THE STUDY OF METAL-FILLER ON GRAPHITE POLYMER COMPOSITE

INDERA KASUMA BIN MOHAMAD YUNUS

This report is presented as a fulfilling requirement part for my Degree of Bachelor in Mechanical Engineering (Structure and Materials)

Faculty of Mechanical Engineering

Universiti Teknikal Malaysia Melaka

JUNE 2012

"I acknowledge that have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of a Bachelor of Mechanical Engineering (Structures & Materials)"

Signature: _____

Supervisor Name: DR MOHD ZULKEFLI BIN SELAMAT

Date: 30th JJUNE 2012





"I declare that this report is my only own work except for the summary and article that each of that I already sited the references"

Signature: _____

Name: INDERA KASUMA BIN MOHAMAD YUNUS Date: 30th JUNE 2012



ACKNOWLEDGEMENT

Alhamdulillah. Thanks to Allah SWT, whom with His willing giving me the opportunity to complete this Final Year Project. This final year project report was prepared for Faculty of Mechanical Engineering, Universiti Teknikal Malaysia Melaka. This FYP basically for student in final year to complete the undergraduate program that leads to the degree of Bachelor of Mechanical Engineering. This report is based on the methods given by the university

Firstly, I would like to express my deepest thanks to, Mister Dr Mohd Zulkifli bin Selamat, a lecturer at UTeM and also assign, as my supervisor who had guided be a lot of task during semesters session 2011/2012. I also want to thanks the lecturers and staffs of Mechanical Engineering for their cooperation during I complete the final year project that had given valuable information, suggestions and guidance in the compilation and preparation this final year project report.

Deepest thanks and appreciation to my parents, family, special mate of mine, and others for their cooperation, encouragement, constructive suggestion and full of support for the report completion, from the beginning till the end. Also thanks to all of my friends and everyone, those have been contributed by supporting my work and help myself during the final year project progress till it is fully completed.

Last but not least, my thanks to Universiti Teknikal Malaysia Melaka, security guard, the cleaner and especially for my PA, for great commitment and cooperation during my Final Year Project.

ABSTRACT

Over the past decade, rapid progress has been made in understanding and development of Polymer Electrolyte Membrane Fuel Cell (PEMFC). Nowadays, the PEM fuel cell is under development to substitute the combustion application in transportation. One of component in PEMFC is bipolar plate which is contributed up to half of effectiveness of fuel cell. This research is about the development of bipolar plate through multi-filler application via Ferum. The composite of G|Fe|PP will increase the effectiveness of bipolar plate that is suitable for application, including control the best requirement needed. Bipolar plates perform as the current conductor between cells, provide conduits for reactant gases flow, and constitute the backbone of a power stack. This study will offers a research work of bipolar plate with combining the Fe into G+PP as second filler while maintaining the good requirement for fuel cell.

ABSTRAK

Sepanjang dekat yang lalu, kemajuan pesat telah dibuat dalam pemahaman dan pembangunan Polymer Electrolyte Membrane Fuel Cell. Pada masa kini, sel bahan api PEM adalah di dalam pembangunan untuk menggantikan system pembakaran dalam pengangkutan. Salah satu komponen dalam PEMFC adalah dwikutub plat yang menyumbang sehingga separuh keberkesanan sel bahan api. Kajian ini adalah tentang pembangunan plat dwikutub melalui penambahbaikan dengan meningkatkan pengisian oleh Ferum. Komposit G|Fe|PP akan meningkatkan keberkesanan plat dwikutub yang sesuai, termasuk mengawal keperluan yang terbaik. Dwikutub plat bertindak sebagai konduktor antara sel-sel, menyediakan saluran bagi gas aliran bertindak balas, dan merupakan tulang belakang timbunan kuasa. Kajian ini akan menawarkan kerja-kerja penyelidikan plat dwikutub dengan menggabungkan Fe ke dalam G+PP sebagai pengisi kedua disamping mengekalkan keperluan yang baik untuk sel bahan api.

