EFFECT OF CARBON BLACK LOADING ON THE PROPERTIES OF GRAPHITE – EPOXY COMPOSITE FOR FLOW CHANNEL FABRICATION

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A report submitted
in fulfillment of the requirements for the degree of
Bachelor of Mechanical Engineering

Faculty of Mechanical Engineering

UNIVERSITI TEKNIKAL MALAYSIA MELAKA

2020

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DECLARATION

I declare that this project report entitled "Effect of Carbon Black Loading on the Properties of Graphite-Epoxy Composite for Flow Channel Fabrication" is the result of my own work except as cited in the references

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Date : 10/08/2020

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APPROVAL

I hereby declare that I have read this project and in my opinion this report is sufficient in terms of scope and quality for the award of the degree of Bachelor of Mechanical Engineering.

Signature : _________________

Supervisor : _________________

Date : _________________

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DEDICATION

To my beloved mother and father

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ABSTRACT

The addition of conducting fillers into composites will increase the electrical conductivity of the composite. However, the electrical conductivity and other performance aspects of the composite such as flexural strength and hardness will have adverse effect when content of fillers such as carbon black and graphite increased beyond certain extend, which is an effect due to percolation threshold. Conductive fillers are commonly added in polymer composite in fabrication of bipolar plate's component such as flow and cooling channels. The percentage content of each filler material and resin must be in correct proportion to achieve the bipolar plate performance target set up by US DOE. This work studies how the variation of carbon black content in an epoxy–matrix composite which contain another conductive filler: graphite can affect the performance of bipolar plate by examine corresponding variation in electrical conductivity, flexural strength, shore hardness, and bulk density. The flow channels produced are examined by their dimensions and compared with drawing to understand the effectiveness and accuracy of hot compression method in fabrication of flow channel used. This work will provide insight to the best practice of correct proportion to be used in preparing a GR/CB/EP composite for best performance in bipolar plate application and suitability of hot compression method in fabrication of flow channel.

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ABSTRAK

Penambahan pengisi konduktif ke dalam komposit akan meningkatkan kekonduksian elektrik komposit. Walaubagaimanapun, kekonduksian elektrik dan aspek prestasi lain komposit seperti kekuatan lenturan dan kekerasan akan merosot apabila kandungan pengisi seperti karbon hitam dan grafit meningkat melebihi komposisi tertentu, disebab kesan ambang perkolasi. Pengisi konduktif biasanya ditambahkan dalam komposit polimer dalam pembuatan komponen plat bipolar seperti saluran aliran dan penyejukan. Kandungan peratusan setiap bahan pengisi dan resin mestilah dalam kadar yang betul untuk mencapai sasaran prestasi plat bipolar yang ditetapkan oleh US DOE. Karya ini mengkaji bagaimana variasi kandungan karbon hitam dalam komposit epoksi-matriks yang mengandungi pengisi konduktif lain: grafit dapat mempengaruhi prestasi plat bipolar dengan memeriksa variasi kekonduksian elektrik, kekuatan lenturan, kekerasan, dan ketumpatan pukal. Saluran aliran yang dihasilkan diperiksa dimensinya dan dibandingkan dengan lukisan untuk memahami keberkesanan dan ketepatan kaedah pemampatan panas dalam pembuatan saluran aliran plat bipolar. Karya ini akan memberi gambaran mengenai amalan terbaik komposisi yang betul untuk digunakan dalam penyediaan komposit GR / CB / EP untuk prestasi terbaik dalam aplikasi plat bipolar dan kesesuaian kaedah pemampatan panas dalam pembuatan saluran aliran.

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ACKNOWLEDGEMENT

First and foremost, praises and thanks to the God, the Almighty, for His showers of blessings throughout my work to finish the FYP.

I would like to express my deep and sincere gratitude to my FYP supervisor, Dr Mohd Zulkefli bin Selamat for his invaluable guidance and dedication throughout the process of completing the research and report. His vision, dynamism, sincerity and motivation have deeply inspired me.

