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"I declare that I have read this thesis 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 (Structure & Materials)"

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# **EFFECT OF STANUM ON THE PROPERTIES OF GRAPHITE -**STANUM COMPOSITE FOR BIPOLAR PLATE

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# This report is submitted to Faculty of Mechanical Engineering as a requirements to get award of

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**Faculty of Mechanical Engineering** Universiti Teknikal Malaysia Melaka

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# DECLARATION

"I hereby declare that the work in this report is my own except for summaries and quotations which have been duly acknowledged."

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#### ABSTRACT

Bipolar plate is an important key component in fuel cell on the basis of its manifold function. Based on these phenomena's there are a lot of effort is going on worldwide to make conductive composites which more high conductive. This research is study the electrical and mechanical properties of Graphite/Stannum (G/Sn) composites as prospective conductive composite to replace the traditional G as bipolar plate in proton-exchange membrane fuel cells (PEMFC). The main problems with the traditional bipolar plate materials such as metal and graphite materials are corrode, too brittle and low in electricity conductivity; but for G-Sn composite have potential to eliminate the above problems. Meanwhile the advantages of Sn as compare other materials are good conductor of electricity, high-strength materials and have the low melting point. In this research, focus is given to Sn and its effects on the properties on G/St composite. The raw materials used to produce thus composite is G as a filler and Sn as a binder or resin. The weight percentage of G/Sn has been be fixed at 80/20, 70/30 and 60/40. Before the composite shaped by using hot press machine, the G and Sn has be mixed used ball mill. The effects of Sn on the electrical conductivity and mechanical properties of G/Sn composite need to be determined as well as the critical loading of Sn in G/Sn composite before can be used as G/Sn composite for bipolar plate. Based on results, the properties of composite such as electrical conductivity and density, the weight percentage of 20 wt% of Sn gives maximum value of electrical conductivity (719.05 S/cm). This value was achieved DOE requirement (>100 S/cm). There are decreasing values of electrical conductivity for higher Sn content. It also interesting to note that with increasing the Sn content, density properties in decreased and satisfied the DOE target which is  $\sim 1.9$  gcm<sup>-3</sup>. From this 3 different composition the test has been done according to ASTM (American Society for Testing and Materials) and composition of 80% G 20% Sn is shows the best result.

#### ABSTRAK

Plat dwikutub merupakan satu daripada komponen penting/utama sel bahan api berdasarkan fungsi pancarongga. Dalam fenomena ini banyak usaha yang sedang dilakukan di seluruh dunia untuk membuat komposit berkonduktif tinggi dengan pengalir elektrik yang baik. Penyelidikan terhadap potensi komposit Grafit / Sn (G / Sn) sebagai pengganti kepada plat dwikutub tradisional sel bahan api protonexchange membrane (PEMFC) perlu dilakukan. Masalah utama yang dihadapi pada plat dwikutub tradisional adalah kakisan, terlalu rapuh dan rendah dalam kekonduksian elektrik. Penggunaan bahan Sn sebagai matrik dalam Grafit komposit diperkenalkan. Kelebihan Sn berbanding bahan matrik yang lain, Sn adalah pengalir elektrik yang baik, kekuatan bahan yang tinggi dan mempuyai takat lebur yang rendah. Dalam kajian ini, tumpuan diberikan kepada kesan Sn (Sn) terhadap sifatsifat komposit Grafit/stamum. Bahan-mentah yang digunakan untuk menghasilkan komposit G/Sn adalah Grafit sebagai pengisi dan Sn sebagai pengikat atau resin. Nisbah G / Sn akan ditetapkan pada 80/20, 70/30 dan 60/40. Sebelum pembentuk komposit dengan menggunakan mesin penekan panas, Grafit dan Sn akan melaui proses pra-pencampura menggunakan pengisar bola. Seterusnya kesan Sn terhadap kekonduksian elektrik dan sifat mekanikal G / Sn komposit akan ditentukan. Pembebanan kritikal Sn dalam G / Sn komposit perlu ditentukan terlebih dahulu sebelum dapat digunakan sebagai plat dwikutub. Berdasarkan keputusan, sifat-sifat komposit seperti kekonduksian elektrik dan ketumpatan telah dapat ditentukan. Jumlah sebanyak 20% Sn memberikan nilai maksimum kekonduksian elektrik (719,05 S / cm). Nilai ini telah melebihi dari United State Department of Energy (US-DOE) (> 100 S / cm). Terdapat penurunan nilai kekonduksian elektrik untuk kandungan Sn tinggi. Ia juga menarik perhatian bahawa dengan meningkatkan kandungan Sn, kepadatan dapat dikurangkan dan berpuas hati dengan sasaran DOE adalah ~ 1.9 gcm<sup>-3</sup>.

