EFFECT OF BINDER AND FILLERS RATIO ON THE PROPERTIES OF GRAPHITE/CARBON BLACK/EPOXY COMPOSITE FOR BIPOLAR PLATE

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Final Report
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JUNE 2015

FINAL YEAR PROJECT

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DECLARATION

"I hereby declare that this report is my only own work except for the summaries and article that each of that I already cited in the references"

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ACKNOWLEDGEMENT

First of all, I would like to express a lot of thank to Allah S.W.T for giving me strength to completely finish my final year project successfully. I would like to express my gratitude to my advisor, Dr. Mohd Zulkefli Bin Selamat for his guidance, support, encouragement, and inspiration during the course of my degree studies. His patience and kindness are greatly appreciated. May Allah S.W.T bless him in this world and hereafter. My final year thesis would not have been possible done it without invaluable guidance and helping from those experiences. His valuable, suggestion and encouragement enabled me to handle all the tasks of this enormity with confidence. He is the best Supervisor that I ever had.

I am indebted to many people who have been helping me to undergo my final year project period where the presences are the essence to make my training successful. They are people of my respects who involve directly or indirectly throughout this project.

I also would like to express my appreciation to UNIVERSITI TEKNIKAL MALAYSIA MELAKA (UTEM) as they have managed to help me to be well organized and providing me a place to conduct my final year project entitled “Effect of Binder and the Fillers Ratio on the Properties of Graphite/Carbon Black/Epoxy Composite for Bipolar Plate”.

Not to forget all of the faculty of Mechanical Engineering's staff members for guiding me and rendered their help during the period of my final year project.

Last but not least, I would like to express a special thanks to my family members and friends for their priceless support, encouragement, constant love, valuable advices, and their understanding of me. Without all of them, I would not go further like where I standing right now.

ABSTRACT

Highly conductive carbon-filled epoxy composites were developed for manufacturing bipolar plates in proton exchange membrane fuel cells (PEMFC). In PEMFC, bipolar plate is one of the main components. The objectives of the research are to study the effect of binder and filler ratio of the properties of Gr/CB/EP composite and determine the suitable loading in Gr/CB/EP composite. The performance of PEMFC is depends on the types of material used to fabricate bipolar plate. The different ratio of graphite (Gr) and carbon black (CB) has been mixed with epoxy to fabricate the conductive composite bipolar plate. The sample is prepared with a weight percentage ratio has been fixed where 70-80% for fillers and 20-30% for binder. The filler materials are Gr and CB as second filler whereas the epoxy as the binder. For fillers materials, the weight percentage of CB will be varied from 5% up to 20% from the total percentage of filler. The sample preparation begin with the material will undergo pre-mixing process in the ball mill machine followed by mixing process using the high speed of mixer. The conductive composite will be fabricated by using motorise hydraulic moulding test press. Properties of the bipolar plate such as electrical conductivity, flexural strength, hardness and bulk density will be measured. The Taguchi's L_9 orthogonal array has been used as a design of experiment (DOE) while the electrical conductivity was measured using four point probes and flexural strength was measured using three point test according to ASTM D638. The optimization parameter had been analyze with Taguchi Design and the fabricated sample has been tested the electrical conductivity, bulk density and shore hardness testing. All the results have been achieved the DOE requirements for bipolar plate. The result for only electrical conductivity is higher than previous finding research which is 108.45 S/cm and fulfil the DOE requirement.

ABSTRAK

Komposit epoksi pengisi karbon yang berkonduksian tinggi dibangunkan untuk plat dwikutub bagi sel polimer pertukaran membran sel bahan api (PEMFC). Dalam PEMFC, plat dwikutub merupakan salah satu komponen utama. Objektif penyelidikan ini adalah untuk mengkaji kesan nisbah bahan pengikat dengan bahan pengisi ke atas sifat-sifat GR/CB/CP komposit. Keupayaan PEMFC adalah bergantung kepada jenis bahan yang digunakan untuk fabrikasi dwikutub plat. Pelbagai nisbah berbeza antara grafit dan juga karbon hitam dicampur dengan epoksi untuk menghasilkan plat dwikutub komposit yang bersifat konduktif. Sampel disediakan dengan nisbah peratusan berat telah ditetapkam di mana 70%-80% untuk pengisi dan 20%-30% untuk pengikat. Bahan penigisi ialah grafit dan karbon hitam seperti pengisi kedua mereka manakala epoksi sebagai pengikat. Untuk bahan pengisi, peratusan berat CB akan dipelbagaikan dari 5% sehingga 20% dari jumlah peratus pengisi. Penyediaan sampel komposit dimulakan dengan proses pra-percampuran dengan menggunakan mesin kempa bebolar dan diikuti mesin pencampur berkelajuan tinggi. Seterusnya komposit difabrikasi dengan menggunakan mesin acuan mampatan. Ciri-ciri plat dwikutub seperti kekonduksian elektrik, kekuatan lenturan, kekerasan dan ketumpatan akan diukur. Orthogonal L_9 Taguchi telah digunakan sebagai Reka bentuk eksperimen (DOE) manakala kekonduksian elektrik adalah diukur menggunakan empat titik prob dan kekuatan lentur ini diukur dengan menggunakan ujian mata tiga mengikut ASTM D638. Hasil daripada ujian tersebut akan dianalisis sama ada sifat-sifat komposit pengalir telah dicapai dan memenuhi keperluan DOE. Parameter pengoptimuman yang telah dianalisis dengan Taguchi Design dan sampel difabrikasi serta diuji dengan ujian kekonduksian elektrik, ujian keliatan, ujian ketumpatan pukal dan kekerasan. Semua keputusan mencapai keperluan DOE untuk plat dwikutub. Keputusan untuk kekonduksian elektrik yang diperolehi lebih tinggi daripada penyelidikan penemuan yang sebelumnya iaitu 108.45 S/cm dan memenuhi keperluan DOE.

