



Short communication

Surface modification of a natural graphite/phenol formaldehyde composite plate with expanded graphite

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ABSTRACT

Natural graphite/phenol formaldehyde (NG/PF) resin composite plates modified with thin layers of expanded graphite (EG) are fabricated by mold compression to lower the contact resistance between the plates and gas diffusion layers (GDLs). The modification considerably reduces contact resistance versus bare NG/PF plates. The extent of the decrease in contact resistance is influenced by the expanded volume of EG used. A low contact resistance of $1.42 \text{ m}\Omega \text{ cm}^2$ persists for the EG (150 ml g^{-1})-modified NG/PF plates despite the PF content, whereas that of bare plates increases from 3.62 to $17.01 \text{ m}\Omega \text{ cm}^2$ as PF content changes from $5 \text{ wt}\%$ to $30 \text{ wt}\%$. With increasing EG thickness on the surface of NG/PF plates, contact resistance at first decreases and then approaches a constant value when the NG layer exceeds $40 \mu\text{m}$. More importantly, the total electrical resistance, as expressed by volume resistance, can be reduced by applying EG layers to NG/PF composite plates. The reduction of total resistance is more remarkable for the composite plates with high PF content because the bulk resistance of the EG layer can be well compensated by the decrease of contact resistance at a proper range of EG layer thickness.

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1. Introduction

The proton exchange membrane (PEM) fuel cell is attractive as an alternative power source for a wide range of applications owing to its high efficiency, high energy density, and low (or zero) emission of pollutants. A PEM fuel cell stack consists of membrane–electrode assembly (MEA), gas diffusion layer (GDL), bipolar plate, end plate, seal gasket, and so on. The bipolar plate, also known as the flow field plate, is a multifunctional component in a PEM fuel cell stack. It provides electrical connection between the individual cells, distributes reactant gases over the whole active area of the MEA on each side, prevents mixing of fuel and oxidant gases, and participates in water and heat management [1–3].

Several different materials have been used to make bipolar plates for PEM fuel cells [4–7]. Graphite is the most commonly used bipolar plate material. Many PEM fuel cell stack producers have used hard graphite to make bipolar plates because of its high bulk conductivity and resistance to corrosion [8]. But hard graphite is rather brittle, and both the material itself and the machining process required to make flow fields on it are expensive [9]. To avoid the problem of brittleness, many choose flexible graphite to make bipolar plates [10]. Flexible graphite is much cheaper than hard

graphite, and flow fields can be easily processed on it by mold compression. However, flexible graphite is usually less conductive and mechanically weaker.

Many fuel cell researchers are also studying metallic bipolar plates. Metal is a promising candidate owing to its excellent mechanical strength, high electrical conductivity, and good processability. Yet metallic bipolar plates tend to dissolve at the anode and to stain at the cathode [11–13], which will degrade fuel cell performance. Complicated and expensive coating or surface modification is usually needed to allay these problems [14,15].

Another popular choice in making bipolar plates is to use graphite–polymer composite materials, with which bipolar plates can be produced via mold compression or extrusion [16–18]. The combination of graphite and polymer resin offers marked advantages including lower cost, lower weight, higher corrosion resistance, and easier manufacture. However, the insulating polymer resin, which tends to accumulate more at the surface layer of the composite, can cause high contact resistance at the interface of the bipolar plate and GDL [19]. This contact resistance not only increases ohmic loss but also may lead to a large quantity of heat, which affects the stability and working time limit of the fuel cell [20].

In this study, we modified an NG/PF composite plate with expanded graphite (EG) to decrease to the contact resistance. A thin layer of EG was firmly stuck to the surface of an NG/PF composite plate by a simple hot mold compression method. Comparisons

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of contact resistance and other properties of the composite plates before and after EG modification were carried out.

