Preparation and properties of thin epoxy/compressed expanded graphite composite bipolar plates for proton exchange membrane fuel cells

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ABSTRACT

Although the composite bipolar plates prepared by the method of the vacuum resin impregnation in compressed expanded graphite (CEG) sheets have been applied in the KW-class stacks, there have been few investigations of the preparation and properties of them so far. In this research, the influences of the microstructure on the physical properties of the thin epoxy/CEG composites (the thickness is 1 mm) are investigated for the first time and the optimum preparation conditions are obtained. Results demonstrated that the mechanical property and the impermeability of the composites increases evidently with the resin content changing from 4% to 30%, while the electrical properties keep nearly constant. It can be attributed to the continuous expanded graphite (EG) conductive network of the raw CEG sheet. The epoxy (30 wt.%)/CEG composite is shown to be the optimum composite, displaying in-plane conductivity of $119.8\,S\,cm^{-1}$, through-plane resistance of $17.13\,m\Omega\,cm^2$, density of $1.95\,g\,cm^{-3}$, gas permeability of $1.94 \times 10^{-6}\,cm^3\,cm^{-2}\,s^{-1}$ and flexural strength of 45.8 MPa. The alcohol scrubbing is the optimum method of surface post-processing. The performance of a single cell with the optimum composite bipolar plates is tested and demonstrated to be outstanding. Above all, the composite prepared by resin vacuum impregnation in the CEG sheet is a promising candidate for bipolar plate materials in PEMFCs.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a promising alternative for various portable electronic devices and transportation applications. Bipolar plate is one of the most significant parts in fuel cells, which accounts for approximately 80% of the fuel cell volume, 70% of the fuel cell weight and as much as 60% of the stack cost [1]. Generally, there are two types of bipolar plates in PEMFCs: the metal-based bipolar plates and the carbon-based bipolar plates. Compared with the former, the carbon-based bipolar plates have preferable corrosion resistance. Recently, the polymer/expanded graphite (EG) conductive composites have become a promising candidate for PEMFC bipolar plates because of lower cost, higher corrosion resistance and easier manufacturing. The bipolar plates that can meet the Department of Energy (DOE) targets (shown in Table 1 [2]) are considered to be suitable for PEMFC application.

Most of the polymer/EG composite bipolar plates were prepared by mixing the EG particle fillers and polymer matrix, followed by compression molding or injection molding [3–14]. Blunk et al. [3] and Du [4] studied the conductive epoxy/EG composite bipolar plates which could show the favorable physical properties. Heo et al. [5] investigated the perform molding technique of the phenol resin/EG composite bipolar plates. Song [6,7] prepared a kind of aromatic polydisulfied/EG nanocomposites, and the short carbon fiber was used to further reinforce the nanocomposites. Furthermore, other kinds of polymers were used to prepare polymer/EG composites, e.g. poly(styrene-co-acrylonitrile) [8,9], PMMA [10,11], polyamide-6 [12], polystyrene [13] and poly(vinyl acetate) [14]. The dispersion of the EG particles and the brittleness are the main handicap of this kind of the composite bipolar plates.

Another method for the preparation of polymer/EG composite bipolar plates with good physical properties was vacuum resin impregnation in compressed expanded graphite (CEG) sheets [15–20]. There have been few literatures about this kind of bipolar plates so far. Ballard Power System Inc. [15–17] firstly investigated CEG-based composite bipolar plates and applied them in the fuel cell vehicles. In this method, the flow fields were firstly embossed on the CEG sheet. Then the CEG sheet was impregnated with resin and cured. DICP (Dalian Institute of Chemical Physics) and Sunrise Power Co. Ltd. [18–20] had also developed polymer/CEG compos-

Table 1
The targets of bipolar plates in PEMFCs.

Characteristic	Targets
In-plane electrical conductivity (S cm^{-1})	>100
Through-plane resistance (mΩ cm^2)	<20
Flexible strength (MPa)	>25
Gas permeability (cm^3 cm^{-2} s^{-1})	<2.00E−06
Thermal conductivity (W (m K)$^{-1}$)	>20
Corrosion (μA cm^{-2})	<1

ite bipolar plates which were already used in the 1 kW and the 10 kW stacks successfully. The bipolar plates was prepared by vacuum resin impregnation, followed by flow field compression and curing. This kind of bipolar plates has outstanding electrical properties and flexibility because of the preparation based on the CEG sheets.

In this paper, a kind of thin epoxy/EG composite bipolar plates (the thickness is 1 mm) was obtained by vacuum resin impregnation with the CEG sheets. The influence of microstructure and the preparing conditions on the physical properties (e.g. electrical property, gas permeability, mechanical property and surface hydrophobicity) of this kind of bipolar plates were investigated for the first time. Besides, I–V curve of a single cell with the optimum bipolar plates was also investigated.

