Development of carbon felt based thermoplastic composite bipolar plates for PEMFCs

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Abstract

Polymer electrolyte membrane fuel cells (PEMFCs) have high efficiency, low operating temperature, and nearly zero environmental emissions. The bipolar plate is one of the main components in the PEMFC because it accounts for a great part in weight, volume and cost. Recently, carbon fiber reinforced thermoplastic composite bipolar plates for PEMFCs have been attracted owing to their simple fabrication method, high flexibility, excellent corrosion resistance, and damage resistance. The efficiency of the PEMFCs predominantly depends on the performances of the bipolar plates, however, the composite bipolar plates have high surface electrical contact resistance because of their resin-rich area.

In this study, the carbon felt made of pan based carbon fiber was used to fabricate the bipolar plate for PEMFCs. Also sol-gel method and the double percolation concept were introduced to improve the impregnation state of the thermoplastic polymer and electrical conductivity of the composite bipolar plates respectively. The electrical conductivity, double percolation morphology, and impregnation state of the newly developed composite bipolar plate were measured by using four-point probe method, transmission electron microscopy analysis and scanning electron microscopy analysis respectively. The results of the experiments were compared with the Department of Energy's(DOE's) technical target value.

1. Introduction

A polymer electrolyte membrane fuel cell (PEMFC) is an electro chemical energy converter that transforms the chemical energy of hydrogen fuel into electricity without creating pollutants. The PEMFCs are composed of bipolar plates, end plates, membrane electrode assemblies (MEAs), and gas diffusion layers (GDLs). Among these component, bipolar plates are main components of PEMFC because they account for a large part of volume, cost, and weight. There are some functional requirements of the bipolar plates such as high electrical conductivity, excellent gas thightness, high flexural strength, good thermal stability, and low density[1-3]. There have been many studies investigated about the development of bipolar plates using various materials with the overall aim of satisfying the requirements of the United States Department of Energy (DOE). Graphite and metallic materials which are conventional materials for the bipolar plate have disadvantages such as poor mechanical strength, high processing cost and low corrosion resistance[4,5]. Recently, thermoplastic or thermosetting composites reinforced with continuous carbon fibers, carbon fabrics and conductive fillers give rise to attention as the promising alternatives to graphite and metallic materials due to their advantages of low cost, good corrosion resistance and low weight. Especially, thermoplastic composites can be easily recycled and have excellent corrosion, impact and damage resistnace. Furthermore thermoplastic composites have fast cycle time than thermosetting composites. However, thermoplastics

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have been used less in bipolar plates than other mateirals due to their lack of electrical conductivity and difficulty to machine the flow channels in the bipolar plates[6,7].

Carbon felts can be used to replace the continuous carbon fibers and carbon fabrics in a thermoplastic composite. The carbon felt which has competitive price and low electrical resistance can be easily machined to make the flow channels. Moreover the carbon felts can be made of recycled carbon fibers, which possibly reduce the material cost and approach to clean technology. However, most carbon felts have over 90% of porosity so it should be impregnated with polymer perpectly to prevent leakage of the fuel.

In this work, carbon felt reinforced thermoplastic composite bipolar plates were made by using the sol impregnation method and double percolation concept to improve the degree of impregnation and electrical property. Isotactic polypropylene (PP) and polyethylene (PE) blend sol were used to introduce the double percolation effect and the MWCNTs were added to increase the electrical conductivity of the carbon felt/PP/PE composite. The electrical conductivity was measured by using the four-point probe method and compared with the DOE's technical target for bipolar plates. Also, The morphological observation of the carbon felt/PP/PE/MWCNT composite and double percolation effect were confirmed by scanning electron microscopy(SEM) and transmission electron microscopy (TEM) analysis.

