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Preparation of graphite composite bipolar plate for PEMFC

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Abstract−This research studied the preparation of graphite composite using liquid thermosetting plastic such as polyester resin (POE), phenolic modified alkyd resin (PhA) and mixed resin (POE with 10% PhA) as a binder. The morphology, physical, electrical and mechanical properties of the graphite composites were analyzed. The results showed that POE could combine with graphite powder (the 66% wt. saturated of graphite powder) better than PhA and mixed resin and gave higher electrical conductivity (4.52 S/cm). It was also found that epoxy resin could improve the mechanical property of composite plate. The addition of TiO_2 and ZnSt slightly decreased the electrical conductivity and the water absorption. Moreover, it was proposed that TiO_2 could improve the mechanical property. Carbon fiber can increase electrical and mechanical properties and water absorption of the composite with POE as a binder. The mixing of wet-lay mixture with graphite, carbon fiber and POE composite improved the mechanical property and decreased the water absorption.

Key words: Graphite Composite, Bipolar Plate, Polyester Resin, PEM Fuel Cell

INTRODUCTION

Proton exchange membrane fuel cell (PEMFC) is suitable for developing and is used as automotive application. It gives high current density and employs low operating temperature and pressure. However, practically, the connection of single fuel cell in series, called fuel cell stack, is usually done in order to increase the cell potential. Hence, bipolar plate is used to separate the adjacent cell in the stack and conduct the electrons. In addition, bipolar plate also provides the fuel gas and the oxidizing gas, water and heat management within the cell. As a consequent, materials used in the fabrication of bipolar plate have to resist the fuel cell operating environment and the fabrication process should not be complicated [1]. Eighty percent of the fuel cell stack's weight is the bipolar plate weight [2]. Thus, the development of bipolar plate for stack cell focuses on its properties, cost and weight of the entire fuel cell.

It's well known that graphite and carbon composites are suitable materials as bipolar plate for fuel cells because they are highly resistant to corrosion or oxidation reaction in fuel cells. The quality, quantity and size of graphite powder have an effect on the properties and function of bipolar plate. The increasing graphite content leads to an increase in plate density and a decrease in impact strength [3,4]. The effect of binders used in carbon composite fabrication is an interesting topic. Using carbon composite with liquid crystal polymer (LCP) as a binder can decrease the amount of carbon material from commercial productivity. This result also leads to the decreasing of density and fragility of the plate [5]. In addition, new methodology such as the wet–lay process is introduced to fabricate the composite plate. The advantage of this process is that there are three ways to cast the plate: direct molding, wet/dry-lay molding and skin-core laminate. The mechanical properties and in-plane electrical conductivity are dramatically increased while maintaining the through-plane electrical conductivity [6]. Jeon et al. studied the performance of silicon-coated graphite particle anodes for lithium ion rechargeable batteries. The result showed that silicon-coated graphite gave high specific capacity and good cycle performance due to the formation of amorphous silicon-carbon black composite layer on the surface of the graphite particles [7]. The electrical conductivity of oxide materials was improved by doping of TiO_2 or ZnO. Fe_2O_3 showed large power factor by doping of TiO_2 [8,9].

In this work, graphite composite bipolar plate was prepared by using thermosetting plastics. The effect of binders and additives on the properties of graphite composite plate was investigated. The graphite composite was used as flow field plate for PEMFC to test its performance.

EXPERIMENTAL

1. Materials

Graphite powder grade RGN-C with average particle size of 0.432 micrometer from Suthee United Carbon, Co., Ltd was used. Polyester resin with 35% styrene monomer (POE) from Roongrojn Fiber Glass, Co., Ltd. and phenolic modified alkyd resin (PhA) from Siam Chemical Industry, Co., Ltd. were used as binders. The hardener and catalyst were used such as methyl ethyl ketone peroxide (MEKP) and cobalt naphthenate from Roongrojn Fiber Glass, Co., Ltd.. The mixing of polyester and phenolic modified alkyd resin was studied. The effect of additives was studied by using TiO_2 (Commercial grade, Behn Meyer, Co., Ltd.) and ZnSt (PURUM, Sigma-Aldrich). Carbon fiber grade PAN AGM 94 (Asbury Graphite Mills, Co. Ltd.) was used to improve electrical conductivity of the composite.

