increase of chain segment mobility. So, it acts as a plasticizer causing
large depression in $T_g$. In contrast, Type II bound water lessens the extent of $T_g$ depression in the water saturated materials as a result of secondary crosslinking. Experimentally determined $T_g$ values represent the combined effect of the two mechanisms. The popular polymer-diluent model used to predict $T_g$ is insufficient when dual-sorption mechanisms are operative under hygrothermal conditions.

Zhou et al. [114] also investigated the hygrothermal effects of water on graphite/epoxy composites. According to their study, the water absorption profiles were slightly different from those of pure cured epoxy resins. They concluded that water sorption in this T300/934 graphite/epoxy composite exhibited both Fickian and non-Fickian diffusion behavior. Diffusion data showed that time for the onset of non-Fickian behavior was inversely related to the exposure temperature. The water gains in the composites were much less than those of pure Fiberate 934 epoxy resin at different temperature.

From the $T_g$ data shown in Table 2.3, they drew the following conclusions: Sorbed water in T300/934 Gr/EP composite materials could be characterized (1) by water residing at crack tips, interfaces and voids, which contributed to excessive weight gain; (2) by physiosorbed water associated with weak Van der Waals type bonding in the resin, which decreased the $T_g$; and (3) by water strongly bonded to hydrophilic groups in the resin, which enhanced the $T_g$ slightly. Irrespective of exposure temperature (in the range of $T/T_g \leq 0.5$), the saturation level of water was the same. However, $T_g$ was affected by the distribution of the chemisorbed versus the physiosorbed water in the material.
2.13 Temperature Effect on Properties of Epoxy Composites

For electrically conductive polymer composites, an interesting phenomenon is a non-linear positive temperature coefficient (PTC) effect shown by a sharp resistivity increase by order of magnitudes upon heating, thus converting the material from electrical conductor to insulator within a narrow temperature range.

The most studied polymer-composite system that exhibits this effect consists of polyethylene (PE) loaded with carbon black (CB). The temperature dependence of the resistivity of one particular PE/CB PTCR material is shown in Figure 2.26 [115]. One can see that at temperatures below 120 °C the resistivity does not depend strongly on temperature, but that within a narrow temperature range around 130 °C, the resistivity rises by many orders of magnitude. This resistivity jump or switch temperature corresponds to the melting point of the crystalline regions of polyethylene. The magnitude of this jump is highly dependent on the crystallinity of the polyethylene, the morphology of carbon black, the details of the composite fabrication process, and the thermal history of the sample. The qualitative description of the PTCR behavior which seems to be generally agreed upon is as follows: Electrical conduction occurs through tunneling between carbon black aggregates. At the crystalline melting temperature, the PE undergoes an abrupt expansion which causes an increased tunneling distance between carbon black aggregates and hence causes an abrupt increase in the electrical resistance.

The unique resistance switching property of these materials forms the base of their applications as current limiting electrical devices for short-circuit protection. In these applications, the PTCR material is placed in series with the electrical circuit to be
protected and designed with dimensions and packaging such that, under normal circuit conditions, the material temperature is below the switch transition and the material is in its low resistance state. When a short-circuit occurs, the joule heating due to the excess current causes the temperature of the materials to rise above the PTCR transition temperature, thereby causing the material to switch to its high resistance state. In this state, the material effectively limits the short-circuit current to an acceptable value and so protects the circuit. When the short circuit is cleared, the device cools to below its switch temperature and normal circuit operation is resumed. Current-limiting devices utilizing PE/CB PTCR materials have been commercially available for many years.

Current limiting devices based on the PTCR effect have all been designed for low power circuit applications. The maximum current density through these materials during switching is typically less than 10 A/cm².

The PE/CB PTCR material used in these experiments was obtained from a commercial current limiting device. The room temperature resistivity and carbon loading of this material was measured to be 0.3 Ω·cm and 53 wt %, respectively. The temperature dependence of the resistivity of this material was measured at atmospheric pressure. They observed that the material exhibits a change in resistivity of 2 orders of magnitude at ~130 °C.

Hedva Bar et al. [116] described the electrical behavior of a thermosetting system, based on epoxy resin, containing metal plated fillers. The percolation threshold values of their composites are 1-2 vol% for epoxy/Cu coated mica flake composite, and 4-6 vol% for epoxy/Cu coated glass fiber composite. Metal coated fillers can be produced by an
electrolysis copper plating process. This process provides electrically conductive fillers with low metal contents, desired high aspect ratios, and particle size distribution. Incorporation of these fillers in thermosetting DGEBA/TETA epoxy matrix provides conductive materials of extremely low metal contents, which offers an improved alternative for conductive adhesives or composites. They observed an extremely large PTC effect for epoxy/copper coated mica composites, increasing the resistivity by more than nine orders of magnitude. The PTC effect is not followed by an NTC effect at temperatures above PTC, owing to the highly crosslinked epoxy matrix that restricts the filler particles’ motion during the heating step. Increasing the copper coated mica concentration raises the PTC temperature of the first temperature cycle, and exposing the material to continuous heating-cooling cycles results in a decrease in the PTC temperature and an increase of its room temperature resistivity.

Supported by TMA analysis, inverse relations were found between the coefficient of thermal expansion and the PTC temperature. There is no relationship between glass transition temperature and the PTC temperature. Accordingly, the mechanism governing the PTC effect in the epoxy-mica composite is based on a larger thermal expansion coefficient of the matrix compared with the ceramic filler, causing destruction of the conducting network upon heating and thus resulting in the PTC temperature. The PTC temperature, at which a sharp increase of resistivity occurs, is the temperature at which the volume fraction of the metal coated filler decreases below the percolation threshold.

The mechanism describing the PTC effect is usually based on the difference of thermal expansion of the filler and matrix, which destroys the continuous conductive
network within the PTC temperature transition. This mechanism appears to be different for semi-crystalline and for amorphous matrices. In a semi-crystalline matrix based conductive composites the PTC transition is usually obtained in the vicinity of the melting region of the polymer due to the high volume expansion of the matrix upon melting. In amorphous matrices the PTC transition is sometimes related to the glass transition temperature of the polymer or—in the case of thermosetting matrices, such as epoxy—to the curing temperature due to internal stresses derived from volumetric shrinkage of the matrix, which increase in high temperature cured matrices [117].

The PTC effect is often followed by a negative temperature coefficient (NTC) effect [115-122], where resistivity decreases at the higher temperatures, which is caused by rearrangement of the conductive particles’ network in the softened polymeric matrix.

The PTC feature makes the materials suitable for applications in the electronic industry, such as temperature/current sensors, self-regulating heaters, or as overcurrent protecting devices, with a potential for multiple use, as opposed to conventional fuses. A desired PTC performance for such applications includes low room temperature resistivity, high PTC intensity, absence of an NTC effect and high reproducibility. Highly crosslinked matrices that restrict the conductive particles motion have shown the potential of meeting such demands [115-122].

2.14 Characterization of Electrical Conductivity

High electrical conductivity is one of the most critical requirements for PEM fuel cell bipolar plates. As Cunningham et al. [123] pointed out that carbon-based polymer
composite have generally lower electrical conductivity than isotropic Poco® elertro-
graphite. Polymer composite bipolar plates have been extensively studied to improve the
electrical conductivity and maintain the strong mechanical properties simultaneously. The
in-plane electrical conductivity of 100 S/cm was required by DOE target. A through-
plane plate area specific resistance of less than 10 mΩ·cm² has been referred to by many
authors [13,23,124-125] to minimize the voltage losses in a stack.

The in-plane electrical conductivity is usually measured by following ASTM
D257-99, through conventional four point probe conductivity measurement device [9].
The through-plane electrical conductivity of the composites is more important to qualify
the composites as bipolar plates. This is usually measured by using a specific designed
fixture whereby the specimen were kept under pressure in the measurement set up, and
the pressure is applied by compression molding machine. The detailed measuring
methods and machine set up were described by Cunningham [123] and Landis [126].

2.15 Summary of Literature Review and Our Contribution to This Field

Fuel cells are of great interest today due to their high efficiency and zero- or low
emissions for a wide range of applications from several watts to megawatts. Among
various types of fuel cells, PEM fuel cell is considered as the most promising candidate
for application in portable electronics and transportation systems, where light-weight, low
cost and compact power sources with quick startup and tolerance to shock and vibration
are needed.
Bipolar plates are a major component in the PEM fuel cells, in terms of weight, volume, cost and functions. Many efforts have been devoted into the research and development of bipolar plates with high performance, light weight, low volume and cost. In the past decades, great advances have been achieved for bipolar plates. Polymer composite bipolar plates and coated metal bipolar plates are two candidates which are considered to be the most promising candidates. Each has its advantages, limitations, and application preferences. The state-of-the-art progress in bipolar plates in PEM fuel cells is described in detail in the above sections.

Metal bipolar plates have high electrical and thermal conductivity, strong mechanical properties, and good gas impermeability. However, the corrosion problem of metal bipolar plates is inherent. Coating a protective layer on the surface of metal bipolar plates can only alleviate, but not completely eliminate the corrosion problem. Coated layers sometimes increase the interfacial contact resistance. Furthermore, metal ions dissolved from metal plates can poison membrane and catalyst, which is harmful for PEM fuel cell’s life and ion conductivity.

Polymer composite bipolar plates have chemical and electrochemical stability, good gas impermeability, and lightweight and low cost. However, polymer composite bipolar plates encounter the problem of low electrical and thermal conductivity. High filler loading is needed to obtain the high electrical and thermal conductivity, but results in poor mechanical properties. Recent development and progress in choosing proper polymer-filler systems and processing methods have improved the electrical and thermal conductivity, and at the same time obtained strong mechanical properties. Several
researchers reported bipolar plates with electrical conductivity much higher than the DOE target of 100 S/cm, and simultaneously possessing strong mechanical properties and good gas impermeability.

In our study, expanded graphite has been chosen as major conductive filler, combined with a small amount of electrically conductive carbon black as a combination. The intrinsic conductivity of graphite is very high about $10^5$ S/cm. A low shear solution mixing method is used, thus the special layered and network structure of expanded graphite can be maintained in the polymer composites and the electron conductive paths of the expanded graphite are kept in the polymer matrix. This layered and network structure of graphite imparts high electrical conductivity of the graphite to the composites. Therefore, high conductivity is obtained for the composites at low filler loadings.

There is a synergistic effect on the electrical conductivity between expanded graphite and carbon black. Incorporation of small amount of electrical conductive carbon black into the expanded graphite filled composites improves the electrical conductivity significantly. This can further reduce the total filler loadings in order to get the high conductivity.

Low filler loading of the composites has another advantage of strong mechanical properties. In addition, surface characterization of the expanded graphite indicates that there are reactive functional groups such as carboxyl, hydroxyl, and epoxide groups on the surface of expanded graphite. These functional groups can react with the polymer matrix, epoxy curing agent DDS, results in strong interface bonding between filler phase
and polymer phase. This reaction between expanded graphite and polymer matrix delivers strong mechanical properties to the composites.

In addition, the thus developed polymer composites also have excellent gas impermeability because of the low filler loading and good interface adhesion between expanded graphite and polymer matrix in the polymer composites.

In this way, the trade off between electrical conductivity and mechanical properties and gas impermeability is solved.

Another contribution of our study is the design of a hygrothermal effect test to simulate and investigate the performance of the bipolar plates under PEM fuel cell service conditions. Very limited research has been done to evaluate the stability of the polymer composite bipolar plates in PEM fuel cell operating conditions. The long-term viability and durability of the bipolar plates in PEM fuel cell are proved to be excellent for the bipolar plates developed in this study.
CHAPTER III

OBJECTIVES

There are vigorous efforts to develop polymer composite bipolar plates to replace the electro-graphite bipolar plates in PEM fuel cell for application in portable electronics and transportation systems. These bipolar plates need to perform excellent multi-functions (specified in Chapter I), and satisfy all requirements (listed in Chapter I) of the bipolar plates in PEM fuel cells.

1. The major objective in this study was to develop a polymer composite material which can satisfy all the requirements specified by DOE targets and the industrial targets. The material should possess high conductivity, higher than the DOE targets 100 S/cm. Strong mechanical properties are required to support fuel cell stack assembly and resist the clamp forces. The material should have tolerance to the shock and vibration for the fuel cell to be used in portable electronics and transportation systems. The materials should have the following mechanical properties: PlugPower’s targets [29]: tensile strength $>$ 41MPa, flexural strength $>$ 59MPa, impact strength $>$ 40.5 Jm.1 (0.75 ft-lb/ in); DOE target [28]: crush strength $>$ 4200 kPa. High thermal conductivity (PlugPower’s
target [29]: \(>10\text{W(mK)}^{-1}\) is required for heat management in PEM fuel cells. Low thermal expansion coefficient is necessary for prevention of micro-cracking and mismatch of the bipolar plates and the neighboring parts during heat-cooling cycles in PEM fuel cells. Chemical and electrochemical stability of the bipolar plates is critical for long-term reliability and durability of the bipolar plates in PEM fuel cells. The material should be thermally stable at the fuel cell operating conditions. Good gas impermeability is required because hydrogen and oxygen are fed into bipolar plates and distribute to MEA through bipolar plates. DOE target [28] for \(\text{H}_2\) permeability (<\(2\times10^{-6}\text{cm}^3/(\text{cm}^2\cdot\text{s})\)) need to be achieved. For PEM fuel cell to be used in portable electronics and transportation systems, bipolar plates should also be lightweight, low cost and compact. Thickness less than 2 mm for applications in automobile vehicles is required. Easy and rapid manufacturability is required to reduce the manufacturing cost.

2. The second objective of this study was to optimize the polymer and filler system and composition of the polymer composites, and the processing methods in order to achieve the major objective mentioned above. For polymer composites, the bulk properties are largely determined by the dispersion of the fillers in polymer matrix, the morphology and microstructure of the composites, especially in this study, expanded graphite was selected as the major conductive filler. Good dispersion of the filler is needed to get the mechanical properties, while filler aggregates is another requirement to form the electron conductive paths to achieve high conductivity of the polymer composites. Thus the filler system which possesses layered and network structure of the
expanded graphite is greatly appreciated as conductive fillers in composites for bipolar plate in PEM fuel cells. For polymer systems, a low viscosity thermosetting resin is preferred as low shear force is encountered during mixing. Low viscosity allows the polymer to penetrate into the pores and voids. The thermoset is then in-situ polymerized during curing to give the final shape. In this study, expanded graphite was selected as the major conductive filler, and electrically conductive carbon black as the minor conductive filler. A synergistic effect on electrical conductivity was found by combining the expanded graphite and carbon black together as filler systems. Low shear, solution intercalation mixing method was chosen to mix the ingredients. By using this processing method, the layered and network structure of the expanded graphite was maintained in the polymer composites, which delivered high conductivity of the expanded graphite to the composites at low filler loadings. Furthermore the functional groups on the surface of the expanded graphite were anticipated to react with the polymer matrix, which impart good adhesion between the interface of the filler and the polymer phases. This interaction between the interface between the filler and polymer further improves the mechanical properties. Good gas impermeability is also achieved by the selection of the polymer and the filler systems and the processing method.

3. The third objective of this study was to develop proper methods to characterize the materials for application as bipolar plates in PEM fuel cells. First, the properties of the composites need to be characterized at the dry state to satisfy all requirements specified by DOE and industry. More important is to investigate the stability of the
properties during the fuel cell service conditions. Therefore the analysis of hygrothermal
effect experiment was conducted to simulate the effects of PEM fuel cells service
conditions and to evaluate the stability of the properties of the composites during the
PEM fuel cell service conditions.

4. Finally, this study also aimed to answer some fundamental questions involving
conduction mechanism of highly loaded polymer composites, processing/structure/
property relationship, the contradiction between conductivity and mechanical properties
in designing polymer composites, and epoxy curing kinetics.

This project also aimed to capture the fundamental understanding of how high
conductivity and good mechanical properties can be obtained simultaneously.

The knowledge developed in this study on highly filled conductive composites
will not only benefit the manufacturing of highly conductive bipolar plates, but also can
have impact on development of conductive electrodes, sensors, electromagnetic shielding
materials, antistatic materials, conductive films, conductive coatings, and phase-transfer
catalysis materials.
CHAPTER IV

EXPERIMENTAL

4.1 Materials

In this study, two types of epoxy resins were selected as the polymer matrix. Expanded graphite (EG), synthetic graphite, and electrically conductive carbon black were chosen as the conductive fillers.

4.1.1 Epoxy Resins

Epoxy resins used in this study have similar ether linkages as that of the Nafion® membranes commonly used in PEM fuel cells. So it is reasonable to select epoxy resins as the polymer matrix in the composite bipolar plates. It was anticipated that the same chemical and electrochemical stability under the PEM fuel cell service conditions as that of Nafion® membranes would be exhibited by the composite bipolar plates [4]. The chemical structures of the epoxy resins — Epon® 826 and Araldite® DY3601, and the curing agent — DDS, are listed in the following Table 4.1.
Table 4.1 Chemical structures of epoxy resins and curing agent.

**Epon 826**: Diglycidyl ether of bisphenol A (DGEBA)

\[ n = 0.085, \text{EEQ} = 178-186 \]

![Chemical structure of Epon 826](image)

**Araldite DY3601**: Polypropylene glycol diglycidyl ether

\[ n = 11.4, \text{EEQ} = 396 \]

![Chemical structure of Araldite DY3601](image)

**DDS**: Diaminodiphenylsulphone

\[ \text{MW} = 248, \text{ENQ} = 62 \]

![Chemical structure of DDS](image)

The polymer matrix used to produce composite bipolar plates is derived from a mixture of the two epoxy resins, an aromatic epoxy resin and an aliphatic epoxy resin, mentioned above and a diamine type curing agent.

The aromatic epoxy, diglycidyl ether of bisphenol A (DGEBA) in the form of Epon® 826, was obtained from Resolution Performance Products (Houston, TX) with epoxide equivalent weight of 178-186, viscosity of 65-95 Pa·s, and specific gravity of 1.15 at 25°C. The aliphatic epoxy is polypropylene glycol glycidyl ether in the form of Araldite® DY3601, received from Vantico (Brewster, NY) with epoxide equivalent weight of 385-405, viscosity of 0.42 - 0.52 Pa·s, and specific gravity of 1.03 at 25°C.
Epon® 826 and Araldite® DY3601 were mixed in the ratio of 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, and 40:60 by weight. These epoxy resin mixtures will be denoted as EP100, EP90, EP80, EP70, EP60, EP50 and EP40 respectively in this study. Properties of these epoxy resin mixtures cured by DDS will be evaluated to optimize the composition of the polymer matrix. A majority of the composites was prepared using EP90 formulation of aromatic and aliphatic epoxy resins due to a favorable glass transition temperature of this formulation.

The curing agent, diaminodiphenylsulphone (DDS) was received from Ciba (Tarrytown, NY) with trade name HT976, melting temperature 180ºC and molecular weight 248 g/mol. The purity is higher than 96 % according to supplier. The curing agent is the diamine type (tetra functional) to facilitate rapid and dense cross-linking of epoxy resins.

As evident from the value of epoxide equivalent weight, Epon® 826 is capable of producing cross-linked epoxy networks much more rapidly and can provide much higher values of storage modulus than Araldite® DY3601 in the fully cured state with the same curing agent. Epon® 826 cured with DDS produced a brittle material, while Araldite DY3601® cured with DDS produced a gum-like material. On the other hand, the mixtures of Epon® 826 with Araldite® DY3601 content higher than 10 wt% yielded more ductile yet strong material when cured with DDS.

DGEBA is the most important epoxy resin system in industry due to its fluidity, mechanical strength in cured state, and low cost. Bisphenols containing thermally stable rigid aromatic rings have been used to synthesize high performance epoxy resins.
Unfortunately, it has unacceptable thermal properties ($T_g < 120^\circ$C) for high performance applications unless specialty aromatic curatives are formulated into the final compounds [100]. Glycidyl groups in an epoxy resin are flexible segments that reduced the viscosity of the resin and enhance the processability. Unfortunately, they also decrease the heat resistance of the cured epoxy resin. The aliphatic linkages in the glycidyl groups are the source of early thermal and thermooxidative degradation of a cured epoxy system.