Secondly, I am extremely grateful to Universiti Teknikal Malaysia Melaka and Faculty of Mechanical Engineering for providing me facilities and resources needed to complete the research which range from journals to laboratories.

Thirdly, I am extending my heartfelt thanks to each of my friends for their patience, helps and understanding throughout the period. I would also like to thank them for their friendship, kindness and great sense of humor.

Last but not least, I am extremely grateful to my parents for their love, caring and continuing support which help me endured each hardships and challenges encountered during the period of completing the FYP.

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LIST OF ABBREVIATIONS

Abbreviation	Full Name
BP	Bipolar Plate
CB	Carbon Black
CMM	Coordinate Measuring Machine
CPC	Conductive Polymer Composite
EP	Epoxy
GCC	Ground Calcium Carbonate
GDL	Gas-Diffusion Layer
Gr	Graphite
MEA	Membrane Electrode Assembly
PCC	Precipitated Calcium Carbonate
PEMFC	Proton-Exchanged Membrane Fuel Cell
US DOE	United States Department of Environment

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CHAPTER 1

ITRODUCTION

1.1 BACKGROUND

Conductive polymer is a composite material which added conductive fillers into polymer. It can conduct electricity but poorer than metal and pure graphite but can work in high corrosive environment which is something that metal cannot achieve. The metal bipolar plate requires extra coating process on its surface to provide corrosion resistance while pure graphite bipolar plate requires resin impregnation to fill up the porous holes and avoid water permeation, these extra processes are costly when mass production in commercial purpose which resulted in the surge of conductive polymer composite (CPC) as the alternative for the bipolar plate material. CPC is largely used as a material to fabricate bipolar plate in fuel cell due to its sufficient electrical conductivity, light-weight, low cost and corrosion resistance. Besides, the high formability also eases the fabrication of flow field design on the bipolar plate.

Most of the researches at the field of CPC up to date have added conductive fillers such as carbon black, carbon nanotube, graphite, metal powders into polymer composites to increase electrical conductivity. Out of all, carbon black is most commonly added into the graphite-based polymer composite due to it can increase the mechanical strength and its high specific surface area can form a conductive network which greatly increase conductivity in plastics even in small amounts. Current researches conducted are focused on how to use the cheapest material to form the most extensive network in the matrix or

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in other word decrease the percolation threshold (Hyun-Jung Choi, et al, 2019).

Bipolar plate is the key component of proton-exchanged membrane fuel cell (PEMFC). Its functions are distributing gas and fuel evenly, remove heat from the active area, conduct electricity from cell to cell, and act as sealant of fuel cell. It represents about 80% of the total weight and 30 to 40% of cost of fuel cell. Hence, it is a great challenge to found materials which possess the mechanical properties and processibility of polymer as well as good conductivity of metal (E. Planes, et al, 2012). These completely different properties are not present at singular material, hence underscore the need of composite material which incorporated all the advantages of different materials.

The US DOE has set up technical targets to achieve for the bipolar plate fabricated for transportation uses. The targets are listed at Table 1.1. Few of them will be served as the benchmark for this study's fabricated bipolar plate samples.

Table 1.1 Technical Targets for Bipolar Plate for Transportation Application (Fuel Cell Technologies Office, 2019)

Characteristic	2015	2020
Cost (\$/kW_{net})	7	3
Plate Weight (kg/kW_{net})	<0.4	0.4
Plate HH_2 permeation coefficient (Std cm^3/ (sec cm^2 Pa) @ 80°C, 3 atm, 100% RH)	0	<1.3 x 10^{-14}
Corrosion, anode (µA/ cm^2)	no active peak	<1 and no active peak
Corrosion, cathode (µA/ cm^2)	<0.1	<1
Electrical conductivity (S/cm)	>100	>100
Areal specific resistance (ohm cm^2)	0.006	<0.01
Flexural strength (MPa)	>34 (carbon plate)	
Forming Elongation (%)	20-40	40

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1.2 PROBLEM STATEMENT

Fuel cell is one of the greenest fuels at the world since its waste product is only water. PEMFC is predicted as the future of the fuel source used in automobile. The production and shipping of PEMFC is increasing yearly mainly due to transportation uses. However, there are still plenty of room for improvement in terms of cell lifetime, tolerance for impurities at electrode, and design optimization.