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LIST OF ABBREVIATIONS

PEMFC	-	Polymer Electrolyte Membrane Fuel Cell
U.S.D.O.E	-	United States Development of Energy
Gr	-	Graphite
CB	-	Carbon Black
EP	-	Epoxy

CHAPTER I

INTRODUCTION

1.1 BACKGROUND

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 ºC. 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. The schematic of Proton Exchange Membrane Fuel Cell as shown below in Figure 1.1.

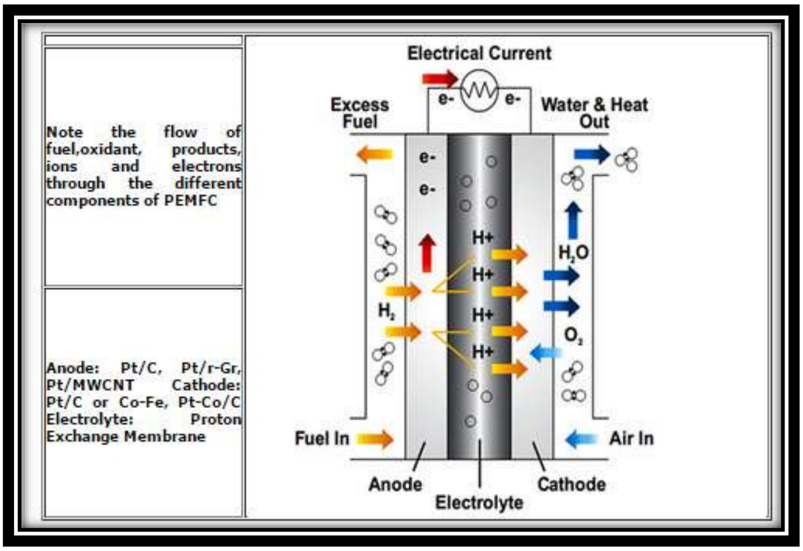

Figure 1.1 Schematic of Proton Exchange of Membrane Fuel Cell
(Source: Haile, 2003)

1.1.1 Working principles of PEMFC

A polymer electrolyte membrane fuel cell (PEMFC) is a good contender for portable and automotive propulsion applications because it provides high power density, solid state construction, high efficiency chemical-to-electrical energy conversion, near zero environmental emissions, low temperature operation (50 -100 ^{o}C), and fast and easy start up. The U.S. Department of Energy (DOE) has also identified the PEMFC as the alternative candidate to replace the internal combustion engine in transportation applications. However, barriers to commercialization remain a major problem. The fundamental and technical understanding of the bipolar plate fabrication is the main challenge in the commercialization of PEM fuel cells. Other challenges include manufacturing and material costs, material durability and reliability, and hydrogen storage and distribution issues. One of the major factors limiting fuel cell is the development of the bipolar plates, which are one of the PEMFC's key components. The requirements of the bipolar plate characteristic pose a major challenge for any type of materials (Metha and Cooper, 2003; Oh, 2005; Wolf and Porada, 2006).

1.1.2 Functions of Bipolar Plate

Therefore, research in materials, designs and fabrications of bipolar plates for PEMFC applications is a crucial issue for global commercialization. The main functions of bipolar plates in the PEMFC are to distribute the process gases (hydrogen and oxygen) to the positive and negative electrode respectively within the cell, to separate the individual components of fuel cells, and to carry the current away from the cell, (Weil, 2004; Mighri, 2004). In order to prepare for a commercialization, the bipolar plate must meet the design requirements such as high electrical conductivity, efficient gas tightness, low permeability, good chemical stability, high corrosion resistance, low volume and high thermal conductivity, and lightweight and acceptable mechanical strength, such as withstanding the stack clamping force. The optimal bipolar plate criteria include low cost, reproducibility, and easy finishing and recyclable (Cunningham, 2005; Blunk, 2006; Krupa, 2004; Thongruang, 2001).