TABLE OF CONTENT

| CHAPTER | ITEMS | PAGES |
|-----------|-------------------------|-------|
| | CONFESSION | ii |
| | DEDICATION | iii |
| | ABSTRACT | iv |
| | ABSTRAK | V |
| | CONTENT | vi |
| | LIST OF TABLES | |
| | LIST OF FIGURES | |
| CHAPTER 1 | INTRODUCTION | 1 |
| | 1.1 Background | 1 |
| | 1.2 Objectives | 3 |
| | 1.3 Problem Statement | 3 |
| | 1.4 Scope | 4 |
| CHAPTER 2 | LITERATURE REVIEW | 5 |
| | 2.1 Fuel Cell | 5 |
| | 2.2 Bipolar Plate | 6 |
| | 2.3 Materials | 9 |
| | 2.4 Fabrication | 19 |
| | 2.5 Testing | 26 |
| CHAPTER 3 | METHODOLOGY | 28 |
| | 3.1 Raw Materials | 29 |
| | 3.2 Pre-mixing | 30 |
| | 3.3 Melt Compounding | 31 |
| | 3.4 Crush and Pulverize | 31 |
| | 3.5 Compression Molding | 31 |
| | 3.6 Testing | 33 |

CHAPTER ITEMS

| CHAPTER 4 | RESULT AND ANALYSIS | 35 |
|-----------|---|----|
| | 4.1 Pre-mixing Outcome | 35 |
| | 4.2 Melt Compounding Outcome | 36 |
| | 4.3 Crush Output | 36 |
| | 4.4 Pulverize Result | 37 |
| | 4.5 Compression Molding Result | 37 |
| | 4.6 Electrical Conductivity Determination | 38 |
| | 4.7 Bulk Density | 39 |
| | 4.8 Shore Hardness | 40 |
| CHAPTER 5 | DISCUSSION | 42 |
| CHAPTER 6 | CONCLUSION & RECOMMENDATION | 44 |
| | 6.1 Conclusion | 44 |
| | 6.2 Recommendation | 45 |
| | REFERENCES | 46 |
| | APPENDICES | 47 |

PAGES

LIST OF TABLES

| TABLE | TITLE | PAGES |
|-------|---|-------|
| 1 | Injection Molding Capabilities [19] | 21 |
| 2 | Raw material properties | 29 |
| 3 | Composition based on weight percentages | 30 |
| 4 | Conductivity of Fe G PP | 39 |
| 5 | Bulk Density of Fe G PP | 40 |
| 6 | Shore Hardness Fe G PP | 41 |

LIST OF FIGURES

| FIGURE | TITLES | PAGES |
|--------|---|-------|
| 1 | Proton Exchange Membrane Fuel Cell [4] | 2 |
| 2 | PEM Fuel Cell [5] | 5 |
| 3 | Fuel Cell Stack [5] | 7 |
| 4 | Mineral Graphite [6] | 9 |
| 5 | Graphite Unit Cell [8] | 10 |
| 6 | Injection molded bipolar plate made of graphite material (ZBT, Duisburg, Germany) [2] | 12 |
| 7 | Iron [15] | 13 |
| 8 | Difference of G PP and G Fe PP | 14 |
| 9 | Low pressure phase diagram of pure iron [7] | 15 |
| 10 | Polypropylene | 17 |
| 11 | Polypropylene [1] | 18 |
| 12 | Injection molding overview [19] | 20 |
| 13 | Injection Molded part | 23 |
| 14 | Compression molding [20] | 25 |

| FIGURE | TITLE | PAGES |
|--------|---|-------|
| 15 | Jandel Multi Height Microp-position Probe and RM3K Test | 26 |
| 16 | Rodwell Hardness Tester [21] | 27 |
| 17 | Automatic Densimeter [22] | 27 |
| 18 | Flow chart | 28 |
| 19 | (a) Graphite, (b) Polypropylene and (c) Ferum | 29 |
| 20 | Ball mill | 30 |
| 21 | Bra-bender | 31 |
| 22 | Crusher | 31 |
| 23 | Centrifugal mill | 32 |
| 24 | Hot Press | 32 |
| 25 | Mold | 33 |
| 26 | Digital Shore Tester | 33 |
| 27 | Electronic Densimeter | 34 |
| 28 | Jandel Multi Four-Point Probe | 34 |
| 29 | Fe+G | 35 |
| 30 | Fe+G+PP from internal mixture | 36 |
| 31 | Fe G PP from crusher | 36 |
| 32 | Fe G PP powder | 37 |
| 33 | Final Specimen | 37 |
| 34 | Graph of conductivity versus Fe wt.%. | 39 |
| 35 | Graph of Density versus Fe wt.%. | 40 |

| FIGURE | TITLE | | PAGES |
|--------|---|------|-------|
| 36 | Graph of shore hardness versus Fe wt.% | | 41 |
| 37 | Fe G PP composite microstructure magnification of 10X & 50X | with | 43 |