2. Preparation of Composite Plate

The carbon composite plate was prepared by mixing graphite powder and binder with overhead stirrer. The amount of graphite powder was varied to study the effect of graphite powder content.

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Then the mixture was placed in the mold and compressed with compression molding at 180 °C and 13.7 MPa. After that the sample was cooled. The effect of additives (TiO_2 and ZnSt) was studied by varying their quantity in the range of 1 to 5 phr (part per one hundred base POE) for graphite composite (66% wt graphite in POE). To improve electrical conductivity, some graphite powder was replaced by carbon fiber while maintaining the same total carbon content.

To increase the overall carbon content, the method of wet-lay mixing [6] was performed. First, polyester resin was mixed with de-ionized water by using the overhead stirrer. Then, 66%wt graphite powder, 7%wt carbon fiber and 2 phr of TiO_2 were added and mixed. After that, the mixture was filtered and dried in the oven at 110 °C before being ground. The ratio of wet-lay powder and different carbon content composites was 1 : 4. The mixture was then molded and compressed at 180 °C and 13.7 MPa.

3. Measurement of Properties

Density and other properties of the composite plates were measured as the following:

- Electrical conductivity: the graphite composite sample (120 mm in length, 20 mm in width and 3 mm in thickness) was measured according to ASTM C611-98 (method B voltmeter technique) [10] to find its electrical conductivity.
- Mechanical property: the flexural strength was measured according to ASTM D790-03 [11] by using the universal testing machine (LLOYD LR 10 K PLUS) which has a span length of 50 mm, and the rate of crosshead is 13.89 mm/min. The specimen bar was 120 mm in length, 10 mm in width and 3 mm in thickness. The durometer hardness tester (REX Gauge 2000) was used to measure the hardness of composite sample according to ASTM D2240-04 [12] (presser foot type B) which has 50 mm in length, 50 mm in width and 6 mm in thickness of the specimen.
- Water absorption: the water absorption measurement was performed according to ASTM D570-98 [13] with 24 hours immersion procedure. The specimen bar was 76.2 mm in length, 25.4 mm in width and 3 mm in thickness.
- Morphology: the composite plates were analyzed morphologically by scanning electron microscope (SEM)
- I-V performance test: a single fuel cell for I-V performance test composed of MEA's and one flow field plate from Electrochem, Co. Inc. and the other plate was graphite composite bipolar plate. The cell was tested in the test station with 100 sccm of saturated H_2 and O_2 flow rates and cell temperature of 60 °C. The moment torque of fuel cell fabrication was varied to study their effects on contact resistance by impedance method.

RESULTS AND DISCUSSION

1. Effect of Binders and Carbon Content

The electrical property of graphite composites prepared by different binders and carbon content was tested. The composite that had high electrical properties will be studied in the next section. The effect of binder and carbon content on electrical conductivity of the composite is shown in Fig. 1. When the carbon content increased, the composite with polyester resin (POE) showed higher electrical conductivity than those with phenolic modified alkyd resin (PhA) or the mixing of POE and PhA. The electrical conductivity of composite plate increased when graphite content increased, especially in graphite composite with POE binder. At carbon content lower than 60% wt, electrical conductivities of composite with POE, PhA and the mixing of POE and PhA were not significantly different. However, when the graphite content was more than 60% wt, electrical conductivity of the composite with POE was higher than that with PhA and mixing binders due to different viscosity of POE (0.4-0.6 Pa·s) and PhA (2-5 Pa·s). Graphite can well combine with low viscosity polymer matrix. Hence, it could uniformly disperse in POE matrix more than PhA matrix. At high graphite powder, it can make a continuous percolation network for electron transfer and improve electrical conductivity. Maximum electrical conductivity was 4.52 S/cm at 66% wt carbon content with POE. The graphite content could not be made any higher due to the limit of compatibility of graphite and polyester resin. As the composite with PhA gave low electrical conductivity, its other properties were not analyzed.