2. Experimental

2.1. Preparation of composites and bipolar plates

The matrices of the composites were CEG sheets (the thickness is 2 mm) with the density of 0.69 g cm^{-3}. The epoxy resin was used as polymer fillers in these experiments, and the phenolic resin was chosen as the curing agent. The alcohol was chosen as the solvent of the epoxy resin and the curing agent.

The preparation process for the composite bipolar plates is shown in Fig. 1. Compared with the compression molding or injection molding, composites preparation with this method is based on the raw CEG sheets. The raw CEG sheets were put into a sealed vessel in vacuum (−0.08 MPa, gage pressure), followed by epoxy resin solution impregnation. After the residual resin on the surface was cleaned with post-processing, the samples were put into Electric Blast Drying Oven to volatilize solvent at 80 °C for 2 h. Then the
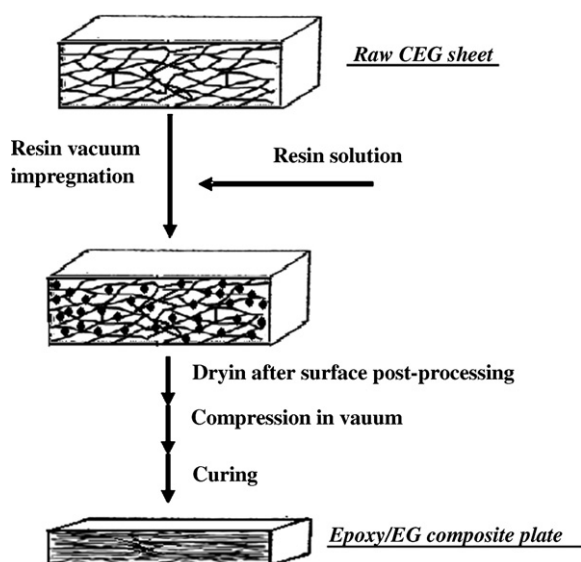
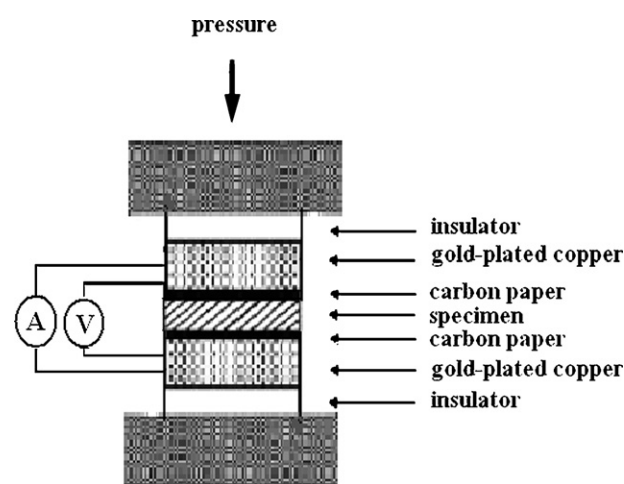**Fig. 1.** The preparation scheme for the epoxy/EG composite bipolar plates.

Fig. 2. Scheme of experimental setup used in the through-plane resistances measurement.

CEG sheets had a compression from 2 to 1 mm, which could increase volume power density to make the composites more applicable for PEMFCs. Finally, the composites were cured at programmed temperatures from room temperature to 175 °C with a constant heating rate of 0.5 °C min^{-1}. Thus, the thin composites were obtained.

The process of the bipolar plates manufacture was similar to that of the composites, except a little difference in the compression procedure. Instead of flat plate, a stainless steel mould was used to shape parallel flow field on the composites surface with a pressure of 10 MPa.

2.2. Characterization of the composites and bipolar plates

2.2.1. Characterization of the microstructure

X-ray diffraction (XRD) was performed on a RINT D/MAX-2500/PC XRD using Cu Kα radiation (λ = 0.154178), generator tension was 40 kV and generator current was 200 mA. Scans were taken from 5° to 60°, and scan rate was chosen as 5° min^{-1}. Scanning electron microscope (SEM, JEOL JSM-6360 LV) was used to study the microstructure of the composites. The porosity of each composite was determined according to the ASTM C20 test procedure.

2.2.2. Measurement of the electrical properties

The in-plane electrical conductivity ($\sigma_{\text{in-plane}}$) of the composite was examined with a digital four-point probe detector (SX1934, Baishen Technology) which has a linear configuration with spacing of 1 mm between the probes. The dimension of the samples is 50 mm × 10 mm × 1 mm.

The through-plane resistance was measured with two gold-plated copper plates by the universal testing machine (WDW-1010), where the sample was kept under a constant pressure (2.0 MPa) (Fig. 2). Samples with a size of 50 mm × 10 mm × 1 mm were placed between two carbon paper layers (Toray TGPH-060) to simulate the interfacial contact in a fuel cell stack. A given current was produced by a programmable power supply (GW INSTEK PSP-2010) through the two gold-coated copper plates, and the resultant voltages were measured by multidisplay multimeter (ESCORT EDM-3150 PRO).