CHAPTER 1

INTRODUCTION

1.1 Background

A fuel cell is an electrochemical device that converts chemical energy from fuel commonly hydrogen into electricity through a chemical reaction. It requires a constant source of fuel and oxygen to produce electricity. Since the fuel cell not requires combustion, it was viewed as viable power source for many applications, including distributed power generation, ground transportation and portable electronics.

There are many types of fuel cell, which is consisting of a cathode, an anode and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrons are drawn through an external circuit from the anode to the cathode, producing direct current electricity. Fuel cells are classified by the type of electrolyte they use and come in a variety of sizes. Single fuel cells produce very small amount of electricity, around 0.7 volts, so cells are "stacked", or placed in series or parallel circuit to increase the voltage and current output to meet an application's power generation requirements. [2]. Fuel cells not only produce electricity, but also involve in producing water and heat depending on the fuel cell source along with nitrogen dioxide and other emissions. The energy efficiency of a fuel cell is generally up to 85% if waste heat is captured for use.

Fuel cell is known as power sources that turn chemical energy from fuel into electrical energy due to chemical reaction with oxygen or another oxidizing agent. [3]. Most common fuel that been used is hydrogen, but hydrocarbons such as alcohol like methanol and natural gas are sometimes used. Fuel cell requires a constant source of fuel and oxygen to run which is different from batteries whereas it can produce electricity continually for as long as these inputs are supplied. The fuel cell for backup and primary power for industrial, commercial and to power fuel vehicles, including automobiles, forklifts, motorcycles, airplane, boats, and submarines. Below is shown a one type of fuel cell.



Figure 1: Proton Exchange Membrane Fuel Cell [4]

Fuel cell is a very promising power sources for residential and mobile application due to attractive features such as high power density, relatively low operating temperature convenient power supply, long life time, etc. [1]. Despite these advantages, commercialization of fuel cell is delayed mainly due to the high fabrication cost. Fuel cell consists of two main components which is bipolar plate and polymer electrolyte membrane. The composite bipolar plates are the promising alternative materials due to their low cost, easy direct molding during processing, good corrosion resistance and low weight. The main composition of bipolar plate is filler and binder. The filler can be non-metal such as graphite, carbon black, and carbon nanotube. Otherwise, it can be a metal such as iron (Ferum), stainless steel, aluminum nickel, and titanium. Besides that, for the binder, it can be a thermoplastic or a thermo-set.

1.2 Objectives

- To study the effect of Iron (Ferum) as a second filler on mechanical and electrical properties of graphite-polypropylene.
- To determine the suitable composition of G|Fe|PP composite for bipolar plate.

1.3 Problem Statement

In this research, graphite is to be used as main filler because of high corrosion resistance and low surface contact resistance but it facing the main handicaps which are brittle and low conductivity. In the other side, iron (Fe) playing role as second filler having a high conductivity but tendency to corrosive. Since the polypropylene (PP) is tough and flexible, it is suitable for binder to provide greater strength and geometric stability. The main concept of using multi filler such as G and Fe is to determine the critical ratio between G and Fe which give the best electrical and mechanical properties for composite G|Fe|PP.

1.4 Scope

In this research, the study will cover on choosing and characterization of raw material to be use which is Iron (Fe), Graphite (G), and Polypropylene (PP). After that, the process of mixing G and Fe by using the ball mill to make it become well fine powder. Next, the mixture from the ball mill will mix with PP through internal mixture. It is by using bra-bender, where the mixture will go through melt compounding under certain condition. After crush the mixture to make it well fine shape, this mixture will be blending using centrifugal mill to become a well powder. In this research also cover for molding process along with hot press for the mixture PP|Fe|G. For hot press stage, this mixture will subjected to certain shape which is disk shape in this research. Lastly, the plate will be tested by using Electronic Densimeter and Digital Shore Tester to determine its density and hardness respectively. For determination of electrical conductivity properties, the plate will be tested by using Jandel Multi Height Four-Point Probe.

