

**EFFECT OF CARBON NANOTUBE ON THE PROPERTIES OF GRAPHITE–
CARBON BLACK-POLYPROPYLENE COMPOSITE FOR BIPOLAR PLATE**

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**A thesis submitted in fulfilment of the requirement for the degree of the Bachelor of
Mechanical Engineering**

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DECLARATION

“I here declare that the result in this report is my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any degree.”

Signature :.....

Name : NUR FITRAH BIN DAINIL

Date : 14 JUNE 2019

DEDICATION

TO

my beloved family

DAINIL BIN MD DEWA

My Supervisor,

PROF MADYA DR. MOHD ZULKEFLI BIN SELAMAT

Other

My friends especially to Muhammad Firdaus Bin Sahrani, Dilip Rhaj A/L Baskaran and Amirul Hanif Bin Mohd Rasid and all people that had guided me throughout completion of this project.

APPROVAL

“I hereby declare that I have read this thesis in my opinion this report is sufficient in term of scope and quality for the award of Bachelor of Mechanical Engineering (with Hons.)”

Signature :.....

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SUPERVISOR'S DECLARATION

I have checked this report and the report can now be submitted to JK-PSM to be delivered back to supervisor and to the second examiner.

Signature :.....

Name of supervisor :

Date :

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ABSTRACT

Nowadays, pure-graphite bipolar plate had been targeted replace to conductive polymer composite (CPCs). This is because CPCs bipolar plate has low manufacturing cost and low density in PEMFCs. The first objective is to study the effect of the CNTs on the properties of G/CB/PP composite. While second objective is to determine the critical loading of CNTs in G/CB/PP composite. In this research, the ratio of filler (G/CNTs) and binder (PP) is fixed at 80:20. The CB fixed at 25%, 10 grams. The additional small amount of CNTs which is 0, 1, 2, 3 wt% (calculate from the total weight of filler 80%) respectively. Before hot press moulding, the G/CB/CNT need to mix with ball mill. Then mix with PP also by ball mill machine in order to determine the effect of CNTs in G/CNTs/PP composite such as electrical and mechanical properties. Moreover, there are several tests to obtain the result which is electrical conductivity, flexural test, density test, shore hardness test (type D) and microstructure analysis. The results show that 2 wt% of CNTs at electrical conductivity test has the highest electrical conductivity which is 124.7544 S/cm. Result of flexural test also has 41.92 MPa for 1wt% of CNTs. 3 wt% of CNTs which has the lowest shore hardness, 1 wt% has the highest result of shore hardness which is 74.2 Shore-D, while increase weight loading of CNTs, decrease of density of composite in result by densimeter.

ABSTRAK

Pada masa ini, plat bipolar grafit tulen telah disasarkan menggantikan komposit polimer konduktif (CPC). Ini kerana plat bipolar mempunyai kos pekilangan rendah dan kepadatan rendah dalam PEMFCs. Objektif pertama adalah mengkaji kesan CNT terhadap sifat komposit G / CB / PP. Tujuan kedua adalah menentukan pemuatan kritikal CNT dalam komposit G / CB / PP. Dalam kajian ini, nisbah pengisi (G / CNTs) dan pengikat (PP) ditetapkan pada 80:20. CB tetap pada 25%, 10 gram. Tambahan kecil CNT adalah 0, 1, 2, 3 wt% berat (dari jumlah berat pengisi 80%). Sebelum proses pembuatan menggunakan penekan panas, G / CB / CNT perlu dicampur dengan pengisar bola mesin. Kemudian campurkan dengan PP juga dengan pengisar bola mesin bagi menentukan kesan CNT dalam komposit G / CNT / PP seperti sifat elektrik dan mekanikal. Tambahan pula, terdapat beberapa ujian untuk mendapatkan hasil seperti kekonduksian elektrik, ujian kekuatan lenturan, ujian ketumpatan, kekerasan ujian kepadatan (jenis D) dan analisis mikrostruktur telah dilaksanakan. Keputusan menunjukkan bahawa 2wt% berat CNT pada ujian kekonduksian elektrik mempunyai kekonduksian elektrik tertinggi iaitu 124.7544 S / cm. Keputusan ujian lenturan juga mempunyai 41.92 MPa untuk 1wt% CNTs. 3 wt% CNT yang mempunyai kekerasan terendah, 1% berat mempunyai hasil kekerasan tertinggi iaitu 74.2 Shore-D. Sementara penambahan beban berat CNT meningkat, tahap ketumpatan komposit dalam hasil oleh densimeter semakin menurun.