2.2.3. Measurement of the gas permeability

Air permeability measurements were carried out in a home-made test facility as shown in Fig. 3. After the circular samples were mounted in the annular specimen chamber, the air was allowed to flow into the upper air chamber. The inferior air chamber was
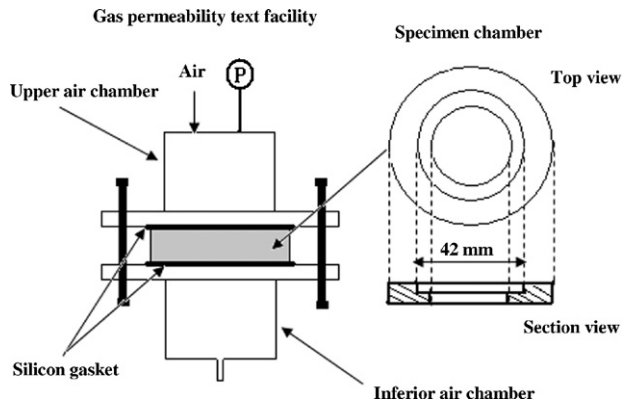
Fig. 3. Scheme of the gas permeability measurement.

open to surrounding. The pressure drop could be totally ascribed to the gas permeation across the specimen, so the gas permeability could be calculated through the descending velocity of the pressure in the upper air chamber. The initial pressure in the upper air chamber was 0.2 MPa (g). The effective diameter of the sample was 40 mm.

2.2.4. Measurement of the mechanical property

Three-point bending tests were carried out with the samples of 50 mm × 10 mm × 1 mm using the WDW-1010 universal testing machine according to ASTM D790-02. The support span was 30 mm, and the cross-head speed was 5 mm min^{-1}. The flexural strength was calculated according to the following equation:

$$\text{Flextural strength} = \frac{3FL}{2Wt^2} \qquad (1)$$

where F is the breaking force of the samples, L is the support span, W is the width and t is the thickness of the sample.

2.2.5. Measurement of the surface hydrophobicity

The contact angles of the samples with water were measured using Drop Shape Analysis System (KRUSS DSA 100).

2.2.6. Single cell test

The composite bipolar plates prepared with optimum properties were used for single cell test. The active area of the single cell was 5 cm^2. The membrane electrode assembly (MEA), which was comprised of a Nafion®212 membrane (DuPont) and two electrodes, was prepared by warming-up for 60 s and then hot pressing at 140 °C and 10 MPa for 60 s. Each electrode was supported by Toray carbon paper (Toray TGPH-060). The Pt loading on the cathode and the anode were both 0.4 mg cm^{-2}.

The cell temperature and the humidification temperature were both kept at 70 °C. The flux of hydrogen and air were 30 sccm (standard cubic centimeter per minute) and 500 sccm, respectively. The pressures of the reacting gases were 0.1 MPa (g) on both sides. Performance of the single cell was evaluated by measuring I–V curve using home-made testing equipment and Arbin BT2000 electrical load (America, Arbin instruments).

3. Results and discussion

3.1. Microstructure of the epoxy/EG composites

EG is a kind of porous, layered modified graphite. With the method mentioned above, the epoxy resin was infused into the pores of the CEG sheet to improve the impermeability and the mechanical property of the composite.

Fig. 4 shows the cross-sectional morphology of the CEG sheets and the epoxy/CEG-based composites obtained by SEM micrographs. Fig. 4(a) shows the layered microstructure of the raw CEG sheet, and the aperture varies from 5 to 63 μm. After the resin impregnation and compression, the composite becomes denser than the raw CEG sheet, and the size of the aperture descends to the range of 2–29 μm (Fig. 4(b)). The further enlarged pictures (Fig. 4(c) and (d)) show that the un-expanded graphite ligaments in the composite maintain the similar structure as the raw CEG sheets. The thickness of the graphite ligaments ranges from 30 to 220 nm. It indicates that the resin impregnation cannot change the graphite conductive network of the raw CEG.

In order to identify whether the resin destroyed the original microstructure of the CEG sheets, XRD measurements of the raw
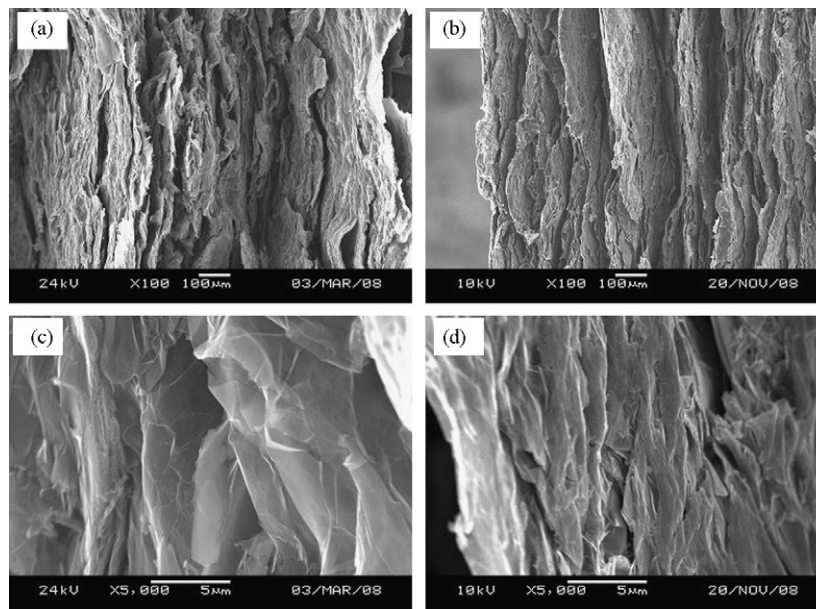