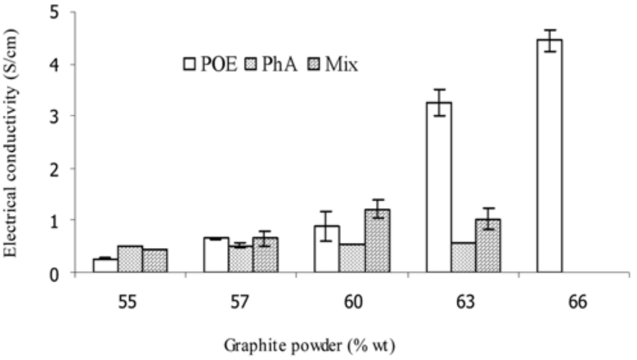

Fig. 1. Electrical conductivity of graphite composite as a function of graphite powder content.

In terms of mechanical property, the flexural strength of POE graphite composite was higher than that of the mix resin graphite composite, as shown in Fig. 2, because graphite powder binds with POE better than with mix resin. This can be confirmed by SEM image as shown in Fig. 3. The POE graphite composite has no hole or void inside the polymer matrix compared with the mix resin. The flexural strength of POE and mix resin graphite composites was not significantly changed at carbon content lower than 63% wt. How-

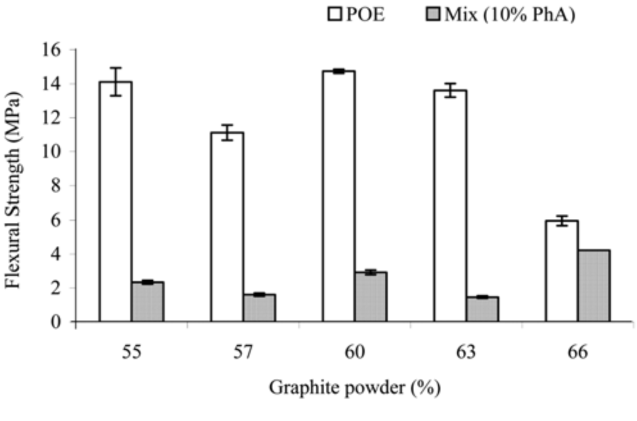

Fig. 2. Flexural strength of graphite composite as a function of graphite powder content.

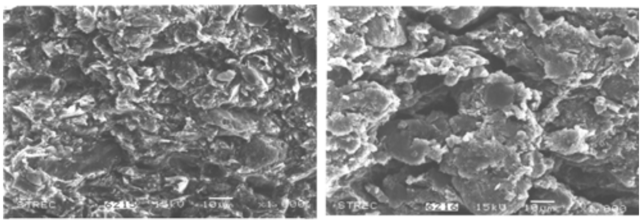
(a) POE graphite composites (b) mix resin graphite composites

Fig. 3. Morphology of POE and mix resin graphite composites.

