UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Mechanical Engineering

ADDITIONAL OF METAL FILLER ON GRAPHITE/CARBON BLACK/POLYPROPYLENE COMPOSITE AS BIPOLAR PLATE MATERIAL FOR PEMFC APPLICATION

Mohd Shakir Bin Ahmad

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Mohd Shakir Bin Ahmad

A thesis submitted

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2015

DECLARATION

I declare that this thesis entitled "Additional of Metal Filler on Graphite/Carbon Black/Polypropylene Composite as Bipolar Plate Material for Pemfc Application" is the result of 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 other degree

Signature : ……………………………

Name : Mohd Shakir Bin Ahmad

Date : ……………………………

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master in Mechanical Engineering

Signature	: ………………………….……….…
Supervisor Name	: Dr. Mohd Zulkefli Bin Selamat
Date	: ……………………..……………

DEDICATION

To my beloved mother, father, wife and son

To my grateful supervisor, Dr. Mohd Zulkefli Bin Selamat and

Dr. Mohd Ahadlin Bin Mohd Daud

To all my sibling and friends.

You all made everything priceless.

ABSTRACT

Polymer electrolyte membrane fuel cell (PEMFC) is expected to be one of the major power sources for future passenger vehicles since it features a high power density at a relatively low operating temperature of about 80◦C. There are several key components in PEMFC and one of them is bipolar plate. This bipolar plate is a multi-functional component. It provides the electrical connection from cell-to-cell and it separates the reactive gases. The known problem related to bipolar plate is the corrosion, weight and high cost. Hence, composite bipolar plate based on thermoplastic material is introduced and solved the general disadvantages of traditional bipolar plate. But, it still has a main limitation which is electrical conductivity and mechanical properties such as brittleness.. Through this research, the effect of secondary filler on electrical and mechanical properties is studied in order to overcome the main limitation of composite bipolar plate. The combination of metal and carbon filler also been studied for the purpose of improvement electrical and mechanical properties of G/PP composite bipolar plate. This study also would propose the fabrication process in producing composite material bipolar plate. The materials used in producing bipolar plate are greatly affecting its final properties. As for binder material, Polypropylene (PP) is used and for main filler material Graphite (Gr) is used. While, second filler used are Iron (Fe), Nickel (Ni) and Carbon Black (CB). The based ratio for this bipolar plate is 80%wt of filler and 20% wt of binder. The addition second filler is varying from 5%wt to 30%wt from the total of 80%wt. The fabrication of sample is done through compression molding method. The measurement that has been done is electrical conductivity, flexural strength, bulk density, shore hardness and microstructures. From result, the addition of CB has shown the most improvement in term of electrical conductivity (218.43 S/cm) and has good mechanical properties (38.03 MPa, flexural strength). While, the addition of Fe and Ni it not quite good but still Fe is better candidate than Ni. From this finding, another sample is introduced which is the combination of Fe and CB as part of second filler and it show the greater result which is 367.59 S/cm in electrical and 44.57 MPa in flexural strength. This result has shown a great improvement in electrical conductivity and acceptable mechanical properties. This framework of study can be used as reference in furthering the research.

