

Performance of an aluminate cement /graphite conductive composite bipolar plate

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Received 10 November 2005; received in revised form 18 December 2005; accepted 20 December 2005
Available online 3 February 2006

Abstract

Aluminate cement/graphite conductive composite bipolar plates were prepared by mould pressing at room temperature. The effects of the graphite content, the mould pressing pressure and mould pressing time on the electrical conductivity and the flexural strength of composite are discussed. The electrical conductivity and the flexural strength of the composite bipolar plates with 60 wt.% graphite content, prepared with a mould pressing pressure of 5 MPa for 10 min, is $>100 \text{ S cm}^{-1}$ and 20 MPa, respectively and can be improved by optimizing the mould pressing conditions, especially mould pressing time. The water content of the composite bipolar plate with different graphite contents was also investigated. The water content of the composite bipolar plate is about 6 wt.% with a graphite content of 60 wt.%. This composite bipolar plate contains capillary pores and has hydrophilicity, which is different from other composite bipolar plates. Therefore, it possesses an inner humidifying function and can use the water produced at the cathode for humidifying the proton exchange membrane during the operation of a PEMFC. In addition, the H_2 permeability of the composite bipolar plate is low.

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Keywords: Graphite; Aluminate cement; Mould pressing; Fuel cell; Bipolar plate

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is a very promising power source for residential and mobile applications with attractive features such as high power density, relatively low operating temperature, convenient fuel supply, long lifetime, etc. [1]. In spite of those advantages, commercialization of the PEMFC has been delayed mainly due to high fabrication cost. Among the PEMFC components, the bipolar plate, for which PocoTM graphite with machined flow channels is the most commonly used, accounts for as much as 60% of the stack cost [2]. Hence, for widespread commercialization of the PEMFC, cost reduction of the bipolar plate is necessary. A composite bipolar plate [3–6] is a promising alternative to PocoTM graphite plate, and has the advantages of low cost, ease in machining and low weight. It is usually prepared using polymers as adhesives and graphite, carbon powder, carbon nanotube

as the conductive fillers and is fabricated by mould pressing [7,8].

In addition, because the NafionTM membrane of the Dupont Company is used in PEMFCs extensively, it is essential to humidify the membrane in the course of operation. Humidifying through external equipment is generally adopted at present, which increases the volume of the fuel cell stack [9]. So, it is a considerable direction to humidify the NafionTM membrane through internal equipment, for example, changing the materials or structure of bipolar plate to give it an humidifying function [10,11]. In this way, the volume and weight of the fuel cell stack can be reduced and it can be integrated.

A aluminate cement [12,13], which is a special type of cement, is widely used as a gel material in concrete and is commercially available. It has a high mechanical strength and can be pulled off a mould easily after solidifying. It can resist acid corrosion because its hydration product has some calcium hydrate. Furthermore, gel capillary pores can form in the concrete in the course of solidification. In this paper, we selected the aluminate cement as the adhesive and graphite as the conductive filler to prepare the hydrophilic conductive composite. We plan to use it

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as the bipolar plate of a fuel cell, which can keep the water in the cooling flow channel or create water in the course of reaction to humidify the membrane of the fuel cell. Papers reporting this approach are not seen in the literature up to the present.

2. Experimental

2.1. Materials

Aluminate cement, having a primary chemical composition of Al_2O_3 (52.3%), CaO (34.7%), was purchased from the special cement factory of Zhengzhou, PR China.

Graphite powder, with a purity of 99.85%, was purchased from the colloid chemical factory of Shanghai, PR China.

The water used was distilled water.

2.2. Composites preparation

Aluminate cement and graphite were mixed evenly in the beaker. Then water was added with 30 min stirring. The mixture was mould pressed adopting a suitable mould and a simple pressure machine at room temperature. Finally, the sample was pulled off the mould and placed for 7 days in 100% relative humidity.

2.3. Measurements of performance

The electrical resistance (R) of composite samples was measured using a TH2512 type testing apparatus for low resistance of direct current (Changzhou). The average electrical resistance of each sample was obtained from three repeated measurements at different locations on the sample. The resistivity (ρ) was calculated as: $\rho = R \times W \times T/L$ and the conductivity (σ) was calculated as: $\sigma = 1/\rho = L/W/T/R$, where L , W and T are length, width and thickness of the sample, respectively.