Fig. 4. SEM micrographs of cross-section of the material: (a) the raw CEG sheet (0.69 g cm^{-3}) with a low magnification (100×), (b) the epoxy (30 wt.%)/EG composite with a low magnification (100×), (c) the raw CEG sheet (0.69 g cm^{-3}) with a high magnification (5000×), and (d) the epoxy (30 wt.%)/EG composite with a high magnification (5000×).
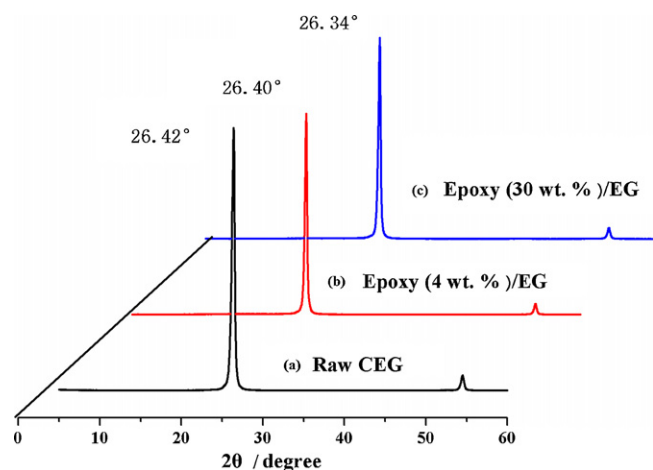
Fig. 5. XRD patterns of raw CEG sheets and epoxy/EG-based composites. (a) The raw CEG sheet (0.69 g cm^{-3}), (b) the epoxy (4 wt.%)/EG composite, and (c) the epoxy (30 wt.%)/EG composite.

CEG sheets and the epoxy/CEG composites were taken. The patterns are shown in Fig. 5. It can be seen that a narrow and sharp diffraction peak (0 0 2) appeared at 26.42° in the raw CEG sheets, reflecting that the d-spacing is 3.37 Å and the crystallite size is 19.5 nm (Fig. 5(a)). Compared with that of the raw CEG sheet, the basal peak (0 0 2) of the epoxy/CEG composite shifts slightly to lower angle (Fig. 5(b) and (c)). With the increasing of the resin content in the composite, the crystallite size changes from 20.4 to 24.9 nm, but the *d*-spacing still keeps nearly at 3.37 Å. This phenomenon suggests that the impregnating of resin has no effect on the basic constituent unit of the raw CEG sheets, i.e. carbon crystal layer, although the crystallite size changes slightly. It tallies with the information obtained from the SEM micrographs (Fig. 4(c) and (d)).

Hence, the characterizations of the microstructure indicate that the method of vacuum resin impregnation with CEG sheets could prepare a kind of composites with continuous conductive network as the raw CEG sheets. The basic conductive network could not be destroyed by resin impregnation and compression.
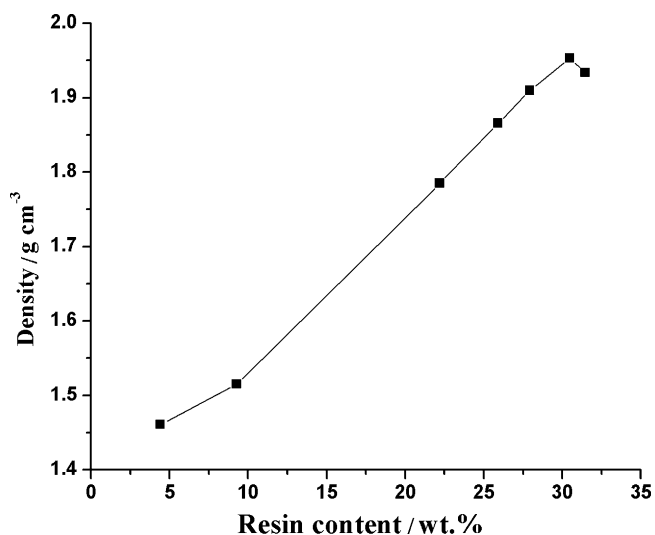