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LIST OF ABBREVIATION

| | |
|--------|---------------------------------------|
| CNTs | Carbon Nanotubes |
| CB | Carbon Black |
| G | Graphite |
| PP | Polypropylene |
| PEMFCs | Proton Exchange Membrane Fuel Cell |
| DC | Direct Current |
| DOE | Department of Environment |
| CPC | Conductive Polymer Composite |

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Proton exchange membrane fuel cells (PEMFCs) is a good contender for portable and automotive propulsion applications because of their advantages of high-power density, solid state construction, high efficiency of conversion of chemical to electrical energy, near zero environmental emissions and low temperature operation.

The bipolar are key components of PEMFCs. They are responsible for functions of vital importance to the long-term operation of these electrochemical devices. The performance of fuel cells is depending on bipolar plate roles in water and gas management, mechanical stability and electrical performance. It is a good application for automotive propulsion because it has high efficiency to convert chemical energy to electrical energy without environment emission. Fuel cell required a very important and expensive component such as bipolar plate. It contributes 70-80 % of stack weight and up to 45 % of the cost [1]. Thus, it shown that it is a critical issue to investigate on cost or performance material of bipolar plate.

Iijima was the first scientist to identify the carbon nanotubes (CNTs) in 1991 [3]. After that, it has been investigated in various field because of it can improve the mechanical and

electrical properties of a component. In 2003, R. Andrews and M.C. Weisenberger were presented their experimental measurements of single shell failure for multiwalled carbon nanotubes that displays fracture strength by using CNTs as discontinuous support for polymer matrices. The strength multiwalled carbon nanotubes had been proved by providing the first direct measurements for tensile fracture strengths of MWCNTs that are near the ultimate strength estimates of quantum mechanics calculation [6].

The metal bipolar plate is usually made of special alloyed steel because of high strength, high chemical stability, ease of mass production and low cost. But, stainless steel is not suitable for bipolar plate due to its very low of surface contact resistance and inexpensive mass production. Thus, graphite is the most currently used material for bipolar plate, because graphite has a good conductivity and higher corrosion resistance under 2g/m^3 of density. However, in term of mechanical strength and ductility of graphite are in low level. In this case, composites materials are the best solution to make sure the bipolar plate criteria of conductivity of electricity performance and mechanical properties are balance. Various graphite with polymer composites and those on the basics of the inorganic binding agent such as Carbon Black, Carbon Nanotubes.

Bipolar plate (BP) is a most costly and main component in PEMFCs, therefore study on performance of bipolar plate (BPs) has become a famous and critical issue now. All materials have standpoint, bipolar plate (BPs) application also should present a balance of physical properties and chemical properties. Thus, the bipolar plates can be different on their properties with the different of composites of BPs. However, the BPs must follow the target properties that specified by Department of Energy (DOE). These targets have been developed with input from the automotive and energy companies and specifically the Fuel Cell Technical Team. The guideline helps to assist component developers in evaluating

progress without testing full systems. The properties requirement shown in Table 1.1 should be satisfied for fabrication of a bipolar plate.

Table 1.1: DOE target for bipolar plate (Source: Yeetsorn et al, 2012 [14])

| Properties | Value |
|-------------------------|----------|
| Electrical conductivity | >100 S/c |
| Thermal conductivity | >10 W/Mk |
| Flexural strength | >25[MPa] |
| Shore Hardness | >50 |
| Bulk Density | <5[g/c] |

To achieve the requirements stated by the U.S. DOE for bipolar plate, materials/composite properties of the CPCs must be considered for achievable design for a fuel cell application, specifically, electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight [2].

1.2 PROBLEM STATEMENT

There are many researches about Polymer Electrolyte Membrane Fuel Cells (PEMFCs) because they want to change of pure graphite or metal based bipolar plates. In

2015, Mohd Zulkefli Selamat was studied the effects of CNTs loading in multi filler with Graphite (G), Carbon Black (CB) and Carbon Nanotubes (CNTs) as reinforcements and Polypropylene (PP) as a polymer matrix. composite for bipolar plate PEMFC shows that incorporating CNTs composites produces a synergistic effect that enhances the electrical conductivity, flexural strength, bulk density and hardness of the composite which are exceeded of Department of Energy (DOE) requirement [4].

By changing bipolar plates can make fuel cell more high-power density, low operating temperature. They are several materials is currently use to produce bipolar plate. The first option material that suitable combination of thermal and electrical properties is pure graphite. It is high corrosion resistant, but inherent brittleness and high manufacturing cost. While another material is metal plate, but it is too heavy compare to pure graphite heavy, corrosion-protective coating is typically required to improve lifetime [4].