2. Experimental

2.1. Materials

Natural graphite (NG) powder, with $\geq 99\%$ purity and $40\text{-}\mu\text{m}$ average granularity, was supplied by Guyu Graphite Company (Qingdao, China). PF with solidifying agent hexamethylene tetramine was purchased from Tianjin Resin Co. (Tianjin, China). The resin powder has an average grain size of $50\text{ }\mu\text{m}$ and softens at $75\text{ }^\circ\text{C}$. Solidification of the resin begins at $100\text{ }^\circ\text{C}$, the temperature under which hexamethylene tetramine starts to decompose. Graphite intercalated with different amounts of acid was obtained from Yingshida Graphite Co. (Qingdao, China). EG of expanded volume ranging from 45 ml g^{-1} to 300 ml g^{-1} were prepared via the intercalated graphite by heating it at $800\text{ }^\circ\text{C}$ for 15 s in a muffle furnace (SX3-4-13, China). Toray carbon paper (TGP-H-090), representing a common GDL, was used as received.

2.2. Preparation of sample plates

The NG and PF powders were mixed at a given ratio in a rotation cutter/blender (FW80, Huanghua, China) at 10,000 rpm for 2 min. The powder mix was put in a mold and compressed at $150\text{ }^\circ\text{C}$ and 50 MPa for 2 min in a hot pressing machine (DY-60, Tianjin, China). The resultant composite plate is disc shaped with a diameter of 30 mm and a thickness of 2 mm.

To prepare modified composite plates as described in the previous paragraph, except for heating at a lower temperature of $90\text{ }^\circ\text{C}$ to avoid cross-linking of the PF. Modification of the prefabricated plate was realized by evenly laying a given amount of EG powder at the bottom of the mold, placing the prefabricated plate on the EG powder, putting another layer of EG powder on top of the plate, and then hot-pressing at $150\text{ }^\circ\text{C}$ and 50 MPa for 2 min.

2.3. Characterization of sample plates

The measurements on the volume resistance, bulk resistance, and contact resistance of the composite plates were conducted via the DC four-electrode method using a digital resistance meter (YY2511, Tianjin, China). During a measurement, the sample plate, sandwiched between two pieces of carbon paper, was placed between the upper and lower electrodes, which were pressed together by a certain pressure (Fig. 1).

The volume resistance R_v of the sample plate is composed of three parts:

$$R_v = R_b + 2R_g + R_{g,b} \quad (1)$$

where R_b is the bulk resistance of the plate, R_g is the bulk resistance of the carbon paper (GDL), and $R_{g,b}$ is the contact resistance between the GDL and the plate. Therefore, the contact resistance can be obtained by

$$R_{g,b} = R_v - R_b - 2R_g \quad (2)$$

To describe the relative change of volume resistance before and after the surface modification of a composite plate, we define a change rate of volume resistance as

$$\Delta R\% = \frac{R_v - R_{vm}}{R_v} \times 100 \quad (3)$$

where R_{vm} represents the volume resistance after modification. Thus, when $\Delta R\% > 0$, the volume resistance becomes lower after modification and vice versa.

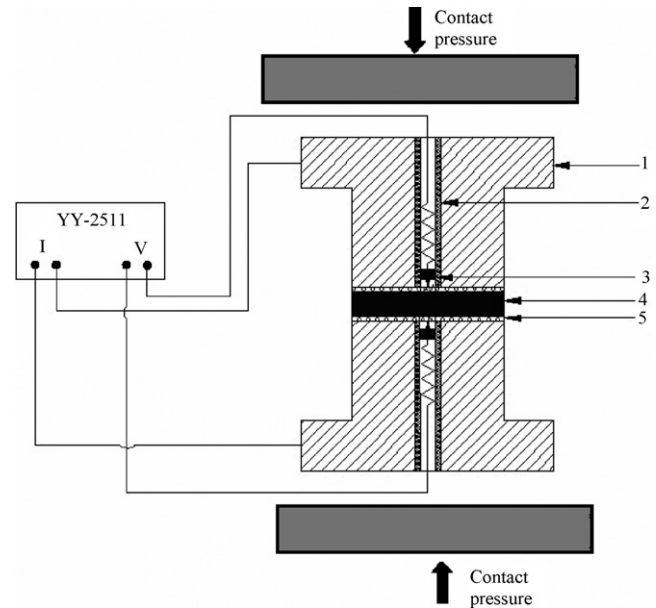


Fig. 1. Four-electrode DC measurement for determination of specific resistance. 1, Cu electrode; 2, isolator; 3, spring probe; 4, sample; 5, carbon paper.