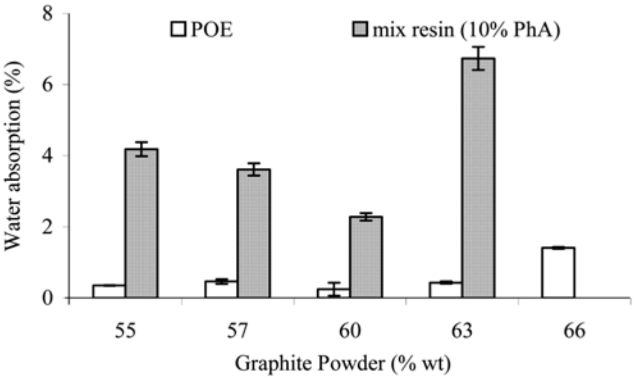

Fig. 4. Water absorption of graphite composite as a function of carbon content.

ever, it decreased by half at 66% wt carbon content, but no change was observed in mix resin composite. This result was the cause of excess graphite powder in the matrix of POE binder which decreased mechanical properties of POE more than that of PhA that had higher viscosity and lower flexural strength. The result corresponded with that of Kuan et al. [3]. It was illustrated that flexural strength of composite plate decreased from 38.47 MPa to 27.3 MPa when carbon content increased from 60%wt to 80%wt, respectively. The durometer hardness of composite with POE (approximately B/90/5 sec) was more than that with mix resin (approximately B/70/5 sec). The density of all composites was the same at approximately 1,650 kg/m^3.

Water absorption was one of the most important properties. The target of water absorption should be lower than 0.3% [14]. High water absorption of bipolar plate could reduce electrical and mechanical properties of the composite plate. It can be seen in Fig. 4 that polyester composite had lower water absorption percentage than mix resin composite. This was the result of two reasons. First, 10% of PhA as a composition in mix resin had hydroxyl groups that could combine with water [15]. Second, the polymer matrix of mix resin composite had many holes or voids that the water molecule could contain water and consequently increase the water absorption. Furthermore, the result showed that carbon content had no effect on water absorption of POE composite except for 66% wt carbon content. However, the water absorption percentage of all POE graphite composites (except for more than 60% wt carbon content) was lower than the target (0.3%). For mix resin composite, its water absorption decreased with increasing carbon content up to 60% wt graphite content. Whereas, at 63% wt graphite content, water absorption percentage increased. This can be explained by the fact that graphite can fill up the void within mix resin composite, leaving less space for water. However, at high graphite content, the composite with polymer was not uniform. Graphite agglomerated in the composite and could absorb more water. It should be noted that water absorption percentage of mix resin composite was higher than 3%.

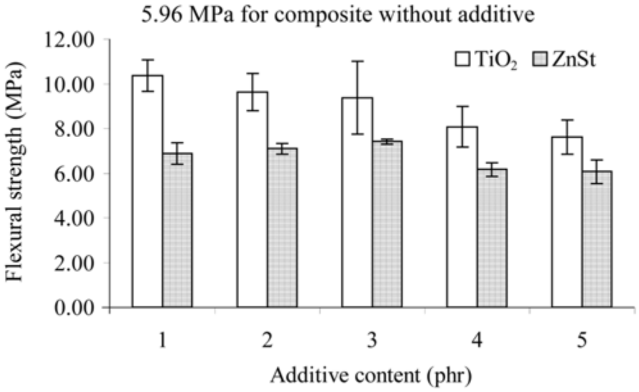

Fig. 5. Flexural strength of graphite composite as a function of polymer additive content (TiO$_2$ and ZnSt) in 66% wt graphite powder and polyester as a binder.

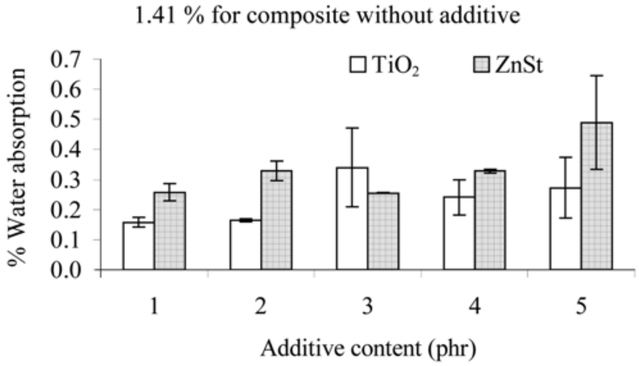

Fig. 6. Water absorption of graphite composite as a function of polymer additive content (TiO$_2$ and ZnSt) in 66% wt graphite powder and polyester as a binder.