The flexural strength of composite samples was investigated using an Instron 5548 micro tester. The width and thickness of the samples were 5 and 2.5 mm, respectively. The adjusted span was 22 mm. The rate of displacement was 0.5 mm min^{-1} .

The section morphology of composite samples was analyzed by a JSM-5610LV type scanning electron microscope (SEM).

3. Results and discussion

3.1. The effect of graphite content on the conductivity of the composite bipolar plate

Keeping the quantity of aluminate cement and water constant and changing the content of graphite, the conductive composites were prepared by using a mould pressing pressure of 5 MPa and mould pressing time of 10 min, and their conductivities were measured (Fig. 1). It can be seen from Fig. 1 that the conductivity of the composite is certain to increase with the increase in the content of graphite and there is no abrupt turning point of the curve.

The above result of the conductivity of composites containing a large quantity of conductive fillers is different from that

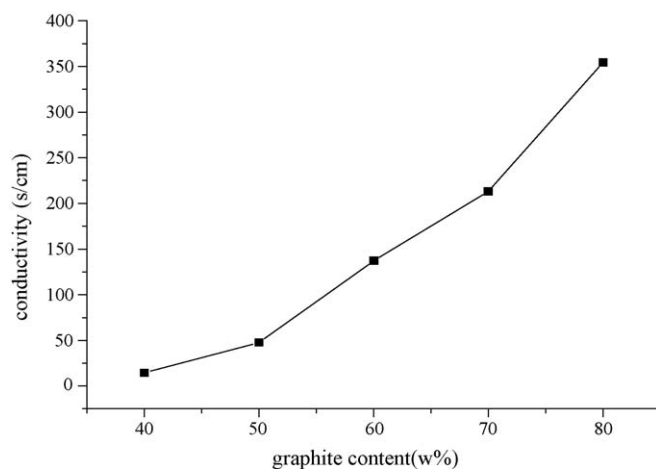


Fig. 1. Effect of graphite content on conductivity.

of composites containing a small quantity of conductive fillers. To composites containing a small quantity of conductive fillers, many experimental results showed that the conductivity of composites do not increase linearly with the increase of the content of graphite, but the conductivity has a increase of several orders of magnitude when the quantity of graphite attains a critical point (percolation threshold). At this critical point, the graphite particles in the composite form a conductive net and the composites transition from insulator to conductor. There is no abrupt turning point on the curve. For composites containing a large quantity of conductive fillers, because the conductive net in the composite has been formed and only the density of the conductive net increases with the increase of graphite, the conductivity of the composite has no abrupt turning point with the increase of graphite.

According to the target value from the American Department of Energy, the conductivity of a bipolar plate in a PEMFC should be greater than 100 S cm^{-1} , so the content of graphite of this composite must be up to 60 wt.%.

The sectional morphology of a composite containing 55 wt.% graphite was investigated by scanning electron microscope (Fig. 2). In Fig. 2, the needles are $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ (C_2AH_8), which is a hydration product of the aluminate cement, and the flaky part is graphite. We can find that the hydration reaction of the aluminate cement is not very complete and there is no hydration reaction aluminate in the composite, which need to be more carefully studied in future experiments. But it has little influence on the formation of the graphite conductive net, so the conductivity of this composite is relatively high.

3.2. The effect of mould pressure on the conductivity of the composite bipolar plate

When the content of the graphite particle is 60 wt.% and mould pressing time is 10 min, the effect of the mould pressing pressure on the conductivity of composite was investigated. The experimental result is shown in Fig. 3, under the pressure of 2.5–7.5 MPa, with the mould pressing pressure increasing, the conductivity of composite increases sharply. On the one