R_{bm} , corresponding to R_b in Eq. (1), is the bulk resistance of composite B, which includes resistance of EG, R_b , and the resistance between EG and composite A. Therefore, the contact resistance between composite B and GDL, $R_{g,bm}$, which corresponds to $R_{g,b}$ in Eq. (1), is

$$R_{g,bm} = R_{vm} - 2R_g - R_{bm} \quad (4)$$

The pressure exerted on the upper and lower electrodes in the electrical resistance measurement was in the range of 0.8–4.8 MPa, under which a PEMFC stack is usually clamped [21].

The resistance to acid corrosion of the composite plates was examined by the potentiostat (Autolab PGSTAT20, Utrecht, The Netherlands). The composite plate to be tested was immersed in $0.01\text{ mol l}^{-1}\text{ H}_2\text{SO}_4$ solution. A conventional three-electrode system was used in the electrochemical measurements. A platinum sheet served as the counterelectrode, a saturated calomel electrode as the reference electrode, and the composite plate as the working electrode. A scanning rate of 1 mV s^{-1} and range from -1 V to 1 V were selected. The corrosion current density was determined via curves of voltage versus current and Tafel fitting by GPES.

The integrity of the modified composite plates was examined by scanning electron microscopy (PHILIPS XL30 ESEM) after immersing the samples in $0.01\text{ mol l}^{-1}\text{ H}_2\text{SO}_4$ solution for 36 h at $80\text{ }^\circ\text{C}$.

The surface wettability of different plates by water was determined via contact angle measurement (JY-82, Chengde, China).

3. Results and discussion

EG modification remarkably decreases contact resistance for different EGs used in our experiments, as shown in Table 1. A maximum reduction to around 37% of the original contact resistance of $3.86\text{ m}\Omega\text{ cm}^2$ was achieved when using EG with expanded volume of 150 ml g^{-1} to modify the composite plate. However, the contact resistance of the modified composite plate varies with the expanded volume of EG and does so in a complex way.

Contact resistance depends not only on the bulk resistances of the two contacting parts but also on the number and area of contacting spots on the interface, or the contact surface, of the two parts. At each contacting spot, so-called constriction resistance

Table 1

Influence of expanded volume of EG on contact resistance and the bulk resistivity of pure EG plate

Expanded volume (ml g ⁻¹)	Contact resistance (mΩ cm ²)	Bulk resistivity (mΩ cm)
–	3.86 ^a	–
45	1.99	21.55
65	2.40	21.79
150	1.42	26.46
250	2.15	35.46
300	2.07	38.31

EG thickness, 0.042 mm; contact pressure, 2.4 MPa.

^a Bare NG/PF composite plate.

arises because of the convergence and divergence of current flow [22]. Mikrajuddin et al. [23] and Kogut and Komvopoulos [24] concluded through theoretical analysis that contact resistance decreases as the number and area of contacting spots at the contact surface increase.

For bare NG/PF composite plate pressed to the GDL, certain parts of the GDL will be in contact with insulating polymer PF, with a probability roughly proportional to the PF content in the composite plate. Such contacting spots will not contribute to the current conduction through the interface of the GDL and the composite plate. With an additional layer of conducting EG at the surface of the NG/PF composite plate after modification, all contacting spots of the GDL and plate are effectively conducting electricity. Besides, the EG layer under pressure is easier to deform than the NG/PF composite material. Therefore, the number and area of contacting spots should be larger for an EG-modified composite plate under the same compression pressure, markedly reducing contact resistance.