ABSTRAK

Elektrolit membran polimer sel bahan api (PEMFC) dijangka akan menjadi salah satu sumber kuasa utama untuk kenderaan penumpang di masa hadapan kerana ia mempunyai ketumpatan kuasa yang tinggi pada suhu operasi yang rendah kira-kira 80◦C . Terdapat beberapa komponen utama dalam PEMFC dan salah satu daripadanya adalah plat dwikutub . Plat dwikutub ini adalah komponen pelbagai fungsi . Ia menyediakan sambungan elektrik dari sel ke sel dan memisahkan gas reaktif . Namun, terdapat beberapa masalah yang telah dikenal pasti berkaitan dengan plat dwikutub ini dan ia adalah kakisan , berat dan kos yang pengeluaran yang tinggi . Oleh itu , komposit plat dwikutub berdasarkan bahan termoplastik diperkenalkan dan boleh menyelesaikan kelemahan umum plat dwikutub ini . Akan tetapi , ia masih mempunyai masalah utama iaitu kekonduksian elektrik dan sifat mekanikal seperti kerapuhan yang rendah.. Melalui kajian ini , kesan bahan pengisi kedua pada sifat elektrik dan mekanikal dikaji untuk mengatasi masalah utama komposit plat dwikutub ini . Gabungan pengisi berasaskn logam dan pengisi karbon juga dikaji untuk tujuan penambah baikan sifat elektrik dan mekanikal G / PP komposit plat dwikutub. Kajian ini juga akan mencadangkan proses fabrikasi yang sesuai dalam menghasilkan bahan komposit plat dwikutub. Bahan-bahan yang digunakan dalam menghasilkan plat dwikutub adalah amat memberi kesan kepada sifat-sifat akhir plat dwikutub ini. Bagi bahan pengikat , Polipropelina (PP) digunakan dan untuk bahan pengisi utama Grafit (Gr) digunakan . Bagi bahan pengisi kedua, pengisi yang digunakan adalah besi (Fe) , Nikel (Ni) dan Karbon Hitam (CB) . Manakala nisbah asas untuk plat dwikutub ini adalah 80 % berat pengisi dan 20 % berat pengikat . Penambahan pengisi kedua adalah berbeza-beza dari 5 % berat hingga 30 % berat dari jumlah keseluruhan pegisi asas iaitu 80 % berat. Fabrikasi sampel pula dilakukan melalui kaedah pemampatan acuan. Bagi bahagian ujian, kekonduksian elektrik , kekuatan lenturan , ketumpatan pukal , kekerasan pantai dan struktur mikro di lakukan . Dari hasil ujian , penambahan CB telah menunjukkan peningkatan yang paling tinggi bagi kekonduksian elektrik (218.43 S / cm) dan mempunyai sifat mekanikal yang baik (38.03 MPa , kekuatan lenturan) . Walaupun , dengan penambahan Fe dan Ni kedalam komposit, namun ia masih tidak memberikan hasil yang baik, tetapi Fe lebih sesuai dijadikan calon bahan pengisi ketiga di dalam kajian ini. Berdasarkan kajian ini, sampel lain diperkenalkan iaitu gabungan Fe dan CB sebagai sebahagian daripada pengisi kedua dan ia menunjukkan hasil yang lebih baik iaitu 367.59 S / cm elektrik dan 44.57 MPa kekuatan lenturan . Keputusan ini telah menunjukkan peningkatan yang besar dalam kekonduksian elektrik dan sifat-sifat mekanik yang boleh diterima pakai . Rangka kerja kajian ini juga boleh digunakan sebagai rujukan dalam melanjutkan penyelidikan di masa depan.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

ABBREVIATION	MEANING
ABS	Acrylonitrile Butadiene Styrene
AFC	Alkaline Fuel Cell
ASTM	American Society for Testing and Materials
BSE	Back Scattered Electron
CB	Carbon Black
CF	Carbon Fiber
CHP	Combined Heat and Power
CHHP	Combined Heat Hydrogen and Power
CL	Cathodoluminescence
CNC	Computer Numerical Control
CNT	Carbon Nanotube
CO	Carbon Monoxide
CPC	Conductive Polymer Composite
DC	Direct Current
DOE	Department of Energy
EBSD	Diffracted Backscattered Electrons
EDS	Energy Dispersive X-ray Spectroscopy
EG	Expanded Graphite
Fe	Iron
GDL	Gas Diffusion Layer
G	Graphite
H_2	Hydrogen
H_2O	Water
ICP	Intrinsically Conducting Polymer
LCP	Liquid Crystalline Polymer
MA	Maleic Anhydride
MCFC	Molten Carbonate Fuel Cell
MEA	Membrane Electrode Assembly
MWCNT	Multi Walled Carbon Nanotube
Ni	Nickel
NiO	Nickel Oxide
O_2	Oxygen
P_+	Platinum
PAFC	Phosphoric Acid Fuel Cell
PEM	Polymer Electrolyte Membrane
PEMFC	Polymer Electrolyte Membrane Fuel Cell