2. Experimental

2.1. Thermoplastic polymer solution preparation

Two immiscible polymer isotactic PP (i-PP) (427883,Sigma-Aldrich Co. LLC., USA) and low-density PE(LDPE) (428043)(Sigma-Aldrich Co. LLC., USA) were used to introduce double percolation effect. The PP and PE solutions were fabricated using i-PP and LDPE by using sol-gel method, respectively, based on our previous work[8]. The two polymers should be dissolved in solvent at a high temperature because of their high solvent resistance. Accordingly, the i-PP and LDPE were dissolved in ortho-dichlorovenzene (*o*-DCB) at 130℃ and 110℃ respectively for 1h to prepare a solution at 20wt%. Then, the 20 wt% of the PP solution (PP sol) and PE solution (PE sol) were poured into liquid nitrogen for the quenching process to maintain the amourphous state at low temperature. The quenched polymer solutions were kept in the freezer for 24h to stabilize the amouphous state of polymer gels. These polymer gels can be re-dissoved more eaily in solvent and cannot be easily crystalized, so they maintain their amorphous phase at low temperatures. After that, the polymer gels were re-dissoved in *o*-DCB at 50℃ to preapre a solution at 8wt%. In the re-dissoving process, the temperature must be kept constant to prevent crystallization cuased by temperature drop. For that reason, the polymer sols were fabricated by heating the solution in a water bath for 1h at 50℃. Then, the PE sol was poured into the PP sol to introduce the double percolation effect and this polymer blend sol was mixed by a magnetic stirrer for 5 min. To elevate the electrical property, 5wt% of MWCNTs (724769, Sigma-Aldrich Co. LLC., USA) without any surface modification were dispersed into the polymer blend sol. After MWCNTs were fed into the polymer blend sol, the mixing was continued for another 15min at 50℃. The overall polymer fabricating process for polymer sol is shown in Fig.1.

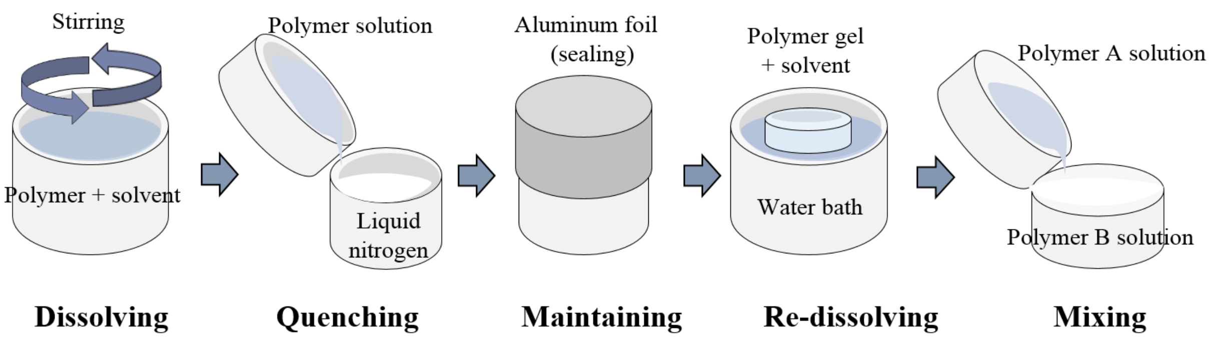

Figure 1. Fabrication process of the PP/PE blending sol

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2.2. Fabrication of the composite bipolar plate

Carbon felt/PP/PE composite filled with MWCNTs were fabricated with a poly-acrylonitirile (PAN) based carbon felt. Two kinds of carbon felts were investigated: XF30A(AAF 304ZS, Toyobo, Japan), Xin Xin carbon felt (Xin Xin, China).

A 150×150 mm area of the carbon felt was placed in a closed mold, and the PP/PE/MWCNT bleding sol was poured onto the carbon felt. Then, the closed mold was pressed at 220℃ under 10 MPa of pressure for 20min, as shown in Fig.2.