To understand the dependence of contact resistance on the expanded volume of EG, we need to notice the change of both physical and mechanical properties at the contact surface when a different EG layer is introduced. The originally loose and porous vermicular EG collapses and deforms when compressed, leaving many closed and half-closed pores of various sizes ranging from nanoscale to microscale [25]. The easy compressibility of the EG layer is attributed to the abundant pores present therein. With EG of larger expanded volume, the resultant EG layer contains more and larger pores and exhibits better compressibility [26]. This will lead to more and larger contacting spots when pressing the EG layer and GDL together, which is good for reducing contact resistance. However, the pores in the EG layer, filled with insulating gas, are barriers for current conduction [27]. Our experiment showed that the bulk resistivity of the EG layer increases with the increase of its expanded volume (Table 1). Therefore, the contact resistance between the EG layer and GDL will increase. We presume that these opposite effects caused by the change of expanded volume result in the complex variation of contact resistance. The lowest contact resistance would correspond to an expanded volume of EG that best balances the compressibility and bulk electrical resistivity of the EG layer.

The effect of contact pressure on the contact resistance of composite plate and GDL was compared under the same thickness conditions as the EG layer (Fig. 2). Higher contact pressure will result in more contacting spots and larger contacting areas. Consequently, the contact resistance decreases as higher contact pressure is exerted.

The variation of contact resistance with the thickness of EG at different contact pressures was also studied. The reduction of contact resistance with increasing EG thickness is sharp when the EG layer is thin. As the EG layer become thicker and thicker, the reduction slows down and eventually stops (Fig. 2). Below a certain thickness, it seems that the deformation of the EG layer is not

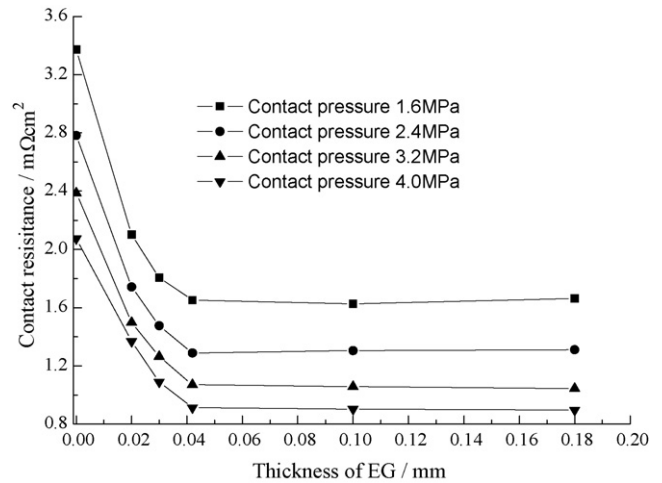


Fig. 2. Influence of EG thickness on contact resistance (PF, 10 wt%; expanded volume, 150 ml g⁻¹).

enough to accommodate a full contact with GDL under a given contact pressure. A thicker EG layer permits larger deformation and better contact. But beyond a certain thickness, 40 μm in our experiments, full contact is realized and further increase in EG thickness makes no improvement.

The ultimate purpose of reducing the contact resistance of the composite plate is to reduce the ohmic losses of a fuel cell stack. Therefore, it is important to study the effect of EG modification on the total resistance of the GDL and composite plate system, which can be expressed by volume resistance as revealed in Eq. (1).

The change rate of volume resistance, $\Delta R\%$, as defined in Eq. (3), as a function of EG layer thickness is shown in Fig. 3. A maximum $\Delta R\%$ is achieved at a moderate thickness of the EG layer. To understand this concept, realize that volume resistance and thus $\Delta R\%$ are affected by both the contact resistance and bulk resistance of the EG-modified composite plate. When the EG layer on the composite plate is thin, $\Delta R\%$ is small because contact resistance improves only slightly. When the EG layer is thick, however, $\Delta R\%$ becomes low again or even becomes negative because the bulk resistance of the EG-modified plate increases linearly with the thickness of the EG layer (Fig. 4), even though the contact resistance is sufficiently reduced. At a moderate thickness of the EG layer, contact