CHAPTER 2

LITERATURE REVIEW

2.1 Fuel Cell

Figure 2 below show a PEM fuel cell which contains flow field plate, an anode, a proton exchange membrane, and a cathode.



Figure 2: PEM Fuel Cell [5]

5

The main processes involved in PEM fuel cell is outlined below [5]:

- 1. Pure hydrogen is passed through the flow plates to the anode (negative) on one side of the fuel cell, and oxygen from the air is passed through to the cathode (positive) on the other side of the fuel cell.
- 2. The anode is coated with a platinum catalyst which enables the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.
- 3. The PEM allows only the protons to pass through to the cathode. The electrons must then travel along an external circuit to the cathode producing an electrical current.
- 4. At the cathode, the electrons and protons from the hydrogen combine with the oxygen to form water. The water then leaves the cell. This is a continuous process so long as hydrogen and oxygen is supplied.

One of the main components that need to stress is bipolar plate may defined as the electrically-conducting plates which join together the anode of one cell to the cathode of another. The end plates are then connected to the electric circuit and current is allowed to flow.

2.2 Bipolar Plate

Bipolar plates act as the backbone of a hydrogen fuel cell power stack, facilitate water and thermal management through the cell, conduct current between cells, and provide conduits for reactant gases namely hydrogen and oxygen. To commercialize fuel cell, bipolar plate are need to be fabricated in mass production and made of materials with excellent manufacturability, which is suitable for costeffective high volume automated production systems. In a fuel cell stack, bipolar plates are conductive plates that act as a cathode for one cell and an anode for the adjacent cell. The plate may be made of carbon, metal or a conductive polymer such as carbon-filled composite or incorporating carbon. Bipolar plate usually incorporates flow channel for the fluid feeds and may be also contain conduits for heat transfer.



Figure 3: Fuel Cell stack [5]

The Figure 3 show one of bipolar plate in fuel cell assembles. There are a lot effort is going on worldwide to make a light weight, high conductivity and costeffective bipolar plate for fuel cell application. In the present research, graphite materials are considered to be used as main materials for bipolar plate. Unfortunately, graphite materials are classified as brittle, low conductivity and permeable to gases with poor cost effectiveness for high volume manufacturing process.

Since these as a main challenge hindering the fuel technology from penetrating the energy market, metallic bipolar plate was given as considerable attention for particular suitability to transportation applications. Metal such as aluminum, stainless steel, nickel, titanium and iron enjoy higher mechanical strength, no permeability, better durability to shock and vibration, and much superior manufacturability and cost effectiveness. There is a lot effort is going on worldwide to make a light weight and costeffective bipolar plate for fuel cell application. In the present research, graphite composite are considered the standard material for bipolar plate. Unfortunately, graphite composite are classified as brittle, low conductivity and permeable to gases with poor cost effectiveness for high volume manufacturing process.

However, metallic bipolar facing a challenge due to corrosion and heavy for PEM fuel cell application. Since the research work currently underway to develop, bipolar plate was made from two main parts which is filler and binder. The filler was made by non-metal and metal material while the binder could be made from thermoplastic and thermo-set.

In polymer electrolyte membrane fuel cell (PEMFC) design, bipolar plate should require as follows [2-3]:

- Good electrical conductivity (>100 S cm⁻¹ bulk conductivity)
- High Shore Hardness (>50)
- Good bulk density (~1.85 g cm⁻³)
- Good flexural strength (>25 MPa)
- High tensile strength (>41 MPa)
- Low permeability for hydrogen ($<2x10^{-6}$ cm³)
- High thermal conductivity (>10 W cm⁻¹)
- High chemical and corrosion resistance ($<1 \ \mu A \ cm^{-2}$)
- Low surface contact resistance
- Mechanical stability toward compression forces
- Low-cost material being process-able with mass production techniques
- Low weight and volume
- Recyclable materials.