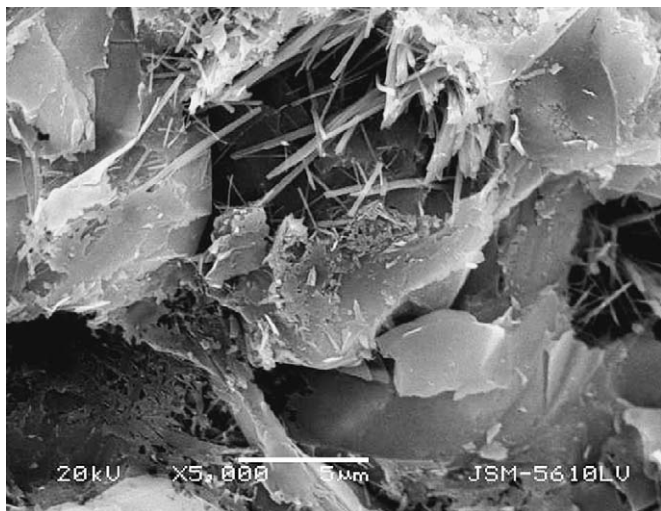


Fig. 2. SEM photographs of composites.

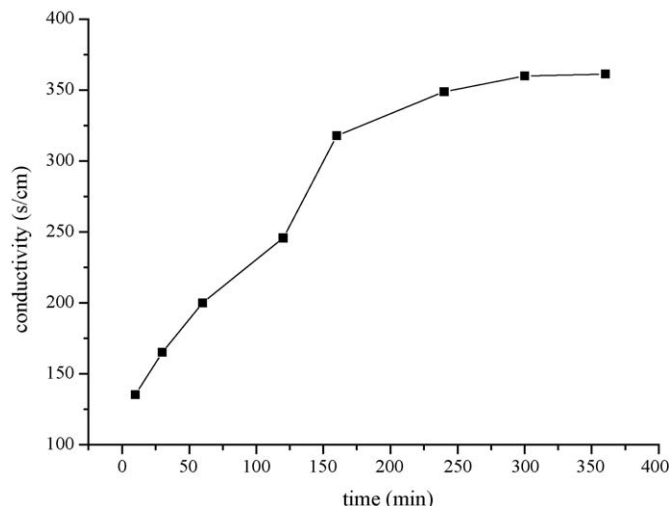


Fig. 4. Effect of mould pressing time on conductivity.

hand, with the increase of the pressure, the quantity of the gel capillary pores in the composite decreased; On the other hand, the contact resistance between the graphite particles decreased also. The contact resistance greatly influences the conductivity of composite. Therefore, with the increase of mould pressure, the contact resistance between two graphite particles decreased and the conductivity of composite increased. But when the pressure reaches 8 MPa, the conductivity of the composite has no obvious change except a small fluctuation with the increase of the pressure. According to the experimental results, 10–12 MPa was selected as mould pressure.

3.3. The effect of mould pressing time on the conductivity of composite bipolar plate

For a content of the graphite of 60 wt.% and a mould pressure of 5 MPa, the effect of mould pressing time on the conductivity of composite was investigated. The experimental results are shown in Fig. 4. During a mould pressing time of 10–240 min,

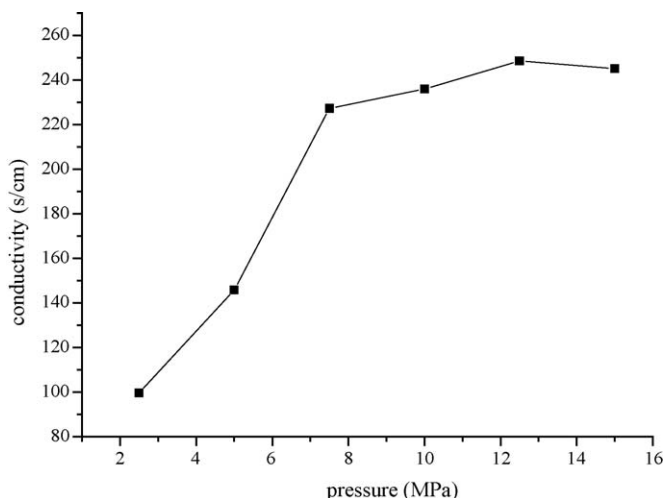


Fig. 3. Effect of mould pressing pressure on conductivity.