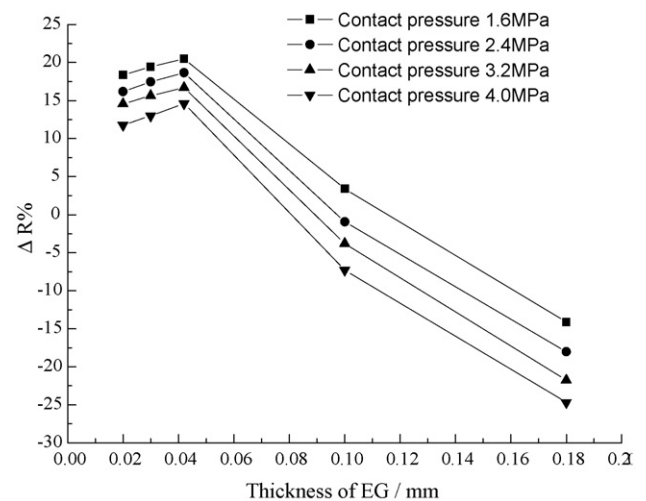


Fig. 3. Influence of EG thickness on change rate of volume resistance (PF, 10 wt%; expanded volume, 150 ml g⁻¹).

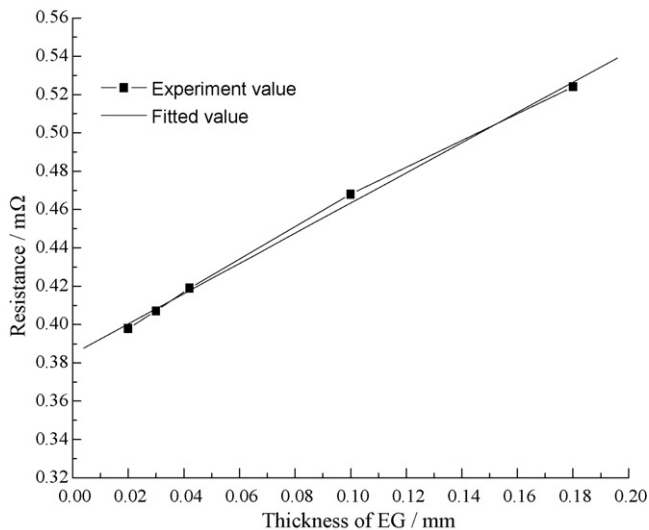


Fig. 4. Influence of EG thickness on bulk resistance of modified plate (PF, 10 wt%; expanded volume, 150 ml g⁻¹).

resistance is greatly reduced and yet the bulk resistance is not high, which results in a maximum $\Delta R\%$.

A noticeable characteristic of the EG-modified NG/PF composite plate is that its contact resistance is not only small in value but is also independent of the PF content (Fig. 5). On the contrary, the contact resistance of the bare NG/PF plate is not only large but also increases strongly with PF content. Actually, the contact resistance for bare NG/PF composite plate increases more rapidly at higher PF content owing to the aggregation of PF resin at the surface of the composite [28]. For application in a PEM fuel cell, high enough PF content in the composite plate is required to ensure good mechanical strength and sufficient blocking of gas permeation. The EG modification method we propose will provide a way of better tailoring the properties of the NG/PF composite plate.