At 66% wt of carbon content in composite POE, the properties of graphite composite can be improved by adding additives and carbon fiber, which will be further investigated.

2. Effect of Mechanical Property

TiO$_2$ and ZnSt were used to improve properties of composite especially the mechanical property. The effect of TiO$_2$ and ZnSt on flexural strength is shown in Fig. 5. It was found that the addition of a small amount of TiO$_2$ and ZnSt increased the flexural strength. However, the flexural strength decreased when the content of TiO$_2$ increased and that of ZnSt was more than 3 phr. The flexural strength of composite with ZnSt was lower than that with TiO$_2$, but it was more than that without any addition of TiO$_2$ and of ZnSt (approximate 6 MPa). The additives had an effect on durometer hardness. They could slightly diminish the durometer hardness of composites (3-5% of diminution).

In addition, the small amount of TiO$_2$ and ZnSt (1-2 phr) could also decrease the water absorption percentage of the composite without additive (1.5% for 66% wt graphite powder with POA) as shown in Fig. 6. Since, small particles of TiO$_2$ and ZnSt could fill in the

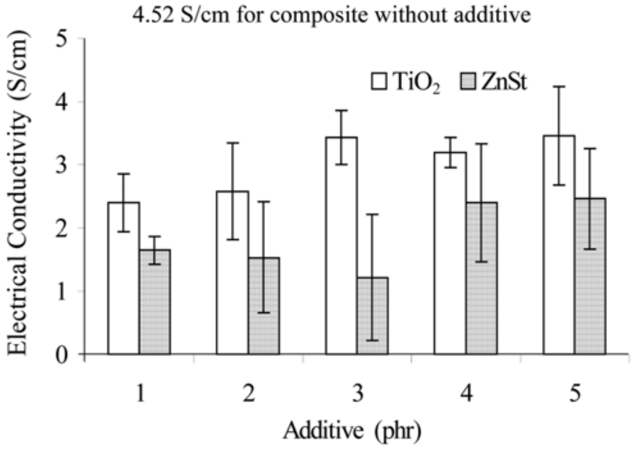

Fig. 7. Electrical conductivity of composite as a function of polymer additive content (TiO_2 and ZnSt) in 66% wt graphite powder and polyester as a binder.

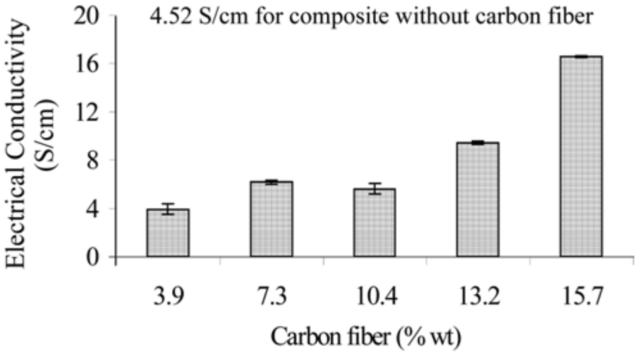

Fig. 8. Electrical conductivity of composite as a function of carbon fiber content for 66% wt overall carbon content and polyester as a binder.

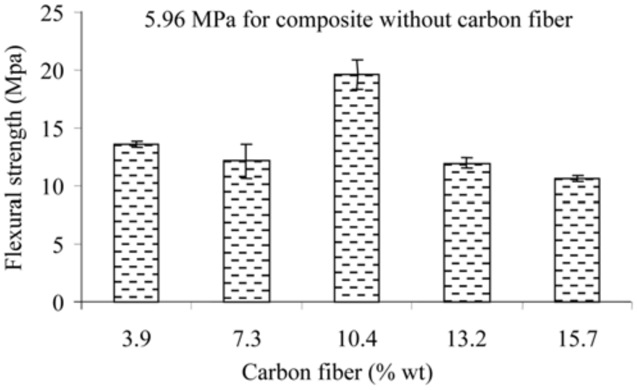

Fig. 9. Flexural strength of graphite composite as a function of carbon fiber content in 66% wt overall carbon content and polyester as a binder.