Currently, the most promising material for mass production of bipolar plate is pure Gr material. However, it is very brittle and difficult to machine to fulfill the specifications needed for fuel cell stacks. Other materials such as metal-based require proper machining process, need special coating, have the extra weight and have a high tendency to corrode even though they have good electrical conductivity. Similarly, carbon-based materials have poor electrical and thermal conductivity, fragile structure and low mechanical strength even though they are easy to form (Acosta, 2006; Ezquerra, 2001; Zou, 2002).

However, the composite materials to be used in a bipolar plate must meet DOE (US Department of Energy) requirement because of its multiple responsibilities and the challenging environment in which the fuel cell operates. The composite properties must be considered for achievable design in a fuel cell application, specifically, electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight (Wu and Shaw, 2004; Hermann, 2005; Middelman, 2003; Selamat, 2011). The material requirements shown in Table 1.1 should be satisfied for the fabrication of a bipolar plate. Graphite powder is the most commonly used material for a bipolar plate. Graphite has a good electrical conductivity and excellent corrosion resistance with a low density of about 2 g cm^{-3}. However, it lacks mechanical strength and has poor ductility. The carbon black powder is introduced to the graphite composite in order to improve the properties of the composite. Epoxy will be used as the binder in this composite.

1.2 PROBLEM STATEMENT

Bipolar plates play the most significant role in weight, volume and the corresponding costs of fuel cells. Initially, metallic and graphite materials had been used for production of bipolar plates due to their electrical conductivity characteristics. Later, these plates due to their deficiency such as corrosion, weight and production expenses were appropriately substituted by composite plates. Generally, there are two types of bipolar plate in PEMFCs that are metal-based bipolar plates and pure graphite bipolar plates. Metallic materials have advantages over pure graphite because of their higher mechanical strength and better electrical conductivity. However, corrosion resistance is a major concern that remains to be unsolved as mortals may develop oxide layers that increase electrical resistivity, thus lowering the fuel cell efficiency. The metal-based bipolar plates have a higher mechanical strength, low gas permeability and much superior manufacturability. However, the main handicap of the metal-based bipolar plate is the lack of ability to combat corrosion in the harsh acidic and humid environment in PEMFCs and considerable power degradation that may be caused by metal ions. Meanwhile, for the pure graphite, it is very expensive and involves a huge amount of money to fabricate it plus it is very brittle. Filler is one of the main materials which influence the electrical properties of bipolar plate. The multiplier is preferable compared to single filler due to its better electrical conductivity. Other than that, the optimal value of weight percentage of both materials of filters and the binder should be determined in order to get the best ratio for filters and binder to be used as bipolar plate. All of these will influence the properties of the bipolar plate in terms of both mechanical and electrical. The Taguchi's L9 orthogonal array has been used as a design of experiment (DOE) while the electrical conductivity was measured using four point probes and flexural strength was measured using three point test according to ASTM D638. The result from the tests will be analyzed whether the properties of conductive composite were achieved and meted be DOE requirement.

1.3 OBJECTIVES

This project is to study the effect of binder and filler ratio on the electrical and mechanical properties of Graphite (Gr) /Carbon Black (CB) /Epoxy (EP) composite for bipolar plates. The filler materials are graphite and carbon black as second filler whereas the epoxy as the binder. The main objectives are:

- Study the effect of binder and filler ratio of the properties of Gr/CB/EP composite.
- Determine the suitable loading in Gr/CB/EP composite.

1.4 SCOPE

This research will study the effect of binder and filler ratio on the electrical and mechanical properties of Gr/CB/EP composite. The critical loading of CB and EP in Gr/CB/EP composite needs to be determined and the optimum composition of Gr/CB/EP composite to be used as bipolar plate. In this research, the samples are prepared with a weight percentage ratio has been fixed where 70%-80% for fillers and 30%-20% for binder. The filler materials are graphite and carbon black as second filler whereas the epoxy as the binder. For fillers materials, the weight percentage of CB will be varied from 5% up to 20% from the total weight percentage of filler. The formation of the composite is produced through compression molding. With the presence of CB, the electrical conductivity and mechanical strength will be determined through electrical and mechanical test.

CHAPTER 2

LITERATURE REVIEW

2.1 OVERVIEW OF LITERATURE REVIEW

This chapter will present the review of bipolar plate in a fuel stack. The review is from the recent and past journals, technical papers, and reference books have been studied to understand the related topic area of this project. Plus, this chapter will go through deeply regarding bipolar plate such as its background, fabrication, and testing used in order to know the properties of the bipolar plate.

