The preparation technique optimization of epoxy/compressed expanded graphite composite bipolar plates for proton exchange membrane fuel cells

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1. Introduction

Bipolar plate is one of the most significant parts in fuel cells, which constitutes the backbone of a fuel cell stack, conducts current between cells, facilitates water and thermal management, and provides conduits for reactant gases. Generally, there are two types of bipolar plates in PEMFCs: the metal-based bipolar plates and the carbon-based bipolar plates. Metal-based bipolar plates have higher mechanical strength, lower permeability, and much superior manufacturability. However, the main handicap of the metal-based bipolar plates is the lack of ability to combat corrosion in the harsh acidic and humid environment of PEMFCs and the considerable power degradation that may be caused by metal ions [1–7]. Compared with the metal-based bipolar plates, the carbon-based bipolar plates have higher corrosion resistance and lower contact resistance, but they are considered as brittle and permeable to gases [7–15]. To develop suitable materials for bipolar plates on the applications in fuel cells, the physical and electrical properties of the bipolar plates should meet the following design requirements (shown in Table 1) [7,16].

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. Vacuum resin impregnation in CEG sheets was reported as one of the proper methods for the preparation of polymer/EG composite bipolar plates with good physical properties [17–23]. For example, Ballard Power System Inc. has investigated CEG-based composite bipolar plates and applied them in the fuel cell vehicles [17–19]. In this method, the CEG sheet was firstly embossed with the flow fields on the surface, and then impregnated with resin and cured. Dalian institute of chemical physics, Chinese academy of sciences (DICP) and Sunrise Power Co., Ltd. [20–23] have also developed polymer/CEG composite bipolar plates which were used in the 1 kW and the 10 kW stacks successfully. This kind of bipolar plates was prepared by vacuum resin impregnation, followed by flow field compression and curing. Although having such differences in preparation technique, both kinds of bipolar plates mentioned above have outstanding electrical properties and flexibility because of the preparation based on the CEG sheets.

The composite bipolar plates prepared by the method of vacuum resin impregnation in CEG sheets have

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Abstract

Vacuum resin impregnation method has been used to prepare polymer/compressed expanded graphite (CEG) composite bipolar plates for proton exchange membrane fuel cells (PEMFCs). In this research, three different preparation techniques of the epoxy/CEG composite bipolar plate (Compression–Impregnation method, Impregnation–Compression method and Compression–Impregnation–Compression method) are optimized by the physical properties of the bipolar plates. The optimum conditions and the advantages/disadvantages of the different techniques are discussed respectively. Although having different characteristics, bipolar plates obtained by these three techniques can all meet the demands of PEMFC bipolar plates as long as the optimum conditions are selected. The Compression–Impregnation–Compression method is shown to be the optimum method because of the outstanding properties of the bipolar plates. Besides, the cell assembled with these optimum composite bipolar plates shows excellent stability after 200 h durability testing. Therefore the composite prepared by vacuum resin impregnation method is a promising candidate for bipolar plate materials in PEMFCs.
already been applied in the kW-class stacks, but few investigations on the preparation technique have been reported in detail so far. In this study, three methods (Compression–Impregnation method, Impregnation–Compression method and Compression–Impregnation–Compression method) were chosen to prepare the epoxy/CEG composite bipolar plates. Their advantages and disadvantages were investigated and the conditions of each preparation technique were optimized. All of the methods were based on the CEG sheets, and epoxy resin was selected as filler. Besides, the composite bipolar plates prepared by the optimum technique were assembled into a single cell to perform 200 h fuel cell durability testing.

2. Experimental

2.1. Materials and preparation methods for the bipolar plates

The matrices of the composites were CEG sheets (the thickness is 7 mm) with the density of 0.20 g cm\(^{-3}\). In these experiments, the epoxy resin was chosen as polymer fillers, and the phenolic resin was used as the curing agent. The alcohol was chosen as the solvent of the epoxy resin and curing agent.