Fig. 6. Variation in the density of the composite with the increasing resin content (wt.%) in the composite.
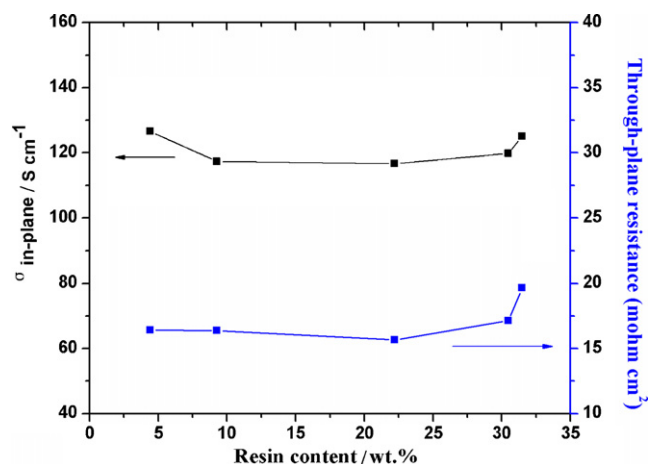

Fig. 7. Variation in in-plane electrical conductivity and through-plane resistance of the epoxy/EG composite with the increasing resin content.

3.2. Physical properties of the composites

3.2.1. The density of the composites

Fig. 6 shows the variation of the density of the composite with the resin content (wt.%) in the composite. The density varies from 1.46 to 1.95 g cm^{-3}, while the resin content in the composites changes from 4% to 31%.

3.2.2. Electrical properties

The variations of the electrical properties of the epoxy/EG composites both in the in-plane and through-plane directions with respect to the resin content are shown in Fig. 7. The in-plane electrical conductivity of the composite maintains nearly at 121 S cm^{-1}, when the resin content changes from 4% to 31%. It is evident that the introduction of the resin has little effect on the in-plane electrical conductivity because of the well conductive network in this direction. The through-plane resistances of the composites also keep nearly constant around 16 mΩ cm^2 with the resin content ranging from 4% to 30%. It suggests that the introduction of the resin cannot change the conductive network of the materials in the through-plane direction when the resin content is below 30%. While when the resin content is above 30%, the through-plane resistance begins to increase. Therefore both the in-plane conductivity and the through-plane resistance keep constant when the resin content is below 30%. Also the electrical properties of all the composites mentioned above could meet the demands of PEMFC bipolar plates (Table 1).

Surface post-processing which could remove the residual resin on the surface after the resin impregnation can improve the electrical properties of the composite bipolar plates. Four methods were chosen for post-processing: alcohol scrubbing, emulsifier OP solution (4%) dipping, hexadecyl trimethyl ammonium chloride (CTAC) solution (4%) dipping and alcohol dipping, respectively. Alcohol is a kind of resin solvent which can dissolve the resin left on the composite surface. Emulsifier OP and CTAC are different kinds of surfactants which can advisably restrain the resin from congregating on the surface. Fig. 8 shows the effects of the four surface post-processing methods on the electrical properties. The composite treated with alcohol scrubbing shows the best through-plane electrical property and takes second place in the in-plane electrical properties. While the composite treated with alcohol dipping shows the best in-plane electrical conductivity, because the dipping can adequately dissolve the residual resin on the surface. The electrical properties of all the composites treated by the four methods meet the bipolar plate criteria (Table 1). It indicates that the
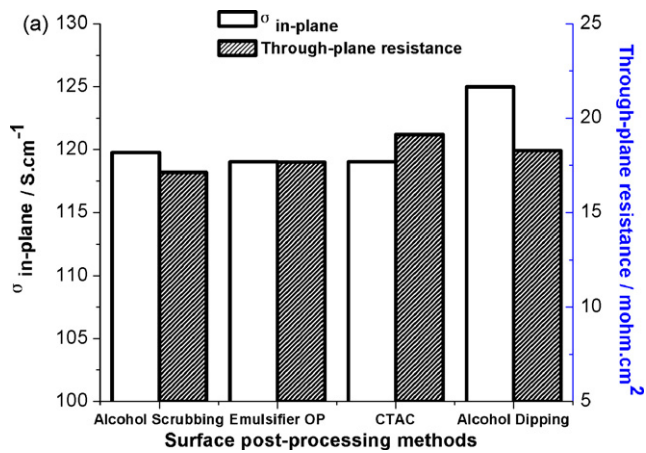
Fig. 8. Effect of different surface post-processing methods on in-plane electrical conductivity and through-plane resistance of the epoxy (30 wt.%)/EG composite.

post-processing methods with alcohol have better effect than the surfactants, although all the four methods could remove the residual resin on the surface effectively.