Both R_v and R_{vm} , the volume resistances before and after EG modification as a function of PF content, are shown in Fig. 6. R_{vm} is always smaller than R_v at the whole range of experimented PF content, thanks to the reduction of contact resistance led by EG modification. Moreover, the increase of R_{vm} with PF content is obvi-

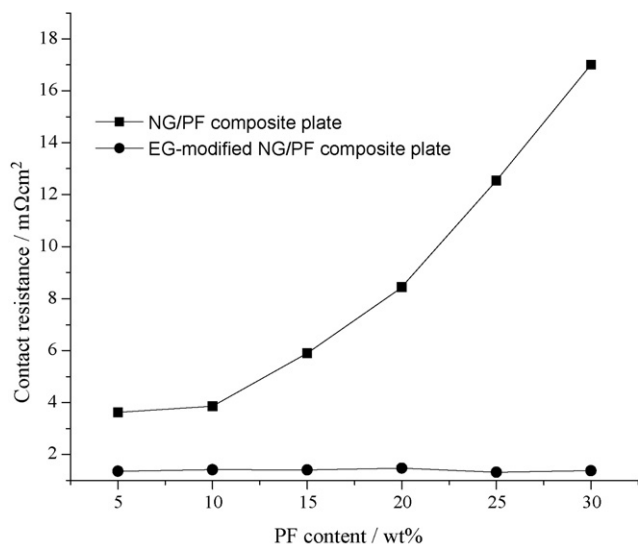


Fig. 5. Influence of PF content on contact resistance (contact pressure, 1.6 MPa; EG thickness, 0.042 mm; expanded volume, 150 ml g⁻¹).

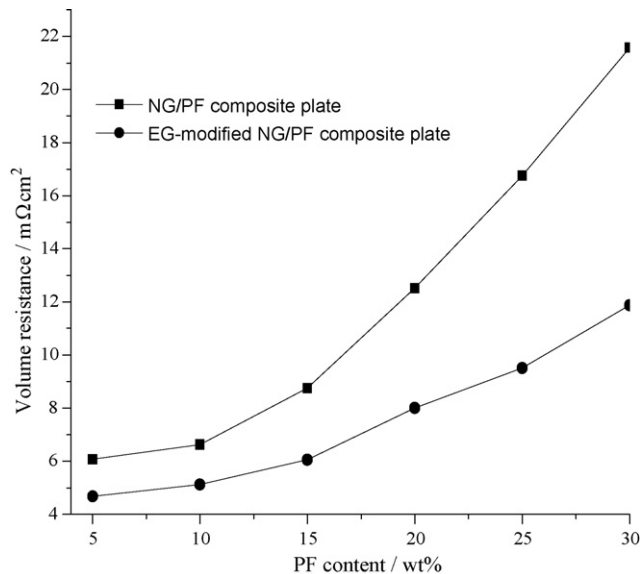


Fig. 6. Influence of PF content on volume resistance (contact pressure, 1.6 MPa; expanded volume, 150 ml g⁻¹; EG thickness, 0.042 mm).

ously slower than that of R_v . That is, the change rate of volume resistance $\Delta R\%$ increases with PF content (Fig. 7). Therefore, the effectiveness of EG modification is more remarkable for the NG/PF composite plate with higher PF content.

Although carbon materials are much better than metal in resisting corrosion in a fuel cell environment, corrosion of the carbon-based flow field plate is still a concern. Therefore, we conducted experiments to compare the corrosion of EG-modified and bare NG/PF plates. As shown in Fig. 8, the polarization curve for the EG-modified NG/PF composite plate consists of two peaks (curve b), whereas that for the single EG plate has only one peak (curve a). The overlapped peaks in curve a and b are due to the corrosion of EG, which exists in both plates. The other peak in curve b is attributed to the corrosion of the NG/PF composite. Through Tafel fitting of the curves, we determine corrosion current densities of 6.3×10^{-4} mA cm⁻² of EG and 2.0×10^{-4} mA cm⁻² of NG/PF, which are well below the 1.6×10^{-3} mA cm⁻² limit set by the U.S.