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# LIST OF SYMBOLS AND ABBREVIATION

Symbols	Title
US-DOE	United State Department of Energy
MEA	Membrane Electrode Assembly
ASTM	American Society for Testing and Materials
PEMFC	Polymer Electron Membrane Fuel Cells
CPCs	Conductive Polymer Composites
GDL	Gas Diffusion Layer
g/cm3	gram/centimeter3
G	Graphite
Sn	Stannum
°C	Degree Celcius
MPa	Mega Pascal
μA	Micron Ampere
Wt.%	Weight Percentage
Е	Young's Modulus
S/cm	Siemen/centimeter

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#### **CHAPTER 1**

#### INTRODUCTION

#### 1.1 Fuel Cell

Fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent. Hydrogen is the most common fuel, but hydrocarbons such as natural gas and alcohols like methanol are sometimes used. Fuel cells are different from batteries in that they require a constant source of fuel and oxygen to run, but they can produce electricity continually for as long as these inputs are supplied. An electrolytic process has to take place inside a cell in which there is an open source fuel which is hydrogen and an oxidant or can be called oxygen [Larminie and Dicks (2003)].

Both the fuel and oxidant are introduced into the cell, where they react and the output product is carried out of the cell and stored. The electrolyte is left as it is inside the cell. This process can take place non-stop for a long time as long as the flow of resources are maintained. There are many types of fuel cells, but they all consists of an anode (negative side), a cathode (positive side) and an electrolyte that allows charges to move between the two sides of the fuel cell. Electrons are drawn from the anode to the cathode through an external circuit, producing direct current electricity. As the main difference among fuel cell types is the electrolyte, fuel cells are classified by the type of electrolyte they use. Fuel cells come in a variety of sizes The result obtained by combining hydrogen and oxygen is water. As a result of this process, electricity is formed. There are mainly three segments.

- i. Anode
- ii. Cathode
- iii. Electrolyte

The type of electrolyte used is what defines the type of fuel cell used. Whatever may be the type of fuel cell, their basic operation is always the same. With the combination of the three segments, two main chemical reactions take place. A catalyst will be present at the anode. This anode catalyst, mostly platinum powder, is used to oxidize the hydrogen fuel. Thus the hydrogen gas turns into ions and electrons. Out of these, the ions make way through the electrolyte to the cathode. As soon as they reach the cathode, they combine with the cathode and then react with the oxidant to produce water. The electrons pass through a wire producing the electricity. Nickel is mostly used as the cathode catalyst.[Thomas and Zalbowitz (2008)]

#### 1.2 Polymer Electronic Membrane Fuel Cell

The Proton Exchange Membrane Fuel Cell (PEMFC), also called the solid polymer fuel cell, was first developed by General Electric in the United States in the 1960s for use by NASA [Larminie and Dicks (2003)]. Currently, the PEMFC is being researched by the automotive industry, government agencies, and educational institutions to replace the internal combustion engine. The PEMFC utilizes hydrogen (fuel) and oxygen (oxidant) to convert chemical energy directly to electrical energy. The by products of this conversion are water and heat. Figure 1.1 illustrates the PEMFC key components and their respective roles in the operation of the fuel cell.



Figure 1.1: Fuel Cell Schematic [http://en.wikipedia.org/wiki/Fuel\_cell].