3.2.3. Porosity and gas permeability

The porosity of the composite descends from 62.2% to 15.4%, when the resin content varies from 4% to 31% (Fig. 9(a)). The pores in the epoxy/EG composites can be classified into two types: open pores and closed pores. Compared with the closed
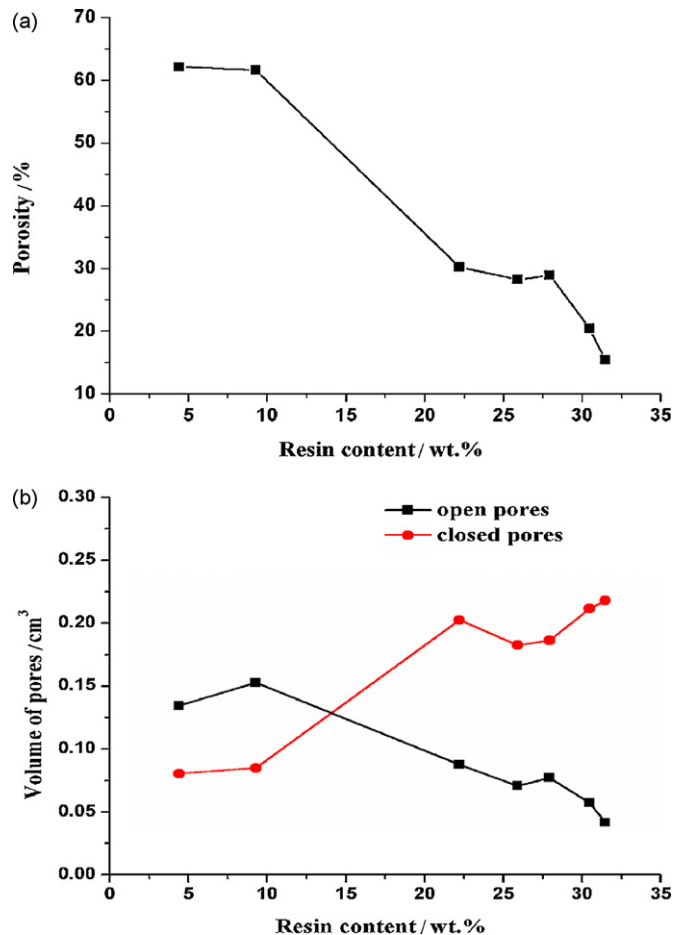

Fig. 9. Variation in (a) the porosity and (b) the pores volume of the epoxy/EG composite with the increasing resin content.
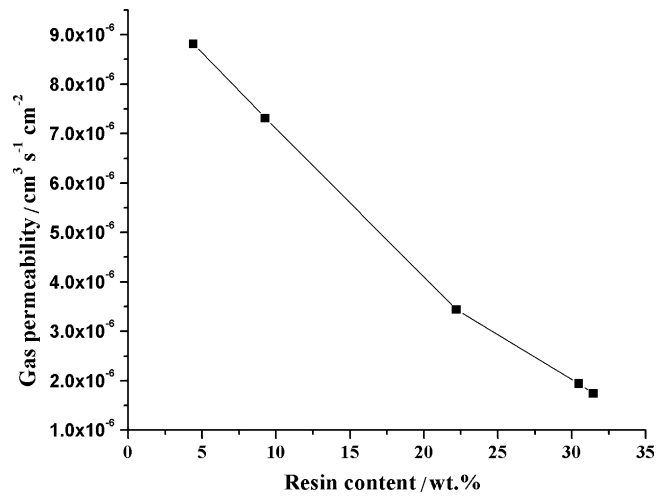

Fig. 10. Variation in the gas permeability of the epoxy/EG composite with the increasing resin content.

pores, the open pores have remarkable effect on the gas permeability. Fig. 9(b) shows the dependence of volume of pores on resin content of the composites. Volume of open pores decreases, while volume of closed pores increases with the increasing resin content.

It is clear that gas permeability of the composites decreases with the increasing resin content (Fig. 10). It owes to that more resin molecules fill the open pores in the CEG sheets, thus the impermeabilities of the composites are improved. When the resin content is above 30% (the volume of open pores in the composite decreases to 0.057 cm^3), the gas permeability of the composites was lower than 2×10^{-6} cm^3 cm^{-2} s^{-1}, the basic permeability request for bipolar plate application (Table 1).

3.2.4. Mechanical property

The relationship between the flexural strength and the resin content is shown in Fig. 11. Compared with the raw CEG sheets (1.9 MPa), the flexural strength of the composites improves evidently. It increases from 20.3 to 49.1 MPa with the ascending resin content. The existence of the resin decreases the porosity of the composite (Fig. 4(b) and Fig. 9(a)) and makes the composite denser, therefore the mechanical property of the composite is improved.
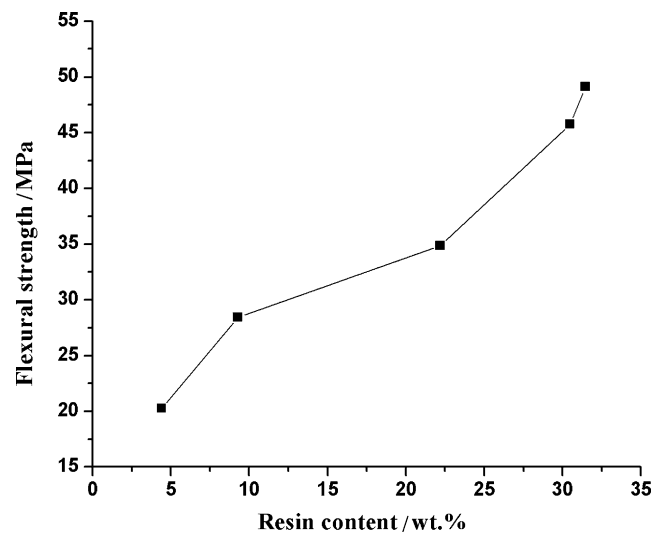

