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The Hybrid Conductive Filler in the Bipolar Plate for Polymer Electrolyte Membrane Fuel Cells

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Abstract: Polymer Electrolyte Membrane Fuel Cells (PEMFC) can be an efficient energy generator as it offers attractive potentials for certain mobile and portable applications. In PEMFC, the bipolar plate is one of the most important components, and it is multi-functional. This study proposes the use of Graphite (G) and Carbon Black (CB) as hybrid conductive fillers, and Epoxy as the material binder in the bipolar plate. G is used as the main filler, while CB as the second filler materials. The hybrid fillers and the binder were shaped through compression moulding. The effects of different CB contents on the properties of the composite were also observed. The results showed that the decreasing of electrical conductivity was correlated with the increasing of CB content. The different CB contents also resulted in some improvements in other properties such as shore hardness and sample bulk density. The findings promise an enhanced performance of the bipolar plate to be used in PEMFC which is beneficial for mobile and portable application industry. A further study on agglomeration and the mechanical properties such as the flexure strength should be pursued.

Key words: PEMFC, Graphite, Carbon Black, Composite Bipolar Plate, Electrical Conductivity

INTRODUCTION

A polymer electrolyte membrane fuel cell (PEMFC) is a good contender for portable and automotive propulsion applications because it provides high power density, solid state construction, highly efficiency chemical-to-electrical energy conversion, near zero environmental emissions, low temperature operation (50 - 100 ^{o}C), and fast and easy startup. The U.S. Department of Energy (DOE) has also identified the PEMFC as the alternative candidate to replace the internal combustion engine in transportation applications. However, barriers to commercialization remain a major problem. The fundamental and technical understanding of the bipolar plate fabrication is the main challenge in the commercialization of PEM fuel cells. Other challenges include manufacturing and material costs, material durability and reliability, and hydrogen storage and distribution issues. One of the major factors limiting fuel cell is the development of the bipolar plates, which are one of the PEMFC's key components. The requirements of the bipolar plate characteristic pose a major challenge for any type of materials (Metha, V. and J.S. Cooper, 2003; Oh, M.H., 2005; Wolf, H. and W. Porada, 2006).

Therefore, research in materials, designs and fabrications of bipolar plates for PEMFC applications is a crucial issue for global commercialization. The main functions of bipolar plates in the PEMFC are to distribute the process gases (hydrogen and oxygen) to the positive and negative electrode respectively within the cell, to separate the individual components of fuel cells, to carry the current away from cell, to connect series of single cell to facilitate water within the cell and to cool the fuel cells system (Weil, K.S., 2004; Mighri, F., 2004). In order to prepare for a commercialization, the bipolar plate must meet the design requirements such as high electrical conductivity, efficient gas tightness, low permeability, good chemical stability, high corrosion resistance, low volume and high thermal conductivity, and lightweight and acceptable mechanical strength, such as withstanding the stack clamping force. The optimal bipolar plate criteria include low cost, reproducibility, and easy finishing and recyclable (Cunningham, N., 2005; Blunk, R., 2006; Krupa, I., 2004; Thongruang, W., 2001).

Currently, the most promising material for mass production of bipolar plate is pure G material. However, it is very brittle and difficult to machine to fulfill the specifications needed for fuel cell stacks. Other materials such as metal-based require proper machining process, need special coating, have extra weight and have high tendency to corrode even though they have good electrical conductivity. Similarly, carbon-based materials have poor electrical and thermal conductivity, fragile structure and low mechanical strength even though they are easy to form (Acosta, J.L., 2006; Ezquerra, T.A., 2001; Zou, J.F., 2002).

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However, the composite materials to be used in a bipolar plate must meet DOE (US Department of Energy) requirement because of its multiple responsibilities and the challenging environment in which the fuel cell operates. The composite properties must be considered for achievable design in a fuel cell application, specifically, electrical and thermal conductivity, gas permeability, mechanical strength, corrosion resistance and low weight (Wu, M. and L.L. Shaw, 2004; Hermann, A., 2005; Middelman, E., 2003; Selamat, M.Z., 2011). The material requirements shown in Table 1 should be satisfied for the fabrication of a bipolar plate. G powder is the most commonly used material for a bipolar plate. G has a good electrical conductivity and excellent corrosion resistance with a low density of about 2 g cm^{-3}. However, it lacks mechanical strength and has poor ductility. The carbon black powder is introduced to the graphite composite in order to improve the properties of the composite. Epoxy will be used as the binder in this composite. However, many significant researches have reported the effect of the combination of various types of conductive fillers, such as G and CB. Combining G with other types of conducting filler has been reported to be an effective way to develop composite with higher conductivity and better mechanical properties (Mohd Zulkefli Selamat, 2011; Dweiri, R. and J. Sahari, 2008; Drubetski, M., 2007; Derieth, T., 2008; Mathur, R.B., 2008). In hybrid fillers, conductive composite such as G and CB have capability to form conductive network with the main filler particles at low concentration (Lee, J.H., 2009; Dweiri, R., and J. Sahari, 2007). However, the systematic results which explain the effects of CB to the G/Epoxy composite have not been much reported. The objective of this study is to investigate the effect of G and CB as hybrid conductive fillers in G/CB/Epoxy composite as bipolar plate.