The fuel cell consists of two bipolar plates, a membrane electrode assembly (MEA), and two seals. The MEA constitutes a membrane, two dispersed catalysts layers, and two gas diffusion layers. Figure shows the conversion of chemical energy to electrical energy using hydrogen as the fuel and oxygen as the oxidant. The anode supplies hydrogen and the cathode supplies oxygen to the gas diffusion layer (GDL). The GDL allows direct and uniform access of the fuel and oxidant to the catalysts layers, which increases the rate of each half reaction. [Borup and Vanderborgh (1995)]

#### 1.3 Bipolar Plate

Bipolar plates constitute the backbone of a hydrogen fuel cell power stack, conduct current between cells, facilitate water and thermal management through the cell, and provide conduits for reactant gases namely hydrogen and oxygen. In the polymer electrolyte membrane (PEM) hydrogen fuel cell design, bipolar plates are fabricated in mass production and they must be made of materials with excellent manufacturability and suitable for cost-effective high volume automated production systems. Bipolar plates have a number of functions within the fuel cell stack;

- i. The reaction gases and water exhaust whereby separating gases between cells.
- ii. Providing a conductive medium between the anode and cathode.
- iii. Providing a flow field channel for the reaction gases.
- iv. A solid structure for the stack.
- v. Transferring heat out of the cell.

Based on United State Department of Energy (US-DOE), the requirements for bipolar plates are as follows,

- i. Good electrical conductivity (>100 S cm<sup>-1</sup> bulk conductivity).
- ii. Low hydrogen permeability  $(<2\times10^{-6} \text{ cm}^3 (\text{cm}^2\text{s})^{-1})$ .
- iii. Good chemical stability and corrosion resistant ( $<1\mu$ A cm<sup>-2</sup>)
- iv. Good flexural strength (>25 MPa).
- v. High tensile strength (>41 MPa).
- vi. High thermal conductivity (>10 W  $(mK)^{-1}$ ).
- vii. Low thermal expansion.
- viii. Efficient process ability.

In a typical cell stack each bipolar plate supports two neighboring cells, constituting about 87 mass percent of the fuel cell stack. The bipolar plate has many

functions within the PEMFC. It disseminates the oxidant (oxygen) and fuel (hydrogen) into the fuel cell. The distribution of the fuel and oxygen throughout the active area are by flow fields in the bipolar plate. The flow fields on the bipolar plate have various patterns which facilitate effective and efficient water and impurity movement so not to compromise fuel cell activity [Kumar and Reddy (2003)]. The bipolar plate also separates the cells from one another, extracts heat from the active area, conducts current from cell to cell, and prevents leakages of gases and coolant [E. Middelman (2003)].

The design criteria of the bipolar plate for the PEMFC takes into account the thickness to minimize stack volume and electrical resistance. The bipolar plate must be gas impermeable to eliminate the mixing of the oxidant and the fuel. The material should be corrosion resistant due to the acidic environment present in the fuel cell. It should also be thermally conductive to remove heat from the fuel cell and electrically conductive to minimize ohmic losses [Nunnery (1998) ]. The bipolar plate should also provide mechanical strength and rigidity to support the electrolyte membrane and withstand the clamping forces [Borup and Vanderborgh (1995)]. In order to achieve the design criteria and function and cost targets of the bipolar plate, researchers tend to focus on the material selection of the bipolar plate.

#### 1.4 Problem Statement

Generally, in current fabrication of bipolar plate, graphite and metal are use as fillers. Meanwhile Polypropylene (PP) is used as a binder. The main problems of metal is high tendency to corrosion, for pure graphite are too brittle and low in electrical conductivity, PP is non conductive material and have a low strength. In this research, stannum is use as a binder and graphite as fillers. Stannum is select as binder because the melting point is low (250°C), good electrical conductivity and its strength is better than PP. It can be replaced PP as a binder in conducting polymer composite.

#### 1.5 Objective

The main objectives of this research are to study the effect of the stannum on the properties of graphite/stannum composite for bipolar plates to be used in fuel cell. In this research is use as a main filler and stannum is used as the binder. The main objectives of the research are;

- i. To study the effects of stannum on properties of graphite composite.
- ii. To determine the critical loading of Stannum, in graphite composite.

#### 1.6 Scope

In this research the raw materials will be used to produce the composite is graphite as a filler and stannum as a binder or resin. The ratio of G/Sn will be fixed at 80/20, 70/30 and 60/40. Before the composite shaped by using hot press machine, the graphite and stannum will be mixed used ball mill. The effects of stannum on the electrical conductivity and mechanical properties of G/Sn composite will be determined. The critical loading of Stannum in G/Sn composite needs to be determined before it can be used as composition of G/Sn composite for bipolar plate.

#### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Conductive Polymer Composites

Conductive polymer composites (CPCs) are obtained by combining an insulating polymer with electrically conductive fillers. The usefulness of these materials as fuel cell bipolar plates requires an understanding of factors which control the electrical conductivity of the composite. In addition to identifying the factors which control electrical conductivity within the composite, developing models that incorporate these principles would result in a more efficient bipolar plate or application specific design. These models would also reduce material usage and time, directly correlating to cost savings for this fuel cell technology. [Pike and Seager (1986)]

Typically, polymers exhibit electrical conductivities in the range of 10-14 to 10-17 Siemens per centimeter (S cm<sup>-1</sup>). Electrical conductivities of typical conductive carbon fillers range from 102 to 105 S cm<sup>-1</sup>. The resulting electrical conductivity of the composite will be heavily dependent on the filler concentration. As the concentration of filler increases to a critical volume fraction (percolation threshold), a conductive network forms due to inter-particle contacts providing a continuous pathway for electron travel and resulting in a dramatic increase in electrical conductivity. This insulator-conductor transition phenomenon seen in materials, especially conductive composites, can be described by the percolation theory. Pike and Seager denoted the percolation theory was a measure of connectivity between regularly or randomly positioned sites within a space [Pike and

Seager (1986)]. To embellish on the definition of Pike and Seager, Stauffer explained percolation theory with the assistance of a square lattice as shown below in Figure 2.1A.



Figure 2.1: Square Lattice Diagram with Cluster Circle

Randomly placed dots are placed in the squares with some squares left empty as shown in Figure 2.1B with a probability, p, that a site will be occupied with a dot. These randomly placed dots form clusters, highlighted in the circles and shown in Figure 2.1.C. A cluster is a group of adjacent squares occupied by dots with a common side. The percolation theory deals with the clusters thus formed, in other words the groups of neighboring occupied sites. In the case of the lattice, percolation occurs at a certain probability where a cluster extends from top to bottom or right to left in the case of these square lattices [Stauffer (1986)]. In conductive resins, the percolation threshold is the measure of the volume fraction of conductive fillers that results in a percolating system.

#### 2.1.1 Percolation Theory

The percolation theory provides an explanation of the composite's electrical conductivity near the critical volume or percolation threshold value. In Figure 2.1, Clingerman graphically described the dependence of conductivity on the filler volume fraction. At low filler loadings, the conductivity is close to that of the pure polymer. At some critical volume fraction, called the percolation threshold, enough filler has been added to form inter-particle contacts, creating a percolating system.

Just beyond this percolation threshold value, the electrical conductivity dramatically increases over a small range of filler concentration. At higher filler loadings, the electrical conductivity plateaus several orders of magnitude above the pure polymer. The percolation threshold value for every conductive composite system varies but share the same characteristic curve (log Electrical Conductivity vs. volume fraction) shown in Figure 2.2. [Clingerman (2003)]



Figure 2.2: Dependence of Electrical Conductivity on Filler Volume Fraction [Clingerman, (2003)]

Many studies have been conducted with the intent of reducing the percolation threshold value so that mechanical integrity and high electrical conductivity can be achieved within the composite. Consequently, fuel cell bipolar plates are fabricated well beyond this critical filler concentration. The percolation threshold value allows our research group to evaluate how effective a conductive filler is at increasing the electrical conductivity of the composite system. The factors that affect this critical volume fraction and the ultimate electrical conductivity of the conductive resin are relevant to this research.

#### 2.2 Bipolar Plate

#### 2.2.1 Graphite Bipolar Plates

Graphite is one of the traditional materials used in producing bipolar plates and has been utilized in space exploration and military applications [Huang (2005)]. Graphite plates have excellent electrical conductivity and corrosion resistance and therefore remain the benchmark for electrical conductivity for other bipolar plate material alternatives. It is a low density material but lacks mechanical strength and lacks ductility which would result in an excessively heavy and voluminous stack [Ajersch (2003)]. Other disadvantages of the graphite bipolar plate are the additional manufacturing processes and high cost incurred in producing the bipolar plate. Due to the porous structure of graphite, an impregnation process is necessary so that the plate is gas impermeable [Baird (2005)]. The post machining of the flow channels limits a mass production technology to be adopted which also increases total cost [Mepsted and Moore (2003)]. As a result, weight and cost become major obstacles in making graphite a viable material selection for bipolar plates in the automotive industry.



Figure 2.3: Graphite bipolar plate [http://image.made-in-china.com/2f0j00oestlwLnnUpP/Graphite-Bipolar-Plate.jpg, 12/12/2012]