Three different methods were selected to prepare the composite bipolar plates in this research. The first method (Method I) was named as Compression–Impregnation method. As shown in Fig. 1, the CEG sheets were compressed directly into the desired shape followed by resin solution vacuum impregnation. After the subsequent processing (e.g. surface post-processing, drying and curing), the composite were obtained. The second method (Method II) was called Impregnation–Compression method. In this method, the CEG sheets were firstly impregnated with resin solution in vacuum, followed by compression and other subsequent processing. The particular process of this method is shown in Fig. 2. The last method (Method III) was Compression–Impregnation–Compression method. Be different from the others, two steps of the compression were applied in this method. The detailed procedure of this method is shown in Fig. 3. The CEG sheets were compressed to a medium thickness (2 mm) by the first step of compression. Then the sheets were impregnated with resin solution in vacuum followed by surface post-processing, drying and the second compression. Finally the sheets were cured and the composite were obtained.

The process of the bipolar plate preparation was similar to that of the composites, except a little difference in the compression proce-
dure (the second compression for Method III). Instead of flat plate, a stainless steel mould was used to shape parallel flow field on the composites surface with the pressure of 10 MPa. The dimension value for channel width, land width and channel depth of the bipolar plate was close to 0.8, 0.6 and 0.4 mm.

2.2. Characterization of the composites and bipolar plates

2.2.1. Characterization of the microstructure

Scanning electron microscope (SEM, JEOL JSM-6360 LV) was used to study the morphology of the composites. The cross-sectional microstructure of the composite was the primary observational object. The dimension of the specimens was 25 mm × 10 mm.

2.2.2. Measurement of the electrical properties

The in-plane electrical conductivity (σ\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 was 50 mm × 10 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. 4). Samples with a size of 50 mm × 10 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

Nitrogen permeability measurements were carried out in a homemade test facility as shown in Fig. 5. After the circular samples were mounted in the annular specimen chamber, the N\textsubscript{2} was allowed to flow into the upper chamber. The pressure in the upper chamber was 0.2 MPa (g). The carrier gas was allowed to the inferior chamber to transmit the gas to SHIMADZU Gas Chromatography (GC-14C). And the gas permeability was obtained. 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 using the WDW-1010 universal testing machine according to ASTM D790-02. The support span was 30 mm, and the crosshead speed was 5 mm min\textsuperscript{-1}. The flexural strength was calculated according to the following equation:

\[
\text{flexural strength} = \frac{3FL}{2Wt^2}
\]

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. Fuel cell durability testing

The composite bipolar plates with optimum properties were used for fuel cell durability testing. The active area of the single cell was 5 cm\textsuperscript{2}. The membrane electrode assembly (MEA), which was comprised of a Nafion\textsuperscript{®} 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\textsuperscript{-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 the homemade testing equipment and Arbin BT2000 electrical load (America, Arbin instru-
Fig. 5. Scheme of the gas permeability measurement.

Fig. 6. SEM micrographs of cross-section of the composites prepared by different methods with 40% resin solution: (a) the composite prepared by Method I with a low magnification (×100), (b) the composite prepared by Method I with a high magnification (×5000), (c) the composite prepared by Method II with a low magnification (×100), (d) the composite prepared by Method II with a high magnification (×5000), (e) the composite prepared by Method III with a low magnification (×100), (f) the composite prepared by Method III with a high magnification (×5000).
ments). The current density of the fuel cell durability testing was 500 mA cm$^{-2}$.

3. Results and discussion

3.1. Microstructure of the epoxy/CEG composites prepared by different methods

Fig. 6 shows the cross-sectional morphology of the three kinds of the epoxy/CEG composites obtained by SEM micrographs. Fig. 6(a) shows layered microstructure of the epoxy/CEG composites prepared by Method I, and the interlamellar spacing varies from 13 to 72 μm. The further enlarged picture (Fig. 6(b)) shows the unexpanded graphite ligaments in the composite. The thickness of the graphite ligament ranges from 110 to 230 nm, and the diameter of the diamond pore changes from 0.92 to 4.59 μm. Fig. 6(c) and (d) shows the microstructure of the composite prepared by Method II at different magnification respectively. Compared with the other composites, the composite obtained by Method II is of less anisotropy. The interlamellar spacing varies from 4 to 33 μm, the thickness of the graphite ligament ranges from 100 to 430 nm, and the diameter of the diamond pore changes from 0.76 to 3.72 μm. Fig. 6(e) and (f) exhibits the morphology of the composite prepared by Method III. The interlamellar spacing varies from 3 to 48 μm, the thickness of the graphite ligament ranges from 90 to 270 nm, and the diameter of the diamond pore changes from 0.93 to 4.84 μm.