There are two ways to alleviate the issues discussed above. First, selection of multiple functionality and low molecular weight of DGEBA to promote high cross-linking density and the rigid structures between two glycidyl groups is the key for improvement of thermal and mechanical properties of the cured epoxy resins. Second, selection of specialty curatives such as aromatic diamines with rigid backbone can bring forth the desired performance of epoxy resins.

Therefore, in our research, we selected Epon® 826, a DGEBA type epoxy resin as the major polymer. It has low molecular weight and thus low viscosity, and high functionality per gram of material. It can promote high cross-linking density and rigid structures between two glycidyl groups. Furthermore, we selected aromatic diamine DDS as the curing agent to further improve the thermal and mechanical properties of the cured epoxy resins. Rigid phenyl rings are particularly useful to provide resins with improved heat and thermal resistance and char formation. Undesirably, too rigid backbone structures also drastically reduce the processability of a resin due to viscosity increase, and produce a relatively still but brittle material. Therefore, aliphatic epoxy resin--
Araldite® DY3601 was selected to combine with Epon® 826 in order to adjust the viscosity of the solution during mixing and provide flexibility to the cured products.

For the polymer matrix system, all components were commercial products, and were used as received, without purification.

4.1.2 Conductive Fillers

Expanded graphite (EG), synthetic graphite (SG), and electrically conductive carbon black (CB) were selected as the conductive fillers. Expanded graphite was selected for their very high intrinsic conductivity. Furthermore, the layered and network structure and large surface area of graphite can deliver the desired high conductivity. Synthetic graphite also has very high intrinsic electrical conductivity. However, compared to expanded graphite, SG has much smaller surface area and large bulk density. Both expanded graphite and synthetic graphite were selected to study the influence of surface area and microstructures of the fillers on the electrical conductivity. Electrically conductive carbon black was selected for its synergistic effect on conductivity when combined with expanded graphite as the conductive fillers.

Electrically conductive carbon black (CB), Ketjenblack® EC-600JD was received from Akzo Nobel Chemicals Inc. (Chicago, IL). The physical properties are listed in Table 4.2 according to the supplier [127].
Table 4.2 Physical properties of Ketjenblack® EC-600JD according to supplier [127].

<table>
<thead>
<tr>
<th>Physical Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical Resistivity</td>
<td>0.01-0.1 Ω·cm</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>10-100 S/cm</td>
</tr>
<tr>
<td>Primary Particle Size</td>
<td>30-100 nm</td>
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<tr>
<td>Specific Gravity</td>
<td>1.8 g/cm³</td>
</tr>
<tr>
<td>Apparent Bulk Density</td>
<td>100-120 kg/m³</td>
</tr>
<tr>
<td>Ash Content, max. wt%</td>
<td>0.1</td>
</tr>
<tr>
<td>Moisture, max. wt%</td>
<td>0.5</td>
</tr>
<tr>
<td>BET Surface Area</td>
<td>1250 m²/g</td>
</tr>
<tr>
<td>Pore Volume (DBP)</td>
<td>480-510 cm³/100g</td>
</tr>
<tr>
<td>PH</td>
<td>8-10</td>
</tr>
<tr>
<td>Grit Content, max</td>
<td>30 mg/kg</td>
</tr>
<tr>
<td>Iodine Adsorption</td>
<td>1.0-1.1 g/g</td>
</tr>
<tr>
<td>Fines&lt;125μm, max wt%</td>
<td>7</td>
</tr>
</tbody>
</table>

Expandable graphite (EG), GRAFGUARD® Expanding Flake 160-50N with high expansion volume of ~ 250 cm³/g at 600°C was obtained from GrafTech (Cleveland, OH). The intrinsic conductivity of expanded graphite is about 10⁵ S/cm. The physical properties are listed in Table 4.3 according to the supplier [128].

Three kinds of primary synthetic graphite powder GP44-R, GP44-B, GP55-B were received from GrafTech Inc. (Parma, OH). The specification of these three types of synthetic graphite is listed in Table 4.4 according to the supplier [129]. Synthetic graphite was selected as conductive fillers to study the morphology effect of the filler particles on the electrical conductivity of conductive composites, as a comparison with that of EG-filled composites.
Table 4.3 Physical properties of GRAFGUARD® Expanding Flake 160-50N according to the supplier [128].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Volume before Expansion</td>
<td>1.25 cm³/g</td>
</tr>
<tr>
<td>Expansion Volume</td>
<td>250 cm³/g at 600°C</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>~ $10^5$ S/cm</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>~ 600 W/m/K</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.88 g/cm³</td>
</tr>
<tr>
<td>Typical Particle Size</td>
<td>300 μm</td>
</tr>
<tr>
<td>Onset Expansion Temperature</td>
<td>160 ºC</td>
</tr>
<tr>
<td>pH</td>
<td>5-8</td>
</tr>
<tr>
<td>Particle Shape</td>
<td>Irregular Flake</td>
</tr>
<tr>
<td>Graphite Weight Content</td>
<td>70 %</td>
</tr>
<tr>
<td>Volatiles by Volume</td>
<td>25 %</td>
</tr>
</tbody>
</table>

Table 4.4 Specification of the synthetic graphite products according to supplier [129].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration of Synthetic Graphite</td>
<td>&gt; 99 wt%</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>2 (Approximate)</td>
</tr>
<tr>
<td>Real Density (Helium)</td>
<td>2.2 g/cc - 2.3 g/cc</td>
</tr>
<tr>
<td>Melting Point</td>
<td>&gt;2760°C (5000°F)</td>
</tr>
<tr>
<td>Particle Size</td>
<td>&lt; 75 μm</td>
</tr>
<tr>
<td>Electrical Conductivity</td>
<td>$10^5$ S/cm</td>
</tr>
</tbody>
</table>

4.2 Preparation of Epoxy Composites

Epoxy composites were prepared by incorporating single or a synergistic combination of conductive fillers into the epoxy matrix by using low shear solution intercalation mixing method.
4.2.1 Preparation of Expanded Graphite

Expanded graphite was prepared by heat shocking of the graphite intercalation compound (GIC) in the form of Expandable graphite, GRAFGUARD® Expanding Flake 160-50N in a high temperature oven. The heat treatment temperatures were set at ~ 900 °C. The oven was preheated to 900 °C. The container-crucible was then preheated to the same temperature in the oven. The expandable graphite was poured into the crucible and allowed to expand. In this way expanded graphite with high expansion ratio was prepared.

4.2.2 Preparation of Polymer Matrix

Various epoxy resin mixtures were prepared by mixing the desired quantities of Epon® 826 and Araldite® DY3601 in a beaker at room temperature, followed by addition of 5 wt% excess of curing agent DDS than necessary to balance the stoichiometry of the epoxide and amine groups. The mixtures were heated up to 135°C and stirred until the system was transparent. Alternatively, the epoxy-curing agent mixtures were prepared by adding all three components into a beaker, followed by addition of acetone as the solvent. The solution was stirred at room temperature until it became clear.

4.2.3 Preparation of EG-based Epoxy Composites

The epoxy composites filled with only EG or with combined EG and CB were prepared by solution intercalation method, whereby expanded graphite and carbon black were added to the mixtures of epoxy resin and curing agent in acetone. The materials...
were mechanically stirred for 6 hours, in order for the epoxy resin to intercalate inside the conductive fillers, especially into the graphite interlayers and pores. After the conductive fillers were mixed with epoxy resins, solvent acetone was evaporated with continuous stirring. The traces of solvent and also moisture were removed by keeping the materials in a vacuum oven for 24 hours at 60°C, and 2 hours at 110°C. The dried materials were obtained in powder form and were compression molded at a pressure of 4000 psi and 180°C and cured for 4-6 hours, followed by post curing in vacuum oven at 200°C for 4-6 hours. The total filler content in the mixture ranged from 40 to 70 wt%, with a maximum of 5 wt% CB. The composite preparation procedure and various stages of intercalation between epoxy resins and expanded graphite and carbon black particles are schematically presented in Figure 4.1.

Figure 4.1 Schematic diagram showing stages in preparation of epoxy composites.
Specimens for measurement of electrical and thermal conductivity, mechanical properties, oxygen permeation rate and etc. were cut from the compression molded sheets in the desired shape.

4.2.4 Preparation of SG-based Epoxy Composites

SG-filled epoxy composites were prepared by solution mixing. SG was added to the mixture of epoxy resins and curing agent in acetone. The solution was mechanically stirred for 30 minutes, then solvent was evaporated, and the materials were dried in a vacuum oven at 60 °C for 24 hours and at 110 °C for another 2 hours. The composites were compression molded into sheets.

4.3 Electrical Properties

High electrical conductivity of the bipolar plates is one of the major requirements in order to obtain efficient fuel cell stacks. High electrical conductivity prevents large voltage drop per plate in the PEM fuel cell stacks. The in-plane and through-plane conductivity and area specific resistance were measured using Keithley 580 (Cleveland, OH) set up with a four point probe method.

4.3.1 In-plane Electrical Conductivity

The in-plane electrical conductivity was measured following ASTM D257-99 standard, through conventional four point probe conductivity measurement device, shown in Figure 4.2 (a).
4.3.2 Through-plane Electrical Conductivity

High through-plane electrical conductivity of the composites is more important for the application of these materials as bipolar plates in PEMFC. The through-plane conductivity of the composites was measured by using a fixture designed in our laboratory whereby the specimen was kept under pressure in the measurement set up (Figure 4.2 (b)). The through-plane resistance of the whole system depends on several resistances in series, including the resistance of two copper electrodes, two carbon paper layers, the bulk resistance of the specimen, and more significantly, the contact resistance between the carbon paper layers and the electrodes and between the carbon paper layers and the specimen. A calibration method was, therefore, used to separately measure the value of bulk resistance of the specimen and the resistance of the overall system, including specimen, carbon papers, and the contact resistances. Figure 4.3 presents the schematic of the set up used in the calibration method. In set up 1, the system resistance ($R_{\text{Setup 1}}$) of one carbon paper (CP) placed between two copper electrodes was measured, while in set up 2, the resistance measured ($R_{\text{Setup 2}}$) included the resistance of two copper electrodes, two CP layers, and the bulk resistance of the specimen, and the contact resistances. Assuming that all contact resistances were the same, the bulk resistance of the specimen can be calculated by using equation 4.1:

$$R = R_{\text{Setup 2}} - 2R_{\text{Setup 1}}$$

(4.1)

where $R$ is the resistance of the composite specimen. Once the value of resistance of the specimen was obtained, the values of conductivity were calculated using the known values of contact area and the specimen thickness.
Figure 4.2  Experimental set-up for measuring (a) in-plane conductivity and (b) through-plane conductivity with four-point probe method. The applied voltage and measured current are respectively $V$ and $I$. CP represents carbon paper.

Figure 4.3 Calibration set-up used for measurement of through-plane conductivity. CP represents carbon paper.
The performance of the composites for through-plane electrical performance via bipolar plates was also evaluated from the measurement of area specific resistance of the composite specimen as shown in set up in Figure 4.2 (b).

4.3.3 Area Specific Resistance (Interfacial Contact Resistance)

While measuring the through-plane conductivity, we found that the resistance of Setup 1 was very close to that of Setup 2 in Fig. 4.4. This can be attributed to large contact resistances of four contact surfaces encountered during measurements (see Figs. 4.3 (b) and 4.4). Thus a better way to characterize the through-plane electrical performance of the composite materials was to measure the values of area specific resistance using Set-up 2 in Fig. 4.4. An area specific resistance of less than 30 mΩ cm\(^2\) has been accepted to minimize the voltage losses in a stack contributed by the bipolar plates [4,25,33]. Typically industrial fuel cell stack prototypes operate at a current density between 1 and 2 Acm\(^{-2}\), and a surface area between 200 and 400 cm\(^2\). Using these typical numbers, the voltage drop per plate can be calculated in the range from 30 to 60mV. This compares favorably to a voltage drop of 50 mV per cell for a well-humidified 100 μm thick Nafion® membrane operated at 1 Acm\(^{-2}\) [26-27]. In our study, the area specific resistances of the system, including two copper electrodes, two CP layers, and one bipolar plate (as shown in Fig. 4.3 (b)), were measured at different pressures controlled by compression molding machine. The electrical through-plane area specific resistance (ASR) can be expressed using the following equation 4.2:

\[
ASR = R \times A \tag{4.2}
\]
where \( R \) is the resistance of Set-up 2 measured by Keithley 580 (Cleveland, OH), and \( A \) is the contact surface area between plates and CP.

4.4 Mechanical Properties of Composites

Strong mechanical performance of the composites are also required for the composites to be used as bipolar plates in PEM fuel cells because the bipolar plates support the soft MEA and the clamping force of the PEM fuel cell stacks. The flexural, impact, and tensile properties were measured according to ASTM D790-03, ASTM D 4812-99, and ASTM D 638-84 methods respectively. For testing flexural properties, the dimension of the specimens was \( 100 \times 12.7 \times 2.5 \) mm, and support span length of the specimens was fixed at 50.8 mm. As for impact strength test, the dimension of the specimens was \( 63.5 \times 12.7 \times 3.2 \) mm. The dimension of composite specimens was \( 100 \times 12.7 \times 2.5 \) mm for tensile property test.

4.5 Thermal Properties

The glass transition temperature (\( T_g \)) of the composites was determined by differential scanning calorimetry (DSC) using TA Instruments, DSC 2920 Modulated DSC (New Castle, DE). Dynamic mechanical analysis (DMA) was also used to characterize the glass transition temperatures of the epoxy resins and composites. A heating rate of 10 °C/min was used for DSC test. DMA was performed with a Pyris Diamond DMA from Perkin Elmer-Seiko Instruments (Boston, MA). Analysis was conducted in sinusoidal tension model at the heating rate of 4 °C/min under nitrogen
atmosphere, and at 1 Hz frequency. The length and width of the specimens for DMA test were $50 \times 10$ mm. The thickness was slightly different for each specimen used as compression molded, around 1-2 mm.

Thermogravimetric analyzer (TGA), TA Instruments TGA 2050 was used to measure the thermal degradation temperatures, such as $T_1$ and $T_2$. The heating rate is 20 °C/min. The weight of each sample was less than 10 mg, usually around 7-8 mg. The values of $T_1$ and $T_2$ were determined from the TGA curves respectively at 5% weight loss and at maximum rate of weight loss.

4.6 Oxygen Permeability

As hydrogen flows through the anode side of the bipolar plates, and oxygen flows through the cathode side of the bipolar plates (see Figure 1.1), the bipolar plates should have good gas impermeability to prevent the gas crossover through the bipolar plates, especially at the desired web thickness. The oxygen permeation rate was investigated as function of expanded graphite loadings and plate thickness.

Oxygen permeability was measured by using the Oxygen Permeation Analyzer 8001 (Chicago, Illinois). The specimens were prepared by compression molding of the composite materials into disks with diameter of 10 cm and thickness of approximately 1.25, 0.5, 0.3 and 0.18 mm.
4.7 Morphology

The morphology of the epoxy composites was characterized by scanning electron microscope (SEM) by using SEM S-2150 from Hitachi (Ibaraki, Japan) at 20 kV. The surfaces of the samples were coated with a thin layer of silver using a K575x sputter coater from Emitech (Kent England) under argon gas atmosphere. The fracture surfaces were prepared by cold fracture under liquid nitrogen.

4.8 Evaluation of Hygrothermal Effects

As bipolar plates are continuously exposed to PEM fuel cells operating conditions of high temperatures around 80 ºC, high humidity and highly acidic environment, with one side contacting with hydrogen flow and the other side contacting with the oxygen flow, it is critical to evaluate the combined effects of these severe PEM fuel cell service conditions on the properties of polymer composite bipolar plates.

Specimens for evaluation of hygrothermal effects were cut from the compression molded sheets. A typical specimen was 100×12×0.5mm. The thickness of the specimen was approximately 0.5 mm. This guaranteed that only one dimensional diffusion of water, perpendicular to the specimen surface, was possible. The edge effect on diffusion was neglected.

The hygrothermal effects were determined by immersing thin specimens of cured epoxy resins and composites in boiling water, boiling aqueous solution of sulphuric acid (pH = 1-2), and boiling aqueous solution of hydrogen peroxide (6 wt%), by allowing continuous reflux for a period of up to 6 months. The pH value of the acid solution was
periodically checked and adjusted to keep in the range of pH = 1-2. The specimens were periodically withdrawn from the reflux apparatus, dried using lint free tissues to remove surface liquid, and weighed. The electrical conductivity was also measured periodically. Finally, the specimens were dried in a high vacuum oven for 3 months at 60°C, and for an additional 3 months at 140 ºC. The glass transition and thermal degradation temperatures were measured after the hygrothermal aging process. The mechanical properties of the epoxy resins and composites were measured by dynamic mechanical analysis (DMA) after the hygrothermal aging process.

4.9 Thermal Conductivity

The basic principle for PEM fuel cells is that hydrogen and oxygen react to generate water, and at the same time generate electricity and heat. To keep the PEM fuel cells at constant operating temperature, heat must be removed from the fuel cell stack through bipolar plates. Thus high thermal conductivity is a requirement for management of heat in PEM fuel cell stack.

Thermal conductivity, \( k \) is the property of a material that indicates its ability to conduct heat. It is defined as the quantity of heat, \( \Delta Q \), transmitted during time \( \Delta t \) through a thickness \( L \), in a direction normal to a surface of area \( A \), due to a temperature difference \( \Delta T \), under steady state conditions and when the heat transfer is dependent only on the temperature gradient, as shown in Equation 4. 3.

\[
k = \frac{\Delta Q}{\Delta t} \times \frac{L}{A \times \Delta T}
\]  

(4.3)
In this study, the thermal conductivity of the composites was measured by a thermal conductivity measurement device built in-house. The functions of the device are schematically illustrated in Figure 4.5. Five thermocouples were used to record the temperature gradient in the reference rod, the temperature gradient of the samples or the calibration specimens, and the temperature difference between the contact surfaces between the two reference rods and the samples. The $L_1$ and $L_2$ represent the length of the reference copper rod and the test samples. The temperatures $T_1$ – $T_5$ represent respectively the temperatures of top reference rod, bottom reference rod, top calibration rod, bottom calibration rod and bottom copper rod.

Figure 4.4 Schematic illustration of thermal conductivity measurement device. The units 1-6 represent respectively the copper plate as the heat source by resistive heating, reference copper rod, testing samples or calibration metal rod, bottom copper rod, copper plate for cooling, and water bath for cooling.
In Figure 4.4 the top copper plate (unit 1) was used for heating, and its temperature was maintained at a constant value of 100 °C. At the bottom, another copper plate (unit 5) was kept at a constant temperature of 25 °C by water flows. Rod-2 was the reference specimen made of copper with known thermal conductivity of 385 W/K/m. Rod-4 was made of copper, the same metal as of Rod-2. Each of the samples or calibration specimens was kept in the device for 30 minutes to allow steady state, after which temperature readings of various thermocouples were registered.

It was assumed that the heat flow rate through the two copper rods (Rod-2 and Rod-4) and the samples was the same under steady state. Three metal rods, brass, copper, and aluminum with the same diameter as that of the reference rods were chosen to calibrate the device. It was found from measurements with three calibration specimens that our assumption of constant heat flow rate through Rod-2, Rod-4 and the sample specimens was correct. The thermal conductivity of the samples were then calculated by the following equations 4.4-4.5.

\[
\frac{\Delta Q}{\Delta t} = \left( \frac{k \times \Delta T \times A}{L} \right)_{\text{reference}} = \left( \frac{k \times \Delta T \times A}{L} \right)_{\text{sample}}
\]

\[
k_{\text{sample}} = \left( \frac{k \times \Delta T \times A}{L} \right)_{\text{reference}} \times \left( \frac{L}{\Delta T \times A} \right)_{\text{sample}}
\]

4.10 Coefficient of Thermal Expansion (CTE)

During heat transfer, most materials expand upon heating and contract upon cooling because an increase in temperature leads to greater thermal vibration of the atoms. Thus the energy stored in the intermolecular bonds between atoms increases and leads to
an increase in the molecular bond length and free volume. This response is expressed as coefficient of thermal expansion (CTE). The linear coefficient of thermal expansion $\alpha$ measures the fractional change in length of a material for each degree of temperature increase in the direction being measured, defined by the following equation 4.6:

$$\alpha = \frac{dl}{l_0 \times dT} \quad (4.6)$$

where: $dl$ = the change in length of material in the direction being measured;

$l_0$ = the original length of the material in the direction being measured;

$dT$ = the change in temperature over which $dl$ is measured.