ABBREVIATION	MEANING
PFSA	Perfluorosulfonic Acid
PC	Polycarbonate
PE	Polyethylene
POA	Poly(axyalkylene amine)
POAMA	Poly(Axyalkylene Amine) bearing Maleic Anhydride
PP	Polypropylene
PPS	Polyphenylene Sulfide
PVDF	Polyvinylidene Fluoride
SEM	Scanning Electron Microscope
SOFC	Solid Oxide Fuel Cell
US	United States
UV	Ultra Violet

LIST OF SYMBOL

π	Pi
I	Current
P	Rho
s	Interprobe spacing
S	Distance of Four Point Probe
V	Voltage
v	Test data

CHAPTER 1

INTRODUCTION

1.1 Background

Since 1950, electrically conductive polymer composite (CPC) have become an interesting research area. CPC is obtained by blending a polymer matrix or conducting polymers (Polyaniline, PANi) with a conductive particle such as Graphite (G), Carbon Black (CB), Carbon Fiber (CF), Carbon Nanotube (CNT) and metal particles. With the polymer matrix being an insulator, the conductivity of these composites demonstrate a sudden jump when critical filler content is reached. This phenomenon is often described as percolation. Typically, 5–20 wt.% of conventional conductive filler (such as G and CB) is added into a polymer matrix to achieve a percolating network. Meanwhile, high filler contents quite often negatively affect the mechanical properties and processability of the resulting composites.

Recently, considerable attention has been given in developing CPC for applications where high electrical conductivity is required such as bipolar plate. Bipolar plate is a conductive plate in a fuel cell stack that acts as an anode for one cell and a cathode for the adjacent cell. The plate may be made of metal or a conductive polymer composite (which may be a carbon-filled composite). The plate usually incorporates flow channels for the fluid feeds and may contain conduits for heat transfer.

The most commonly used bipolar plate material is pure G. Among the advantages of graphite are its excellent corrosion resistance, light weight and low-bulk resistivity. On the other hand, the disadvantages are difficulties in machining, and its brittleness as stated by Kamarudin et. al., (2006), Onischak et. al., (1999) and Larminie et.al., (2001). Other material that can be used as bipolar plate are metals, Wang et. al., (2004) in his study describe that thin metal sheet is also a good material for a bipolar plate because it offers the attributes of good electrical conductivity, low-cost, excellent mechanical strength and ease to fabrication, but suffers from low-corrosion resistance.

A composite bipolar plate is a promising alternative to both metal and pure G, and has the advantages of low-cost, ease in machining or in situ molding of complex flow fields during processing, good corrosion resistance and light weight. Kyungmun et. al., (2013) also stated the same advantages of composite bipolar plate. A carbon/polymer combination was thought to be an ideal component for producing such plates. The advantages with addition of carbon are light weight, available in different structural forms to provide varied electrical, thermal, and mechanical properties.

1.2 Problem Statement

The fuel cell stack is the heart of a fuel cell power system. It generates electricity in the form of direct current (DC) from chemical reactions that take place in the fuel cell. A single fuel cell produces enough electricity for only the smallest applications. Therefore, individual fuel cells are typically combined in series into a fuel cell stack. A typical fuel cell stack may consist of hundreds of fuel cells.