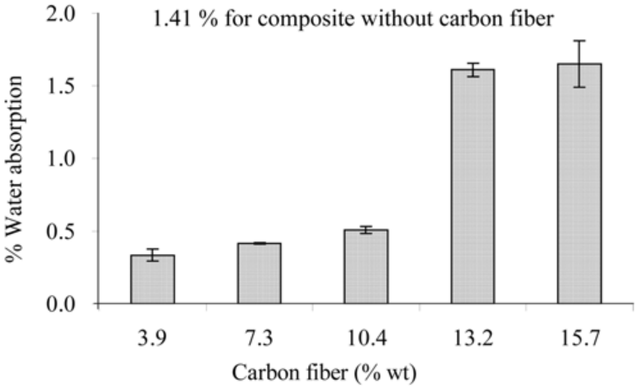

Fig. 10. Water absorption of graphite composite as a function of carbon fiber content in 66% wt overall carbon content and polyester as a binder.

holes of polymer matrix and could decrease the chance of water molecule that would form the covalent bond with the polymer matrix. However, the composite with TiO_2 gave a little lower water absorption than that with ZnSt. It was the cause of different morphology of additives. By using SEM, the morphology of TiO_2 showed small spherical particles and smooth surface but ZnSt showed dendrite surface and larger particle size than TiO_2.

To observe the effect of TiO_2 and ZnSt on electrical properties, the electrical conductivity of composites was tested. The result showed that the electrical conductivity of composites was in the range of 1 o 3.5 S/cm (Fig. 7). It was less than that without both TiO_2 and ZnSt (4.5 S/cm).

From these results, it can be concluded that TiO_2 and ZnSt were not interesting to be used for improvement of composite properties. So in the next section, a type of carbon was used to improve electrical conductivity.

3. Improvement of Electrical Property

The properties of a composite can be improved by increasing the carbon content and choosing a suitable type of carbon. In this study, carbon fiber was used to replace some graphite in the composite with POE for 66%wt of carbon content. The carbon content was increased by wet-lay mixing [6]. The electrical conductivity of composites was first considered.

Fig. 8 shows the effect of increasing of carbon fiber content on electrical conductivity. The electrical conductivity increased exponentially with increasing carbon fiber content. At 15.7% wt of carbon fiber, the electrical conductivity of composite was 16.5 S/cm more than that of composite without carbon fiber. In addition, the carbon fiber could improve flexural strength of composites by 2 or 3 times of that without carbon fiber, as shown in Fig. 9. When adding the carbon fiber (CF), used as reinforced fiber, into the polyester graphite composite, the flexural strength increased as carbon fiber content increased and the maximum flexural strength was 19.6 MPa at 10% carbon fiber content. Besides, at carbon fiber content more than 10%, the flexural strength decreased due to the cluster of carbon fiber in the polymer matrix.

Regarding the effect of carbon fiber content (Fig. 10), the water absorption increased with the increasing carbon fiber content. This was because the N-H bond and C-H bond in the chemical structure of carbon fiber were highly active with O-H bond in water molecules and formed a covalent bond with water. Even if the increasing of carbon fiber could raise the electrical conductivity, the water absorption also increased with carbon fiber content, which could affect the performance of the cell.