The linear thermal expansion coefficient was measured by dynamic mechanic analysis (DTMA) in the F-control Mode under nitrogen atmosphere by using Perkin Elmer Pyris Diamond DMA from Perkin-Elmer Instruments. The samples (50×8×2 mm) were set onto the DMA clamp, heated and expanded without external force. The original length of the sample was fixed at 20 mm. The heating rate was 4 °C/min. DMA recorded the length of the sample as a function of temperature during heating.

With typical linear CTE in the range of 0-200 ppm/K for polymers and composites, the changes in length are extremely small. As such small changes in length are difficult to measure, the linear CTE of polymers and their composites were usually characterized by thermomechanical analyzer (TMA) or interferometry by different authors [130-133]. In this study, DTMA was used to measure the linear CTE of epoxy resin and composites. In order to ensure the data obtained in our study comparable with the literature data, DTMA was calibrated using strips of copper with purity of 99.999% to determine the contribution of the expansion or contraction of the DTMA fixtures.
respectively under heating and cooling cycle. The linear CTE of pure copper determined in this study was compared with that of the pure data and the difference was identified as the contribution from DTMA fixture. The subsequent experimental data were corrected by taking into account this contribution. It was found that the CTE of DMA fixture fell between $7 \times 10^{-6}$ and $8 \times 10^{-6}$ m/m/K. Typical CTEs of polymers are much larger than this value. Therefore, we conclude that data measured by DTMA would be accurate when the CTE of the sample is larger than that of copper $16.7 \times 10^{-6}$ m/m/K.

However, when the CTE of the composites is smaller than the CTE of the DMA fixture, negative data would be obtained.

4.11 Surface Characterization of Graphite Oxide and Expanded Graphite

As is well known, certain functional groups such as carboxyl, carbonyl, hydroxyl, and epoxide groups are present on the surface of the graphite oxide and expanded graphite. In this study, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared attenuated total reflection (FTIR-ATR) spectroscopy are used to characterize the surface chemistry of graphite oxide and expanded graphite.

XPS measurements were performed in a VG ESCALAB Mk II system under high vacuum conditions (around $10^{-9}$ mbar). The aluminum anode on a Mg/Al X-ray source was used at a power of 180 W with a fixed analyzer transmission energy of 100 eV.

The IR spectra were recorded on a Nicolet Nexus 870 FT spectrometer equipped with a Thunderdom® ATR accessory. The samples were pressed gently on a Ge crystal window and each spectrum was averaged over 64 scans at a 4 cm$^{-1}$ bandwidth.
4.12 Influence of Graphite on Curing Kinetics of Epoxy

In this study, large amounts of EG were added to the epoxy resins in order to obtain high values of electrical conductivity. It was acknowledged that such large quantities of EG might influence the cure kinetics of the epoxy resins. So it was felt important to characterize the cure kinetics of epoxy resins. DSC was used to characterize the influence of expanded graphite and carbon black on the curing temperatures and heat flow. For this purpose, a TA Instruments 2920 Modulated DSC (New Castle, DE) was used with a heating rate of 10 °C/min.

4.13 Influence of Curing Conditions on the Properties of Epoxy Composites

In this study, epoxy composites were cured at high temperatures (~180 °C) under high pressure by using compression molding machine. The cure temperature, pressure and time needed to be optimized because these curing conditions were expected to influence the properties of the epoxy composites. In this study, the influence of curing pressure on the electrical conductivity was investigated. The curing pressure significantly affected the electrical conductivity and the mechanical properties of the composites due to the porosity and powder-liked raw materials before curing. Higher curing pressure reduced the porosity of the composites, and resulted in higher electrical conductivity and stronger mechanical properties. This study was conducted by using a compression molding machine to apply and record the curing pressures and temperatures.
4.14 Temperature Effect on Electrical Conductivity

Some researchers reported that conductive epoxy composites have the positive temperature coefficient (PTC) effect [134-136]. As the composites were developed for application as bipolar plates in PEM fuel cell, the usage temperatures would be around 60-140 °C. We felt it was important to investigate the temperature effect on the electrical conductivity of the epoxy composites. The experiment was conducted by using Keithley 580 (Cleveland, OH) to measure the resistance of the composites at different temperatures. The temperature of the composite samples was controlled by a compression molding machine.
CHAPTER V

OPTIMIZATION OF POLYMER MATRIX COMPOSITION

5.1 Introduction

The polymer matrix of the composites was derived from a mixture of two types of epoxy resins, an aromatic and an aliphatic epoxy resin cured by a diamine curing agent. The aromatic epoxy was DGEBA in the form of Epon® 826. The aliphatic epoxy was polypropylene glycol glycidyl ether in the form of Araldite® DY3601. DDS was selected as the curing agent. Epon® 826 and Araldite® DY3601 were mixed in the ratio of 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, and 40:60 by weight – these composites will be denoted as EP100, EP90, EP80, EP70, EP60, EP50, and EP40 respectively. Approximately 5 wt% excess DDS than necessary with balanced stoichiometry was added to the epoxy resin mixtures to for curing.

As evident from the value of epoxide equivalent weight, Epon® 826 is capable of producing cross-linked epoxy networks much more rapidly and can provide much higher values of storage modulus than Araldite® DY3601 in a fully cured state with the same curing agent. Epon® 826 cured with DDS produced a brittle material, while Araldite DY3601® cured with DDS produced a gum-like material. On the other hand, the mixture
of 10 wt% Araldite® DY3601 with Epon® 826 (EP90) yielded more ductile material when cured with DDS.

DGEBA contains thermally stable rigid phenyl rings in the backbone and have been used to synthesize high performance epoxy resins in industry due to its fluidity, physical strength after curing, and cost advantage. Unfortunately, it has unacceptable thermal properties ($T_g < 120^\circ C$) for high performance applications unless specialty aromatic curatives are included in the final compounds. Glycidyl groups in an epoxy resin are flexible segments that reduced the viscosity of the resin and enhance the processability. Unfortunately, they also decrease the heat resistance of the cured epoxy resin. The aliphatic linkages in glycidyl groups are the source for early thermal and thermooxidative degradation of a cured epoxy system.

There are two ways to solve the problems listed above. First, multiple ($\geq 2$) functionality and low molecular weight to promote high cross-linking density and rigid structures between two glycidyl groups are key solutions to the improvement of thermal and mechanical properties of the cured epoxy resins. Second, development of specialty curatives such as aromatic diamines is a good method for the improvement of the performance of epoxy resins.

Thus in this study, Epon® 826, a DGEBA type epoxy resin was selected as the major constituent of the polymer matrix. It has very low molecular weight and thus low viscosity and high content of functional groups per gram of resin. Therefore it can promote high cross-linking density and rigid structures between two glycidyl groups. Moreover, we selected aromatic diamine DDS as the curing agent, which can further
improve the thermal and mechanical properties of the cured epoxy resins. Rigid phenyl rings are particularly useful to provide resins with improved heat and thermal resistance and char formation. Undesirably, the rigid structures also drastically reduce the processability of the resin due to solubility reduction and viscosity increases and also add brittleness to the materials. In view of this, an aliphatic epoxy resin, Araldite® DY3601 was selected to combine with Epon® 826 in order to adjust the flexibility of the resultant crosslinked epoxy resins.

The composition of the polymer matrix such as the weight ratio of Epon® 826 to Araldite® DY3601 needed to be optimized to obtain the desired mechanical properties, thermal properties and the material processibility. The following polymer matrix compositions were considered in this study: (1) The ratio of Epon® 826 to Araldite® DY3601 were 100:0, 90:10, 80:20, 70:30, 60:40, 50:50, and 40:60 by weight and the respective formulations were defined as EP100, EP90, EP80 and EP70, EP60, EP50, and EP40 respectively. (2) DDS with 5 wt% access above the stoichiometric quantities was added into the above epoxy resin mixtures.

The evaluation of thermal properties and mechanical properties of the resultant cured epoxy resins were carried out to obtain an optimum composition of the polymer matrix systems.

5.2 Glass Transition Temperatures and Dimensional Stability

As the PEM fuel cells are operated at 60-140 ºC, it is important that the bipolar plates are thermally stable at these temperatures. Specifically, the materials should not
deform appreciably or should not undergo thermal degradation over a long period of time. DSC and DMA were used to characterize the $T_g$ of the resultant polymer matrix systems to optimize the formulation of the polymer matrix and obtain an idea of the upper bound of the usage temperature.

Figure 5.1 shows the DSC thermograms and the glass transition windows of various epoxy resin formulations with different compositions. EP100 with the composition of Epon® 826 : Araldite® DY3601 = 100:0 has the highest glass transition temperature of 223 ºC. The glass transition temperature of EP90 is 190 ºC. These two epoxy resin systems have glass transition temperatures much higher than the PEM fuel cell operating temperatures (60-140 ºC). These resins should be dimensionally stable at PEM fuel cell operating temperatures.

Figure 5.1 Glass transition curves of different epoxy resins measured by DSC. The glass transition temperatures of different epoxy systems are shown in the figure.
Figure 5.1 also shows that EP80 has the glass transition temperatures of 156 °C, slightly higher than the PEM fuel cell operating temperatures. All other epoxy resin systems with high content of Araldite® DY3601 showed glass transition temperatures lower than 120 °C. These materials such as EP70, EP60 EP50 and EP40 are thought to be not suitable for application as bipolar plates in PEM fuel cells as these materials may deform at the higher end of PEM fuel cell operating temperatures.

DMA was also used to evaluate the loss factor \( \tan \delta \) of the epoxy resin systems with different formulations as function of temperature shown in Figure 5.2. From Figure 5.2, we again observed that the glass transition temperatures of EP100 and EP90 are higher than the PEM fuel cell operating temperatures. EP80 has glass transition temperature slightly higher than PEM fuel cell operating temperatures. The other resins, EP70, EP60, EP50 and EP40 showed glass transition temperatures lower than the PEM fuel cell operating temperatures as already found by DSC.

The glass transition temperatures determined from DSC thermograms and \( \tan \delta \) plots of DMA are summarized in Table 5.1. From the glass transition temperatures of the epoxy resin systems shown in Figures 5.1-5.2 and Table 5.1, we can infer that the EP100 and EP90 are dimensionally stable at the PEM fuel cells operating temperatures. On the other hand, EP80 had glass transition temperature slightly higher than 140 °C, and EP70, EP60, EP50, and EP40 had \( T_g \) lower than 140 °C. Therefore, EP70-EP40 resins were not included in further study.
Figure 5.2 Plots of $\tan \delta$ as a function of temperature of different epoxy resin formulation measured by DMA. Peak temperatures of different epoxy systems are shown in the figure.

Table 5.1 Glass transition temperatures of different epoxy formulations of Epon® 826 and Araldite® DY3601 measured by DSC and DMA.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (ºC) (DSC)</td>
<td>223</td>
<td>199</td>
<td>156</td>
<td>115</td>
<td>92</td>
<td>56</td>
<td>50</td>
</tr>
<tr>
<td>$T_g$ (ºC) (DMA)</td>
<td>216</td>
<td>188</td>
<td>160</td>
<td>131</td>
<td>106</td>
<td>65</td>
<td>53</td>
</tr>
</tbody>
</table>
Epoxy systems of EP100, EP90 and EP80 had high glass transition temperatures. However, these materials also needed to be mechanically strong enough to support the PEM fuel cell assembly and the clamping force. Therefore, mechanical properties of these epoxy resin systems were evaluated below.

5.3 Mechanical Properties

Storage modulus of the resins by DMA, flexural strength, and impact strength were measured to evaluate the mechanical performance of the material for application as bipolar plates in PEM fuel cells. First DMA was used to measure the mechanical properties of the epoxy resin systems, as shown in Figures 5.3 and 5.4.

Figure 5.3 Storage modulus as function of temperature for different epoxy formulations measured by DMA.
From Figure 5.3, we observed that the EP100 and EP90 resins had much higher storage modulus and maintained high values of mechanical properties at temperatures as high as 180 °C. The storage modulus of EP100 and EP90 did not change at the temperature range of 60-140 °C, and values higher than 1400 MPa were obtained. For EP80, at low temperatures, the storage modulus is also very high, but with the increase of temperature, the storage modulus decreases rapidly at the temperature range of 60-140 °C, as shown in Figure 5.4. The other resins such as EP70, EP60, EP50 and EP40 did not show stable values of storage modulus at the PEM fuel cell operating temperatures.

Figure 5.4 Storage modulus as a function of temperature for epoxy resins with different formulations at the PEM fuel cell operating temperatures of 60-140 °C.
From the experimental data of the glass transition temperatures \((T_g)\) and storage modulus presented above, we concluded that EP70, EP60, EP50, EP40 are not suitable for application as bipolar plates in PEM fuel cells. These four epoxy resin systems showed low glass transition temperatures and poor mechanical properties.

Flexural strength, toughness and impact strength of the materials were also measured to evaluate the mechanical properties of EP100, EP90, EP80 and EP70 resins. The flexural stress vs. strain behavior is shown in Figure 5.5. The flexural strength is the maximum value of the flexural stress obtained from stress vs. strain curves as in Figure 5.5. The toughness of the materials is calculated from the area of the flexural stress vs. strain plots. The data are presented in Table 5.2.

![Figure 5.5 Flexural stress vs. strain for epoxy resin with different formulations.](image-url)
From Table 5.2, we observed that EP90 has the highest flexural strength, followed by EP80, EP100, and EP70. Note that EP100 was derived from aramotic Epon® 826 cured by DDS, and contained the largest amount of phenyl rings in the backbone of the system, which gave the system rigidity and high modulus. However, high content of phenyl rings in the backbone also gave rise to brittleness in the material. Incorporation of small amount of aliphatic epoxy Araldite® DY3601, e.g. EP90, brought some flexibility to the system. Thus EP90 has highest flexural strength among the epoxy resins with different formulations. However, large amount of aliphatic epoxy decreased the rigidity of the epoxy backbones, therefore EP80 and EP70 became too soft and the flexural strength decreased. Toughness of the materials —measured by the area under the curves in Figure 5.5, is also shown in Table 5.2. EP90 has higher toughness than EP100 because incorporation of 10 wt% of aliphatic Araldite® DY3601 to the epoxy system gave rise to flexibility to the resultant materials. EP80 and EP70 did not break during test because they were relatively soft and flexible due to the presence of large amount of aliphatic epoxy in the system. Consequently, the toughness of EP80 and EP70 were also high.

<table>
<thead>
<tr>
<th>EP resins</th>
<th>Flexural Strength (MPa)</th>
<th>Toughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP100</td>
<td>136</td>
<td>3.91</td>
</tr>
<tr>
<td>EP90</td>
<td>141</td>
<td>5.58</td>
</tr>
<tr>
<td>EP80</td>
<td>138</td>
<td>7.69</td>
</tr>
<tr>
<td>EP70</td>
<td>114</td>
<td>4.79</td>
</tr>
</tbody>
</table>
The impact strength of the materials was also evaluated by following ASTM D 4812-99 method. The results are presented in Figure 5.6. From Figure 5.6, we see that the impact strength increased with the increase of Araldite® DY3601 content at first. It is seen that EP80 has the highest impact strength ~ 559 J·m. The impact strength decreased slightly with further increase of aliphatic epoxy content.

![Figure 5.6 Impact strength of epoxy resin systems with different compositions.](image)

5.4 Summary

In this chapter, the glass transition temperatures and mechanical properties of epoxy resin systems with different compositions of Epon® 826 and Araldite® DY3601 were evaluated. EP100 and EP90 showed high values of glass transition temperature,
much higher than the PEM fuel cell operating temperatures, and EP80 slightly higher than 140 °C. EP70, EP60, EP50, and EP40 exhibited glass transition temperatures lower than 120 °C, thus are not suitable for application as polymer matrix in composite bipolar plate. Comparing EP100, EP90 and EP80, the storage modulus maintained high values for EP100 and EP90 up to temperatures of 180 °C, but for EP80, it decreased significantly at the temperature range of 60-140 °C. The flexural strength, toughness, and impact strength of EP100 is slightly lower than EP90 because of the rigidity and brittleness of the material. EP80 has acceptable glass transition temperature, high toughness and impact strength. However, the storage modulus at the PEM fuel cell operating temperatures decreased rapidly with the increase of temperatures.

EP90 with the composition of Epon® 826 : Araldite® DY3601 = 90:10 cured with 5 wt% access than stoichiometry of DDS, exhibited high enough glass transition temperature and good mechanical properties. In view of this, EP90 was selected as the polymer matrix for further investigation.
CHAPTER VI

OPTIMIZATION OF CONDUCTIVE FILLER SYSTEMS

In Chapter V, EP90 was determined as the most suitable polymer matrix system for this work. In this chapter, a suitable conductive filler system will be determined and optimized. Note that graphite has very high intrinsic electrical conductivity (~ $10^5$ S/cm) and it is chemically stable under acidic environment. Therefore, synthetic graphite (SG) and expanded graphite (EG) were considered as conductive fillers for development of conductive composites. In this study, three types of synthetic graphite, GP55B, GP44B and GP44R were used. One grade of expanded graphite, Grafeguard® expandable graphite flake160-50N was used. Electrically conductive carbon black (CB) Ketjenblack EC600J was also chosen as a minor conductive filler. This carbon black had porous and fibrillious structures and its intrinsic conductivity was 10-100 S/cm.

The electrical conductivity of the composites filled with single conductive filler as well as combined fillers were evaluated to optimize the filler systems below.
6.1 Electrical Conductivity of EP90/SG Composites

The values of in-plane electrical conductivity of the EP90/SG composites were measured by a Keithley 487 picoammeter-voltage source (Cleveland, OH) and calculated according to ASTM D 257. The data are shown in Figure 6.1. SG content of 40 wt% or higher was used to obtain the desired electrical conductivity. From Figure 6.1, we observed that the conductivity of the composites increased with the increase of graphite content for all three synthetic graphite grades. Also, GP55B gave the highest conductivity at the same filler loadings compared to GP44B and GP44R. However, the overall conductivity of the composites is low, only about 10 S/cm even at the filler loading as high as 80 wt%. This conductivity is still much lower than the DOE target value of 100 S/cm. We also observed that the resultant materials were very brittle. Therefore, we conclude that the composites filled with single filler SG are not suitable for fabrication of bipolar plates due to their low electrical conductivity and poor mechanical properties.

Figure 6.1 In-plane electrical conductivity of EP90/SG composites.

130
6.2 Electrical Conductivity of EP90/SG/CB Composites

Further, we evaluated the electrical conductivity of the composites with combined fillers of SG and CB --Ketjenblack® EC600J. In this case, carbon black content was maintained at 5 wt%. The data are shown in Figure 6.2. It is seen that the electrical conductivity increased with the increase of the total filler content. The highest conductivity for EP90/GP55B/CB composites achieved was 15 S/cm. The in-plane conductivity of composites increased slightly, with the incorporation of 5 wt% carbon black, compared to single filler composites shown in Figure 6.1. However, the conductivity is still much lower than the DOE target value of 100 S/cm even at the filler loading as high as 80 wt%. This observation is surprising as the intrinsic conductivity of graphite is about $10^5$ S/cm. It was realized that the electrical conductivity of the composites depends not only on the intrinsic conductivity of the fillers, but also on the micro-structures, and the level of dispersion of the fillers.

![Figure 6.2 Electrical Conductivity of EP90/SG/CB composites with 5 wt% CB.](image-url)
Figure 6.3 SEM images of synthetic graphite GP4B (a), (b) and (c); and GP4R (d), (e), and (f).
Figure 6.4 Comparison of SEM images of expanded graphite (a), (b) and (c) with SEM images of synthetic graphite GP55B (d), (e) and (f).
All three types of synthetic graphite had bulk density approximately 2.2 g/cm$^3$, and the surface area is low. The particle size of the synthetic is large, of the order of 75 μm. The morphology of synthetic graphite is shown in Figure 6.3. From the SEM images, we can see that the synthetic graphite has very dense structures. Thus in the composites, the graphite particles were possibly coated by a thin layer of epoxy resin, resulting in very low electrical conductivity of the composites.