Bipolar plate is one of the important components in the fuel cell stack. Traditional bipolar plate usually is made from metal alloy and G. However, the main issues about this traditional bipolar plate are their corrosion resistant, weight and cost. Currently, the researcher tends to focus on improving this problem and they come out with the solution with the use of polymeric material to overcome the drawback of traditional bipolar plate, but by using this polymeric material it make the electrical conductivity lower than the traditional bipolar plate. For example Polypropylene (PP)/G composites are among the polymer composites that have been used to produce bipolar plates. PP does not include any polar groups in its backbone, it is thought that homogenous dispersion of the G layers in PP is not realized and thus a relatively low electrical conductivity is obtained. Moreover, hardly any interaction occurs between PP and chemically inert G layers.

Renato et. al., (2011) in his review stated that one of the main challenges of PEM fuel cell manufacturers is to maximize the power density of these devices. The pathway to reach this goal is closely related to the reduction of ohmic losses within the fuel cell stack. In this context, the optimization of the electrical conductivity of polymer matrix composite bipolar plates plays a leading role thereby demanding many efforts to the development of increasingly conductive materials. The science behind this quest comprises of a conjunction of characteristics owing to materials, processing and their mutual interaction. Reza (2014) in his review mentions that polymer-carbon composite BP such as PP/G has a lower electrical properties, mechanical properties and also non-stampability. Lim J.W. et.al.,(2014), in his work mention that carbon composite bipolar plates have a higher gas permeability and bulk resistance than those of conventional graphite bipolar plates, which compromises the efficiency of a PEM fuel cell. Lim J.W. et.al.,(2014) also mentions that the greatest handicap for carbon-polymer composite bipolar plate is the lack of electrical conductivity which is critical to the final application of PEMFC.

In order to overcome this limitation other carbon-based conductive fillers besides conventional graphite can be incorporated into the polymer matrix. These fillers include carbon black (CB), multi-walled and single-walled carbon nanotubes (MWCNT and

SWCNT), carbon fibers, expanded graphite and combinations thereof. Metal filler such as Fe, Ni, and Cu also can be a possible candidate. In this work, the combination of second filler material in the composite bipolar plate is studied. CB, Iron powder (Fe) and Nickel (Ni) is the second filler material that been used. It is an additive characterized by a smaller particle size (10–50 µm) than graphite.

1.3 Objectives

The objectives of the research are:

1. To study the effects of CB, Fe, and Ni content on the electrical conductivity and mechanical properties of G/PP composite material for bipolar plate.
2. To improve the electrical conductivity and mechanical properties of G/PP composite by introducing the combination of metal and carbon based filler as bipolar plate material.
3. To propose the fabrication process in producing composite material for bipolar plate application in PEMFC.

1.4 Scope of Work

Electrical conductivity of carbon–polymer composite bipolar plates can be favorably tailored through the correct choice of materials and manufacturing methods. The knowledge of materials properties is the basic tool to start a successful research project. In this way, it is necessary to understand how different carbon based fillers behave owing to the percolation phenomena in specific organic matrices. The development of composite bipolar plates may be guided by understanding the effect of second filler material which is added in order to improve the electrical conductivity and flexural strength of the bipolar plates. The aspect ratio of the conductive filler particles will be maximized in order to reduce the percolation threshold and increase the electrical conductivity of the composite. Finally the rote of process in producing bipolar plate can be established.

This research focuses on the usage and content of CB, Fe and Ni on the PP/G composite as bipolar plate. The scope of study that consisted in this project accomplishment is the fabricated composite are focused to the use of G as main filler. As for secondary conductive filler material, CB, Fe and Ni are used. For binder, PP is used in the fabrication of composite bipolar plate sample. The composition ratio of filler to binder will be vary from 70-80 : 30-20. While the secondary conductive filler will be vary from 5 to 30 wt% of total ratio filler content. The composite specimen will be tested for investigating purpose on the electrical conductivity, flexural strength, shore hardness, bulk density and microstructure of the sample due to the use of various weight ratios of CB, Fe and Ni in the total ratios of the filler material.