Bipolar plates which is one of the key components of PEMFC need to provide electrical conduction between the cells, high resistant to chemical corrosion and has very low gas permeability. These requirements are steep challenges for any class of materials, none of them can fits the needs totally. This has leaded to the only resolution: invention of new material. Many researches have been conducted to find out appropriate materials to fabricate bipolar plate.

Up to date, there are several options which have potential to be materials for bipolar plates to realize target of commercialization of PEMFC which are metal with or without coating, non-porous graphite and graphite based polymer composite. The weakest point of polymer composite is low electrical conductivity when compared to metal and graphite materials although it is lower in weight, cost and ease in fabrication. Hence, the current challenge faced by scientists around the world is to invent composites with better electrical properties at low cost. Various types of conductive fillers such as graphite, carbon nanotubes, carbon black and metallic powders are employed to increase the conductivity. The percentage of fillers and binder in a composite are investigated in many researches to find out the most optimum parameters for various requirements as stipulated in US DOE targets for bipolar plate in transportation application at lowest cost.

The flow field design and flow channel dimensions also affect the local current density, temperature and water content of PEMFC (S. Shimpalee, 2011). Proper design of the dimensions of flow channel can avoid flooding at electrode and dehydration of MEA which affect the performance of PEMFCs significantly.

There are various fabrication processes for flow channel such as machining and hot compression method. Machining method made use of CNC machine to cut out a high accuracy

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dimension of flow channel at graphite plate but is time consuming and high cost. In contrast, hot compression method is easy and cheaper to employ in fabrication of flow channel, but the dimension accuracy is inferior to machining method.

1.3 OBJECTIVES

1. Study the effect of Carbon Black on the properties of Graphite/Epoxy composite.
2. Determine the parameter dimension of flow channel.

1.4 SCOPE OF PROJECT

The effect of carbon black on the properties of graphite/epoxy composite will be determined using 3 different weight percentages of carbon black and graphite fillers with fixed weight percentage of epoxy as binder. This composite will be fabricated through hot compression molding. During fabrication process the flow and cooling channel will be fabricated on the surface of the sample. The properties determined from mechanical and electrical tests will be analyzed to get the critical loading of carbon black in the composite. The dimension of flow channel will be determined after fabrication of bipolar plates and compared with mold to analyze the difference in dimension.

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CHAPTER 2

LITERATURE REVIEW

2.1 FUEL CELL

39 years after the invention of the world first battery, fuel cell is invented which its biggest difference with the previous is it acts as a device to convert external fuel source, hydrogen to react with oxygen where the chemical process generates electricity, instead of storing energy. Fuel cell generates electricity in a simple step through chemical reaction when compared with existing power plant which undergone many processes to generate electricity. This enable fuel cell as future energy source due to its clean, green and efficient characteristics.

Fuel cell can be varying in the forms of different electrolytes which are potassium hydroxide solution (alkali fuel cell), metal carbonates salt (molten carbonate fuel cell), phosphoric acid (phosphoric acid fuel cell), polymer sheet (proton exchange membrane fuel cell) and metal ceramic compound (solid oxide fuel cell). The first three of the electrolytes are in liquid form while the last two are in solid form.

All kinds of fuel cell operated in slightly different conditions but the process can be summarized as hydrogen oxidized at anode and reduced by oxygen at cathode to form water, the emission of electron during oxidation process will induced a DC current flow through external circuit.