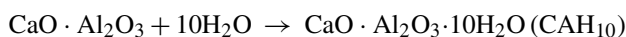
with increase in pressing time, the conductivity of the composite increased linearly. On the one hand, when prolonging the mould pressing time, under a certain pressure, the quantity of pores that form in the course of the aluminates cement hydration will decrease and the compactness of composite improved. On the other hand, prolonging the mould pressing time was favorable for the direct contact of graphite particles. These all make the conductivity of the composite increase. A mould pressing time of 300 min does not increase the conductivity any more.

It also can be seen from Figs. 3 and 4 that for the composite with a 60 wt.% graphite content under the preparation conditions of: mould pressure of 5 MPa and mould pressing time of 10 min, prolonging the mould pressing time increases the conductivity of the composite more than increasing the mould pressing pressure. The conductivity of the composite can only increase 71% by increasing the mould pressing pressure and an increase of 150% was obtained by prolonging the mould pressing time. Considering the production cycle time of mould pressing a bipolar plate, the conductivity and the water content of the composite, the optimum mould pressing time needs to be investigated more in future experiments.

3.4. The effect of graphite content on the flexural strength of the composite bipolar plates

Conductive composites were prepared with a mould pressure of 5 MPa and a mould pressing time of 10 min, and the effect of the graphite content on the flexural strength of the composite bipolar plate was investigated (Fig. 5). It can be seen from Fig. 5 that the flexural strength of the composite decreases with increase in the graphite content.

A primary composition of the aluminates cement is calcium $\text{CaO} \cdot \text{Al}_2\text{O}_3$, (CA). The primary hydration reaction of CA at room temperature is



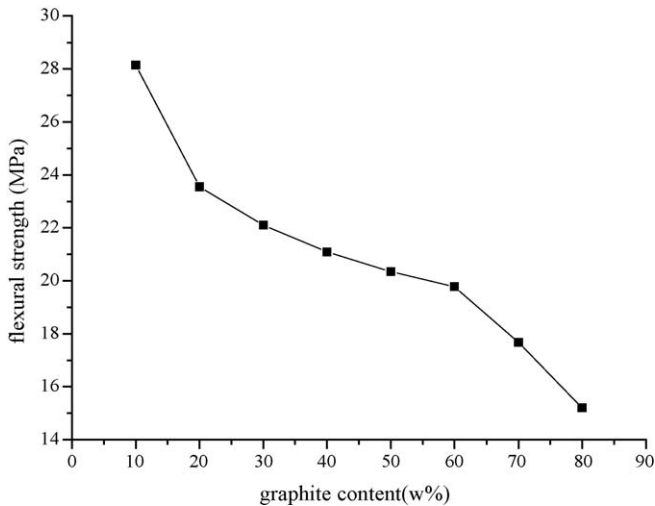
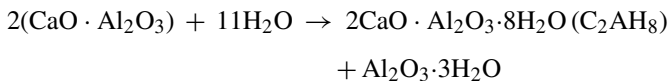


Fig. 5. Effect of graphite content on flexural strength.



Because the mutual penetration and crossover of the hydration product are flake crystal CAH_{10} and needle crystal C_2AH_8 , aluminate cement/graphite conductive composites have good mechanical strength. When the graphite content of this composite is 60 wt.%, the flexural strength of the composite is 20 MPa while the flexural strength of Poco™ graphite bipolar plate can attain 45 MPa. However, this aluminate cement/graphite conductive composite bipolar plate should be not broken under the normal cell assembling and operating conditions [4].

3.5. The effect of mould pressing pressure on the flexural strength of composite bipolar plate

For a content of graphite of 60 wt.% and a mould pressing time of 10 min, the effect of the mould pressure on the flexural strength of the composite was investigated. The experimental result is shown in Fig. 6. With increase of pressure, the quantity of the pores among the graphite particles decreased and the adhesion between the hydration products of the aluminate cement and the graphite became stronger. Consequently, the flexural strength of composite bipolar plate increased as the mould pressure increased. However, the flexural strength of composite bipolar plate could only increase 3 MPa from 21 MPa (at a pressure of pressure 5 MPa) to 24 MPa (at a pressure of 10 MPa).