Fig. 11. Variation in the flexural strength of the epoxy/EG composite with the increasing resin content.
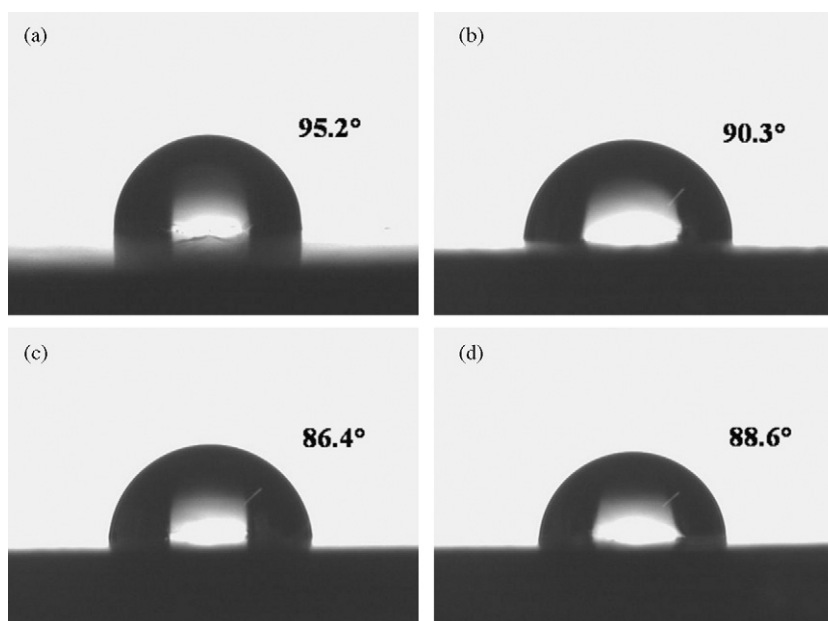
Fig. 12. Effect of different surface post-processing methods on the contact angle of the composite with water. (a) Alcohol scrubbing, (b) emulsifier OP solution (4%) dipping, (c) (CTAC) solution (4%) dipping, and (d) alcohol dipping.

When the resin content is above 8%, the composites can satisfy the bipolar plate criteria of flexural strength (Table 1).

Different from the composites obtained by the compression molding or injection molding, when the resin content increased from 4% to 30%, the electrical properties of the composites prepared with this method kept at constant and the mechanical property increased. The conflict between the electrical properties and the mechanical property was avoided owing to the continuous conductive network remained from the raw CEG sheets (Fig. 4(c) and (d)).

3.2.5. Hydrophobicity/hydrophilicity of the surface

Hydrophobicity/hydrophilicity of the surface is one of the most important features affecting the fuel cell performance particularly at high current densities. The hydrophobic nature of the composite will let the water remain in the form of droplets which can be swept away easily by the gas stream in the gas flow channels of the composite bipolar plate. The hydrophilic tendency can result in the formation of water film which will effectively increase the pressure drop inside the channels. Hence the hydrophobic surface of the bipolar plate is suitable for the application of the PEMFCs.

The surface post-processing method has remarkable effect on the hydrophobicity/hydrophilicity of the surface. The values of contact angle of the composites are shown in Fig. 12. The water contact angle of the composites by the methods of alcohol scrubbing, emulsifier OP solution dipping, CTAC solution dipping and alcohol dipping are 95.2°, 90.3°, 86.4° and 88.6°, respectively. The data shows that the alcohol scrubbing method provides the most hydrophobic surface which is the nearest to the surface of the raw CEG sheet (96.2°). It indicates that the alcohol scrubbing is proved to be the optimum surface post-processing method in these methods.

