The Effect of Polyaniline Addition on The Properties of Carbon-Based Polypropylene Composite

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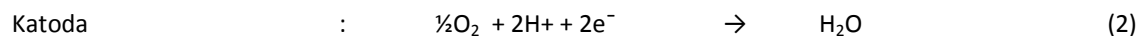***Email :*** *lieswisojo@hotmail.com*

Abstract :

One of the main component of a Proton Exchange Membrane Fuel Cell (PEMFC) is the cell main frame, which consists of individual bipolar plates. Bipolar plates take 40% and more of stack cost. An investigation is made to prepare alternatives bipolar plate from local material. A carbon-based Polypropylene composite bipolar plate for PEMFC has been developed that has high electrical conductivity, high strength, light weight, and has the potential for being produced at low cost. The plate were prepared by solution blending of graphite and polymer with appropriate solvent and continued by compression molding. Specimens were made in different ratio of graphite (G), carbon black (CB) and polypropylene (PP); and various processing temperature. Then it was characterized for density, porosity, electrical conductivity, hardness, tensile strength and morphology. The electrical conductivity reaches 66.2402 S/cm by combination 95% G/CB and 5% PP. To increase electrical conductivity, Polyaniline (PANi) as conductive polymer was added by 5% weight of total polymer. Because of this addition, the electrical conductivity increase from 66.2402 S/cm to 99.2688 S/cm for 95% G/CB and 5% PP/PANi. While the commercial bipolar plates require 100 S/cm electrical conductivity. The density has fulfill the requirement for commercial bipolar plate, not more than 5 gr/cc.

Keywords: bipolar plate, composite, polyaniline, polypropylene

1. Introduction

Proton Exchange Membrane Fuel Cell (PEMFC), a type of polymeric fuel cell is a type of fuel cell that has broad application opportunities. This fuel cell has the advantage of: large energy density (2.6 to 3.8 kW/m^2), very low emissions (zero emission), low operation temperature (± 80 º C), convenient fuel supply (requires only H_2 and O_2) (Equation 1 to 3 showed the basic reaction for PEMFC, consume only hydrogen and oxygen), high efficiency (> 45%), portable shape, reliable and low maintenance cost, light weight, and very quite [1]. The key components of a PEMFC are the polymer electrolyte, catalyst layer, gas diffusion layer and bipolar plate. Of the various advantages, the PEMFC can be used as an alternative energy for transportation, portable, large and small stationary and military applications.

Anode	:	H_2	$\rightarrow$	2H+ + 2e$^-$	(1)
Katoda	:	$\frac{1}{2}O_2$ + 2H+ + 2e$^-$	$\rightarrow$	H_2O	(2)
Total reaction of fuel cell	:	$2H_2 + O_2$	$\rightarrow$	$2H_2O$ + Eo	(3)

Among components of PEMFC, bipolar plates (BPPs) provide the following main functions within the fuel cell stack: provide a distribution of fuel gases within the cell, promote water management over the whole cell and exhibit excellent electrical conductivity as a current collector and provide adequate mechanical strength to resist the clamping force while the stack was assembled. This BPP is takes more than 40% of stack cost [2]. In this direction a lot of effort is going on worldwide to make light-weight and cost-effective BPP for PEMFC application. In order to stack-up to form a PEMFC, and to generate useful currents and voltages, numerous single cells with BPPs stacked and connected in series.
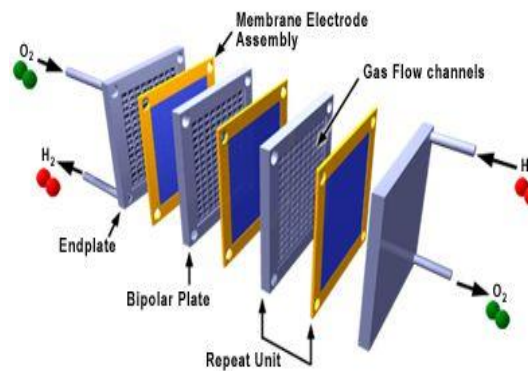
Figure 1. Bipolar plate in fuel cell stack