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2.2 POLYMER ELECTROLYTE MEMBRANE FUEL CELL (PEMFC)

PEMFC has an anode which acts as negative terminal and cathode acts as positive terminal of the cell. At anode, hydrogen molecules undergo oxidation to eliminate electrons to become hydrogen ion. The electrons emitted are conducted through external circuit. The ionized hydrogen is then reduced to water by oxygen at cathode. The half chemical equations are:

$$H^2 - 2e^- = 2H^+ \text{ (Anode)}$$

$$O_2 + 4e^- + 4H^+ = 2H_2O \text{ (Cathode)}$$

The schematic diagram of the working order for a single PEMFC is shown in Figure 2.1.

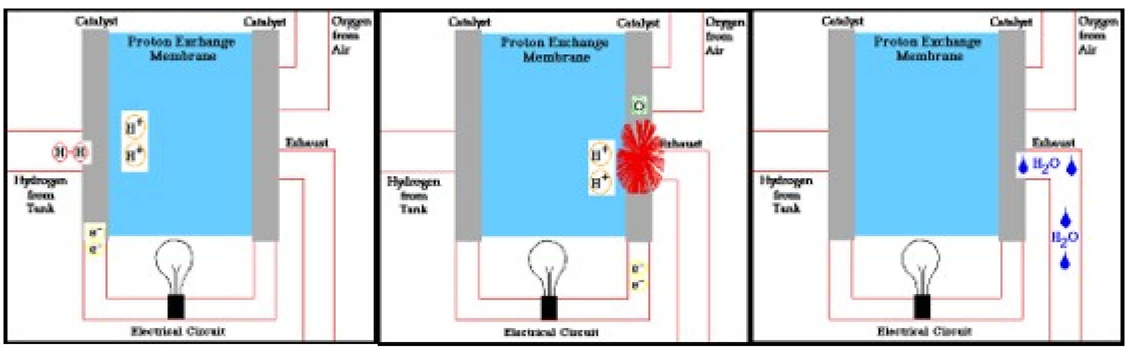

Figure 2.1 Single PEMFC (Smithsonian, 2017)

There is a channel connected to each terminal of the cell to provide hydrogen and oxygen supply to anode and cathode respectively. Since both of the electrodes at the terminals are made up of precious metal and has low operating temperature (< 100 °C), pure fuel and oxygen sources are needed. The electrolytes used in PEMFC is ion-selective membrane made up of ionomers. The combination of ionomeric membrane sandwiched between two electrodes thin films is known as membrane electrode assembly (MEA) which is the key component of PEMFC.

There are two bipolar plates at the end of single fuel cell which usually made up of high density graphite. There are gas flow field machined on the plates to allow even distribution of react gases with electrodes which is further aided by presence of gaskets which helps limit the flow of gases on the effective area and gas-diffusion layers (GDL) which enable direct access of the gases with catalysts. PEMFC is stacked to provide voltage according to demand. The current is conducted from one cell to another through the bipolar plates. The main components

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of single PEMFC is shown in Figure 2.2. Since the PEMFCs is dynamic, light weight and able to operate under low temperature, it is usually used in vehicle.