2.2 PEM FUEL CELLS

2.2.1 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 of a fuel cell is shown below:

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

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

Net reaction : $2H_2 + \ O_2 \rightarrow \ 2H_2O$

The pressurized hydrogen gas (H2) entering the fuel cell on the anode side. This gas is forced through the catalyst by pressure. A H2 molecule splits into two H+ ions and two electrons (e-) 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 (O2) 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+ ions through the membrane, where they combine with two of the electrons from the external circuit to form a water molecule (H2O). 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.

PEMFC's 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.

2.2.2 Components of PEM Fuel Cell Stack

Figure 2.1 shows the major components in a single PEM fuel cell, which includes: the membrane electrolyte assembly (MEA) (which is an electrolyte membrane with catalyst layer on both sides), gas diffusion layers, gaskets, bipolar plates, current collectors and endplates. There are four main components of PEM fuel cell: Membrane Electrode Assembly (MEA), Bipolar Plate, End Plate and Current Collector.

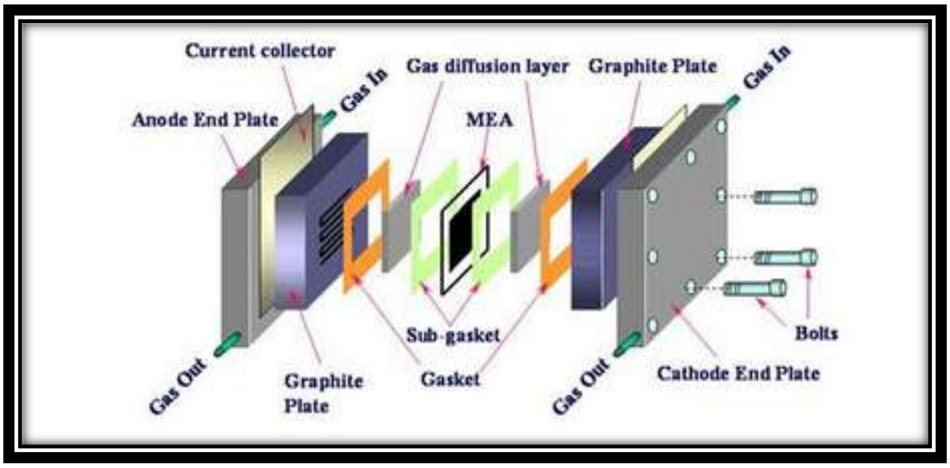

Figure 2.1: Polymer Electrolyte Membrane Fuel Cell
(Source: Beth , 2009)

Table 2.1: Primary components of a PEM fuel cell
(Source: Wang, 2006)

Component	Material	Functionality
Membrane electrode Assembly (MEA)	Solid polymer electrolyte impregnated with catalyst layers for the anode and cathode Porous carbon paper or cloth for gas diffusion layer (GDL)	Consists of the two electrodes, a membrane electrolyte and two GDLs. The membrane separates (with a gas barrier) the two half-cell reactions and allows protons to pass through from anode to the cathode. The dispersed catalyst layers on the electrodes promote each half reaction. The GDL evenly distributes gases to the catalyst on the membrane, conducts electrons from the active area to the bipolar plates and assists in water management.
Bipolar plate	Graphite, stainless steel, or thermoplastic materials	Distributes gases over the active area of the membrane. Conducts electrons from the anode of one electrode pair to the cathode of next electrode pair. Carries water away from each cell.

Endplate	Material with good mechanical strength (normally steel or aluminum)	Provides integrated assembly for the entire fuel cell stack.
Current collector	Metal material with good electric contact and conductivity, normally copper.	Collects and transfers the current from the stack to an external circuit.

2.3 BIPOLAR PLATE

According to Lee et. al., (2009), bipolar plate can categorized as the major components in PEMFC where it consists of huge portion of the stack volume and cost. Bipolar plate can either comesfrom metal based, graphitic based or polymer composite. For a commercialization, bipolar plate must meet the design requirement that had been listed by Department of Energy (DOE). The optimal bipolar plate criteria should include all the requirements such as low cost, easy finishing and reproductivity.

2.3.1 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:

Table 2.2 Requirement properties of the bipolar plate (DOE target)

Property	Value
Electrical conductivity	> 100 [Scm $^{-1}$]
Flexural conductivity	> 25 [MPa]
Shore conductivity	> 50
Bulk density	< 5 [g/cm^3]

2.3.2 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.

2.3.2.1 Electro-graphite Bipolar Plates

According to Wang and Turner, (2004), 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. 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