Compared to synthetic graphite, the expanded graphite exhibited porous structures, low density and large surface area. The morphology of expanded graphite particles was compared with those of SG in Figure 6.4. Figure 6.4 shows that expanded graphite particles possess layered and network structures. It was expected that the layer and network structures if kept in the composites, would result in high electrical conductivity of the composites.

6.3 Electrical Conductivity of EP90/EG/CB Composites

In this study, expanded graphite particles were made by a thermal shock of the expandable graphite flake 160-50N at 900 ºC. This thermal shock of the acid treated expandable graphite gave it highly porous structures with associated voids between the graphite layers. The solution mixing method with low shear force was used to prepare the composites. Thus the layered and network structures of the expanded graphite were maintained in the composites. These layered and network structures formed large fractions of electron conducting paths in the composites, resulting in high electrical conductivity. The electrical conductivity of the EP90/EG/CB composites was measured
by conventional four point probe conductivity measurement device and the data are shown in Figure 6.5.

![Figure 6.5 Electrical conductivity of EP90 composites filled with single filler-EG, and EG combined with 5 wt% of CB.](image)

Figure 6.5 Electrical conductivity of EP90 composites filled with single filler-EG, and EG combined with 5 wt% of CB.

From Figure 6.5, we observed that the electrical conductivity increased with the increase of the total filler content for both composites filled with EG and composites filled with EG combined with 5 wt% CB. It is also seen that incorporation of 5 wt% of CB increased the electrical conductivity. For both composites, the electrical conductivity is higher than the DOE target of 100 S/cm at the total filler loading as low as 40 wt%. For SG filled composites, the conductivity was only 15 S/cm at the filler loading as high as 80 wt%. Therefore, EG is much more effective as conductive filler compared to synthetic graphite. Composites with combined fillers of EG and small amount of CB has higher conductivity compared to single filler EG filled composites.
From the above study, we can see that the electrical conductivity increased when small amounts of CB was added to the systems for both EG and SG filled composites at the same filler loading content. There is positive synergistic effect between graphite and CB. The optimization of CB content is discussed below. The electrical conductivity of epoxy composites filled with 60 wt% total filler content of EG and CB was measured and presented in Figure 6.6. In this case the CB content was varied between 0 and 13 wt%.

![Conductivity vs CB Content](image)

Figure 6.6 In-plane electrical conductivity of EG filled epoxy composites as a function of CB content. The total filler content was 60 wt%.

From Figure 6.6, we can see that the in-plane electrical conductivity increased with the increase of the CB content up to 5 wt%, and then decreased with further increase of the CB content. Composites with 5 wt% CB showed the highest electrical conductivity. This is due to positive synergistic effect on electrical conductivity between EG and CB. However the intrinsic conductivity of CB is much lower than that of EG, thus incorporation of higher content of CB into the composites decreased the electrical
conductivity. In the rest of this study, 5 wt% of CB was selected as the minor conductive filler loading.

6.4 Summary

From the SEM images of synthetic graphite and expanded graphite shown in Figures 6.3 -6.4, we observed that the synthetic graphite had dense regular sphere particles of a typical size of 75 μm. Expanded graphite possesses layered and network structures, as compared in Figure 6.4. We see that it is much easier for fillers with layered and network structures to form electron conductive paths compared to dense regular sphere conductive particles at the same filler loadings. The dispersion and electron conducting path formed for both SG and EG are schematically shown in Figure 6.6.

![Figure 6.7 Conductive fillers of spherical particles (a) and fillers with layered and network structures (b) and (c).](image)

With the solution intercalation mixing method, the epoxy resins penetrated into the pores of the expanded graphite and in-situ polymerized between the graphite layers. Therefore, the layered and network structures of EG were maintained in the composites, thus delivering high electrical conductivity to the composites. With the total filler loading
as low as 40 wt%, the electrical conductivity of the composites is seen to be much higher than the DOE target value of 100 S/cm. When combined with 5 wt% of CB, the electrical conductivity of the composites of EG is much higher than the composites filled with single filler EG.

From the study in this chapter, expanded graphite or expanded graphite combined with 5 wt% carbon black was selected as the conductive filler systems due to the high electrical conductivity of the composites. Other properties of the EP90/EG/CB composites were also evaluated as presented in the next chapters.
CHAPTER VII

SURFACE CHARACTERIZATION OF GO AND EG

The surface chemistry of the expanded graphite is very important for the mechanical and hygrothermal properties of EG reinforced composites. The mechanical properties of the composites can be controlled by tailoring the structure of the EG surface and the interface between the EG and the polymer matrix. Some reactive functional groups on the surface of EG can react with the polymer matrix during mixing and curing, resulting strong interfacial adhesion between the polymer matrix and the filler. Therefore, it is critical to characterize the surface chemistry of the expanded graphite particles.

X-ray photoelectron spectroscopy (XPS), thermogravimetical analysis (TGA) and Fourier-transform infrared attenuated total reflection spectroscopy (FTIR-ATR) were used to characterize the functional groups on the surface of the expanded graphite (EG) and graphite oxide (GO).

7.1 Surface Chemistry of GO and EG by XPS

Figures 7.1-7.2 show the XPS spectra of graphite oxide and expanded graphite respectively. In the case of graphite oxide, C (1s) at about 277.5 eV and O (1s) at about 527 eV generated two significant peaks, which indicated that there are large amounts of
oxygen containing functional groups present at the surface of graphite oxide. Figure 7.2 shows that the $sp^2$ carbon produced a significant peak while oxygen peak is much weaker. This indicates that expanded graphite has much less oxygen containing functional groups. The C (1s) peak of EG is much stronger compared to GO, which means most of the oxidized carbon in GO is reduced to $sp^2$ carbon.

By determining the area under each peak, it is possible to analyze the relative amounts of the elements identified on the surface of the graphite. The data shown in Table 7.1 shows that the oxygen content is about 21% in GO, and 3.9% in EG. Therefore, there are still some functional groups on the surface of EG, but much less than that on the GO. Also, approximately 96% of the carbon element is restored to graphitic network of $sp^2$ bonds in EG, compared to only 73% carbon element in GO.

The amount of $sp^2$ bonds in EG can also be verified by measurement of electrical conductivity, as higher fraction of carbon elements are at $sp^2$ bonding states, could give rise to higher electrical conductivity. But when the carbon is oxidized such as in GO, the hybridization changes to $sp^3$ and the material becomes an insulator. The EG and GO powder were hand packed into two plastic cylinders and pressed to form a solid material for measurement of electrical conductivity. The electrical conductivities of the two cylinders were measured by conventional four point probe device. It is seen from the data presented in Table 7.2 that EG has much higher electrical conductivity than GO.
Table 7.1 Surface chemical composition of GO and EG determined by element analysis using XPS.

<table>
<thead>
<tr>
<th>Element</th>
<th>GO (wt%)</th>
<th>EG (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>73.3</td>
<td>96.1</td>
</tr>
<tr>
<td>Oxygen</td>
<td>21.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Sulphur</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Sodium</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

Figure 7.1 XPS spectrum of graphite oxide.
Table 7.2 Electrical conductivity of GO and EG.

<table>
<thead>
<tr>
<th>Materials</th>
<th>GO</th>
<th>EG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity (S/cm)</td>
<td>$10^{-10}$</td>
<td>1100</td>
</tr>
</tbody>
</table>

From XPS data in Figures 7.1-7.2, we know that GO particles contained larger amounts of oxygen containing functional groups on GO compared to those on EG. High resolution XPS was used to analyze the types of functional groups on both GO and EG particles. Figures 7.3-7.4 show the deconvolution of the C (1s) peaks from high-resolution XPS of GO and EG particles respectively.
In Figure 7.3, the oxygen-containing functional groups can be clearly seen from the asymmetry of the C (1s) peak toward higher binding energies corresponding to non-graphitic C (1s). These functional groups are mostly C-O- bonds, such as epoxide and hydroxyl groups with the binding energies around 279 eV, and C=O bonds such as carboxyl and carbonyl groups with the binding energies around 282.5 eV.

In Figure 7.4, there are still some C-O functional groups such as epoxide and hydroxyl groups at the binding energies around 279 eV, and C=O bonds such as carboxyl and carbonyl groups at the binding energies around 282.5 eV.

The XPS spectra of the surface chemistry of the GO and EG particles show that there are large quantities of C-O bonds and C=O bonds on the surface of GO, and small amounts of functional groups on EG. The content of oxygen element is about 21 wt% on GO, and 3.9 wt% on EG. Comparing these XPS data with literature data [108-110,137-146], we conclude that functional groups with the C-O bonds were most probably epoxide and hydroxyl groups, and the C=O bonded functional groups were mostly carboxyl and carbonyl groups.
Figure 7.3 Narrow XPS spectrum of C (1s) region of graphite oxide.

Figure 7.4 Narrow XPS spectrum of the C (1s) region of EG.
7.2 TGA Analysis of the GO and EG

TGA was used to verify the amount of volatile materials and to determine the thermal stability of the functional groups on GO and EG. The TGA was carried under nitrogen atmosphere. The data are shown in Figures 7.5-7.6.

Figure 7.5 shows a sharp weight loss of GO at the temperature range of 200-400ºC. Note that GO was an expandable graphite flake 160-50N in this study. It is known from the supplier that the expansion starts at a temperature around 160 ºC. That is the reason that a dramatic weight loss was observed at relatively low temperatures. During this dramatic weight loss, most of the functional groups were removed from the GO, and the material turned into EG. The residual weight of the GO was about 78 wt%, indicating that at least 22 wt% functional groups existed on GO before thermal treatment in the TGA machine. The data is comparable to the XPS result of 21 wt% of oxygen content.

![Figure 7.5 Weight loss of GO measured by TGA under nitrogen atmosphere.](image-url)
Figure 7.6 shows the weight loss of EG as a function of temperature. It is seen that there was not much weight loss for EG. The residual weight of EG was 98.5 wt%. A small weight loss at the temperatures around 400 °C occurred. The TGA data of EG shows that there are small amount of functional groups on EG, the amount is at least 1.5 wt%, which is slightly lower than what was supported by XPS result of 3.9 wt% of oxygen.

7.3 Surface Characterization of GO and EG by FTIR-ATR

The surface chemistry of GO and EG was also studied by Fourier transform-infrared attenuated total reflection (FTIR-ATR) spectroscopy. The IR spectra were recorded on a Nicolet Nexus 870 FT spectrometer equipped with a Thunderdom® ATR
accessory. The samples were pressed gently on a Ge crystal window and each spectrum was averaged over 64 scans at a 4 cm\(^{-1}\) bandwidth.

The FTIR-ATR spectra in the region of 0-4000 cm\(^{-1}\) are shown in Figure 7.7. Three sharp and significant peaks at 864 cm\(^{-1}\), 1039 cm\(^{-1}\), and 1161 cm\(^{-1}\), and a broad and asymmetric peak at 1680-1737 cm\(^{-1}\), were observed for GO particles. There are also four corresponding peaks on in the spectra for EG particles, but these peaks are very weak. This means that there are large quantities of functional groups on the surface of GO, and relatively small amounts of functional groups on the surface of EG particles.

The broad and asymmetric peak in the region about 1680-1704 cm\(^{-1}\) in the spectrum of GO are probably due to the C = O stretching vibration of carboxyl and carbonyl groups [147]. The peak in the region about 1716-1737 cm\(^{-1}\) can be regarded as the C = O stretching vibrations of carboxyl groups and lactone groups. The sharp and symmetric peak at 1161 cm\(^{-1}\) could be assigned to C-O symmetric vibration, and 1039 cm\(^{-1}\) and 864 cm\(^{-1}\) peaks are probably due to C-O asymmetric vibration [147-148]. These peaks most probably corresponded to epoxide, hydroxyl and ether groups [147-148].

EG spectrum has the same set of peaks, indicating EG has the same functional groups, such as carboxyl, carbonyl, epoxide and hydroxyl groups. The difference is that EG has much less functional groups on the surface than GO. The thermal treatment of GO removed most of the functional groups, resulting in a reduction of carbon in GO back to \(sp^2\) bonded graphitic carbon. That is the reason that EG is a perfect electrical conductor, while GO is an insulator. The FTIR-ATR results agree well with the data from XPS and
TGA, and the data on the electrical conductivity of hand-packed GO and EG consolidated materials.

Figure 7.7 FTIR-ATR spectra of GO and EG. Bottom line is the spectrum of GO, and the upper line is the spectrum of EG.

7.4 Summary

In this chapter, the surface chemistry of GO and EG was characterized by XPS, TGA, and FTIR-ATR. The results of three different characterization methods agree with each other very well.
The analysis of graphite particles by XPS, TGA, and FTIR-ATR provided evidence that there were large quantities of oxygen-containing functional groups such as carboxyl, carbonyl, hydroxyl, epoxide and lactone groups on the surface of GO. The presence of these functional groups gave GO the ability to undergo large expansion upon thermal shock. There were still small fractions of functional groups present on the surface of EG particles after the heat treatment of GO. These functional groups were most probably carboxyl, carbonyl, epoxide, and hydroxyl groups. These functional groups are very important for the mechanical properties of the resultant composites. Among these functional groups, carboxyl and epoxide groups can readily react with the curing agent DDS of the epoxy matrix, potentially resulting in strong interfacial adhesion between the polymer matrix and EG particles.
CHAPTER VIII

CHARACTERIZATION OF PROPERTIES OF EP90/EG COMPOSITES

In the previous chapters, EP90 was determined as the polymer matrix system, expanded graphite was selected as the major conductive filler, and Ketjenblack® EC600J carbon black was selected as the minor conductive filler. In this chapter, the properties of the EP90 composites filled with EG or combined EG and CB were characterized to evaluate the performance for application as bipolar plates in PEM fuel cells. First, we discuss electrical conductivity in greater detail as high electrical conductivity is an important requirement for the composites to be used as bipolar plates in PEM fuel cells.

8.1 Electrical Conductivity of EP90/EG/CB Composites

High electrical conductivity of 100 S/cm is required for polymer composites to be used as PEM fuel cell bipolar plates. In-plane electrical conductivity is very important for the bipolar plates to avoid voltage loss of the cell due to the potential difference on the surface of the bipolar plates. Through-plane electrical properties are more important for bipolar plates because current flows through the bipolar plates from one cell to the next cell. There are two ways to measure the through-plane electrical properties: one is to measure the electrical conductivity of the composite plate itself, and another way is to
measure the interfacial area specific resistance. The area specific resistance is more
practical for bipolar plates, which allows the engineers to quickly estimate the voltage
loss of each plate. The in-plane and through-plane electrical conductivity, and interfacial
area specific resistance were evaluated and discussed below.

8.1.1 In-plane Electrical Conductivity of Composites

The in-plane electrical conductivity was largely influenced by the total filler
content as well as the filler type and the degree of filler dispersion in the polymer matrix.
In Figure 8.1, CB content was fixed at 5 wt%, and EG content was increased up to 85
wt%. It is seen that the conductivity of epoxy composites increased with the increase of
EG content. The conductivity increased monotonically with the increase of filler content
up to 600 S/cm for 75 wt%, and then jumped sharply to above 1000 S/cm at 85 wt% EG.
The very high electrical conductivity of larger than 1000 S/cm at 85 wt% can be
attributed to physical contacts between the filler particles, which established large
numbers of electron conducting pathways. One can argue that EG content as high as 85
wt% should be used to capitalize on the very high values of electrical conductivity.
However, the mechanical properties were found to be poor when the content of EG was
greater than 65 wt%. It was found that compression molded laminates with filler content
greater than 70 wt% were fragile and in some case can be fractured easily with the
application of small load by hand. In view of this, we focused in this study on
composites containing 35-65 wt% EG and a maximum of 5 wt% CB.
Next, in-plane electrical conductivity of EP90 composites without CB was measured and compared with that of EP90 composites with 5 wt% CB, as shown in Figure 8.2. It is seen that composites with 5 wt% CB provided higher conductivities over those without CB at the same total filler loading. This indicates that CB particles effectively formed additional conductive networks in the composites. This is counter-intuitive, as the intrinsic conductivity of EG is $10^5$ S/cm, much higher than the value 10-100 S/cm of CB and the presence of CB particles should have lowered the overall conductivity instead of increasing it. This can be interpreted in terms of a positive synergistic effect between EG and CB on electrical conductivity. Clingerman et al. [77] also noticed positive synergistic effects using a combination of CB, synthetic graphite, and carbon fiber.
Figure 8.2 In-plane electrical conductivity of EP90 composites as a function of total filler content.

The same positive synergistic effect on electrical conductivity was observed for other epoxy mixtures. In order to study the synergistic effects of EG an CB on electrical conductivity, three composites with different epoxy formulation were made and filled with EG or combined EG and CB. The data are shown in Figures 8.3-8.5. All three epoxy composites showed the same trend: the electrical conductivity of the composites filled with combined fillers of EG and CB is higher than that of the corresponding composites filled with the single filler EG at the same total filler loadings.
Figure 8.3 In-plane electrical conductivity of EP100 composites. Bottom line represents the electrical conductivity of EP100 composites filled with EG. Upper line represents the electrical conductivity of EP100 composites filled with combined EG and 5 wt% of CB.

Figure 8.4 In-plane electrical conductivity of EP80 composites. Bottom line represents the electrical conductivity of EP80 composites filled with EG. Upper line represents the electrical conductivity of EP80 composites filled with combined EG and 5 wt% of CB.
Figure 8.5 In-plane electrical conductivity of EP70 composites with or without 5 wt% of CB.

The synergistic effect can be explained on the basis of additional conductive pathways formed in the presence of CB particles. Note that the intrinsic conductivity of EG is around $10^5$ S/cm and that of CB is between 10-100 S/cm. Nevertheless, the macroscopic resistance of polymer composites depends on two contributions [99]: (1) the resistance of aggregates, $R_a = \rho_i / d$, where $\rho_i$ is the resistivity of the filler, and $d$ is the diameter of the contact area; (2) the resistance of the inter-aggregate space $R_e$, which results from the tunneling resistance. An expression of $R_e$ can be written as $R_e = \rho_t / A$, where $\rho_t$ is the tunneling resistivity, and $A$ is the contact surface area of the particles. The total resistance of the composite, $R$, is the sum of all aggregate resistances $R_{a,i}$ and inter-aggregate space resistances $R_{e,i}$, and given as

$$R = \Sigma R_{a,i} + \Sigma R_{e,i}.$$  (8.1)
Figure 8.6 schematically shows how various resistances contribute to the total resistance of the composites. The resistance of EG particles is very small owing to high value of intrinsic conductivity. In this case, therefore, the total resistance comes primarily from the resistance of the inter-aggregate space, $R_e$ (Figure 8.6a). Accordingly, CB particles, present in the composites, provided additional connections between EG layers, thus reducing the value of $R_e$, and hence the total resistance, $R$ (Figure 8.6c). Note also that CB can efficiently impart electrical conductivity with a minimum loading because of highly branched and hollow structures, high surface area, and small aggregate sizes.

Figure 8.6 Schematic illustration of (a) how various resistances act in series and define the overall resistance, $R$; (b) CB particles placed between two graphite platelets to help reduce the value of $R_e$.

An evidence of the structural arrangement of EG and CB particles included in the resistivity model in Figure 8.6 can be obtained from the SEM images presented in Figure 8.7. These SEM images clearly show that CB particles uniformly distributed in
epoxy/EG/CB composites, and that many CB aggregates were present between graphite layers (Figure 8.7b), thus imparting both high in-plane and through-plane conductivity between the adjacent graphite layers. In this manner, \( R_e \) was substantially reduced, resulting in a lower total resistance or higher total conductivity of the composites.

![SEM images](image)

Figure 8.7 SEM images of (a) EP90/EG/CB (50/50/0), (b) EP90/EG/CB (50/45/5). The granular images inside circles in (b) indicate CB particles.