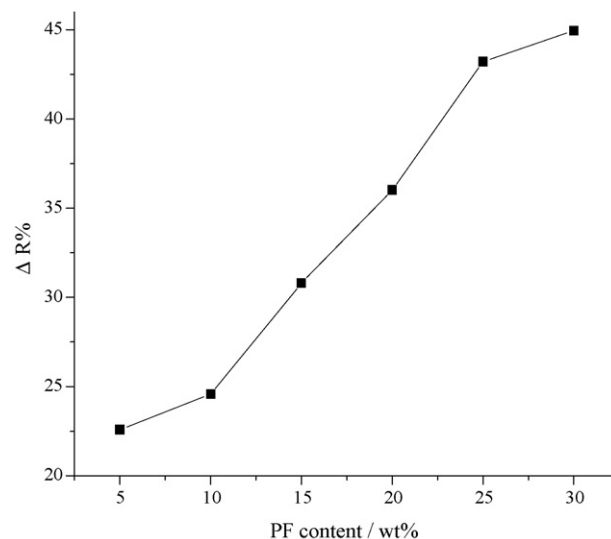


Fig. 7. Influence of PF content on change rate of volume resistance (contact pressure, 1.6 MPa; expanded volume, 150 ml g⁻¹; EG thickness, 0.042 mm).

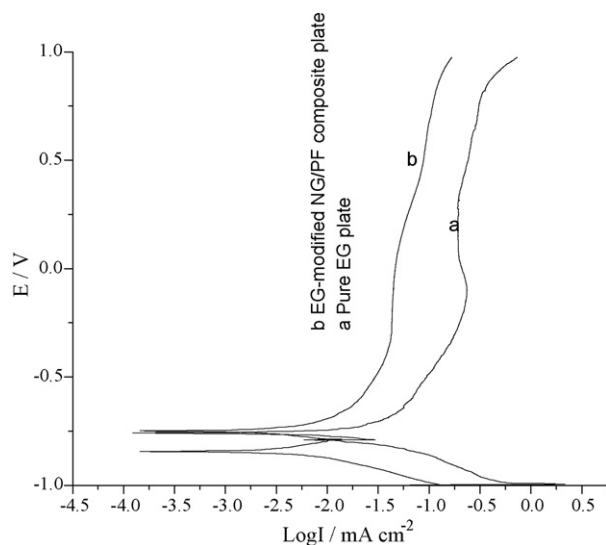


Fig. 8. Polarization curve of (a) modified composite plate (PF, 10 wt%; expanded volume, 150 ml g⁻¹; EG thickness, 0.042 mm) and (b) pure EG plate (EG expanded volume, 150 ml g⁻¹).

Department of Energy for flow field plates [29]. Therefore, the modification of the NG/PF composite plate with EG does not impair its suitability for fuel cell application in corrosion concerns.

The water contact angle at the surface of the EG-modified NG/PF composite plate was approximately 95°. This value is consistent with measurements on similar EG materials. The hydrophobic nature of the EG-modified plate is propitious to the removal of liquid water from its surface, which is important for water management in PEM fuel cells, especially at the cathode side [30]. To test whether the EG layer would stick to the NG/PF surface stably under fuel cell environment conditions, we immersed the EG-modified composite plate in 0.01 mol l⁻¹ H₂SO₄ solution for 36 h at 80 °C and observed any changes of the plate via scanning electron microscopy. We found no tearing or other damage from the surface and cross-section views of the samples.

4. Conclusions

We modified an NG/PF composite plate with EG by using a simple and inexpensive mold compression technique. Marked reduction of electrical contact resistance and volume resistance can be achieved when choosing EG with proper expanded volume and moderate thickness. The modified composite plate exhibits satis-

factory corrosion resistance, and the EG layer sticks to the NG/PF substrate stably in a simulated PEM fuel cell environment. Our method for modifying the NG/PF composite plate provides a way of better tailoring the properties of a carbon composite bipolar plate for PEM fuel cell application.