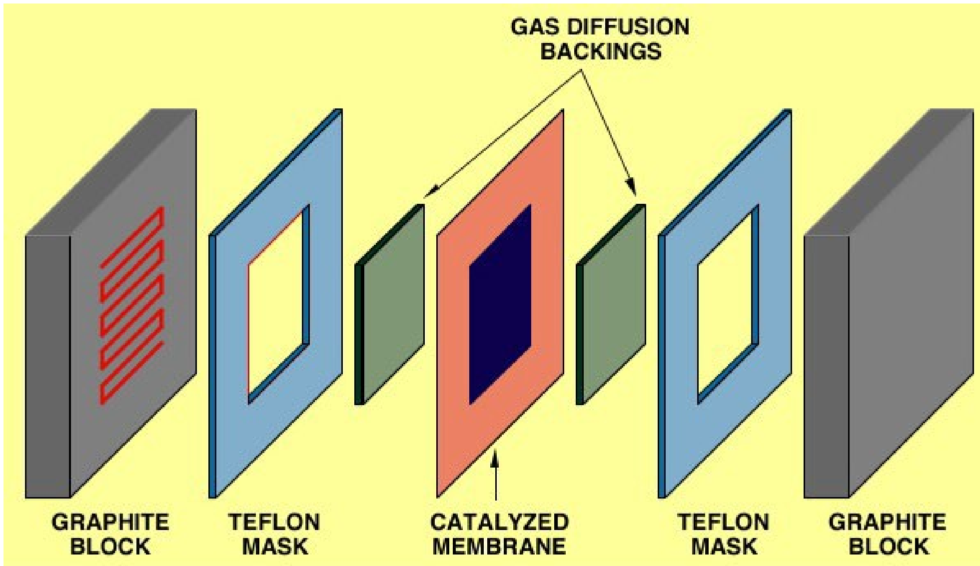

Figure 2.2 Main Components of Single PEMFC (Gottesfeld, n.d.)

2.3 FLOW CHANNEL

A flow channel is the channel on bipolar plates which helps to provide adequate amount of react gases (hydrogen and oxygen) to gas diffusion layer (GDL) and surface of the catalysts meanwhile maintain the flow pressure. It comes with different often-used shapes as shown in Figure 2.3.

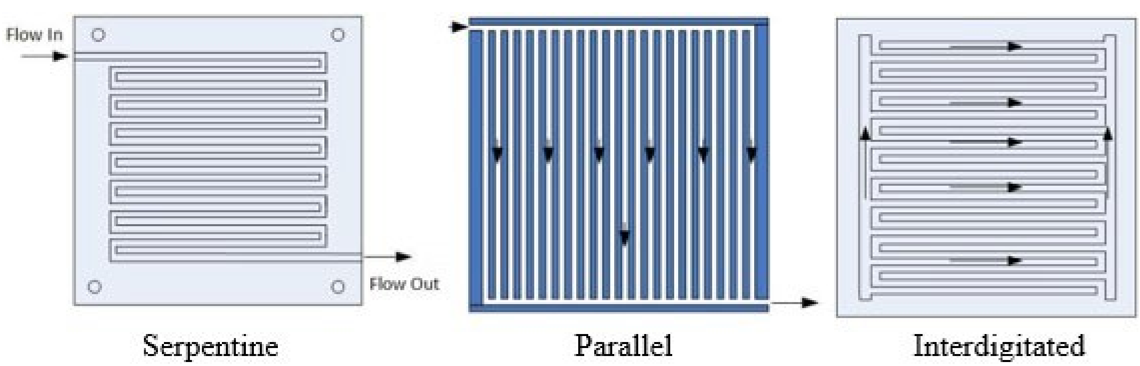

Figure 2.3 Flow Channel Shapes (Spiegel, 2017)

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Serpentine flow field design is relatively efficient at providing flow distribution across the electrode surface of the fuel cell. This design may cause pressure loss due to the relatively long flow path (Spiegel, 2017). The most qualitative flow field for PEMFC applications proved to be the serpentine flow field, having a higher pressure drop than parallel flow field and efficiently removing accumulated water from the channels (Ionescu, 2018).

Flow channel dimensions also affect the performance of PEMFC. To achieve the highest power density in a PEM fuel cell, it requires that both the total width and the rib ratio be small. In the small total width, the flow channel width is small and water can easily diffuse from the corner to the middle of the channel (in cross-section) to hydrate the membrane, which increases the membrane conductivity and thus the cell performance (Liu, 2013). According to Perng, S.-W., & Wu, H.-W. (2015), the larger angle and height of trapezoid baffles significantly strengthen the blockage effect and thus promote the cell performance. However, the baffles of 1.5 mm and 90° cause local high temperature (>372 K) to damage the membrane of PEMFC and the maximum pressure drop. As a result, the maximum enhancement of cell net power from a novel PEMFC with baffles of 60° and 1.125 mm is about 90%.