Traditionally, the most used material for bipolar plate is prepared by machining graphite plate because it provides excellent corrosion resistance, low bulk density and high electrical conductivity [3]. However, the main difficulty in using graphite to produce bipolar plate is the time consuming and costly step of machining flow channels in the surfaces. Nowadays, commercial manufactures of fuel cells are associated with major problems of high fabrication cost and insufficient reliability of fuel cells [4]. Especially for bipolar plate (which accounts for nearly 38-42% in a fuel cell stack cost), it is one of the most costly components in PEMFCs. Hence, the investigation on suitable materials for bipolar plates on the applications in fuel cells has become a critical research issue.

In recently reports, the various polymer were used as binder in injection molding process to meet the nanocomposite materials, such as polypropylene with carbon nanotube, phenolic resin, epoxy resin and nano carbon filler/CNT, poly(phenylene sulfide) in wet lay method, novolac type phenol formaldehyde resin. The bipolar plate with coating technique is also have been developed using polyaniline and polypyrrole which could reach up the conductivity in acidic condition and reduced corrosion.
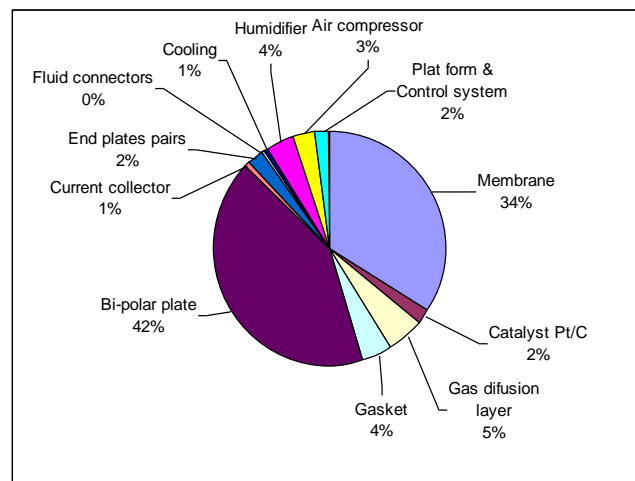

Figure 2. Cost per component to built up 500 W PEM fuel cell

In this investigation effort was made to develop graphite-composites BPP by compression molding technique to achieve the requisite goal. The composites plates were prepared by using thermoplastics polymer polypropylene as polymer matrix precusor in its liquid form. The composites were characterized for physical and mechanical will be discused in this paper.

2. Material and Methods

2.1. Materials

Graphite and acetylene black used was received from PT International Chemical Industry (ABC Battery) as conductive powder/ filler. Thermoplastic polymer Polypropylene (PP) that are produced by Tri Polyta Company was used as binder. Xylene from Merck used as a solvent, it works to dilute the PP. Polyaniline as conductive polymer was synthezised from Aniline and Ammonium Peroxydisulphate from Merck as described in previous report **[5]** with slightly modification.

2.2 Preparation of polyaniline

Ammonium peroxydisulphate was added into 150 mL aquadest water then was stirred for 15 minutes. 2.04 mL aniline was added into the solution by drop wise with constant stirring until the solution became dark green. After that, stirring process was stopped and continued by polimerization reaction for 24 hours. 500 mL aquadest was added into the solution for washing. Filtration was done to obtain polyaniline. Wet polyaniline was dried in vacuum oven until it become powder.

2.3. Sample preparation

Thermoplastics composite materials were generated using a slurry-making process where PP is dissolved in Xylene then graphite, acetylene black and polyaniline, for comparison, were mixed in the solvent for 30 minutes to get a homogenous condition. Then these were hot pressed in a hydraulic press machine for 75 and 150 kgf/cm^2 at 200^0 C using mold of 14 cmø. Variations in composition (wt%) between filler (G : AB = 5 : 1) and binder (PP) are 95:5, 90:10, 85:15, 80:20 and 75:25. For comparison, we used polyaniline as conductive polymer with composition between filler (G : AB = 5 : 1) and binder (PP and PANi, PP) and polyaniline are 80:15:5 and 70:25:5. The density, porosity, conductivity and hardness of those composites were determined.