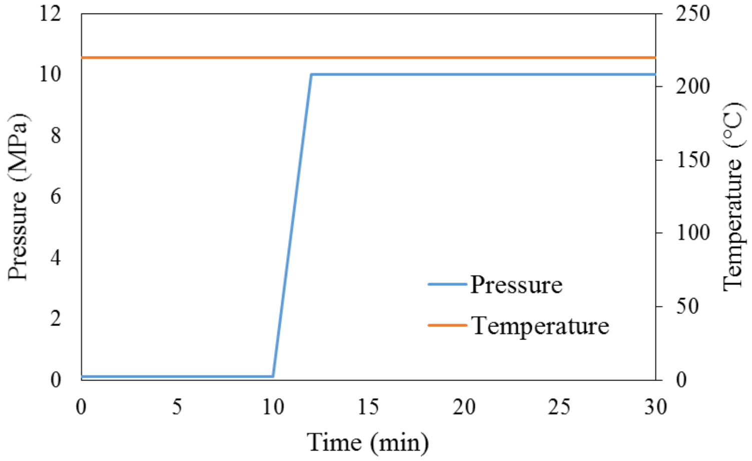

Figure 2. Molding cycle of carbon felt/PP/PE composites filled with MWCNTs

The carbon fiber/PP/PE/MWCNT composite bipolar plates were fabricated with a poly-acrylonitrile (PAN)-based 3k plane-woven carbon fabric (CF-3327EPC, Hankuk Carbon, Korea) to compare the properties of carbon felt/PP/PE/MWCNT composites. The carbon fabric already sized with bisphenol A diglycidyl ether epoxy by the manufacturer was heated under vacuum for 3h at 550℃ to remove the sizing layer. The fabricating procedure of the carbon fiber/PP/PE/MWCNT composite was the same with those of the carbon felt/PP/PE/MWCNT composites. In addition, the carbon fiber reinforced PP composites were fabricated using the conventional film-staking method to confirm the effect of sol-gel method. All of the specimens were reinforced with 5 wt% of MWCNT and their sample naming with repect to the composition is summarized in Table 1.

Sample	*Fabrication condition*
PP-film	Carbon fiber reinforced composite made of **PP film with 5 wt% MWCNTs**
PP-sol	Carbon fiber reinforced composite made of **PP sol with 5 wt% MWCNTs**
PP/PE-sol	Carbon fiber reinforced composite made of **PP/PE blending sol with 5 wt% MWCNTs**
CFT-PP/PE-sol	Toyobo carbon felt reinforced composite made of **PP/PE blending sol with 5 wt% MWCNTs**
CFX-PP/PE-sol	Xin Xin carbon felt reinforced composite made of **PP/PE blending sol with 5 wt% MWCNTs**

Table 1. Sample naming convention with repect to the composition of the composite

2.3. Characterization

The in-plane electrical conductivity of the composite bipolar plates was measured using a four-point

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probe (CMT-SR1000N, AiT, Korea) and the dimension of the composite specimen was 110×110 mm. The morphology of the carbon felt/PP/PE composite filled with MWCNTs was examined with scanning electron microscopy(AIS1800C, Seron Technologies Inc, Korea). To observe the cross section of the composite, the sample was firstly immersed into the liquid nitrogen and cutting process was perfomed.Transmission electron microscopy (H-7650, Hitachi, Japan) observation was performed with voltages of 100 kV. Ultrathin sections of cryo-microtomed PP/PE/MWCNT composite films were prepared with an ultramicrotome (Leica EM U C6, Leica-Microsystmes GmbH, Austria) to confirm the double percolation effect of the PP/PE/MWCNT composite. The cryo-microtoming was conducted below its grass transition temperature using liquid nitrogen.

3.Results and discussion

Fig. 3. shows the electrical conductivity of the composites bipolar plates with respect to the composition and fabricating method. Among them, the PP/PE-sol specimen exhibited the highest electrical conductivity at a given MWCNT wt% because the MWCNTs form the electrical path through the polymers by selective localization. The electrical conductivity value of the CFX-PP/PE-sol specimen was 25.4 S/cm and this value is higher than the conventionally fabricated PP-film specimen. Although, the CFX-PP/PE-sol specimen has improved electrical property than the PP-film specimen, the electrical conductivity is so low to satisfy the Department of the energy's(DOE's) technical target value.

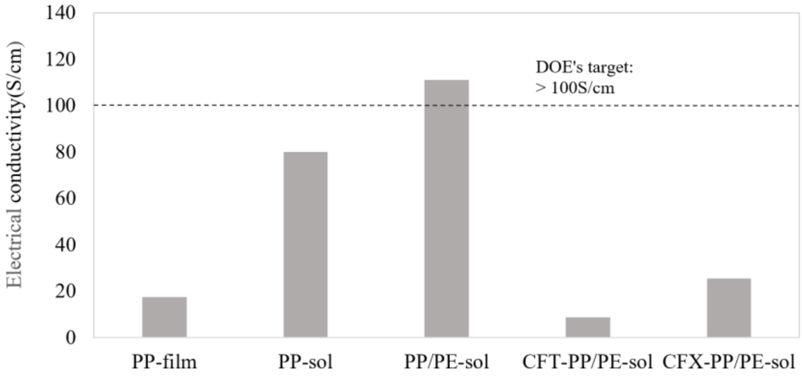

Figure 3. Electrical conductivity of composite specimens with respect to the composite fabrication method