3.6. The effect of mould pressing time on the flexural strength of composite bipolar plate

For graphite 60 wt.% and a mould pressure of 5 MPa, the effect of mould pressing time on the flexural strength of the composite was investigated. The experimental results are shown in Fig. 7, when prolonging the mould pressing time under a certain pressure, the hydration reaction of the aluminate cement

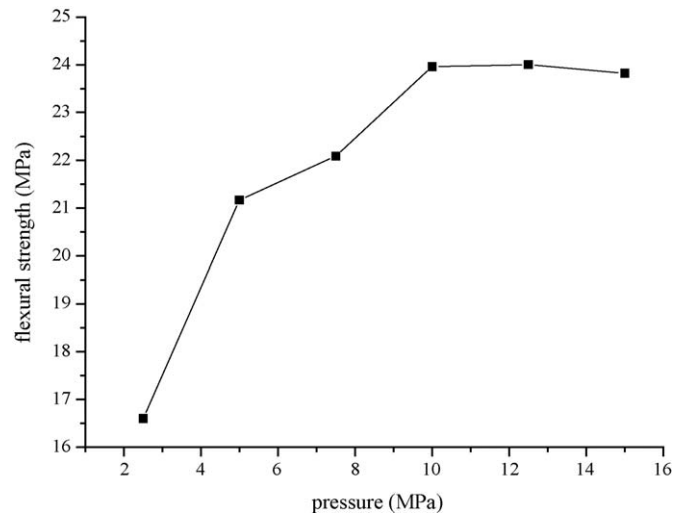


Fig. 6. Effect of mould pressing pressure on flexural strength.

occurred under a certain pressure. So it was favorable for hydration products of the aluminate cement to blend with graphite particles and the compactness of the composite was also improved. Consequently, the flexural strength of the composite bipolar plate increased as the mould pressing time increased. The flexural strength of the composite bipolar plate can increase 7 MPa from 21.5 MPa (for a time of 10 min) to 28.5 MPa (for a time of 160 min).

3.7. The water content and hydrophilicity of the composite bipolar plate

After cooking a sample in water of 80 °C for an hour, the wet weight of the sample was measured. After baking this sample in oven at 80 °C for 2 h, the dry weight of the sample was measured. The difference between the wet weight and the dry weight is the water content of this sample. The average water content of each sample was obtained from three repeated mea-

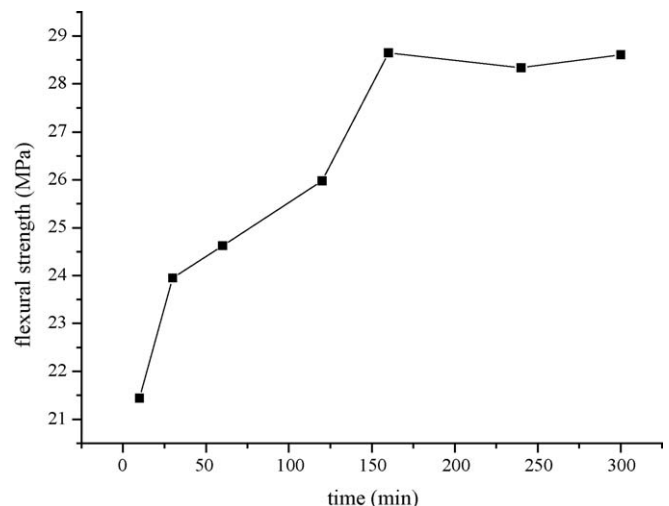


Fig. 7. Effect of mould pressing time on flexural strength.

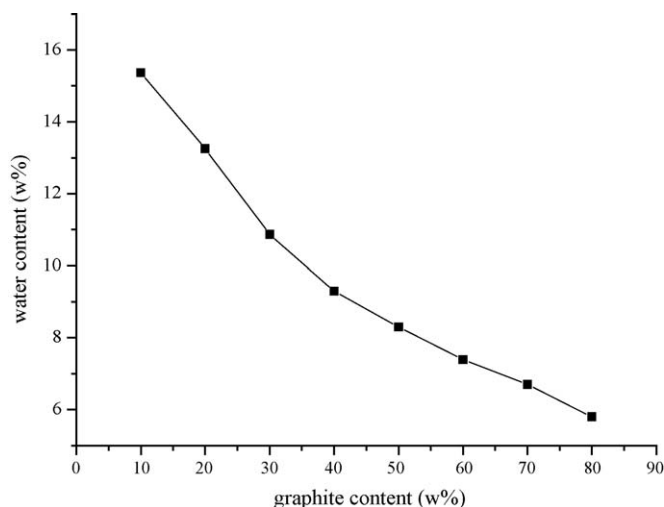


Fig. 8. Effect of graphite content on water content.