2.4. Analysis and measurement

The porosity of each sample was determined according to the ASTM C20 test procedure **[6]**. The specimen was weighed in air and the value was recorded as dry weight (D). Then completely immersed in water at a temperature of 100 °C for 2 hours and cooled in water for 12 hours. The specimen was weighed in water and record as suspended weight (S). The specimen was then dried and weighed as *saturated weight* (W).

The porosity (P) was then calculated as:

$$P(\%) = \frac{(W - D)}{(W - S)} \times 100\%$$

(4)

The density of each sample was determined according to the ASTM D792 test procedure **[7]**. The specimen was weighed in air and the value was recorded as *A*. Then completely immersed in water at temperature of $\pm$ 28 °C. The specimen was weighed and recorded as *B*. The density of the sample was calculated as:

$$\rho = \frac{A}{(A - B)} \times \rho_t \quad \text{(g/cm}^3\text{)}$$

(5)

The bulk resistance and electrical conductivity of the graphite composite was examined using pour point probe method. We used four point probe K 705 RS. The bulk resistivity (ρ), bulk resistance (*R*), and conductivity (σ) calculated using equations 4-6.

$$\rho = 2\pi s \frac{V}{I}$$

(6)

$$R = \rho \frac{l}{A}$$

(7)

$$\sigma = \frac{1}{\rho}$$

(8)

where *s* is distance between two probes, *V* is voltage, *I* is electric current, *l* length, and *A* is Surface area of the specimen.

Vickers method of hardness was determined by Wolpert DIA Testor 2RC instrument. Tensile strength were determined by Instrontester Seri Strograph-RI Toyoseiki. Structure and morphology was tested by Scanning Electron Microscope.

3. Results And Discussion

In this paper, thermoplastics polymer polypropylene were used as binder in order to produce of BPP by injection molded method. Polypropylene (PP), also known as polypropene, is a thermoplastic polymer used in a wide variety of applications including packaging and labeling, textiles (e.g., ropes, thermal underwear and carpets), stationery, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. An addition polymer made from the monomer propylene, it is rugged and unusually resistant to many chemical solvents, bases and acids.

Polypropylene is normally tough and flexible, especially when copolymerized with ethylene. This allows polypropylene to be used as an engineering plastic, competing with materials such as ABS. Polypropylene is reasonably economical, and can be made translucent when uncolored but is not as readily made transparent as polystyrene, acrylic, or certain other plastics. It is often opaque or colored using pigments. Polypropylene has good resistance to fatigue.

The composition of graphite powders were done in 5:1 to acetylene black as filler for increasing the hardness and conductivity. The third component is polymer whereas polypropylene were easily obtained. Synthesis method in slurry condition is easily obtained homogenous composition of composite materials.

The BPP should be strong enough to withstand the compressive stresses generated during assembling the stacks of the plates in a fuel cell. This is one of the reasons for replacing the conventional monolithic graphite plates which are brittle and have low-strength. The BPPs should depend upon the nature of filler contents and the bonding with the resin system used. Herein we focused the composition of polymer as binder in graphite/acetylene black powder is 5 to 25 wt% in order to get light weight and high strength.