8.1.2 Through-plane Electrical Conductivity of Composites

The through-plane electrical conductivity changed only slightly in the presence of CB particles, e.g., from 77 S/cm for composite EP90/EG/CB (50/50/0) to 79 S/cm for
composite EP90/EG/CB (50/45/5). Recall that the numbers in the parenthesis represent parts by weight of components in the composites. Such small contribution to through-plane conductivity by the synergistic combination of fillers is counter-intuitive in view of large enhancements observed in the case of in-plane electrical conductivity (Figure 8.2). This can be attributed to large contact resistances encountered during measurements (see Figures 4.2). Specifically, the resistance of Set up 1 was found to be very close to that of Set up 2 in Figure 4.3, apparently due to significant contributions from the contact resistances of four contact surfaces. In view of this, we felt that a better way to characterize the through-plane electrical performance of the composite materials was to measure the values of area specific resistance using Set up 2 in Figure 4.3.

Table 8.1 Through-plane electrical properties of epoxy composites.

<table>
<thead>
<tr>
<th>EP/EG/CB</th>
<th>Through-plane Conductivity (S/cm)</th>
<th>ASR(mΩ·cm²) (1000 psi)</th>
<th>ASR(mΩ·cm²) (2000 psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50/0</td>
<td>77</td>
<td>21</td>
<td>13</td>
</tr>
<tr>
<td>50/45/5</td>
<td>79</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>40/60/0</td>
<td></td>
<td>18</td>
<td>16</td>
</tr>
<tr>
<td>40/55/5</td>
<td></td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>DOE target</td>
<td></td>
<td></td>
<td>&lt; 30</td>
</tr>
</tbody>
</table>

An area specific resistance of less than 30 mΩ·cm² has been accepted to minimize the voltage losses in a stack contributed by the bipolar plates [33]. Typically industrial fuel cell stack prototypes operate at a current density between 1-2 A/cm², and a surface area between 200-400 cm². Using these typical numbers, the voltage drop per plate can
be calculated in the range from 30-60mV. In our study, the area specific resistances of the system, including two copper electrodes, two CP layers, and one bipolar plate (as shown in Figure 4.2 (b)), were measured at different pressure, as shown Table 8.1.

All composites developed in this study have area specific resistance less than 30 mΩ·cm². In view of this, the voltage loss for these composites falls in the range from 20-40 mV. This compares favorably to a voltage drop of 50 mV/cell for a well-humidified 100µm thick Nafion® membrane operated at 1 A/cm² [23,33].

8.2 Mechanical Properties

Bipolar plates must possess good mechanical properties to support thin membranes and electrodes, and to withstand high clamping forces for the stack assembly. However, high loading of conductive fillers required to reach high electrical conductivity, may also introduce voids and defects in the resulting composites, especially if the filler loading is higher than a critical volume concentration, known in additive industry as the critical pigment volume concentration (CPVC) [33,98-99]. In view of this, it is difficult to obtain simultaneously high electrical conductivity and sufficient mechanical strength from the same materials. In this study a solution intercalation method was used to mix the epoxy and fillers with low shear force, which to some extent preserved the layered and network structures of EG particles in the composites. Also, low viscosity allowed epoxy resins and the curing agent to penetrate into the EG gallery and fill the micro- and macro-pores of the EG particles. In addition, the large pressure
applied during epoxy curing led to reduction of the voids and defects. Furthermore, synergistic combination of EG and CB allowed substantial reduction of total filler loading to reach high electrical conductivity. Thus several measures were taken in composite preparation method to eliminate possible sources of voids and defects.

Table 8.2 lists the mechanical properties of the composites. Impact strengths of the samples, 173 and 144 J/m for composites epoxy/EG/CB (50/50/0) and epoxy/EG/CB (50/45/5) respectively, significantly exceed the DOE target value of 40.5 J/m [28-29]. The flexural strengths of epoxy composites without CB are also higher than the DOE target value of 59 MPa [28-29], although the flexural strengths decreased with the addition of 5 wt% CB. The tensile strengths of epoxy composites are lower than the DOE target value of 41 MPa except in the case of 50:50:0 ratio of EP90/EG/CB.

In Section 8.1, a synergistic effect of combination of EG and CB on the electrical conductivity was observed, because of the additional conductive bridges formed by CB between graphite layers. However, from Table 8.2, we see that incorporation of 5 wt% of CB into the EP90/EG composites reduced the mechanical properties compared with single filler EG composites at the same total filler loadings. This is probably due to the disturbance of interfacial adhesion between EG particles and epoxy in the presence of CB particles. Note that small amounts of reactive functional groups such as carboxyl and epoxide groups on the surface of expanded graphite might have readily reacted with the epoxy matrix and developed strong adhesion between the interface of EG particles and epoxy matrix. This in turn
resulted in stronger mechanical properties. The CB particles on the other hand did not contain much reactive functional groups on the surface, and the surface area was much smaller than that of EG particles. Thus incorporation of CB into epoxy/EG composites generated poor adhesion between the interface of CB and polymer matrix and, thereby, resulted in inferior mechanical properties compared with those without CB.

Table 8.2 Mechanical properties of EP90/EG/CB composites.

<table>
<thead>
<tr>
<th>EP90/EG/CB</th>
<th>Flexural Modulus (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Tensile Strength (MPa)</th>
<th>Impact Strength (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60/40/0</td>
<td>$1.77 \times 10^4$</td>
<td>61</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>60/35/5</td>
<td>$0.75 \times 10^4$</td>
<td>40</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>50/50/0</td>
<td>$2.08 \times 10^4$</td>
<td>72</td>
<td>45</td>
<td>173</td>
</tr>
<tr>
<td>50/45/5</td>
<td>$1.49 \times 10^4$</td>
<td>44</td>
<td>26</td>
<td>144</td>
</tr>
<tr>
<td>40/60/0</td>
<td>$2.66 \times 10^4$</td>
<td>82</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>40/55/5</td>
<td>$1.76 \times 10^4$</td>
<td>56</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Target Value [28-29]</td>
<td>59</td>
<td>41</td>
<td>40.5</td>
<td></td>
</tr>
</tbody>
</table>

The mechanical properties data presented in Table 8.3 compares well with the properties of commercial bipolar plates or research reported in literature. For example, composites of PPS and polyethyleneterephthalate with graphite and carbon nanofibers provided in-plane and through-plane conductivity of 230-271 S/cm and 18-25 S/cm respectively [82]. In addition, PPS composites provide flexural strengths of 96 MPa and tensile strength of 58 MPa [82]. Therefore, the polymer composites developed in this study have the advantages of higher electrical conductivity and better mechanical properties over the commercial bipolar plates.
Table 8.3 Comparison of mechanical properties of bipolar plates developed in this study with literature data [82].

<table>
<thead>
<tr>
<th>Manufacturers/ Patent</th>
<th>Polymer</th>
<th>Filler (wt %)</th>
<th>σ (S/cm)</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>In-plane</td>
<td>Thru-plane</td>
</tr>
<tr>
<td>US 6,248,467 (LANL)</td>
<td>Vinyl Ester</td>
<td>68% GP</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>Commercial</td>
<td></td>
<td></td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>Premix Inc.</td>
<td>Vinyl Ester</td>
<td>68% GP</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>BMC 940</td>
<td>Vinyl Ester</td>
<td></td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Plug Power</td>
<td>Vinyl Ester</td>
<td>68 %GP</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>US 4,214,969 (GE)</td>
<td>PVDF</td>
<td>74% GP</td>
<td>119</td>
<td></td>
</tr>
<tr>
<td>US 5,942,347 (GTI)</td>
<td>Phenolic</td>
<td>77.5%GP</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>US 6,171,720 (ORNL)</td>
<td>Phenolic</td>
<td>CF</td>
<td>200-300</td>
<td></td>
</tr>
<tr>
<td>DuPont</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SGL</td>
<td></td>
<td></td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>H2 Economy</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Virginia Tech</td>
<td>PPS</td>
<td>76%GP&amp;CF</td>
<td>271</td>
<td>19</td>
</tr>
<tr>
<td>U Akron</td>
<td>Epoxy</td>
<td>50%EG&amp;CB</td>
<td>300-500</td>
<td>77-79</td>
</tr>
<tr>
<td>DOE target Value</td>
<td></td>
<td></td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>
The flexural modulus and flexural strength of the epoxy composites as function of filler content are presented in Figure 8.8-8.9. We see that both flexural modulus and flexural strength are higher for epoxy composites filled with the single filler EG than those of epoxy composites filled with combined EG and CB. It is also seen that both flexural modulus and flexural strength increased with the increase of total filler content. However, the flexural strain decreased with the increase of the total filler content, as presented in Figure 8.10. This shows that the materials became brittle at higher filler loadings.

Figure 8.8 Flexural modulus of epoxy composites filled with EG or with combined EG and CB fillers.
Figure 8.9 Flexural strength of epoxy composites filled with EG or filled with combined EG and CB fillers.

Figure 8.10 Flexural strain of epoxy composites filled with EG or filled with combined EG and CB fillers.
The tensile strength of both EP90/EG and EP90/EG/CB composites are presented in Figure 8.11 as function of total filler content. Figure 8.11 shows that tensile strength of EP90/EG composites is higher than that of EP90/EG/CB composites for filler content. It is evident that the tensile strength first increased with filler content up to 50 wt%, and then decreased when the filler content further increased from 50 wt% to 60 wt%. This is because hard fillers can reinforce the polymer at relative lower filler loadings, beyond which, the materials become brittle. Incorporation of hard fillers also reduces the elasticity of the composites, which results in lower tensile strength and reduced flexibility of the composites.

Figure 8.11 Tensile strength of epoxy composites filled with EG, and composites filled with combined EG and CB fillers.
In view of the data presented in Table 8.2 and Figures 8.8-8.11, it can be inferred that the composite materials, especially EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites, developed in this study offer strong mechanical properties required for application as bipolar plates in PEM fuel cells.

In Section 8.1, we also reported that high electrical conductivity of 300-500 S/cm was achieved for both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites. Several approaches were taken to deliver the composites both high electrical conductivity and strong mechanical properties simultaneously. First, expanded graphite with layered and network structures was used as conductive filler. This expanded graphite has high intrinsic conductivity for each layer. Second, solution intercalation mixing method with low shear force was used, thus the layered and network structures of expanded graphite were maintained in the composites, as shown in Figure 8.12.

Figure 8.12 Morphology of epoxy composites showing layered and network structures of EG.
Third, expanded graphite has pores and voids in the network and large surface area. Low viscosity epoxy resin penetrated into these pores and voids before it was in-situ polymerized. Furthermore, the reactive functional groups on expanded graphite potentially reacted with the epoxy matrix, thus imparting strong interfacial adhesion between the polymer matrix and the filler layers. This resulted in strong mechanical properties.

8.3 Thermal Stability

As PEM fuel cells are operated at high temperatures, e.g., 60-140 °C, it is important to characterize the thermal stability of the polymer composites. Glass transition temperatures \( T_g \) and thermal degradation temperatures \( T_1 \) and \( T_2 \) of epoxy resins and composites were measured using DSC and TGA respectively, and the data are presented in Table 8.4. It is seen that thermal degradation temperatures \( T_1 \) of all epoxy resins and composites are higher than 360°C, and \( T_2 \) are higher than 400°C. The glass transition temperatures of EP90 resin and composites are around 180°C (also see Chapter VI), which is much higher than 140°C, the highest PEM hydrogen fuel cell operating temperature. These data indicate that EP90 composites are thermally stable, and no thermal deformation and degradation would occur, at the operating temperatures of PEM fuel cells.
Table 8.4 Glass transition and thermal degradation temperatures of EP90 resin and composites.

<table>
<thead>
<tr>
<th>EP90/EG/CB</th>
<th>( T_g ) (°C)</th>
<th>( T_1 ) (°C)</th>
<th>( T_2 ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0</td>
<td>182</td>
<td>390</td>
<td>424</td>
</tr>
<tr>
<td>50/50/0</td>
<td>177</td>
<td>389</td>
<td>414</td>
</tr>
<tr>
<td>50/45/5</td>
<td>174</td>
<td>370</td>
<td>403</td>
</tr>
<tr>
<td>40/60/0</td>
<td>179</td>
<td>385</td>
<td>415</td>
</tr>
<tr>
<td>40/55/5</td>
<td>179</td>
<td>368</td>
<td>402</td>
</tr>
</tbody>
</table>

8.4 Thermal Conductivity

It was discussed earlier that hydrogen and oxygen react to generate electricity in PEM fuel cells, and at the same time generate water and heat. The heat is removed from the PEM fuel cell stack through bipolar plates partly by air flowing through cooling channels inside bipolar plates and partly as sensible heat leaving with water. Thus the bipolar plates are required to possess good thermal conductivity for heat management in PEM fuel cells. The requirement is that the thermal conductivity of the bipolar plate materials should larger than 10 W/m/k.

A great deal of work has been done on improvement of thermal conductivity of polymer composites by incorporation of metal-based particles such as alumina and copper, and carbon-based fillers such as carbon fibers, carbon nanotubes, and graphite into polymer matrix [149-155]. The intrinsic thermal conductivity of crystalline graphite could be as high as 3000 W/m/k [149]. The bulk thermal conductivity of expanded graphite sheet is around 600 W/m/k. Unfilled epoxy resins have very low thermal
conductivity of 0.01-0.3 W/m/k. Therefore, graphite offers a promising route for producing nano-scale polymer composites with high thermal conductivity. Fukushima et al. [149] reported that a nylon 6 nanocomposite filled with 20 vol% of exfoliated graphite, provided thermal conductivity of approximately 4 W/m/k, which is much higher than the thermal conductivity around 0.3 W/m/k of the nylon 6 matrix. Ye et al. [151] developed high density polyethylene (HDPE) composites filled with expanded graphite. It was shown that the thermal conductivity of HDPE composite reached 1.6 W/m/k with 7 vol% of expanded graphite.

In this study, the thermal conductivity of the composites was measured by a device designed in our laboratory, and the data are presented in Figure 8.13 for both epoxy composites filled with EG and epoxy composites filled with EG combined with 5 wt% of CB.

Figure 8.13 shows that the thermal conductivity of EP90/EG composites is slightly higher than that of EP90/EG/CB composites at the same total filler loadings. This is because the intrinsic thermal conductivity of graphite is about 600 W/m/k, while that of Ketjenblack® EC600JD carbon black has relatively low thermal conductivity due to its amorphous carbon and porous structures [149]. Thus composites with single filler of EG have higher thermal conductivity than composites filled with combined EG and CB. The thermal conductivity increased with the increase of the total filler content for both composites. Furthermore, there is a significantly jump in thermal conductivity when the filler loading was increased from 40 wt% to 50 wt% for both composites.
Figure 8.13 Thermal conductivity of epoxy composites.

It is seen that EP90/EG composites showed a thermal conductivity of 13.5 W/m/k with 40 wt% of filler content, which is higher than the target value of 10 W/m/k. The thermal conductivity, however, jumped to 56 W/m/k with 50 wt% of EG. Further increase of the EG content led to only smaller increase in thermal conductivity.

Thermal conductivity of EP90/EG/CB composites also increased with the increase of EG content. There is a sharp jump of the thermal conductivity from 9.6 W/m/k with total filler loading of 40 wt% to 54 W/m/k with 50 wt% total filler loading.

In both cases, a sharp jump in thermal conductivity is observed in Figure 8.13 as the filler content was increased from 40 wt% to 50 wt%. This indicates that conductive paths formed due to the physical contacts between the filler particles as the filler content was raised to 50 wt%.
From the study of electrical and thermal conductivity, mechanical properties, and thermal stability of the composites, we found that the most promising composition of the composites are EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5). Both of them possess high electrical conductivity of 300-500 S/cm, high thermal conductivity larger than 50 W/m/k, strong mechanical properties and desired thermal stability. All of these properties either met or exceeded the DOE target values.

8.5 Coefficient of Thermal Expansion

PEM fuel cells are used in many applications where frequent thermal cycles are encountered, for example, to power vehicles. Consequently, composite bipolar plates may undergo changes in dimension with temperatures. Therefore, low thermal expansion coefficient is required to avoid unmatched expansion of the bipolar plates and the neighboring components. As is well known, polymers have large values of positive thermal expansion coefficient. This drawback restricts the application of polymers in areas where sample dimensions play an important role. Many authors have reported work on reduction of the thermal expansion coefficient of polymers by polymer modification [156], and more frequently by incorporation of carbon fiber, carbon nanotube, graphite, ceramic particles, clay, and various negative thermal expansion materials such as PbTiO$_3$, ZrW$_2$O$_8$ [156-175].

In this study, linear coefficient of thermal expansion in the length direction of epoxy resin and composites were measured by DTMA using the F-control mode. The data are presented in Figures 8.14-8.18 and summarized in Table 8.5.
Figure 8.14 Thermal expansion of unfilled EP90 in the temperature range of (a) 20-250 °C; (b) 60-140 °C; (c) T>T_g.
Figure 8.15 Thermal expansion of EP90/EG/CB (90/5/5) composite in the temperature range of (a) 20-250 °C; (b) 60-140 °C; (c) T>T_g.
Figure 8.16 Thermal expansion of EP90/EG/CB (90/10/0) composite in the temperature range of (a) 20-250 °C; (b) 60-140 °C; (c) T>T_g.
Figure 8.17 Thermal expansion of EP90/EG/CB (50/50/0) composite in the temperature range of (a) 20-250 °C; (b) 60-140 °C; (c) T>T_g.
Figure 8.18 Thermal expansion of EP90/EG/CB (90/45/5) composite in the temperature range of (a) 20-250 °C; (b) 60-140 °C; (c) T>Tg.
Table 8.5 Linear thermal expansion coefficient of epoxy resin and composites.

<table>
<thead>
<tr>
<th>EP90/EG/CB</th>
<th>CTE ($\times 10^{-6}$ W/m/k)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At Room Temperatures</td>
</tr>
<tr>
<td>100/0/0</td>
<td>55</td>
</tr>
<tr>
<td>90/10/0</td>
<td>33</td>
</tr>
<tr>
<td>90/5/5</td>
<td>28</td>
</tr>
<tr>
<td>60/40/0</td>
<td>--</td>
</tr>
<tr>
<td>60/35/5</td>
<td>--</td>
</tr>
<tr>
<td>50/50/0</td>
<td>--</td>
</tr>
<tr>
<td>50/45/5</td>
<td>--</td>
</tr>
</tbody>
</table>

From the data in Table 8.5, we can see that with the incorporation of fillers, such as EG and CB, the linear CTE decreased dramatically in the whole temperature range of measurement. With EG content as low as 10 wt%, the CTE already decreased by half from 87 m/m/k to 45 m/m/k at the PEM fuel cell operating temperature range. The linear CTE became to be almost zero or even negative when the filler content reached 40 wt% of EG. According to the work conducted by Ishikawa et al. [156], the longitudinal CTE of graphite-epoxy laminates composites was almost zero in a very wide temperature range of 100-500 K. They also reported negative CTE of $-0.5 \times 10^{-6}$ m/m/k. These negative values were observed because the CTE of the developed materials were low and smaller than the CTE of the testing set-up and the pure copper strip used for calibration. Hacker et al. [175] investigated the coefficient of thermal expansion of nuclear graphite with increased degree of thermal oxidation. They reported a large difference between room-temperature values of the CTE of the graphite crystals measured perpendicular to
the basal planes ($\alpha_c = 27.0 \times 10^{-6} \text{ K}^{-1}$), and parallel to the basal planes ($\alpha_a = -1.5 \times 10^{-6} \text{ K}^{-1}$). This large difference is due to the contrast between the strong $sp^2$ C-C bonds within basal planes (a-axis) and the weak Van der Waals interaction between the basal planes (c-axis). They reported that the CTE of isotropic moderator graphite measured in the range 20-120 °C lie in the range $4-6 \times 10^{-6} \text{ K}^{-1}$.

Composites with only EG filler show lower CTE than composites filled with EG combined with CB, as shown in Table 8.5 and Figure 8.19. The CTE of EG is almost zero, but the CTE of CB is much higher [156], that is why EG is a more effective filler to reduce the linear thermal expansion coefficient than CB. Another reason is that the surface area of expanded graphite is much larger than CB, thus EG can contact with more polymer chains and thus restrict the movement of these polymer chains and segments.