In order to study the effect of the overall carbon content on the

Table 1. The properties of graphite composite mixed with wet-lay powder

Property	Graphite composite					
	POE 66		7.3CF		15.7 CF	
	no mixed	mixed	no mixed	mixed	no mixed	mixed
Electrical conductivity (S/cm)	4.5	3.4	6.2	5.6	16.4	16.6
Flexural strength (MPa)	5.96	13.8	13.6	19.9	10.67	17.6
Durometer hardness (B/_/5 sec)	86.1	86.4	86.3	86.8	87.4	89.3
Water absorption (%)	1.41	0.21	0.42	0.21	1.65	1.86
Density (g/cm^3)	1.69	1.77	1.68	1.77	1.68	1.68

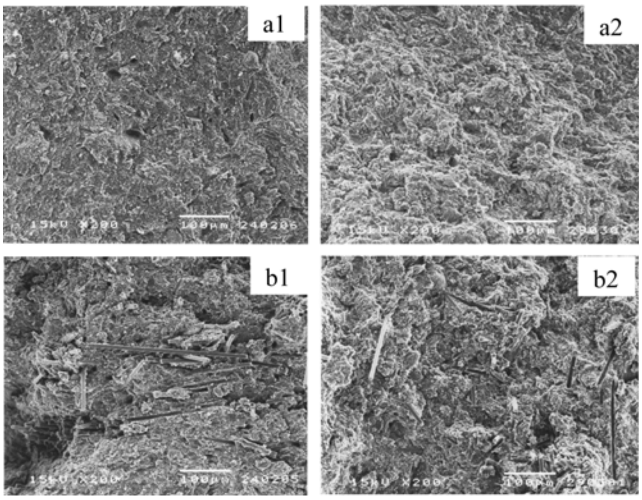

Fig. 11. Cross sectional SEM image of graphite composite sample; a1-a2: POE 66 without and with WL 73 powder, respectively, b1-b2: 7.3CF without and with WL 73 powder, respectively.

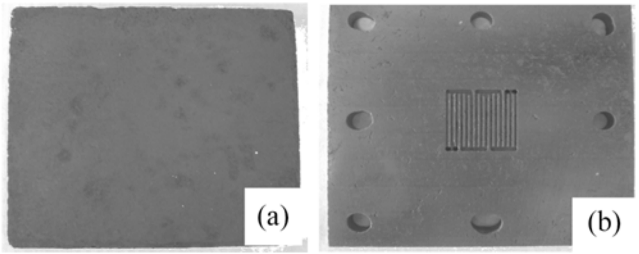

Fig. 12. Graphite composite plate before (a) and after (b) complete the serpentine flow channel.

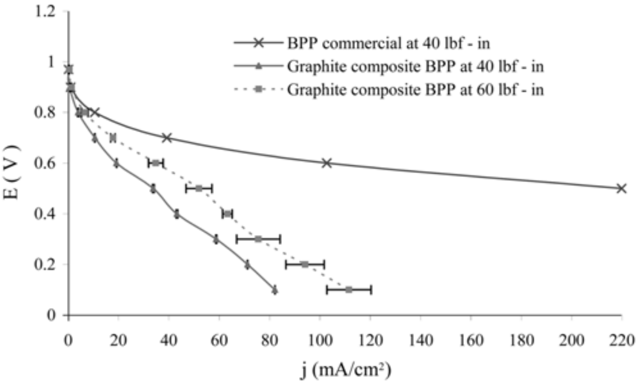

Fig. 13. Polarization curve of PEMFC single cell with one WL73 & 7.3CF graphite composite compare with commercial PEMFC single cell from Electrochem, Inc.

electrical conductivity, wet-lay powder was mixed at different composition of composites. Table 1 shows the effects on properties of these composites. The electrical conductivity of the composites after mixing was not significantly different from the initial composition. In terms of mechanical properties, the flexural strength was dramatically increased (around 40% from the original composition), as seen in Fig. 12. Since the wet-lay powder was a small particle, it could fill the holes or voids of the polymer matrix and make it dense. So the structure of the composite was more strengthened. The durometer hardness and density of composites remained the same. The water absorption of all composites mixed with wet-lay powder, except for 15.7 CF composite, was 40% decreased due to the small particles of wet-lay powder that filled the holes in the polymer matrix. This would prevent the water molecule from forming a covalent bond with the polymer matrix. The SEM image (Fig. 11) shows the dense cross sectional structure after mixing the composition with wet-lay particles.