Table 1. Properties of BPPs without PANi

Composition	Hotpress pressure	Density (g/cm^3)	Porosity (%)	Conductivity (S/cm)	Tensile strength (kg/cm^2)	Hardness (kg/mm^2)
	75	1.219	1.075	66.240	27.709	7.536
95:5	150	1.346	3.614	74.709	35.190	4.051
	75	1.391	1.163	56.958	50.899	4.051
90:10	150	1.482	1.219	74.170	45.792	4.207
	75	1.315	3.030	41.290	55.455	4.207
85:15	150	1.429	2.500	56.482	81.923	4.139
	75	1.402	6.173	23.588	90.842	4.139
80:20	150	1.462	1.163	26.978	69.403	4.518
	75	1.364	3.960	27.894	83.019	4.518
75:25	150	1.421	4.819	20.717	60.449	4.314

In compression molded methods the slurry composite was preheated in hotpress tools with mold size of 14 cm diameter in 15 minutes, then in order to remove air inside the composite the slurry was pressed slowly and pressed at 200^0C with 75 and 150 kgf/cm^2 in 15 minutes. The results of BPPs components properties are shown at Table 2. The polymer type of PS was choosen as thermoplastics polymer. A density of all variant composites are less than 2 g/cc that was consider to many references. The electrical conductivity decresed with increasing of polymer contents **[8]**. And high presure of 150 kgf/cm^2 were give a good effect to increase all variants conductivity.

Table 2. Properties of BPPs with PANi

Composition	Hotpress pressure	Density (g/cm³)	Porosity (%)	Conductivity (S/cm)	Tensile strength (kg/cm²)	Hardness (kg/mm²)
	75	1.266	3.488	99.269	21.429	4.649
95:5	150	1.359	5.940	59.213	23.811	7.572
	75	1.333	5.825	35.315	43.081	4.416
90:10	150	1.113	2.752	47.279	31.393	4.656
	75	1.377	2.531	44.189	49.886	5.669
85:15	150	1.343	2.678	38.161	43.436	5.410
	75	1.258	4.396	31.131	88.147	5.641
80:20	150	1.532	6.186	36.208	88.258	5.194
	75	1.325	6.667	44.108	104.014	6.902
75:25	150	1.352	3.797	29.880	59.639	4.566

The density of all variant composites is less than 2 g/cm³ that was consider in many references. The electrical conductivity increased with increasing of graphite contents because graphite has good conductivity. The electrical conductivity reaches 66.2402 S/cm by combination 95% G/CB and 5% PP. To increase electrical conductivity, Polyaniline (PANi) as conductive polymer was added by 5% weight of total polymer. Adding of PANi to the composite gives higher electrical conductivity as shown in Table 1 and Table 2. The electrical conductivity increase from 66.2402 S/cm to 99.2688 S/cm for 95% G/CB and 5% PP/PANi. While the commercial bipolar plates require 100 S/cm electrical conductivity. This observation appears to agree with that of Kakati B.K., et al. [9], who found a positive influence of the PANi on the electrical conductivity of G/PP composites. These synergistic effects were explained by enrichment of the PANi at the interface between G and PP. High pressure of 150 kgf/cm² were shown to give a good effect to increase all variants conductivity.

As comparison, commercial bipolar plate from local industry (paralel model and serpentine) and electrochem bipolar plate were measured by the same method. It results electrical conductivity 40.646 S/cm, 87.291 S/cm and 98.013 S/cm, respectively. The electrical conductivity of ABS composite is approaching the commercial ones.
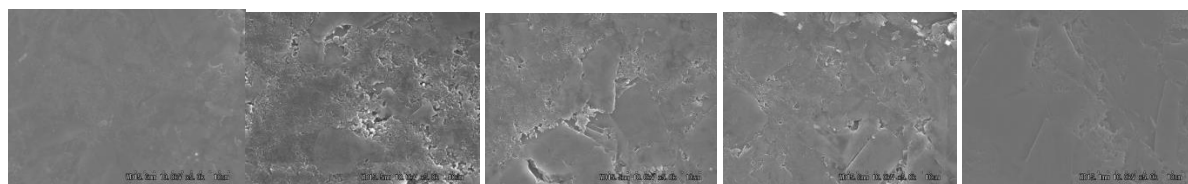