Figure 8.19 Linear CTE of epoxy resin and composites.
The values of CTE of composites remained almost constant at temperatures lower than \( T_g \). However, they were much at temperatures closer to the glass transition temperatures of the resin and the composites. This phenomenon can be clearly seen in Figures 8.14-8.18 (a). The values of CTE became constant again with much higher values at above the glass transition temperatures. Upon heating, the mean distance between the atoms, the molecules and the polymer chains increases, and materials expand. As the temperature reaches the glass transition temperatures, secondary, non-covalent bonds between the polymer chains become weak, polymer chains and segments undergo larger plastic deformation, and higher thermal expansion values are obtained. For unfilled epoxy resin, the CTE jumped from 87 m/m/k at temperatures below \( T_g \), to 214 m/m/k above \( T_g \). For epoxy composites, CTE still jumped to higher values above \( T_g \), however this jump is much less for 10 wt% filler loading in composites, as EG potentially restricted the movement of the polymer chains and segments.

This is another reason why the polymer matrix should have higher \( T_g \) than the PEM fuel cell operating temperatures so as to avoid large thermal expansion at temperatures higher than \( T_g \).

In summary, the CTE of both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites are very low in the PEM fuel cell operating temperature range of 60-140 °C. The CTE of EP90/EG/CB (50/45/5) composite is 2.2 m/m/k, and almost zero for EP90/EG/CB (50/50/0) composite. Thus both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites satisfied the requirement for low thermal expansion coefficient for application as bipolar plates in PEM fuel cells.
8.6 Oxygen Permeation Rate

As hydrogen and oxygen flow through the flowing channels in bipolar plates in PEM fuel cell, good gas barrier properties are required for bipolar plates to separate the reactant gases and to reduce the voltage loss due to gas crossover [33,176-181]. At the same time, bipolar plates with good mechanical properties, area specific resistance less than 30 mΩ·cm² [33], and plate thickness less than 2 mm are also required to meet the vehicular volumetric power density target (>2kW/L) for application in cars [33]. However, it is difficult to meet all these targets simultaneously when using polymer composite bipolar plates. The DOE target requires that the H₂ permeation rate of the composite should be less than $2 \times 10^{-6}$ cm³/cm²/s at the web-thickness of 0.3 mm for the composite to be used as bipolar plates. Polymer composites are brittle and have some porosity at high conductive filler loadings necessitated by the requirement to obtain high electrical and thermal conductivity. It is more likely to generate a high convection-driven H₂ and O₂ permeation rates at high graphite loadings and at thin plate thickness. Therefore, it is important to study the gas permeability of the polymer composites. Figure 8.20 schematically illustrates the gas flow channels within bipolar plates. The plate thickness is less than 2 mm, and the web thickness is usually <0.3 mm.

Figure 8.20 Schematic illustration of H₂ and O₂ flow within the bipolar plates.
In this study, oxygen permeation rate of the polymer composites with thickness of 0.3 mm and the oxygen pressure of 344 KPa was measured at different graphite loading levels, as shown in Figure 8.21.

![Graph showing oxygen permeation rate of epoxy composites at different graphite loadings. The plate thickness is 0.3 mm and the oxygen pressure is 344 KPa.](image)

Figure 8.21 Oxygen permeation rate of epoxy composites at different graphite loadings. The plate thickness is 0.3 mm and the oxygen pressure is 344 KPa.

Figure 8.21 shows that the oxygen permeation rate of epoxy composites decreased with the increase of the graphite loading at filler loading less than 20 wt%. However oxygen permeation rate increased with further increase of the graphite loading after 20 wt%, and there is a sharp increase when the filler loading exceeded 50 wt%. This can be explained as follows using the argument that expanded graphite used in this work had layered structures which in turn provided barrier resistance. Most of the layers are at nano-scale, and the graphite layers have better gas barrier property than the polymer because it has high density. Therefore, incorporation of small amount of graphite decreased the oxygen permeation rate at low filler loadings (as shown in Figure 8.22 a).
At filler loading higher than the percolation threshold concentration for electrical conduction but below the second critical filler concentration, the composite should not contain any void between graphite particles. The second critical filler concentration ($\phi_2$) is termed as critical pigment volume concentration (CPVC) in paint industry. Thus permeation occurs solely by molecular diffusion (Brownian motion) through the polymer phase due to a partial pressure or concentration gradient. In view of this, the dense graphite layers acted as gas barrier, which increased the tortuosity of gas diffusion paths, thus decreasing the oxygen permeation rate. However, the electrical and thermal conductivities were still low (see Sections 8.1 and 8.4) at these compositions, and not enough to meet the fuel cell composite plate targets.

However, with further increase of graphite loading, the gas permeation rate began to increase. This is because voids began to generate in the composites. When the graphite content was increased to above the $\phi_2$, large amounts of voids were generated in the composites due to insufficient polymer matrix to contain all the graphite particles. Locally, these voids might connect with each other to form a gas permeation path (as shown in Figure 8.22 c), thus the gas permeation mechanism changed from diffusion-driven to convection-driven permeation mechanism at higher filler loading. Therefore, oxygen permeation rate increased dramatically when the graphite concentration approached the $\phi_2$. At the same time, the electrical conductivity (as shown in Figures 8.1-8.2) and thermal conductivity (as shown in Figure 8.13) increased significantly around $\phi_2$ due to direct contact between neighboring graphite particles. The electrical conductivity jumped sharply at the graphite concentration around 70 wt% (see Figure 8.1), and the
thermal conductivity changed significantly at the graphite loading of 50 wt% (see Figure 8.13). On the other hand, oxygen permeation rate increased sharply at 60 wt% filler loading (see Figure 8.22). From the data on electrical and thermal conductivity and oxygen permeation rate, we can see that the value of $\phi_2$ of epoxy/graphite composites is approximately 60-70 wt%.

![Diagram](image)

Figure 8.22 Proposed oxygen permeation mechanism in polymer and composites at different filler loading levels: (a) unfilled polymer, diffusion-driven permeation; (b) graphite loading higher than percolation threshold but below $\phi_2$, diffusion-driven permeation; (c) Graphite content at or above $\phi_2$, convection-driven permeation at thin plate section. The symbol $\bigcirc$ represents voids, and black lines represent graphite layers. The film thickness is $t_f$.

Oxygen permeation rates of epoxy composites with 50 wt% EG at different plate thickness ($t_f$) were also measured, and the data are shown in Figure 8.23. With the increase of plate thickness, the oxygen permeation rate decreased significantly.

From the data in Figure 8.21, we can see that the oxygen permeation rates are very low, less than $8.0 \times 10^{-10}$ cm$^3$/cm$^2$/s, for the whole range of EG loading for a plate...
thickness of 0.3 mm, even at EG loading as high as 60 wt%. Therefore, we can conclude that the EP90/EG composites developed in this work are good gas barrier materials.

Figure 8.23 Oxygen permeation rates of epoxy composites with EG content of 50 wt% at different plate thickness of 0.18mm, 0.3mm and 0.5mm.

The DOE target requires H₂ permeation rate of less than $2 \times 10^{-6}$ cm³/cm²/s at plate thickness of 0.3mm, which was not measured in this study. However, according to gas diffusion and Graham’s law, the gas permeation rate of different gases is reversely proportional to the square root of the molecular weight of the gas as shown in the following Equation 8.2.

$$\frac{R_{H_2}}{R_{O_2}} = \sqrt{\frac{m_{O_2}}{m_{H_2}}} = \sqrt{\frac{32}{2}} = 4 \quad (8.2)$$

The H₂ permeation rate was calculated by Equation 8.2 to be around $8.4 \times 10^{-10}$ cm³/cm²/s at the filler loading of 50 wt% with the plate thickness of 0.3mm. This is much
lower than the DOE requirement about the hydrogen permeation rate. Therefore we can say that the composites developed had good gas barrier properties.

According to gas diffusion and Graham’s law, we also anticipate that the results of H₂ permeability measurement would follow the same trends as what was seen in oxygen permeation measurement.

8.7 Processing Methods on Properties

The electrical and thermal conductivity, gas permeation rates and mechanical properties of the composites not only depend on the filler content, but also depend on the extent of dispersion and structures of the filler particles in the polymer matrix. High electrical and thermal conductivities of the composites are required for bipolar plates, which need high conductive filler loading level and filler aggregates to form global conductive paths in the composites. However, in order to achieve good mechanical and gas barrier properties, low filler loading level and good filler dispersion are required. These two requirements contradict each other for both layered fillers and spherical fillers.

In this study, EG was selected as conductive filler, which possesses layers at nano-scale, resulted in good dispersion and good mechanical and gas barrier properties. These EG layers were connected with each other and formed global network, which delivered high electrical and thermal conductivity. The key point is that the layered and network structures of the EG should be maintained in the polymer composites. Therefore selection of the proper mixing methods is very important.
Figure 8.24 Electrical conductivity vs. sonication time for epoxy composites with 50 wt% EG loading.

Figure 8.25 Electrical conductivities of different composites before and after 1 hour sonication.
There are two methods of preparation of polymer composites, one is melt mixing and the other is solution mixing. Melt mixing methods use high shear force, which can easily damage the graphite network structures. Solution intercalation mixing method was selected in this work. During processing, both mechanical stirring and sonication method were used. The electrical conductivities of the composites prepared by sonication are shown in Figures 8.24-8.25.

From Figure 8.24, we see that the electrical conductivity decreased dramatically with the increase of sonication time at the beginning, then leveled off with further increase of the sonication time for the EP90/EG/CB (50/50/0) composites. With 10 minutes of sonication, the electrical conductivity reduced from 325 S/cm to 120 S/cm. This is because that the global network structures of the expanded graphite were damaged by sonication, resulting in break down of the electron conductive paths.

The electrical conductivities of several epoxy composites after one hour of sonication were also measured, as presented in Figure 8.25. The conductivities decreased to approximately 50 S/cm for all four composites after one hour of sonication. Sonication can produce good dispersion of the filler in the polymer composites, however it also damage the global conductive network structure of expanded graphite. A typical scenario is schematically shown in Figure 8.26. Figure 8.26 (a) shows the layered and network structures of expanded graphite. Figure 8.26 (b) shows the morphology of EG-filled composites produced by using mechanical stirrer. We can clearly see that the layered and network structures were retained in the composites. Epoxy resin penetrated into the pores of expanded graphite and in-situ polymerized. Therefore, both good dispersion and global
Conductive networks were achieved by this solution intercalation mixing method without sonication. Figure 8.26 (c) shows that sonication broke down the network structures of the expanded graphite into platelets, which led to good dispersion. However, it was found that the electrical conductivity of the composites prepared by sonication was much lower than those prepared by mechanical stirring.

Figure 8.26 Effect of mechanical stirring and sonication on the network structures of expanded graphite: (a) expanded graphite; (b) expanded graphite after mechanical stirring in composites; (c) Expanded graphite after sonication. Top row is the schematic illustration of the effect of mixing on the morphology of expanded graphite. Bottom row are the SEM images of expanded graphite with different processing.

In summary, we conclude that solution intercalation mixing method without sonication kept the layered and network structures of expanded graphite in the
composites. Therefore, high electrical conductivity and good mechanical properties were achieved simultaneously for the composites, while sonication is an effective way to obtain good dispersion of fillers in polymer matrix. However sonication damaged the network structures of expanded graphite, and resulted in much reduced electrical conductivity even with 10 minutes of sonication. Therefore, mechanical stirring without sonication was selected as the mixing method in this study.

8.8 Effect of Curing Pressures on Electrical Conductivity

The curing pressure was expected to significantly influence the electrical conductivity of the composites in view of the porous structure of EG and the high loadings of filler content. In this study, electrical conductivities of EP90/EG/CB (50/45/5) composite cured at different pressures were measured, as shown in Figures 8.27-8.28. Figure 8.27 shows that the electrical conductivities of the composites increased with the increase of the curing pressures due to the reduction of the distances between EG particles and formation of more electron conductive paths. The electrical conductivity of the composites did not change much when the curing pressures increased above 3000 psi. In view of this, the curing pressure was set at 4000 psi in the rest of the study. We also observed that the materials were still in the powder form after curing when the curing pressure was lower than 1000 psi. The composites were very brittle under the curing pressure of 2000 psi. The composites became mechanically strong when the curing pressure was reached 3000 or 4000 psi. The electrical conductivities of composites with different total filler loadings were measured for curing pressures at both 3000 psi and
4000 psi, as shown in Figure 8.28. For both curing pressures, electrical conductivity of the composites increased with the increase of total filler content. Composites cured at 4000 psi had slightly higher electrical conductivity than those cured at 3000 psi.

Figure 8.27 Electrical conductivities of EP90/EG/CB (50/45/5) composites cured at different curing pressures. Zone I means the cured materials were still in the powder form. Materials in Zone II were obtained in bulk consolidated form.

Figure 8.28 Electrical Conductivities of epoxy composites with 5 wt% of CB as a function of total filler content cured at 3000 psi and 4000 psi.
The morphology of the resulting composites cured at different pressures is compared in Figure 8.29. From the SEM images, we see that the composites cured at low pressure had very porous structure, and even gap between graphite layers are visible. However, when the curing pressure was increased to 3000 psi or 4000 psi, dense composites resulted and no obvious voids were observed.

![Figure 8.29 Morphology of epoxy composites at different curing pressures: (a) 1000 psi; (b) 3000 psi; and (c) 4000 psi.](image)

In summary, the electrical conductivity of the epoxy composites increased with the increase of curing pressure. Dense composites were achieved with high electrical conductivity when cured at 3000 psi and 4000 psi. The composites cured at 4000 psi offered the highest electrical conductivity. Other curing parameters, such as curing temperature and curing time were chosen according to literature survey [182-192]. Detailed information will be presented in Section 8.10.
8.9 Temperature Effect on Electrical Conductivity

Some researcher reported positive (PTC) and negative temperature coefficient (NTC) effects on the electrical resistivity of polymer composites, which usually occurred at the conductive filler content slightly above the percolation threshold concentration \([71,134,193-204]\). These phenomena were schematically shown in the following Figures 8.30-8.32 respectively.

![Figure 8.30 Schematic illustration of percolation threshold concentration of conductive polymer composites. \(V_f\)—percolation threshold concentration.](image)

\[0 5 10 15 20 25\]

\[V_f\]

\[\log \sigma (\text{S/cm})\]

\[V_c\]
Figure 8.31 Schematic illustration of NTC effect on electrical resistivity. The electrical conductivity jumps at the transition temperature of the polymer matrix, which is either a glass transition temperature or melting point, represented by $T_{\text{trans}}$ here.

Figure 8.32 Schematic illustration of PTC effect on electrical resistivity. The electrical conductivity jumps at the transition temperature of the polymer matrix, which is either a glass transition temperature or melting point, represented by $T_{\text{trans}}$ here.
Bar et al. [203] observed PTC effect on the electrical resistivity for DGEBA/TETA epoxy filled with copper coated mica composites at the temperatures around glass transition temperature, and at the filler contents which were slightly above the percolation threshold concentration. This PTC effect on electrical resistivity at temperatures close to transition temperatures can be explained as follows. Thermal expansion coefficient of most polymers increases significantly at temperatures close or above their transition temperatures. When the filler content is slightly above the percolation threshold concentration, the electron conductive paths begin to form because of physical contact between the conductive particles. The conductive network between the particles will be destroyed due to large thermal expansion at temperatures close to or above the transition temperatures. In this case, the electrical resistivity increases sharply as the temperature is raised.

NTC effect on electrical conductivity is not common for conductive polymer composites. In some cases, the conductive polymer composites show PTC effect on electrical resistivity when the temperature increases to around glass transition temperature. This is followed by NTC effect with further increase of the temperature, as observed by Di et al. [198] in low-density polyethylene (LDPE) filled with CB and carbon fiber (CF). As a result, the complete PTC/NTC phenomena occurring in the same materials can be described by the following: the electrical resistivity first increases with the increase of temperature close to glass transition temperature of the polymer. This is followed by a dramatic drop in resistance at temperatures higher than the glass transition temperatures. Conductive particles disconnect the electron conductive paths upon large
thermal expansion at temperatures around $T_g$, but the conductive particles reaggregate to form electron conductive paths at higher temperatures, resulting in NTC effect.

As the PEM fuel cells operate at 60-140 °C, it is important to characterize electrical conductivity of the composites at the whole operating temperatures to make sure the plate materials developed in this work are capable of maintaining high electrical conductivity.

In this study, electrical conductivity of both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites were investigated as a function of temperatures, as shown in Figure 8.33. It was seen that for both composites, the electrical conductivity did not change much. Only a slightly decrease at the temperatures higher than 200 °C was observed. No PTC or NTC effects on electrical resistivity were observed. In this case, the electrically conductive filler loadings were much higher than the percolation threshold concentration for both composites, thus large quantities of electron conducting paths were formed in the composites. In addition, expanded graphite had layered network structures, which could not be easily destroyed by thermal expansion. Furthermore, the thermal expansion of the composites with such high filler loading was measured to be very low, even at temperatures higher than $T_g$. Therefore, electrical conductivity of both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites did not change much upon heating, even at temperatures above $T_g$. 

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Figure 8.33 In-plane electrical conductivities of epoxy composites as a function of temperature.

In summary, both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites developed in our laboratory maintained stable electrical conductivity at elevated temperatures, much higher than the DOE target value of 100 S/cm at a very wide temperature range.

8.10 Influence of Graphite on Curing Kinetics of Epoxy Resin

It is important to study the influence of graphite on curing kinetics of epoxy resin to optimize the curing temperature and time.
8.10.1 Curing Chemistry of Amine-Epoxy Polymer System

According to literature survey [182-191], the curing reactions of epoxy with DDS are known, as shown in the following Equations 8.3-8.6:

(1) Primary amine – epoxy reaction:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{C} \\
\text{O} & \\
\text{H} & + \text{RNH}_2 \\
\text{H}_2\text{C} & \quad \text{C} \\
\text{N} & \quad \text{R} \\
\text{H} & \\
\text{OH} & \\
\end{align*}
\]

(2) Secondary amine – epoxy reaction:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{C} \\
\text{OH} & \\
\text{H}_2 & + \text{C} \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{NR} & \\
\text{H}_2\text{C} & \quad \text{C} \\
\text{N} & \quad \text{H} \\
\text{H} & \\
\text{OH} & \\
\end{align*}
\]

(3) Etherification reaction:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{C} \\
\text{O} & \\
\text{H} & + \text{CH} \\
\text{OH} & \\
\text{CH} & \quad \text{CH} \\
\text{O} & \quad \text{CH}_2 \quad \text{CH} \\
\text{OH} & \\
\end{align*}
\]

Epoxy – DDS curing reaction:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{C} \\
\text{O} & \quad \text{C} \\
\text{H} & + \text{NH}_2 \quad \text{SO}_2 \quad \text{NH}_2 \\
\text{OH} & \quad \text{H}_2\text{C} \quad \text{CH}_2 \\
\end{align*}
\]
The mechanism and kinetics of epoxy-amine curing reaction have been widely analyzed [182-191]. Three principal reactions happen in the system, as shown in Equations 8.3-8.5. The first step is the reaction of the primary amine hydrogen with the epoxide group, as shown in Equation 8.3, followed by secondary amine hydrogen reacting with another epoxide group, as shown in Equation 8.4. The tendency of the etherification reaction depends on the curing temperature, the type of diamine, and the initial ratio of epoxy-amine. Riccardi et al. [183] suggested that the etherification reactions should be taken into consideration when aromatic diamines were used. They used IR spectroscopy to characterize the cured samples and provided evidence of the presence of the etherification reaction when cured at 180 °C. This etherification reaction occurred at the last stage of curing, especially at high curing temperatures.

Table 8.6 Glass transition temperatures of DGEBA/DDS system under different curing temperatures [185].