1.5 Thesis Layout

This study consists of five chapters. Chapter 1, covers the introduction and the basics of the study. This includes the objectives, scopes and problem statement. Chapter 2, presents recent and previous studies from all related resources. Chapter 3, consists the detail of method and materials used for this study. Chapter 4 will present the analysis and discussion of all data taken from the experimental job done in this study and in Chapter 5 is a conclusion part for the study has been done.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Fuel cell is a device that uses a hydrogen and oxygen to create electricity by an electrochemical process. A single fuel cell consists of an electrolyte and two catalyst-coated electrodes (Ryan et.al., 2009). While there are different fuel cell types, all fuel cells work similarly:

1. A fuel (such as hydrogen) is fed to the anode where a catalyst separates hydrogen's negatively charged electrons from positively charged ions (protons).
2. At the cathode, oxygen combines with electrons and, in some cases, with species such as protons or water, resulting in water or hydroxide ions, respectively.
3. For polymer electrolyte membrane and phosphoric acid fuel cells, protons move through the electrolyte to the cathode to combine with oxygen and electrons, producing water and heat.
4. For alkaline, molten carbonate, and solid oxide fuel cells, negative ions travel through the electrolyte to the anode where they combine with hydrogen to generate water and electrons.
5. The electrons from the anode cannot pass through the electrolyte to the positively charged cathode; they must travel around it via an electrical circuit to reach the other side of the cell. This movement of electrons is an electrical current.

2.2 Types of Fuel Cells

Fuel cells are classified by the kind of electrolyte used. This classification also determines what kind of chemical reactions that take place in the cell, the kind of catalysts required, the temperature range which the cell operates, the fuel required, and other factors. These characteristics effect can be used for the applications 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. Their types and comparisons are as shown in Table 2.1

Table 2.1 : Advantages and disadvantages of different type fuel cell source from (EERE, 2012)

Fuel Cell Type	Operating Temperature (°C)	Application	Advantages	Disadvantages
Polymer electrolyte membrane (PEMFC)	50-100 Typically 80	• Backup power • Portable power • Distributed generation • Transportation • Specialty vehicle	• Solid electrolyte reduces corrosion and electrolyte management problem • Low temperature • Quick start-up	• Expensive catalysts • Sensitive to fuel impurities • Low temperature waste heat
Alkaline (AFC)	90-100	• Military • space	• Cathode reaction faster • Low cost component	• Sensitive to CO_2 in fuel cell air • Electrolyte management
Phosphoric acid (PAFC)	150-200	• Distributed generation	• Higher temperature enables CHP • Increase tolerance to fuel impurities	• Pt catalyst • Long start up • Low current and power
Molten Carbonate (MCFC)	600-700	• Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use variety of catalyst • Suitable for CHP	• High temperature corrosion and breakdown of cell component • Long start up • Low power density
Solid oxide (SOFC)	700-1000	• Auxiliary power • Electric utility • Distributed generation	• High efficiency • Fuel flexibility • Can use variety of catalyst • Suitable for CHP & CHHP • Solid electrolyte • Hybrid/GT cycle	• High temperature corrosion and breakdown of cell component • High temperature operation requires long start up time and limits

2.3 Polymer Electrolyte Membrane (PEM) Fuel Cells

Polymer electrolyte membrane fuel cell is also known as proton exchange membrane fuel cells (PEMFC). PEMFC delivers high power density, and is low in weight and volume as compared to other type of fuel cells. Solid polymeric electrolyte and porous carbon electrodes containing platinum catalyst are used in PEMFC. PEMFC only needs hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some other fuel cells.

PEMFC usually operate at relatively low temperatures, around 80°C (176°F). Low operating temperature means it allows fuel cell to start quickly (less warm-up time), less wear on system components and results in better durability. However, PEMFC requires a noble-metal catalyst (typically platinum) be used for separate the hydrogen's electrons and protons, which is quite costly for the system. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reactor to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Developers and researchers are currently exploring platinum/ruthenium catalysts that are more resistant to CO.