Figure 5. SEM surface micrographs of G/CB/PP at: (a) 25 wt% PP; (b) 20 wt%; (c) 15 wt%; (d) 10 wt%; (e) 5 wt%.
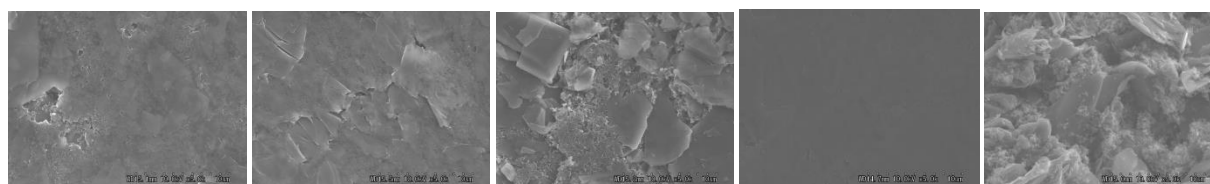

Figure 6. SEM surface micrographs of G/CB/PP/PANi at: (a) 25 wt% PP/PANi; (b) 20 wt%; (c) 15 wt%; (d) 10 wt%; (e) 5 wt%.

The scanning electron micrographs in Fig 5-6 reveal that graphite primary particles aggregate into larger clusters with low aspect ratios. These tend to disperse more evenly into the polymer matrix, thereby resulting in fewer particle contacts at given loading level and, consequently, a lower conductivity polymer composite. In other words, the filler particles do not make contact with the nearest neighbor due to partial wetting by the polymer. Dawson and Adkins [10] proposed that conductivity in G-filled polymers is regulated by inter-particle electron transfer at low filler loadings and by intra-particle electron transfer at high filler loadings. Solution blended

G/CB/PP/PANi has higher conductivity than of G/CB/PP. This can be attributed to better distribution of graphite rather than to the addition of PANi.

It was difficult, however, to prepare well-dispersed PP/G composites with simple mixing techniques. The surface properties of the filler and polymer have a significant effect on the conductivity of the composite by influencing the interaction between them. How well the polymer wets the surface of the filler can be quantified by the difference between the surface energies of the two materials. Smaller differences between the two surface energy values lead to better wetting of the filler by the polymer. Better wetting means that larger amounts of the polymer are coating the filler surface, which will alter the distribution of the filler within the matrix. This will increase the percolation threshold and the overall resistivity of the composite because larger amounts of the filler are required before the particles will come in to contact with each other. PP is hydrophobic and has relatively low surface free energy ($\sim$20-25 mJ/m^2) [11]. G is also strongly hydrophobic these may be a small difference between its surface energy and that of PP [12] which might lead to partial wetting and hence lower conductivity. This would explain why a somewhat larger difference between the surface energy of the filler and the polymer is desirable.

As described in results properties, the graphite-carbon black powder with various polymer matrixes composite have an opportunity as new BPP materials. However, on the concept of commercial manufacturing for fuel cells, they are associated with major problems of high fabrication cost and insufficient reliability of fuel cells. The BPP is one of the most costly component hence this research should be continued to get optimum formula of matrix contain and has become a critical research issue.

4.   Conclusion

The composite BPPs were investigated using PP as binder and graphite with acetylene black which were done by simple hot pressing. Higher loading filler must be added in order to improve conductivity to meet the requirements of the BPP. The filler contents must be limited otherwise it can lead to poorer mechanical properties, as shown in this research results. Furthermore, this project is still being investigate to determine the correlation between polymer contents and graphite/acetylene black with temperature and holding time in manufacture to get optimum properties. However, on the concept of commercial manufacturing for fuel cells, they are associated with major problems of high fabrication cost and insufficient reliability of fuel cells. The BPP is one of the most costly component hence this research should be continued to get the optimum formula of matrix contained and has become a critical research issue. The study has generated useful insight into processing of composite plate with tailored properties to meet further stringent requirements to achieve higher power densities at economical rates in a fuel cell stack.

Acknowledgement

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