For Method I, the compression process before the resin solution impregnation makes the CEG sheets denser and the resin content in the composite lower. Therefore, the interlamellar spacing of the composites prepared by Method I is the largest in all the composites. Contrarily, because of the highest resin content in the composite obtained by Method II, more resin molecules are infused into the CEG sheets, hence the interlamellar spacing of this kind composite is the lowest. The thicknesses of the graphite ligaments of the composites prepared by Method I and Method III are similar. It indicates that resin molecules prefer the interlayer pores to the diamond pores for the Method I and Method III. Hence the graphite conductive network in the composites has no significant change. Compared with the other composites, Method II makes the thickness of the graphite ligament of the composite increase slightly and the diameter of the diamond pore decrease slightly. It indicates the resin molecules can enter into both the interlayer pores and the diamond pores when the density of the CEG sheet is low. Therefore, the microstructure of the composites prepared by Method II has a little difference with those of the other composites.

3.2. Physical properties of the composites

3.2.1. The thicknesses and the resin contents of the composites

The thicknesses and the resin contents of the composites prepared by three methods are shown in Fig. 7.

3.2.2. Electrical properties of the composites

The variations of the electrical properties of the epoxy/CEG composites with respect to the resin solution concentration are shown in Fig. 8. Fig. 8(a) and (b) shows the in-plane conductivities and the through-plane resistances of the composites, respectively.

For Method I, with the increasing of the resin solution concentration, the in-plane conductivity keeps constant, and the thickness of the composite prepared by Method II increases. The compression step in Method I compresses the CEG sheets to the desired thickness firstly, and the latter steps cannot affect the thickness of the composite, hence the thickness of the composite is constant. The first compression step in Method III can decrease the resin content in the composite to maintain the desired thickness of this kind of composite. For Method II, the increasing resin content in the composite makes the CEG sheet hard to be compressed, and meanwhile the thickness ascends. It indicates that the thin composite is difficult to be obtained in Method II when the resin solution concentration is high.
Fig. 8. The effect of the resin solution concentration on electrical properties of the composites prepared by different methods: (a) in-plane electrical conductivity of the epoxy/CEG composite and (b) through-plane resistance of the epoxy/EG composite.

Fig. 9. The gas permeabilities of the epoxy/CEG composites prepared by different methods.

3.2.3. Gas permeabilities of the composites

The gas permeabilities of the composites prepared by three different methods are shown in Fig. 9. When the resin solution concentration increases, the permeabilities of the composites prepared by Method I and Method III decrease. But for Method II, with the increasing of the resin solution concentration, the permeability decreases firstly and then keeps constant when the resin solution concentration is above 10%.

The permeability of the composite prepared by Method I is the highest in all the composites. The high density of the CEG sheet obtained by the first compression step can inhibit the resin molecules from entering into the pores in the CEG sheet. Hence the largest porosity (Fig. 6(a)) leads to the highest permeability. Only when the resin solution concentration is high (40%), the gas permeability of the composite is lower than $2 \times 10^{-6} \text{cm}^3 \text{cm}^{-2} \text{s}^{-1}$ (Table 1), the basic permeability request for bipolar plate application of Department of Energy (DOE).

The composite prepared by Method II has excellent gas impermeability. Because of the loose and porous structure of the raw CEG sheet, the resin molecules can enter into the pores easily (Fig. 6(c)) to decrease the porosity. The compression step after the impregnation can further reduce the porosity to improve the impermeability of the composite. Except the composite prepared by 5% resin solution, all the other composites can meet the request of the DOE targets (Table 1).

Two compression steps used in Method III can control the resin content in the composite, so the permeability of the composites prepared by Method III is between those of the other composites. When the resin solution concentration is above 20%, the gas permeability can satisfy the basic request of the DOE targets (Table 1).