Now, new bipolar plate material has been developed and through composite approached where two types of materials were used. That materials are fillers and binder. Normally the fillers or conductive fillers such as G, CB and carbon fibre. While the binders used thermoplastic or thermoset. The mixer of these material is Conducting Polymer Composite (CPC). CPC have advantage such as ease of shaping, low density and wide range of electrical conductivities as well as corrosion resistance when compare with the metallic conductor [8].

Mostly researcher used for bipolar plates is graphite material because it has good corrosion resistance, high electrical conductivity and low density than other materials. On the other hand, graphite is a very high cost of machining channels into the surface and their vulnerability will cause the fuel cell stack becomes heavy and voluminous [7].

1.3 OBJECTIVE

The main objective of this research is:

- To study the effect of Carbon Nanotubes (CNT) on the properties of Graphite (G), Carbon Black (CB) and Polypropylene (PP) composite.
- To determine the critical loading of CNT in G, CB, and PP composite.

1.4 SCOPE OF PROJECT / GENERAL METODOLOGY

This research will study the effect of CNT loading on the electrical and mechanical properties of G, CB, and PP composite. The critical loading of CNT in G/CB/PP composite needs to be determined and to be used as composition of G/CB/CNT/PP composite for bipolar plate. The ratio of filler (G/CNT) and binder (PP) is fixed at 75:25. The amount of G also will be fixed 25% and by adding of small amount of CNTs into CB/CNT/PP composite thus will gives synergy effect on electrical conductivity and mechanical properties. The small amount of CNTs which is 0, 5, 10 and 15 wt. % (from the total weight of fillers 75 %) will be added into G/CB/PP composite. The filler of G, CB and CNTs will be mixed used ball mill before the fabrication process using the hot press. To determine the effect of CNTs content in G/CNT/PP composite, the tests such as electrical conductivity, flexure test, density test, hardness and microstructure analysis will be performed.

CHAPTER 2

LITERATURE REVIEW

2.1 FUEL CELL

Fuel cell is a device of electrochemically like a battery that can convert from chemical potential energy of gaseous or liquid reactant into direct current (DC) electricity. The different between fuel cell with battery is the fuel cell requires the source of hydrogen (fuel) and oxygen (air) as reacting gases to generate electrical energy. Fuel cell also can produce electricity continuously for as long as fuel and oxygen are supplied.

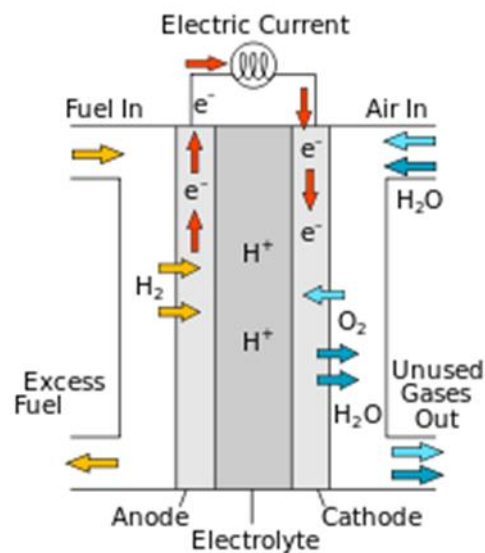


Figure 2.1: Basic Fuel Cell [15]

Fuel cell consist of anode cathode and electrolyte that block the negative charged of electron pass through was shows in figure 2.1. At anode, the fuel (H₂) will undergo oxidation reaction to form positively charged hydrogen ions and electron. At the same time, electron from anode flow from anode to cathode though external circuit produce direct current electricity. At cathode, there are form of water by the reaction of hydrogen ions, electron and oxygen [9]. There are many types of fuel cells as shown at table 2.1. All types of fuel cells require a fuel that reacts with oxygen and in the process releases the chemical energy contained in the fuel.

| Low Temperature Fuel Cells | | | | High Temperature Fuel Cell | | |
|-----------------------------------|--|---|-------------------------------------|--|---|--|
| | DMFC Direct Methanol Fuel Cell | PEMFC Proton Exchange Membrane Fuel Cell | AFC Alkaline Fuel Cell | PAFC Phosphoric Acid Fuel Cell | MCFC Molten Carbon Fuel Cell | SOFC Solid Oxide Fuel Cell |
| Electrolyte | Proton-conducting membrane | Proton-conducting membrane | Caustic Potash solution | Concentration phosphoric acid | Molten Carbonate | Ceramic |
| Temperature Range | < 100 °C | < 100 °C | < 100 °C | ~200 °C | ~650 °C | 800-1000 °C |
| Fuel | Methanol | Hydrogen | Hydrogen | Hydrogen | Natural gas, coal | Natural gas, coal |
| Power Range | Watts/ kilowatts | Watts/ kilowatts | Watts/ kilowatts | Kilowatts | Kilowatts / megawatts | Kilowatts/ megawatts |
| Application Example | Vehicle/ small appliances | Vehicles/ small generator, domestic supply, power station | Outer space | Block type heat, power station | Power plant, combined heat and power | Power plant, combined heat and power |