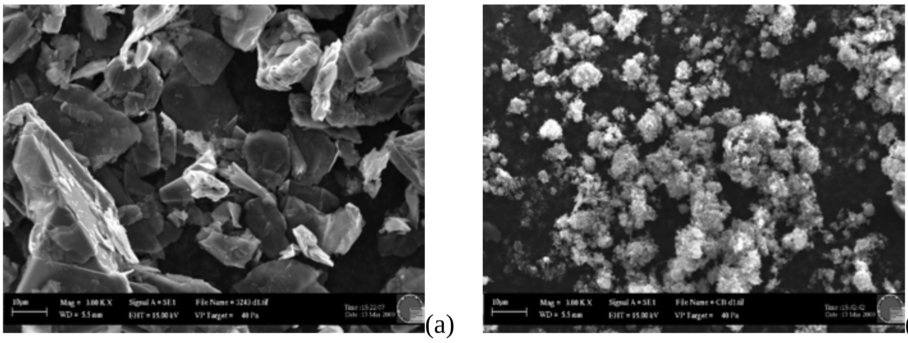
Table 1: Requirement properties for the bipolar plate (DOE target) [5, 6 and 8].

Property	Value
Electrical conductivity	> 100 [Scm^{-1}]
Thermal conductivity	> 10 [$W(mK)^{-1}$]
Flexural strength	> 25 [MPa]
Shore Hardness	> 50
Bulk Density	<5 [g/cm^3]

MATERIALS AND METHODS

Materials:

The materials used to produce conducting polymer composite samples in the present work are natural G and CB powder. The representative scanning electron microscope (SEM) images of powder, which was used in this study, are shown in Figure 1 (a) G powder and (b) CB powder with a magnification of 3000 times, a bisphenol-A based Epoxy resin with a viscosity of 6 Poise was used as a binder in this study. The curing temperature of the Epoxy resin that was recommended by the manufacturer was 80 ^{0}C. The curing agent, 4-Aminophenylsulphone and it is diamine type (tetra functional), which facilitate rapid and dense cross linking in the epoxy resin. A low-viscosity epoxy matrix was selected for its better wetting conditions with conductive fillers. Meanwhile, Table 2 shows the main materials properties.



(a) (b)

Fig. 1: (a) G flake and (b) CB particle, with of magnification of 3000 times

Table 2: Material property of G, CB and Epoxy.

Material	CB	G	Epoxy
Grade	5303	3243	105/206
Density	1.7~1.9 g/cm^3	1.74 g/cm^3	1.15 g/cm^3
Thermal stability	3000°C	3500-4000 ºC	180-220 ºC
Size	≤5 um	≤60µm	-
Shape	Flake	Particle	Liquid
Resistivity	0.314 Ωcm	0.036 Ωcm	1(1014Ωm)

Methods:

Four hybrid fillers samples of different composition ratio of G/CB/Epoxy composite were selected, as shown in Table 3. The process in obtaining the sample of the hybrid composite started with the pre-mixing process. The G and CB were mixed by using ball mill machine. A ball mill is a cylindrical device used in grinding (or mixing) raw material materials of G and CB. The mixed G and CB then went through the stirring process in which the Epoxy was introduced in the hybrid fillers. Then, the mixed hybrid fillers and the binder are quickly placed in the mold for the compression molding process. In this process, the pressure was applied at 20 tonnes; the temperature was set at 80°C. The mold went through the pre-heating stage about 6 minutes before the pressure was applied and then, the mold was hold with pressure for 30 minutes. The sample was removed from the mold after all the processes were completed. The sample was pressed as shown in Figure 2. The effect of CB loading on the properties of G/CB/Epoxy composite, such as electrical conductivity, shore hardness and bulk density were observed. The electrical conductivity was measured using the Jandel Multi Height Four Point Probes as shown in Figure 3. The Shore hardness (scale D) was measured by using the Shore Durometer and the bulk density was measured by using weight balance tests, (Densimeter) complying to ASTM D792.

Table 3: The composition ratio between G, CB and Epoxy.

Specimen	Weight Percentage (wt.%)		
	G	CB	Epoxy
1	65	15	20
2	60	20	20
3	55	25	20
4	50	30	20

Fig. 2: Samples of G/CB/Epoxy composite.