2.4 CONDUCTIVE POLYMER COMPOSITE (CPC)

Bipolar plates (BP) is one of the key components of PEMFC which transport react gases, water and conduct electron. According to Ehsan Zarmehri, et al. (2013), BP has the most significant role in weight, volume and corresponding costs of fuel cells. In order to be used in automotive applications, BP must be light weight and small in volume, have shock resistance and can withstand harsh operating environment. A lot of researches has been done to find out better materials to build BP which range from metals to composites, which are more cost effective and feasible than traditionally used high-density graphite. This is due to pure graphite is brittle, porous and complicated in machining flow field (Heinzel et al., 2009).

Conductive polymer composite (CPC) is graphite composite material which is used to fabricate BP used in static PEMFC applications. It utilizes the combination of conductive fillers such as carbon nanotubes, carbon blacks, graphene and binder such as epoxy and phenolic resins,

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polyester, polypropylene to provide low cost, light weight, high conductivity, process ability, corrosion resistance and mechanical strength properties. According to Heinzel et al. (2009), the conducting fillers form a percolation network within the polymer matrix with a required good quality of dispersion via a kneader or extruder, and usually incorporated with graphite fibers to increase mechanical strength.

2.5 MATERIALS

Materials used in production of BP in this project are CPC, made up of Gr and CB as fillers while EP as binder. The physical properties of the materials used to produce BP samples are listed in the Table 2.1.

Table 2.1 Physical Properties of Gr/CB/EP

Properties	Gr	CB	EP
Density (g/cm^3)	2.09 - 2.23	1.8 - 2.1	1.54
Electricity Conductivity at 20°C (S/m)	3.3×10^2	-	-
Volume Resistivity (ohm-cm)	-	-	$> 10^{10}$
Thermal Conductivity (W/mK)	< 1950	-	1.30 - 2.88
Flexural Strength (MPa)	15.5 - 207	-	1.12×10^8

2.5.1 Filler

Filler can increase specific properties and reduce the cost of composite. The top filler materials used are ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), kaolin, talc, and carbon black (Market Study: Fillers (3rd edition), 2014). Fillers mainly used to fill up space in targeted area, increase material strength, conductivity and surface smoothness.

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2.5.1.1 Carbon Black (CB)

Carbon black is the generic name for a family of small-size, mostly amorphous, or para crystalline carbon particles grown together to form aggregates of different sizes and shapes, primary particle size, chemistry, porosity and surface area according to commercial grades. CB is formed in the gas phase by the thermal decomposition of hydrocarbons in the absence or presence of oxygen in sub stoichiometric (Michael E. Spahr, Roger Rothon, 2016).

According E.B. Sebok, et al. (2001), ~93% of CB usage is in rubber applications, and can be classified into two main categories: tires and mechanical rubber goods (e.g. automotive belts and hoses). The reinforcing properties of carbon black provide enhanced performance and durability to the rubber compounds in which they are used.

CB also used in graphite-polymer composite bipolar plate due to its structural characteristics such as morphology and size have decisive influence on the final properties of bipolar plates. The small carbon black particles helped to make conducting tunnels between graphite particles, increasing conductivity (Renato et al., 2011).

2.5.1.2 Graphite (Gr)

Graphite (Gr) is a crystalline form of the element carbon with its atoms arranged in a hexagonal structure. This structure enables Gr has high degree of anisotropy which determine its properties. It is extremely soft, cleaves with very light pressure, and has a very low specific gravity. In contrast, it is extremely resistant to heat and nearly inert in contact with almost any other material (King, n.d.). According Isabel Suárez-Ruiz, et al (2008), Gr shows a high directional strength and is highly inert, although its reactivity increases as the temperature rises and therefore it reacts with oxygen at temperatures higher than 300–400°C.

Gr is a common material used to make bipolar plate. The corrosion for graphite-base composite is negligible compared with metallic bipolar plate. It offers advantages in weight, formability and cost. However, it has lower strength and electrical conductivity than steel plates.

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