Table 2.1: Type of Fuel Cells Characteristic

2.2 PROTON EXCHANGE MEMBRANE FUEL CELLS (PEMFCs)

The Department of Energy (DOE) is focusing on the PEMFCs as the most important of vehicles applications. There have been many successful shows of this technology in recent years. It able to efficiently to generate high power density and low operating temperature about 60 to 80 degrees Celsius. Despite PEMFCs have many advantages such as hydrogen can be produced in an environment friendly manner, while oil extraction and refining are very damaging, clean exhaust gases, modular design and low noise production [9].

The purpose of Proton-exchange membrane fuel cells (PEMFCs) are to changes the energy for suitable applications with difference requirements. The material combinations of PEMFCs that used also must difference. But need to get the properties of bipolar plates the properties for bipolar plates are as follows:

- Have electrical conductivity that $>100 \text{ S cm}$ bulk conductivity.
- The thermal conductivity must $>20 \text{ Wcm}$
- High chemical and corrosion resistance.
- Mechanical stability toward compression forces.
- The low permeability for hydrogen.
- Mass production techniques must have low-cost material being process able.
- Low volume and weight.

2.3 MAIN COMPONENT OF PEMFCs

Figure 2.3 shows the structure diagram of PEMFCs. There are three main components of PEMFCs which are Membrane Electrode Assembly (MEA) Bipolar plate (BPs) and End plate.

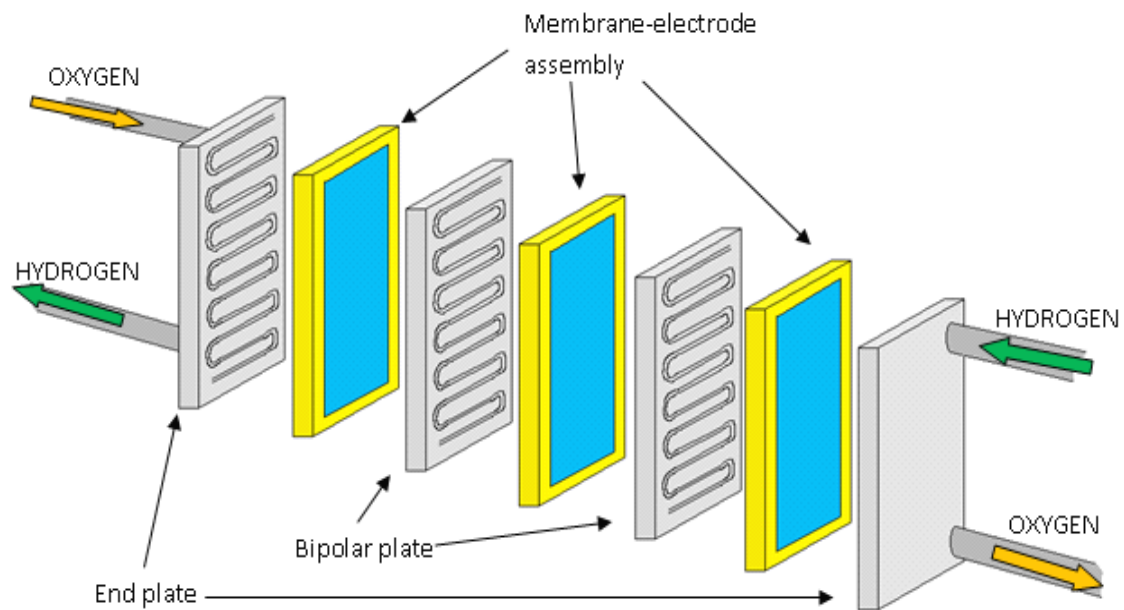


Figure 2.3: Structure Diagram PEMFCs, [15].

2.3.1 Membrane Electrolyte Assembly (MEA)

The MEA is the heart component of PEMFCs and work currently being done to find cheaper and thinner membranes whilst maintaining durability.

2.3.2 Bipolar Plates (BPs)

Allen Hermann, [10] stated that bipolar plates (BPs) play major role with multifunctional character of proton exchange membrane fuel cells (PEMFCs). The BPs can distribute fuel gas and air uniformly, remove heat from the active area, conduct electrical