Fig. 3: Four-point Probe for electrical conductivity measurement.

RESULTS AND DISCUSSION

The Effects of CB on Electrical Conductivity:

Figure 4 shows the electrical conductivity of G/CB/Epoxy composite with various contents of CB. The result showed that the electrical conductivity decreased as CB contents increased until 30 wt.% CB. The value of electrical conductivity for G/CB/Epoxy showed the highest value at 15 wt.% CB (118.21S/cm) and the electrical conductivity dropped with increasing CB loading than the value has decreasing sharply from 20 wt.% CB to 30 wt.% CB (16.8 S/cm). Although the smaller size of CB particles in comparison with the G particles forms a conductive path and creates more conducting tunnels between the G particles, the CB contents was above the critical loading, the additional CB was not wetted well with the Epoxy resin, consequently, the conductivity of the composite deteriorated due to lack of compaction.

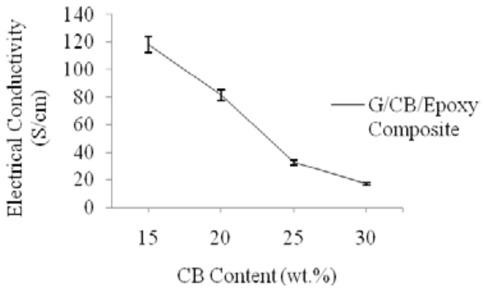


Fig. 4: Electrical Conductivity of various CB content.

Effect CB on Bulk Density:

Figure 5 shows the variation in the bulk density of the composites of the bipolar plate with increasing CB weight percentage. Due to lower density of CB, the bulk density of the composites decreased with the increase of CB content. Initially, at 15 wt % of CB, the bulk density was 1.71 g/cm^3. However, it started to moderately decrease as the CB content increased. The minimum value of the bulk density was 1.41 g/cm^3 at 30 wt % of CB.

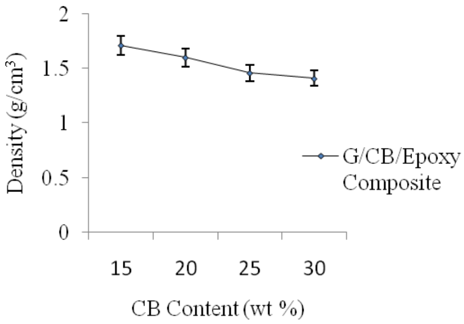


Fig. 5: Bulk density of various content of CB.

The Effects of CB on Hardness:

Figure 6 shows the variation in the Shore hardness (D) with the increase of CB content. The shore hardness showed an increase except for the specimen with 25 wt % and 30 wt % of CB. The value of shore hardness for the specimen with 15 wt % of CB is 8.71, and it increased to 11.05 at 20 wt % of CB. Then, the value continued to decrease until 30% wt. CB, which was 5.4. This is due to the compactness of the composite as the CB content increases. The interconnectivity and interactions between the reinforcing constituents are getting lesser. This suggests that the wetting limitation of Epoxy plays an important role for the hardness of the sample.

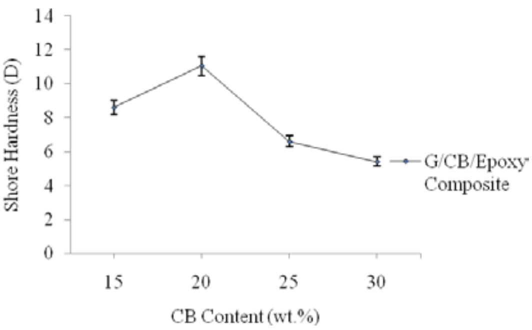


Fig. 6: Shore Hardness of various content of CB.

Conclusion:

The CB content has significant effects and influences on the electrical properties, bulk density and hardness of G/CB/Epoxy composite. The addition of CB as the second filler material offers an effective way to develop higher hybrid conductivity composites. The best conductivity value was 15 wt % of CB and the value of electrical conductivity was 118.21 S/cm. However, the electrical conductivity of this composite decreased after 15 wt % of CB; this is due to several conditions of the binder material such as the wetting of the filler and the level of compaction. The bulk density for all compositions showed a decrease as the CB loading increases in the G/CB/Epoxy composite. Meanwhile, the hardness of CB increased until 20 wt % of CB but decreased after the

CB loading increased. Finally, the result indicated that the electrical conductivity the result (15 wt % of CB) has shown that it was over the targeted value which is more than 100 S/cm. The bulk density was less than 5 g/cm^3. A further study on agglomeration and the mechanical properties such as the flexure strength should be pursued.

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