3.3. Single cell test

According to the bipolar plate criteria in PEMFCs, the epoxy (30%)/EG composite bipolar plate with the predominant properties is considered to be the most suitable candidate. I–V and I–P performances of the single cell assembled with this kind of the composite bipolar plates are given in Fig. 13. From I–P character-
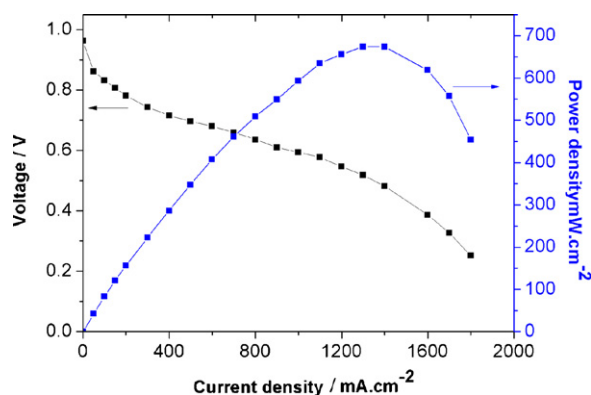

Fig. 13. The PEMFC performance curves of the single cell with the epoxy (30 wt.%)/EG bipolar plates.

istic, it is observed that the power density of the cell continuously increases up to the current density of 1400 mA cm^{-2} corresponding to the maximum power density of 674 mW cm^{-2}. The good performance of the single cell indicates that the method of resin vacuum impregnation with CEG sheets could prepare outstanding composites, which are suitable for the application of the preparation of the PEMFC bipolar plates.

4. Conclusion

A kind of thin epoxy/CEG-based composite bipolar plates was developed by the resin vacuum impregnation with CEG sheets. When the resin content changed from 4% to 30%, the electrical properties both on the in-plane and the through-plane directions stayed constantly. Meanwhile the flexural strength ascended with the increasing of the resin content. The conflict between the electrical property and the mechanical property was eliminated. It attributed to the continuous EG conductive network provided by the CEG sheets. With the increasing of the resin content, the density of the composite bipolar plate ascended, meanwhile the porosity and the gas permeability of the composite descended. When the

resin content was above 30%, the corresponding volume of open pores was below 0.057 cm^3, and the gas permeability was lower than 2.0×10^{-6} cm^3 cm^{-2} s^{-1}, which was suitable for the basic permeability request for bipolar plate application. Because of favorable electrical properties and hydrophobic surface (95.2°) of the composite, the methods of alcohol scrubbing was considered to be the best surface post-processing method.

Considering the DOE targets of the bipolar plates, the epoxy (30%)/EG composite bipolar plate was considered to be the most suitable candidate for PEMFCs. The favorable performance of the single cell test indicated that this kind of composites was a promising candidate for bipolar plate material. Liquid permeability and stability of the materials in PEMFCs will be focused on in the future works.

Acknowledgements

References

[1] D.P. Davies, P.L. Adcock, M. Turpin, S.J. Rowen, J. Appl. Electrochem. 30 (1) (2000) 101–105.
[2] Orest Adrianowycz, DOE Hydrogen Program Review, (2007).
[3] R. Blunk, M.H. Abd Elhamid, D. Lisi, Y. Mikhail, J. Power Sources 156 (2006) 151–157.
[4] L. Du, S.C. Jana, J. Power Sources 172 (2007) 734–741.
[5] S.I. Heo, K.S. Oh, J.C. Yun, S.H. Jung, Y.C. Yang, K.S. Han, J. Power Sources 171 (2007) 396–403.
[6] L.N. Song, M. Xiao, X.H. Li, Y.Z. Meng, Mater. Chem. Phys. 93 (2005) 122–128.
[7] L.N. Song, M. Xiao, Y.Z. Meng, Compos. Sci. Technol. 66 (13) (2006) 2156–2162.
[8] G. Zheng, J. Wu, W. Wang, C. Pan, Carbon 42 (2004) 2839–2847.
[9] W.P. Wang, C.Y. Pan, J.S. Wu, J. Phys. Chem. Solids 66 (2005) 1695–1700.
[10] W. Zheng, S.-C. Wong, Compos. Sci. Technol. 63 (2003) 225–235.
[11] W. Zheng, S.-C. Wong, H.-J. Sue, Polymer 43 (25) (2002) 6767–6773.
[12] F.M. Uh, Q. Yao, H. Nakajima, E. Manias, C.A. Wilkie, Polym. Degrad. Stabil. 89 (2005) 70–84.
[13] Y. Ishigure, S. Iijima, H. Ito, T. Ota, H. Unuma, M. Takanashi, Y. Hikichi, H. Suzuki, J. Mater. Sci. 34 (1999) 2979–2985.
[14] P. Liu, K. Gong, P. Xiao, M. Xiao, J. Mater. Chem. 10 (2000) 933–935.
[15] P.R. Gibb, Europe Patent WO0041260 (1999).
[16] A. Donald, US Patent 2004/0231530 A1 (2004).
[17] R.A. Mercuri, US Patent 6923631 B2 (2005).
[18] X. Yan, M. Hou, H. Zhang, F. Jing, P. Ming, B. Yi, J. Power Sources 160 (2006) 252–257.
[19] H. Zhang, M. Hou, China Patent 200410020906 (2004).
[20] H. Xu, Y. Fu, X. Luo, P. Ming, China Patent 200710158892.8 (2007).