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References

- [1] J.H. Huang, D.G. Barid, J.E. McGrath, J. Power Sources 150 (2005) 110–119.
- [2] V. Mehtar, J.S. Cooper, J. Power Sources 114 (1) (2003) 32–53.
- [3] A. Kravtsov, M. Auinat, Y. Ein-Eli, J. Power Sources 164 (2) (2007) 697–703.
- [4] H. Tawfik, Y. Hung, D. Mahajan, J. Power Sources 163 (2) (2007) 755–767.
- [5] S. Radhakrishnan, B.T.S. Ramanujam, A. Adhikari, S. Sivaram, J. Power Sources 163 (2) (2007) 702–707.
- [6] L.N. Song, M. Xiao, Y.Z. Meng, Compos. Sci. Technol. 66 (13) (2006) 2156–2162.
- [7] A. Hermann, T. Chaudhuri, P. Spagnol, Int. J. Hydrogen Energy 30 (12) (2005) 1297–1302.
- [8] R. C. Emanuelson, W. L. Luoma, W. A. Taylor, US Patent, 4,301,222, (1981).
- [9] R.C. Makkus, A.H.H. Janssen, F.A. Brujin, R. Mallant, Fuel Cells Bull. 3 (17) (2000) 5–9.
- [10] O. Ottinger, J. Bacher, W. Langer, US Patent, 6,746,771 (2004).
- [11] S. Joseph, J.C. McClure, R. Chianelli, P. Pich, P.J. Sebastian, Int. J. Hydrogen Energy 30 (12) (2005) 1339–1344.
- [12] D.R. Hodgson, B. May, P.L. Adcock, D.P. Davies, J. Power Sources 96 (1) (2001) 233–235.
- [13] M.C. Li, C.L. Zeng, S.Z. Luo, J.N. Shen, H.C. Lin, C.N. Cao, Electrochim. Acta 48 (12) (2003) 1735–1741.
- [14] C.-Y. Liao, S.-K. Chen, P.-J. Chiu, M.-H. Chang, T.-T. Hung, T.-H. Ko, J. Power Sources 176 (1) (2008) 276–281.
- [15] Y.J. Ren, C.L. Zeng, J. Power Sources 171 (2) (2007) 778–782.
- [16] H.-C. Kuan, C.-C.M. Ma, K.H. Chen, S.K. Chen, J. Power Sources 134 (1) (2004) 7–17.
- [17] E.A. Cho, U.S. Jeon, H.Y. Ha, S.A. Hong, I.-H. Oh, J. Power Sources 125 (2) (2004) 178–182.
- [18] T.M. Besmann, J.W. Klett, J.J. Henry, E. Lara-Curzio, J. Electrochem. Soc. 147 (2000) 4083–4086.
- [19] Z.H. Liu, Y.X. Wang, Chin. J. Mater. Res. 19 (6) (2005) 651–656.
- [20] R. Guenter, B. Sven, CFI-Ceram. Forum Int. 82 (4) (2005) E33–E36.
- [21] A. Heinzl, F. Mahlendorf, O. Niemi, C. Kreuz, J. Power Sources 131 (1–2) (2004) 35–40.
- [22] R. Holm, Electrical Contacts, 4th ed., Springer, New York, 1967, pp. 9–16.
- [23] A. Mikrajuddin, F.G. Shi, H.K. Kim, K. Okuyama, Mater. Sci. Semicond. Proc. 2 (4) (1999) 321–327.
- [24] L. Kogut, K. Komvopoulos, J. Appl. Phys. 94 (5) (2003) 3153–3162.
- [25] W. Jia, R. Tchoudakov, M. Narkis, Polym. Compos. 26 (4) (2005) 526–533.
- [26] J.L. Gu, Y. Gao, New Carbon Mater. (China) 16 (1) (2001) 53–58.
- [27] J.L. Gu, W.Q. Cao, W.C. Shen, Y.J. Liu, Carbon (China) 3 (1996) 1–6.
- [28] Z.H. Liu, L. Xu, Y.X. Wang, J. Chem. Ind. Eng. (China) 57 (2) (2006) 403–408.
- [29] R.P. Biswa, G.R. Ramana, J. Power Sources 153 (1) (2006) 125–129.
- [30] X.Q. Yan, M. Hou, H.F. Zhang, F.N. Jing, P.W. Ming, B.L. Yi, J. Power Sources 160 (1) (2006) 252–257.