3.2.4. Mechanical properties of the composites

The relationship between the flexural strength and the resin solution concentration is shown in Fig. 10. For Method I and Method III, the flexural strength increases with the increasing of the resin solution concentration. More resin content which decreases the porosity can improve the flexural strength. When the resin solution concentration is above 25% and 10% respectively, the flexural strength of the composites prepared by Method I and Method III can meet the DOE targets of the bipolar plates (Table 1). Contrarily, the flexural strength of the composite prepared by Method II decreases when the resin solution concentration increases. It could be attributed to the increasing of the thickness of the composites. But all the composites prepared by Method II can meet the DOE targets (Table 1). Hence the Method II can provide the composites with the best flexural strength in the three methods.

3.3. The advantages and disadvantages of the techniques

According to the physical properties and microstructure of the composites, the advantages/disadvantages and the optimum conditions of the technique methods are discussed as follows:

- Method I can provide the thin bipolar plate with excellent electrical properties. The technique process is simple and easy to shape.
But because of the one-time formation in the first step, the low resin content in the composite can affect the mechanical property and the gas impermeability of the composite. Hence for Method I, the high resin solution concentration (40%) is considered to be the optimum condition to prepare the composites which can meet the demands of PEMFC bipolar plates.

Method II can prepare the bipolar plate with outstanding gas impermeability and mechanical property. The technique process is also easy. But the loose and porous structure of raw CEG sheet leads to high resin content in the composite. If resin solution with high concentration is chosen to prepare composite with Method II, the electrical properties and the thickness is hard to meet the basic request for bipolar plate application. Therefore for Method II, the low resin solution concentration (<10%) is considered to be optimum.

Method III can provide the thin bipolar plate with satisfying electrical, mechanical properties and gas permeability. Compared with Method I and Method II, the optimum range of the resin solution concentration is broad for Method III. When the resin solution concentration changes from 25% to 40%, the composites can all reach the demands of PEMFC bipolar plates.

When the optimum conditions are chosen, all these methods above can provide the favorable epoxy/CEG composite bipolar plates which can satisfy the request of PEMFC application. But considering the overall properties, the composite obtained by Method III with 25% resin solution concentration is optimum. It indicates that Method III is the most suitable candidate in the three methods.

3.4. Fuel cell durability testing

200 h performance of the single cell assembled with the optimum composite bipolar plates (Method III, 25% resin solution concentration) is given in Fig. 11. After 200 h testing, no significant performance degradation of the cell is found. The waves which appear at 30, 70, 100, 120, 140 and 180 h are due to the shut-downs in order to fill water into the humidifier.

Fig. 12 shows the I–V performance and resistance of the cell before and after 200 h testing. It is obvious that no evident performance decline of the cell is observed, although the resistance of the cell increases slightly.

The steady performance of the cell indicates that the method of Compression–Impregnation–Compression (Method III) could prepare outstanding composites, which are suitable for the application of the preparation of the PEMFC bipolar plates.

4. Conclusion

Three types of preparation methods of the composite bipolar plates are investigated in this paper. Compression–Impregnation method (Method I) can provide thin bipolar plate with excellent electrical properties at the sacrifice of partial gas impermeability and mechanical property. Contrarily, Impregnation–Compression method (Method II) can prepare the bipolar plate with outstanding gas impermeability and mechanical property, but the electrical properties will decrease partly at the same time. Compression–Impregnation–Compression method (Method III) can provide the thin bipolar plate with excellent electrical, mechanical properties and gas permeability, although two-step compression steps are necessary.

Although having different characteristics, bipolar plates obtained by all the techniques can meet demands of PEMFC application as long as the optimum conditions are selected. For Method I, the high resin solution concentration (40%) is the optimum condition for preparation. For Method II, the low resin solution concentration (<10%) is the optimum range. For Method III, the optimum range of the resin solution concentration is between 25% and 40%.

Considering the overall physical properties of the composites, the epoxy/CEG composite bipolar plate prepared by Method III
25% resin solution concentration is regarded as the most suitable candidate for PEMFCs. The steady 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 PEMFC bipolar plates. The liquid permeability, the stability and the cost of the epoxy/CEG composite bipolar plate in PEMFCs will be focused on in the future works.

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