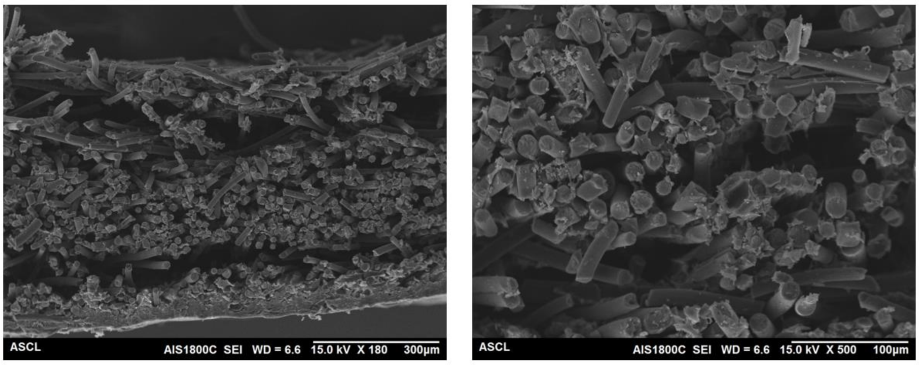

Figure 4. SEM topographies of the CFX-PP/PE-sol composite cross section with different magnifications

To confirm the impregnation state of the composites, the cross-sectional view of the composites were observed by SEM. Fig. 4. shows the SEM topographies of the carbon felt based PP/PE/MWCNT composite with different magnifications. Large amount of voids were detected in the cross section of the sample which means poor impregnation state of the composite. These unimpregnated area of the

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composite caused by the high pressure applied during the compression molding so that the excessive polymer resin was squeezed out from the stack. As a result, the electrical conductivity of the composite are strongly influenced by the unimpregnated area and voids. In this respect, the applied pressure and amount of the PP/PE/MWCNT sol must be optimized to improve the impregnation state.

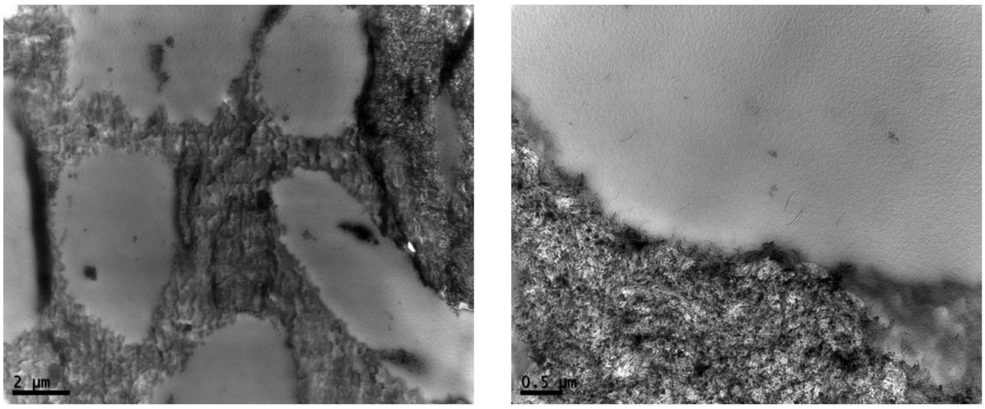

Figure 5. Transmission electron micrographs of the PP/PE/MWCNT composites with different magnifications.

The morphology of the carbon nanotube-filled PP/PE composite was investigated by TEM at different magnifications to confirm the double percolation effect. The double percolation effect of two immiscible polymer blends improved the electrical conductivity of the composite by positioning MWCNTs selectively in the one polymer phase or at their interface. Fig.5. shows the micrographs of the PP/PE composite containing 5wt% carbon nanotubes. These TEM images reveal the explicitness of the CNT location within the dark phase, which formed the conductive network in the composite.

4. Conclusions

In this study, carbon felt/PP/PE composite bipolar plates for PEFMCs filled with MWCNTs were fabricated by using the sol gel method and double percolation effect to improve the degree of impregnation and dispersion of MWCNTs with enhanced electrical properties. The following conclusions were derived from the results:

(1) At a given MWCNT content, carbon felt based PP/PE/MWCNT composite has higher electrical conductivity than the conventionally fabricated PP-film specimen.
(2) The large amount of void and unimpregnated area were confirmed from the SEM images of CFX-PP/PE-sol specimen. These defects of the composite bipolar plate resulted in the low electrical conductivity.
(3) From the TEM images, the double percolation effect was confirmed. The selective distribution of the MWCNTs improved the electrical conductivity of the composite without an excessive increase in viscosity.

Acknowledgments

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