2.3 Materials

2.3.1 Filler

About 80% of the bipolar plate is filler which is come from metal material such as titanium, aluminum, stainless steel, iron and etc. The filler also can be a nonmetal material such as graphite, carbon black, carbon fiber and etc. This percentage is based on the total weight of overall bipolar plate. In bipolar plate, filler provide influences of mechanical and electrical conductivity properties. In this research, we will go through the material to be used for filler of bipolar plate which is graphite as a main and iron as side filler and polypropylene as binder to provide a greater strength.

i. Graphite

Graphite acts as main filler inside the bipolar plate. In this research, we will study about the general information of graphite. The mineral graphite is one of the allotropes of carbon which can be seen in the Figure 4 below.



Figure 4: Mineral Graphite [6]

Graphite is well known used as an electrical conductor, semimetal. Under standard conditions, graphite is the most stable form of carbon. Therefore, it widely used as the standard state for defining the heat of formation of carbon compound in thermo-chemistry.

a. Structure

Graphite has a layered, called planar structure. In each layer, the carbon atoms are arranged in hexagonal lattice with separation of 0.142 nm, and the distance between planes is 0.335 nm. [7]. The two known forms of graphite , alpha (hexagonal) and beta (rhomohedral), have a very similar physical properties, except for graphene layers stack slightly differently. [8].The hexagonal graphite may be either flat or buckled. Through mechanical treatment, the alpha form can be converted to beta form and when heated above 1300°C, the beta form can be reverting to alpha form. [9] This structure is shown in the Figure 5 below:



Figure 5: Graphite Unit Cell [8]

b. Properties

Graphite able to conduct electricity via the vast electron delocalization within the carbon layers called aromaticity because valence electrons are free to move. However, the electricity is primarily conducted within the plane of the layers. The conductive properties of powdered graphite allowed its use as a semiconductor substitute in early carbon microphones. Graphite and graphite powder has solely lubricating properties due to the loose interlamellar coupling between sheets in the structure but its poor lubricant in vacuum environment. [10]. This observation led to the discovery that the lubricant is due to the presence of fluids between the layers, which are naturally adsorbed from the environment. Superlubricity is an effect can account for graphite's lubricating properties. The tendency to facilitate pitting corrosion in some stainless steel and to promote Galvani corrosion between dissimilar metals cause the limiting of graphite's used. Hexagonal boron nitride is another high-temperature lubricant; called white graphite has the same molecular structure and similar properties. Graphite loses it lubrication properties when a large number of crystallographic defects bind these planes together known as pyrolytic carbon. Besides, it will float in mid-air above a strong magnet because of highly diamagnetic. Therefore, natural and crystalline graphite are not often used in pure form as structural materials because of shearplanes, brittleness and inconsistent mechanical properties. [11].

c. Graphitic bipolar plate materials

Many efforts have been done to develop bipolar plate to become applicable in transportation. In phosphoric acid fuel, G was already known to suitable material in bipolar plate application. Bipolar plate made from pure graphite has an excellent chemical resistance, lower density form metal and good thermal plus electrical conductivity. The challenge is, to machining the flow fields is complicated and costly. Besides, graphite plate is porous and brittle, so that, it have to be coated to become impermeable to fuel and oxygen. Therefore, bipolar plate made from graphite is nonviable to become low-cost PEMFC component.

Graphite composite materials with polymer binders are more suited to achieve the desired properties and to improve manufacturing technologies for bipolar plates including the flow fields and cooling channels. These composite materials are made of commercially available polymers as binders and a high loading of conductive carbon compounds (e.g., natural or synthetic graphite powder, carbon blacks, and carbon nano-tubes), which increases the conductivity. The polymers are either thermoplastics such as polyvinylidenefluoride, polyethylene, polypropylene, liquid crystal polymers, and polyphenylene sulfide, or thermo-sets, such as vinyl ester, phenolic resins, and epoxy resins [2]. The conducting particles form a percolation network within the polymer matrix. The composite materials, owing to the polymer matrix, retain the processability of the polymer. A good quality of dispersion of the conductive component particles within the polymer binder is needed to obtain a mechanically stable bipolar plate with low permeability.

Generally, thermo-sets bonded graphite composite is complicated to process. In order to achieve sufficient stability, after injection molding, it has to be postcured. A thin polymer-rich skin layer has to be removed from the surface of the bipolar plate after the injection molding of thermo-sets and thermoplastic. This can be done by processes such as abrasive blasting to reduce the contact resistance to the gas diffusion layer (GDL).



Figure 6: Injection molded bipolar plates made of graphite composite material (ZBT, Duisburg, Germany) [2]