<table>
<thead>
<tr>
<th>Insothermal Condition (°C)</th>
<th>Curing Time (min)</th>
<th>Conversion (%)</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>465</td>
<td>64</td>
<td>118</td>
</tr>
<tr>
<td>130</td>
<td>421</td>
<td>72</td>
<td>140</td>
</tr>
<tr>
<td>140</td>
<td>384</td>
<td>83</td>
<td>155</td>
</tr>
<tr>
<td>150</td>
<td>342</td>
<td>84</td>
<td>162</td>
</tr>
<tr>
<td>160</td>
<td>208</td>
<td>87</td>
<td>173</td>
</tr>
<tr>
<td>170</td>
<td>183</td>
<td>91</td>
<td>185</td>
</tr>
<tr>
<td>180</td>
<td>175</td>
<td>93</td>
<td>186</td>
</tr>
</tbody>
</table>
In our study, high $T_g$ is required for the composites to be capable of using as bipolar plates in PEM fuel cells. Therefore high curing temperature is preferred. But too high a curing temperature might result in etherification reaction at the last curing stage as reported by Riccardi et al. [182] and a brittle polymer matrix. Therefore 180 °C was selected as the curing temperature in this study, and the curing time was 4 hours, followed by a post-cure processing to complete the curing at 200 °C for another 4 hours.

In our study, DGEBA/DDS cured at 180 °C and post-cured at 200 °C offered $T_g$ of 223 °C measured by DSC, and 216 °C measured by DMA.

8.10.2 Influence of EG on the Cure Kinetics of Epoxy Resin

It is important to investigate the influence of EG and CB on the cure kinetics of epoxy resins. The influence of EG and CB on epoxy cure kinetics were characterized by DSC using temperature sweep of the curing process. The heating rate was set at 10 °C/min. The heat release during temperature sweep is shown in Figures 8.34-8.38, summarized in Table 8.7.

Table 8.7 Curing kinetics of epoxy resin and composites.

<table>
<thead>
<tr>
<th>EP90/EG/CB</th>
<th>Curing Peak T (°C)</th>
<th>Heat Flow (J/g sample)</th>
<th>Heat Flow (J/g epoxy)</th>
<th>Curing T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0</td>
<td>230</td>
<td>269</td>
<td>269</td>
<td>172</td>
</tr>
<tr>
<td>50/50/0</td>
<td>218</td>
<td>134</td>
<td>268</td>
<td>159</td>
</tr>
<tr>
<td>50/45/5</td>
<td>216</td>
<td>125</td>
<td>250</td>
<td>162</td>
</tr>
<tr>
<td>40/60/0</td>
<td>216</td>
<td>99</td>
<td>248</td>
<td>160</td>
</tr>
<tr>
<td>40/55/5</td>
<td>218</td>
<td>97</td>
<td>243</td>
<td>163</td>
</tr>
</tbody>
</table>
Figure 8.34 Curing curve of unfilled epoxy resin with DDS at a heating rate of 10 °C/min.
Figure 8.35 Curing curve of EP90/EG/CB (50/50/0) composite by DSC at a heating rate of 10 °C/min.
Figure 8.36 Curing curve of EP90/EG/CB (50/45/5) composite by DSC at a heating rate of 10 °C/min.
Figure 8.37 Curing curve of EP90/EG/CB (40/60/0) composite by DSC at a heating rate of 10 °C/min.
Figure 8.38 Curing curve of EP90/EG/CB (40/55/5) composite by DSC at a heating rate of 10 °C/min.
According to data in Table 8.7, we see that the epoxy curing temperature and curing peak temperature of unfilled epoxy were 172 °C and 230 °C respectively. The curing temperature range was very wide, from 93 °C to 350 °C for unfilled epoxy resin, as shown in Figure 8.34. The epoxy curing temperatures and curing peak temperatures of all composites decreased to approximately 160 °C and 217 °C respectively. The curing temperature range was narrow, starting from a much higher temperatures of 120 °C and finished curing at a lower temperature of around 330 °C (as shown in Figure 8.35-8.38), which indicates that the curing temperature windows became narrow and the curing occurred faster with the incorporation of EG and CB.

Higher curing temperature results in faster curing and higher $T_g$, but a brittle material. From the resulted data in Table 8.7, we can see that curing temperature of unfilled epoxy is the highest, 172 °C. In this study, curing temperature of 180 °C was selected as the curing temperatures for all epoxy resin and composites in this study.

The heat generated during curing for composites slightly decreased with the increase of filler loadings. The heat flow of composites with 5 wt% of CB even decreased more than only EG filled composites at the same total filler loadings.

In summary, the curing temperature was determined to be 180 °C for all epoxy resin and composites. Incorporation of EG and CB decreased the curing temperatures, and also accelerated the curing process and narrowed the curing temperature windows of the epoxy.
8.11 Summary of Properties of EG-filled Epoxy Composites

In this Chapter, the properties of EG-filled epoxy composites were investigated. The study showed that highly conductive epoxy composites can be developed using synergistic combinations of EG and CB as conductive fillers. The data on electrical conductivity, thermal and mechanical properties indicate that these composites will be very suitable for bipolar plates in PEM hydrogen fuel cells. Specifically, the composites developed in this study exceeded many specifications set by DOE targets and industry. Both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites provide in-plane conductivity of ~200–500 S/cm, high through-plane conductivity of 77 S/cm, low area specific resistance, high glass transition temperatures ($T_g \sim 180 \, ^\circ\text{C}$) and high thermal degradation temperatures ($T_2 \sim 415 \, ^\circ\text{C}$). The thermal conductivity is larger than 50 W/m/K. The linear CTE is extremely low at the total filler loading of 50 wt%. The composites maintained high electrical conductivity at high temperatures.
CHAPTER IX

HYGROTHERMAL EFFECT ON PROPERTIES OF EPOXY COMPOSITES

As bipolar plates is used under the PEM fuel cell operating conditions of high temperatures, high humidity, and highly acidic environment, it is important to investigate the hygrothermal effects of these conditions on mechanical, thermal, and electrical properties of highly conductive graphite-based epoxy composites. The hygrothermal aging experiments were designed to simulate the PEM fuel cell service conditions by using water, acid and hydrogen peroxide reflux. Specifically, the composite specimens were immersed in boiling water, aqueous sulphuric acid solution, and in aqueous solution of hydrogen peroxide (6 wt%). Water uptake by specimens, surface appearance, specimen dimensions, glass transition temperatures, thermal stability, electrical properties, and mechanical properties were evaluated. It was found that the water uptake is reversible and increased linearly with the square root of time, and finally reached a plateau, as in linear Fickian diffusion behavior. The presence of graphite significantly reduced the rate of water uptake and hence water diffusivity. No discernible changes in surface appearance and specimen dimensions were recorded. The electrical conductivity and mechanical properties remained unchanged, and SEM images showed no discernible changes in morphology. The glass transition temperatures of the wet specimens showed
slight reduction, apparently due to the plasticization effect of the absorbed water, and slightly increased after re-drying the specimens. The values of $T_1$ decreased slightly, which can be attributed to water evaporation from the specimens at around 200°C. Nevertheless both $T_1$ and $T_2$ were greater than 350°C, and the composites maintained high electrical conductivity of about 300-500 S/cm, and good mechanical properties.

9.1 Introduction

Recent literature shows significant progress in graphite-based composite bipolar plates with useful contributions of light-weight and low cost with desired properties [71]. Polymer composite bipolar plates are now commercially available from such suppliers as DuPont, H2 Economy, ICM Plastics, NedStack, to name a few. This shows that the technology of polymer composite bipolar plates is maturing [71]. However, many challenges still exist. For example, PEM fuel cells are operated at temperatures greater than 80 °C, and under high humidity and highly acidic environment. Thus bipolar plates are continuously exposed to high temperatures, under high humidity, and to highly acidic membranes and gaseous oxygen. It is critical to evaluate the combined effects of these severe PEM fuel cell in-service conditions on the properties of polymer composite bipolar plates. A very limited literature exists on investigation of hygrothermal reliability and durability of polymer composite bipolar plates at the PEM fuel cell service conditions. In view of this, we undertook a study on the effects of hygrothermal aging on the properties of polymer composite bipolar plates with specific emphasis on expanded graphite (EG) – epoxy composites.
We developed polymer composites with high electrical conductivity and glass transition temperatures greater than 170°C. In addition, the polymer composites also possess strong mechanical, good thermal and chemical properties, and good gas tightness at dry states. It is imperative that the polymer composites bipolar plates should also exhibit long term resistance to hygrothermal aging fatigue, chemical corrosion, and thermal degradation under PEM fuel cell service conditions in order to be viable for application in economically successful PEM fuel cells.

It is learned from existing literature that hygrothermal aging is a degradation process that combines the effects of moisture and temperature and results in substantial deterioration of the thermal and mechanical properties of polymers and composites. A large number of studies reported the effects of hygrothermal aging on polymers and fiber reinforced polymer laminate composites [205-255]. Some researchers suggested multiple water diffusion mechanisms, ranging from the simplest case, a Fickian model, where diffusion is driven by the water concentration gradient, to the more complex stress-dependent, history dependent, and dual phase diffusion models. Although Fickian diffusion is often assumed, diffusion in thermosetting polymers usually involves the concentration-gradient driven Fickian diffusion, and a time-dependent relaxation process. This results in phased or pseudo-Fickian response, usually called the two-stage diffusion model [220]. Fickian diffusion behavior is observed when no chemical degradation occurs in materials [112,224,246,252], thus indicating that the hygrothermal effects are reversible. Non-Fickian diffusion behavior, on the other hand, usually relates to either
chemical degradation of the materials or matrix cracking, and interface debonding between the fillers and the polymers [216,223,238,242-248].

Hygrothermal exposure of polymers and composites can often lead to significant drop in glass transition temperature (T\text{g}) of the materials [112-114,217,220,223,240,242-244,251,254-255]. Such drop in T\text{g} can sometimes be more than 50°C as reported by Cornelia [254-255] for the bismaleimide (BMI)- and polyimide (PI)-carbon fiber composites, and in some rare cases can be as high as 100°C. Mechanical properties, such as tensile modulus and tensile strength, flexural modulus and strength, and adhesion strength also show significant deterioration [114,205,210-215,221-222,224-225,228-229,235-236,241,245,251,253]. For example, Ishak et al. [224] reported a reduction of tensile properties for short glass fiber reinforced poly(butylene terephthalate) composites. A number of other researchers also reported either no change or a slight increase in mechanical properties after hygrothermal exposure [210,217,221-222,241]. Botelho et al. [222] reported that no changes in mechanical properties for the Glare laminate hybrid composites for high performance aerospace applications. Long term hygrothermal exposure can also cause matrix swelling and cracking, moisture vapor induced microvoids, interface debonding behavior between fillers and matrix, surface blistering, and microstructural and composition change due to chemical degradation, such as oxidation and hydrolysis [208-215,225,229,243-244,246-248,251]. These detrimental changes will eventually cause damage to the materials and hence failure of the components.
A ramification of reduction in wet $T_g$, can be microvoids and surface blistering. For example, if the wet $T_g$ approaches the fuel cell operating temperature, the elevated internal moisture vapor pressures can be sufficiently high to generate both interior microvoids and small surface blistering. This is aided by accelerated polymer relaxation at temperatures higher than wet $T_g$. In addition, the intrinsic properties of the polymers and the composites, such as mechanical properties, can significantly deteriorate. Consequently, the values of wet $T_g$ set the acceptable upper limit of the service temperature. In view of this, water diffusion behavior in polymer composite bipolar plates plays a crucial role in determining the wet $T_g$ and hence the performance towards microvoid generation and mechanical failure.

In view of the importance of wet $T_g$, it is useful to fully understand the mechanism of water diffusion in polymer composites. In addition, the effects of the PEM fuel cell service conditions on the properties of the polymer composite bipolar plates must be studied before they can be confidently used in PEM fuel cells. This paper investigates water diffusion mechanism, hygrothermal aging effects on the thermal, chemical, mechanical, and electrical properties of epoxy resins, and graphite/epoxy composites.

Specimens for evaluation of hygrothermal effects were cut from the compression molded sheets. The thickness of the specimen was approximately 0.5 mm. This guaranteed that only one dimensional diffusion of water, perpendicular to the specimen surface, was possible. The edge effect on the diffusion can be neglected. A typical specimen was $80 \times 10 \times 0.5 \text{mm}$. 

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The hygrothermal effects were determined by immersing thin specimens of cured epoxy resins and composites in boiling water, boiling aqueous solution of sulphuric acid (pH=1-2), and boiling aqueous solution of hydrogen peroxide (6 wt%), by allowing continuous reflux for a period of up to 6 months. The pH value of the acid solution was periodically checked and adjusted to keep in the range of 1-2. The specimens were periodically withdrawn from the reflux apparatus, dried using lint free tissues to remove surface liquid, and weighed. The electrical conductivity was also measured periodically. Finally the specimens were dried in a high vacuum oven for 3 months at 60ºC, and for an additional 3 months at 140ºC. The glass transition and thermal degradation temperatures were measured after the hygrothermal aging process. The mechanical properties of the epoxy resins and composites were measured by dynamic mechanical analysis (DMA) after the hygrothermal aging process.

9.2 Water Absorption Profile

The mechanism of water diffusion was studied from the amount of water uptake by the specimens. The water uptake content was calculated from Equation 9.1 as following:

\[ M\% = \left( \frac{W - W_d}{W_d} \right) \times 100\% \]  

(9.1)

where \( M \) is water uptake in percent by weight of the dry specimen, \( W \) is the weight of the specimen at time \( t \), and \( W_d \) is the weight of the dry specimen.

Water absorption profile for the epoxy resin and composites are shown in Figure 9.1. It is apparent that the water absorption in all materials followed the Fickian diffusion
model, whereby the amount of absorbed water increased linearly with the square root of time in the early periods and gradually reached the equilibrium water content after about 100 hours. This is contrary to what was observed by other researchers. For example, Zhou et al. [114] reported non-Fickian water diffusion behavior in graphite/epoxy laminate composites at reflux temperature greater than 90ºC. Bao et al. [216,246-248] reported two-stage diffusion model for the bismaleimide matrix carbon fiber composites system with the first and the second stages being diffusion- and relaxation- controlled respectively. It is seen from Figure 9.1 that the maximum water uptake is about 1.8 % by weight for composites, and 4.3% by weight for unfilled epoxy resin. A reduction in total water absorption in composites can be attributed to the presence of EG and CB fillers. Specifically, incorporation of EG made the composites more hydrophobic in nature, which was reflected in reduction of total water absorption. A positive ramification of this can be easier water management in the operation of fuel cells. The water generated in the PEM fuel cells from reactions between hydrogen and oxygen can form small water droplets on the surface of bipolar plates, which can be easily removed from the fuel cells due to the hydrophobic nature of the bipolar plate surfaces.

Although water absorption profiles in Figure 9.1 present a clear trend, it is interesting to determine and compare the values of water diffusivity in the epoxy resin and composites. Water diffusivity, D, in epoxy resins and composites were calculated by Equation 9.2 [112], the initial slope of the water absorption profiles shown in Figure 9.1. Such data is presented in Table 9.1.

\[
D = \frac{\pi}{16} \left( \frac{h}{M_m} \right)^2 \left( \frac{M_{t_2} - M_{t_1}}{\sqrt{t_2} - \sqrt{t_1}} \right)^2
\]  

(9.2)
where $h$ is the thickness of the specimen, $M_m$ is the maximum water uptake of the specimen, $M_{t1}$ and $M_{t2}$ are the weights of the specimen at times $t_1$ and $t_2$ respectively. The values of times $t_1$ and $t_2$ were chosen from the linear regime in Figure 9.1.

Figure 9.1 Water absorption profiles of epoxy resin and composites during refluxes.

A clear trend is apparent from the data in Table 9.1. Water diffusivity of composites is almost an order of magnitude lower than those of epoxy resins. This can be attributed to the hydrophobic nature and the layered structure of EG particles which induced higher barrier to diffusion of water molecules.
Table 9.1 Water Diffusivity of epoxy resin and composites in water, acid and H$_2$O$_2$ reflux.

<table>
<thead>
<tr>
<th>Material Epoxy/EG/CB</th>
<th>Medium</th>
<th>$M_m$ (%) (6 months)</th>
<th>$D$ ($\times 10^{-6}$) (mm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0/0 Water</td>
<td>4.22</td>
<td>8.4</td>
<td></td>
</tr>
<tr>
<td>100/0/0 Acid</td>
<td>4.20</td>
<td>10.2</td>
<td></td>
</tr>
<tr>
<td>100/0/0 H$_2$O$_2$</td>
<td>4.21</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>50/50/0 Water</td>
<td>1.62</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>50/50/0 Acid</td>
<td>1.59</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>50/50/0 H$_2$O$_2$</td>
<td>1.61</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td>50/47/3 Water</td>
<td>1.77</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>50/47/3 Acid</td>
<td>1.72</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>50/45/5 Water</td>
<td>1.46</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>50/45/5 Acid</td>
<td>1.52</td>
<td>0.66</td>
<td></td>
</tr>
</tbody>
</table>

9.3 Water Desorption Profile

Water desorption profile was obtained by drying the specimens at 60 °C for 3 months, referred to as Step I, and then at 140 °C for another 3 months, referred to as Step II, shown in Figure 9.2. The amount of water desorbed was calculated from Equation (9.3):

$$M_{loss} \% = \frac{M_m - M_t}{M_m} \times 100\%$$

(9.3)

$$M_t = W_t - W_d$$

(9.4)

where the $M_{loss} \%$ is the percentage of weight loss due to desorption of water, $M_m$ is the maximum water uptake by the specimens obtained from the data in Figure 9.1, $M_t$ is the weight of water that remained in the specimens at time $t$, $W_t$ is the weight of the specimens at time $t$, and $W_d$ is the weight of the dry specimens.
Figure 9.2 Water desorption profiles of epoxy resin and composites after water and acid reflux. Step I: the specimens were dried in a vacuum oven at 60 °C for 3 months; and Step II: the specimens were dried in a vacuum oven at 140 °C for another 3 months.

Figure 9.2 reveals that the weight of desorbed water also showed linear behavior with time at the beginning, and reached a plateau at long time at the drying temperature of 60 °C (Step I). Not all water absorbed by the sample could be removed in Step I. Approximately 4 wt% of the absorbed water could not be removed from the specimens with further increase of drying time at 60 °C. This residual water in the specimens is
referred to as locked-in water [112] and can only be removed at temperatures higher than the boiling temperature of water. In view of this, the drying temperature was elevated to 140 °C in Step II. Zhou [112] postulated the existence of two types of bound water in cross-linked epoxy resins. Type I water (as in Step I) is bound by Van der Waals forces or by single hydrogen bonding, while the residual water molecules (removed in Step II) are usually multiply hydrogen bonded with the epoxy molecules, as defined as Type II bound water. Thus the trend seen in Figure 9.2 reveals that both Type I and Type II bound water were presented in the materials considered in this work.

The water that was removed at 60°C may have resided in the free volume of the samples or was bound with epoxy molecules by Van der Waals and/or single hydrogen bonding. Figure 9.2 reveals that this Type I bound water was easily removed from the samples and constituted the majority of water absorbed in the samples. The water removed by drying at 140°C was Type II bound water, and was multiply hydrogen bonded with the epoxy molecules.

It is seen in Figure 9.2 that the original weights of the specimens were recovered after drying at temperature of 140 °C for 3 months. This indicates that water absorption-desorption process is reversible, a ramification of which is the absence of chemical degradation, such as hydrolysis of epoxy, during the reflux process. However, some researchers reported weight loss after hygrothermal aging process, indicating the possibility of chemical degradation [208-215,225,229,243-244,246-248,251], which was not the case in this study.
We can also see that the water desorption rate of the graphite/epoxy composites is much lower than that of unfilled epoxy resin. The graphite not only slows down the water absorption rate as seen in Figure 9.1, but also slows down the water desorption rate. After the drying Step I, epoxy resin almost recovered to its original weight, but there is still some locked-in water remained in all graphite/epoxy composites. The locked-in water was finally removed from the samples after the drying Step II. As will be seen later, this behavior affected the value of thermal degradation temperatures $T_1$.