4. I-V Performance Test

Although, at 7.3%wt carbon fiber, the composite had a relatively lower electrical conductivity, water absorption was approximately four times lower than the composite with 15.7% wt carbon fiber. Since water adsorption was the strongest influence on the resistance of composite and water management of a cell, the composite of wet-lay powder mixing with 7.3%wt carbon fiber, 58.7%wt graphite and 34%wt POE composition was used to test its performance in proton exchange membrane fuel cells (PEMFC). The composite plate was made with flow channel in serpentine model (Fig. 12).

In I-V performance test, commercial MEA's, one flow field plate from Electrochem Co. Inc. and one of flow field composite were used. The conditions of the test run were 100 sccm of humidified hydrogen and oxygen flow rates and 60 °C cell temperature. The result of the polarization curve is in Fig. 13. The polarization curves of graphite composite bipolar plate (BPP) are lower than that of commercial fuel cell (Electrochem Co. Inc.). The current density at 0.6 V of single cell with one graphite composite bipolar plate was 19 mA/cm^2 lower than the commercial single cell (102.7 mA/cm^2) due to the lower electrical conductivity of the graphite composite bipolar plate. To reduce the contact resistance between the compo-

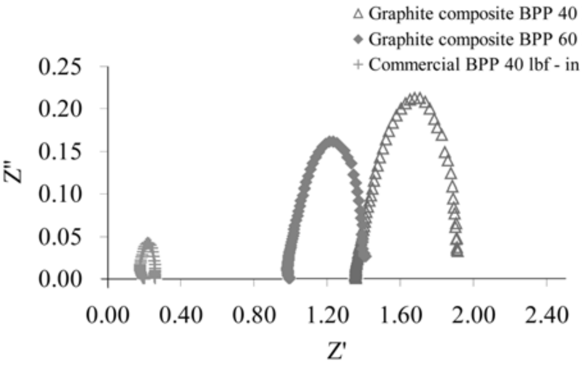

Fig. 14. Nyquist plot of PEMFC single cell with graphite composite and commercial bipolar plates at 0.6 V as a function of moment torque.

nents of the single cell, the moment torque was increased from 40 lb$_f$-in to 60 lb$_f$-in. The performance was slightly increased, especially in the range of ohmic loss because the increasing of moment torque made the components more attached and electrons could be transferred from plate to plate conveniently. The current density at 0.6 V increased from 19 mA/cm^2 to 34 mA/cm^2 and the ohmic resistance decreased from 1.36 ohm to 0.99 ohm, as shown in Fig. 14 for the Nyquist plot. The performance of the graphite composite bipolar plate was still lower than that of the commercial plate. This is attributed to the fact that the ohmic resistance of the graphite composite bipolar plate was higher than commercial bipolar plate. This result complied with the polarization curve. The graphite composite bipolar plate in this study was still not suitable for use as bipolar plate in PEMFC. Its electrical conductivity needs to be improved by using a highly conductive binder and carbon.

CONCLUSION

The graphite composite with 66% wt carbon with POE as a binder had better performance than other binders. The addition of carbon fiber can increase electrical and mechanical properties. Whereas, increasing TiO_2 can only improve the mechanical property of the composite plate with the optimal content of 2 phr. Mixing the graphite composite mixture with wet-lay powder can increase the mechanical properties and reduce the water absorption. The graphite composite plate had water absorption and density in the range of standard (<0.3% for water absorption and <5 g/cm^3 for density). However, the electrical and mechanical properties could be improved by performing further study on conductive binder.

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