The water desorption profiles of epoxy resin and composites in hydrogen peroxide solution hold the similar trends to those in water and acid solution. The weight of the desorbed water also showed linear behavior at the beginning, and then reached a steady state at the drying temperature of 60 °C. There were some residual water could not be removed at this drying temperature. The final weight was recovered to their original weight before hygrothermal test.

9.4 Dimensional Stability and Morphology

The specimens subjected to water, acid and hydrogen peroxide reflux presented no discernible change in material dimension and surface appearance by observation. The dimensional stability of the epoxy composites were characterized by recording the thickness of the samples during the hygrothermal testing, as shown in Figure 9.3. The thickness of specimens recorded before and after reflux and drying steps did not show any change from the original specimens, indicating that the specimens had excellent dimensional stability under the PEM fuel cell operating conditions.
Figure 9.3 Thickness of the samples for EP90/EG/CB (50/50/0) composites as a function of square root reflux time.

The morphology of fractured surfaces of composites is shown in Figures 9.4-9.5. The SEM images of both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites, show that there was no interface debonding between graphite layers and epoxy, no micro-cracking or micro-voids in the composites. Some researchers reported that hygrothermal aging processes caused micro-cracking, micro-voids, or water debonding behavior in the interface between fillers and polymer matrices [209,226]. In this work a highly cross-linkable epoxy resin, Epon® 826, was selected. The highly cross-linked thermosetting resin is more resistant to cavitation and associated macro-blistering or micro-cracking than a thermoplastic because thermoset cavitation requires rupture of covalent cross-linked molecular segments. So no micro-structural changes were observed by examining the SEM images.
Figure 9.4 Fracture surface SEM morphology of EP/EG/CB (50/45/5) (a) before hygrothermal exposure, (b) after hygrothermal reflux.
Figure 9.5 Fracture surface morphology of EP/EG/CB (50/50/0) (c) before hygrothermal exposure, (d) after hygrothermal exposure.
The absence of interface debonding between graphite and polymer matrix can be interpreted as follows. Graphite layers are known to contain the functional groups, such as carboxyl, epoxide, hydroxyl, and carbonyl on the surface [108-110,137,256-258]. Of these functional groups, carboxyl and epoxide can react with the –NH₂ amine groups of the curing agent DDS, and result in covalent bonding between graphite and epoxy, as shown in Figures 9.6-9.7. The strongly bonded interface thus formed delivers high resistance to water attack on the interface. The reactions at the interface between functional groups of graphite and DDS can go as follows:
Figure 9.7 Interaction between reactive functional groups on the surface of expanded graphite with curing agent DDS of the epoxy matrix. – represents graphite layers.

The functional groups on the surface of expanded graphite were characterized by XPS, TGA and FTIR-ATR, as detailed in Chapter VII. There were large quantities of oxygen containing functional groups on the surface of GO, and after thermal treatment of GO, there were still small amount of oxygen containing functional groups such as carboxyl and epoxide groups on the surface of expanded graphite. The oxygen content was about 3.9 wt% as measured by XPS. Therefore, the proposed interaction reactions between graphite and epoxy in Figures 9.6-9.7 are reasonable.
9.5 Electrical Conductivity

In view of application as bipolar plates in PEM fuel cells, the highly conductive graphite/epoxy composites must satisfy the requirement to have very high electrical conductivity not only at the dry state, but also maintain high electrical conductivity during the service life. Thus one aim of this study was to monitor the electrical conductivity of the composites during the hygrothermal exposure. The electrical conductivity of the epoxy composites was measured periodically during the hygrothermal aging processing, and the data are shown in Figure 9.8. It is seen from Figure 9.8 that electrical conductivity of the specimens decreased only slightly due to hygrothermal effects up to 6 months, and all specimens maintained electrical conductivity higher than 400 S/cm. Note that the content of the conductive fillers in these composites was substantially higher than the percolation threshold. Thus water uptake has very little influence on the global filler network structures in these composites.

![Figure 9.8 Hygrothermal effect on electrical conductivities of epoxy composites.](image)

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The electrical conductivity of the specimen after hydrogen peroxide reflux showed the same trends as that of water and acid reflux. The conductivity decreased slightly during hygrothermal test, however, it maintained at levels higher than 400 S/cm.

9.6 Mechanical Properties

The polymer composite bipolar plates should also retain good mechanical properties so as to support thin membranes and electrodes, and withstand the clamping forces for the PEM fuel cell stack assembly. Thus hygrothermal effects on mechanical properties of epoxy resin and composites also need to be monitored. In this study, the mechanical properties were characterized by dynamic mechanical analysis (DMA) of the materials after hygrothermal exposure. For the purposes of this investigation, the values of storage modulus (G’) and the loss factor (tan δ) were measured, as shown in Figures 9.9-9.14.

![Figure 9.9 Storage modulus of unfilled EP90 before and after water and acid reflux by DMA.](image)

Figure 9.9 Storage modulus of unfilled EP90 before and after water and acid reflux by DMA.
Figure 9.10 $\tan \delta$ of unfilled EP90 before and after water and acid reflux by DMA.

Figure 9.11 Storage modulus of EP90/EG/CB (50/50/0) composite before and after water and acid reflux by DMA.
Figure 9.12 $\tan \delta$ of EP90/EG/CB (50/50/0) composite before and after water and acid reflux by DMA.

Figure 9.13 Storage modulus of EP90/EG/CB (50/45/5) composite before and after water and acid reflux by DMA.
Figure 9.14 tan δ of EP90/EG/CB (50/45/5) composite before and after water and acid reflux by DMA.

It is seen that the values of storage modulus in Figures 9.9, 9.11, and 9.13, were either the same or increased slightly in some cases after hygrothermal exposure, which is counter-intuitive. The increase is more apparent for composites than for the unfilled epoxy resin. This also indicates that no degradation occurred in the materials as we already mentioned in Sections 9.3 to Section 9.4.

The loss factor (tan δ) vs. temperature plots of epoxy resin and composites are also shown in Figures 9.10, 9.12 and 9.14. The peaks of tan δ shifted to higher temperatures for all composites after reflux, indicating that the glass transition temperatures, T_g increased slightly as a result of the hygrothermal exposure. Table 9.2 presents values of T_g as function of the type and the amounts of fillers. This was also verified by glass transition temperatures measured by differential scanning calorimetry (DSC) in the next section. It is also seen that the peaks of tan δ for composites became
very broad and even split into two peaks. This kind of splitting of the peaks of tan \( \delta \) was observed earlier by other authors [220,226].

Table 9.2 Glass transition temperatures of epoxy resin and composites determined by peak temperatures of tan \( \delta \) by DMA.

<table>
<thead>
<tr>
<th>Epoxy/EG/CB</th>
<th>( T_g (\degree C) ) (DMA)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>100/0/0</td>
<td>186</td>
</tr>
<tr>
<td>50/50/0</td>
<td>190</td>
</tr>
<tr>
<td>50/49/1</td>
<td>188</td>
</tr>
<tr>
<td>50/48/2</td>
<td>187</td>
</tr>
<tr>
<td>50/47/3</td>
<td>189</td>
</tr>
<tr>
<td>50/46/4</td>
<td>185</td>
</tr>
<tr>
<td>50/45/5</td>
<td>189</td>
</tr>
<tr>
<td>50/44/6</td>
<td>186</td>
</tr>
</tbody>
</table>

The slightly increase in both storage modulus and glass transition temperatures measured by DMA can be attributed to slow post-curing that occurred during long term (6 months) exposure of the specimens to boiling water and boiling acid solution. The gradual rearrangement of epoxy molecular chains caused a reduction in free volume and thus a gradual increase in density towards the equilibrium value and a reduction in molecular mobility during hygrothermal aging at elevated temperatures. Barral et al. [260] and Bauwens-Crowet et al. [261] also reported the same trend in phenol novolac epoxy system cured by DDS. The molecular chain rearrangement and the post-curing effect
resulted in the increase of the modulus and the glass transition temperatures of the epoxy resin and composites. Thus the hygrothermal aging process slightly increased the mechanical properties and the glass transition temperatures.

As we also observed that the tan δ peaks broadened and even splitted into two peaks for the composites after hygrothermal aging. This can be explained as following: The absorbed water was bonded with epoxy molecular chains with multiple hydrogen bonding. This part of water acted as a plasticizer in the composites, and the mobility of hydrogen bonded water was higher than the cured epoxy network. But this part of water was not free water. Therefore, the tan δ peaks broadened and even splitted into two peaks. Furthermore, the height of tan δ peaks of the samples after water and acid reflux also increased for all epoxy resin and composites. This is also attributed to the mobility of the absorbed water, which increased the ability of the materials to dissipate energy.

Specimens of hydrogen peroxide reflux showed the same trends in mechanical properties as those of water and acid reflux.

In summary, hygrothermal aging slightly increased the mechanical properties and the glass transition temperatures of the epoxy resin and composites. This is because the molecular chain rearrangement and post-curing effect of the epoxy matrix. Therefore, we can see that the composites developed are mechanically stable for a long term in PEM fuel cell operating conditions.
9.7 Thermal Stability

The polymer composite bipolar plates should also exhibit substantial thermal stability under PEM fuel cell operating conditions. The thermal stability of the composites was characterized in terms of glass transition temperatures ($T_g$) and thermal degradation temperatures ($T_1$ and $T_2$), measured respectively by using differential scanning calorimetry (DSC) technique and thermo-gravimetric analyzer (TGA). The values of $T_g$, $T_1$, and $T_2$ of composites are summarized in Table 9.3 and Figures 9.15-9.16.

From Table 9.3, we can see that $T_g$ of wet specimens after hygrothermal exposure decreased slightly. But after re-drying, the values of $T_g$ were recovered to their original values obtained for specimens before hygrothermal exposure. A slight increase is also seen for some re-dried specimens. The reduction in $T_g$ of wet specimens can be attributed to the moisture-induced plasticization, while the increase in $T_g$ of the re-dried specimens was due to post-curing of epoxy. Some researchers [220,262] suggested that in some cases, the possibility of loss of small molecules during long term hygrothermal exposure, may also cause an increase in $T_g$. In our case, however, the water desorption data showed that there was no dissolution loss from the epoxy resin and the composites. Thus the increase in $T_g$ should be attributed to the post-cure progress of the specimens during hygrothermal exposure. For wet samples with absorbed water, however, the plasticization effect dominates over the effect of post-cure. Thus a decrease in $T_g$ was observed for all epoxy resin and composites.
Table 9.3 Glass transition temperatures and thermal degradation temperatures of epoxy resin before and after water and acid reflux.

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions</th>
<th>$T_g$ (°C) (DSC)</th>
<th>$T_1$ (°C)</th>
<th>$T_2$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>Before</td>
<td>182</td>
<td>390</td>
<td>424</td>
</tr>
<tr>
<td></td>
<td>Wet-water</td>
<td>171</td>
<td>367</td>
<td>424</td>
</tr>
<tr>
<td></td>
<td>Wet-acid</td>
<td>172</td>
<td>352</td>
<td>424</td>
</tr>
<tr>
<td></td>
<td>Redried-water</td>
<td>187</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redried-acid</td>
<td>186</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/50/0</td>
<td>Before</td>
<td>177</td>
<td>392</td>
<td>415</td>
</tr>
<tr>
<td></td>
<td>Wet-water</td>
<td>170</td>
<td>371</td>
<td>416</td>
</tr>
<tr>
<td></td>
<td>Wet-acid</td>
<td>169</td>
<td>345</td>
<td>413</td>
</tr>
<tr>
<td></td>
<td>Redried-water</td>
<td>182</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redried-acid</td>
<td>181</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50/45/5</td>
<td>Before</td>
<td>174</td>
<td>370</td>
<td>402</td>
</tr>
<tr>
<td></td>
<td>Wet-water</td>
<td>168</td>
<td>363</td>
<td>393</td>
</tr>
<tr>
<td></td>
<td>Wet-acid</td>
<td>167</td>
<td>358</td>
<td>395</td>
</tr>
<tr>
<td></td>
<td>Redried-water</td>
<td>179</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Redried-acid</td>
<td>180</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 9.15 Thermal degradation of unfilled epoxy resin before and after water and acid reflux measured by TGA.
Figure 9.16 Thermal degradation of EP90/EG/CB (50/50/0) composite before and after water and acid reflux measured by TGA.

Figure 9.17 Thermal degradation of EP90/EG/CB (50/45/5) composite before and after water and acid reflux measured by TGA.
Thermal degradation temperatures, $T_1$ and $T_2$, are temperatures at 5% weight loss and at the maximum weight loss rate respectively. After water and acid refluxes, $T_2$ of epoxy resin and composites remained at the same high temperatures as before reflux. However, the value of $T_1$ decreased after reflux due to water evaporation upon heating, which were still higher than 350°C. The small peaks in the derivative of weight loss data for all graphite/epoxy composites corresponded to the removal of water at the temperature around 200°C, as shown in Figures 9.16-9.17. However, there are no corresponding small peaks in derivative weight loss of unfilled epoxy resin, as shown in Figure 9.15. In order to observe the phenomenon better, we have enlarged the derivative weight loss for epoxy/EG/CB (50/45/5) composite, as shown in the insert in Figures 9.17. As we have already mentioned in Section 9.3, the incorporation of graphite into epoxy prevented the water from being removed from the specimens. There is relatively more locked-in water in composites, so during the thermal degradation test, there are small peaks at the temperature of around 200°C for all composites, which correspond to the water evaporation peak. For epoxy resin, the water has been almost removed at lower temperatures, so there is no water evaporation peak.

The glass transition temperatures and thermal degradation temperatures of the specimens after hydrogen peroxide reflux showed the similar trends as that of water and acid reflux. The DSC and TGA data indicates that the epoxy composites studied in this work are thermally and chemically stable under the PEM fuel cell service conditions.
9.8 Summary

Effects of long term hygrothermal exposure of the graphite-based epoxy composites developed were investigated in this study. Under the experimental conditions, water diffusion behavior followed the linear Fickian diffusion model for both epoxy resin and composites, indicating that no chemical degradation occurred. Incorporation of EG delivered hydrophobic nature to the composites, and significantly decreased the maximum water uptake and water diffusivity, which is favorable for the water management in PEM fuel cells. There was no change in surface appearance and thickness of the specimens, indicating that the composites were dimensionally stable. SEM images showed no morphology change, no matrix-cracking, micro-voids or interface debonding behavior between graphite and epoxy. The water desorption profile showed that water absorption process was reversible, indicating no chemical degradation of epoxy, such as hydrolysis, or thermal oxidation. DSC and TGA data indicated that the composites were thermally and chemically stable under the PEM fuel cell service conditions. Long term hygrothermal exposure had very little effect on the electrical conductivity and mechanical properties of the epoxy composites.
10.1 Conclusions

Highly conductive carbon-filled epoxy composites were developed for potential application as bipolar plates in proton exchange membrane (PEM) fuel cells. These composites were prepared by solution intercalation mixing, followed by compression molding and curing. Electrical conductivity, thermal and mechanical properties, gas barrier properties, and hygrothermal characteristics were determined as functions of carbon-filler type and content. Expanded graphite and carbon black were used as synergistic combination to obtain desired in-plane and through-plane conductivities.

These composites showed high glass transition temperatures ($T_g \sim 180^\circ$C), high thermal degradation temperatures ($T_d \sim 415^\circ$C), and in-plane conductivity of 200-500 S/cm with carbon fillers as low as 50 wt%. In addition, strong mechanical properties, such as flexural modulus, flexural strength, and impact strength of respectively $2 \times 10^4$ MPa, 72 MPa, and 173 J/m were obtained, which are much higher than the target requirements. Both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites had excellent thermal conductivity of greater than 50 W/m/K. The linear coefficient of thermal expansion decreased dramatically with graphite loading. The linear coefficient of thermal expansion of both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5)
composites are very low in the PEM fuel cell operating temperature range of 60-140 °C. The CTE of EP90/EG/CB (50/45/5) composite is 2.2 m/m/k, and almost zero for EP90/EG/CB (50/50/0) composite. Thus both EP90/EG/CB (50/50/0) and EP90/EG/CB (50/45/5) composites satisfied the requirement for low thermal expansion coefficient for application as bipolar plates in PEM fuel cells. The gas barrier properties were investigated by testing the oxygen permeation rate (OPR). The gas barrier properties increased with incorporation of small amount of expanded graphite particles, but decreased with further increase of filler content after 20 wt%. The gas barrier properties dropped dramatically at 60 wt% loading of expanded graphite.

The electrical conductivity increased sharply at the graphite concentration around 70 wt%, and the thermal conductivity jumped significantly at the graphite loading of 50 wt%. On the other hand, oxygen permeation rate increased sharply at 60 wt% filler loading. The tensile strength of the composites began to decrease significantly around the total filler content of 50 wt%. From analysis of the data on electrical and thermal conductivity, oxygen permeation rate, and mechanical properties, a critical pigment volume concentration (CPVC) of epoxy/graphite composites is assumed to be approximately 60-70 wt% of total filler loading.

Surface chemistry of graphite oxide and expanded graphite was characterized by XPS, TGA, and FTIR –ATR. The XPS and FTIR-ATR spectra show that there are large quantities of oxygen containing functional groups and the oxygen content is about 22 wt% on the surface of graphite oxide. While, there are only small amounts of oxygen containing functional groups left on the surface of expanded graphite, and the oxygen is
about 3.9 wt% measured by XPS and 1.5 wt% measured by TGA. These functional groups could contain carboxyl, hydroxyl and epoxide groups verified by XPS and FTIR-ATR spectra. These functional groups are reactive with curing agent DDS in epoxy matrix. Therefore, the potential interaction between graphite particles and epoxy matrix delivered good interfacial adhesion between graphite particles and epoxy matrix and thus strong mechanical properties to the composites.

As PEM fuel cells are operating at high temperatures, under high humidity and acidic environment, hygrothermal effects on the properties of the composites were investigated to provide long-term reliability and durability of the bipolar plates in PEM fuel cell operating conditions. Under the experimental conditions, water diffusion behavior followed the linear Fickian diffusion model for both epoxy resin and composites, indicating no chemical degradation occurred. Incorporation of EG delivered hydrophobic nature to the composites, and significantly decreased the maximum water uptake and water diffusivity, which is favorable for the water management in PEM fuel cells. The presence of expanded graphite and carbon black fillers helped reduce water uptake from 4-5 wt% for unfilled epoxy resins to 1-2 wt% for composites. There is no change in surface appearance and thickness of the specimens, indicating that the composites were dimensionally stable. SEM images showed no morphology change, no matrix-cracking, no micro-voids or interface debonding behavior between graphite and epoxy. The water desorption profile showed that water absorption process is reversible, indicating no chemical degradation of epoxy happened, such as hydrolysis or thermal oxidation. DSC and TGA data indicated that the composites are thermally and chemically stable under
the PEM fuel cell service conditions. Long term hygrothermal exposure has very little effects on the electrical conductivity and mechanical properties of the epoxy composites. Long-term hygrothermal test shows that the graphite-based polymer composites developed in this study are electrically, thermally, chemically and mechanically stable in the PEM fuel cell service conditions.

Experimental data indicate that the composites developed in this work meet many requirements of bipolar plates. The composites developed in this study are suitable for application as bipolar plates in PEM fuel cells.

10.2 Recommendations

1. The mechanical properties of the materials were tested by the ASTM standards in this study. It is important to know the relationship between the mechanical property data and the thickness of the final plates. So it is recommended that future study investigates the effects of different plate thickness on mechanical properties. The thickness of plates would be an important design variable of PEM fuel cell.

2. In this study, the content of the minor conductive filler CB was fixed at 5 wt% due to an optimum in electrical conductivity. However, the resultant composites with or without CB provided electrical conductivity much higher that what is required by DOE target. In addition, incorporation of CB gave higher coefficient of thermal expansion than composites filled with only expanded graphite. In view of this, a future study should explore other attributes of CB in the system, e.g., on curing kinetics of epoxy.
3. The storage moduli of the epoxy resins showed slight increase at temperatures higher than glass transition temperatures as shown in Figures 5.3. This slight increase of the mechanical properties is assumed to be caused by the larger thermal expansion at temperatures higher than glass transition temperatures or post curing effect during DMA test. A future study should investigate the proper reasons behind this.
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