surements. The experimental results are shown in Fig. 8. With the content of graphite increasing, the water content decreased gradually. When the content of graphite was greater than 60 wt.%, the water content of the composite bipolar plate was about 6 wt.%. Whereas, the water content of the composite bipolar plate which was prepared using a polymer organic adhesive was almost 0 wt.%. The basic reason why these composites have a water-retaining property is that the hydration products of the aluminate cement can form gel capillary pores in the composites during hydration and solidification.

The surface water contact angle of the composite was also investigated by a CA-XP150 Contact Angle Meter from Consonance Interface Co. Ltd. of Japan. The surface water contact angle of the composite with 60 wt.% graphite content was about $73^\circ (<90^\circ)$, which indicates that this composite bipolar plate has hydrophilicity.

This composite bipolar plate has hydrophilicity and contains capillary pores, which is different from other composite bipolar plates.

It has hydrophilicity, which can save the water produced at the cathode during the PEMFC operating [5]. This not only can prevent the accumulation of water on the cathode side, flooding catalyst, but it also can promote the distribution of water throughout the bipolar plate. As a result, the water contacting this composite bipolar plate material has the tendency of forming a film rather than droplets on the surface of the plate. In the presence of water throughout the plate, the potential coming from the mixture of the reactant gases across the bipolar plate is substantially reduced [10].

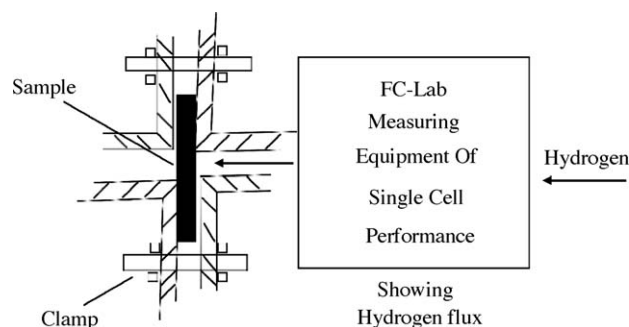


Fig. 9. the schematic drawing of testing H_2 permeability of composite bipolar plate.

In addition, negative pressure on the surface of the bipolar plate possibly comes into being due to consuming of the reactant gases while the PEMFC operates, so the water in the capillary pores of the bipolar plate can release from this composite bipolar plate and humidify the reactant gases. Or, if the pressure difference, which can be obtained by adjusting reactant gases pressure, is well applied across the bipolar plate, and if the capillary pores in the bipolar plate are connected, water can be transported from the cathode side of the bipolar plate to the anode side by capillarity action [14], which can only humidify the hydrogen while the PEMFC operates.

3.8. The H_2 permeability of the composite bipolar plate

The H_2 permeability of composite bipolar plate was examined by FC-Lab of Electro Chem. Inc., USA. Fig. 9 shows a schematic drawing of the testing for H_2 permeability of a composite bipolar plate. The sample was not placed into the setting and the vent was closed, the H_2 flux was recorded on the condition of a stable H_2 pressure. In the same way, the H_2 flux was also recorded when the sample was placed into the setting. The H_2 permeability of the composite bipolar plate was calculated by the H_2 flux difference between the above two experiments. The experimental sample is a round sample of diameter 3 cm. The testing results are shown in Table 1.

It can be seen from Table 1 that the H_2 flux difference between the experiments with no sample and experiments with sample is small and the H_2 permeability is 10^{-4} to $10^{-5} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$. Although there are capillary pores in this composite bipolar plate, the capillary pore sizes are very small and there is water in the capillary pores. So, the H_2 permeability is low for low H_2 pressure and the single cell performance with this composite bipolar plate can be measured by the FC-Lab from Electro Chem. Inc., USA. The potential decline resulting from the mixture of

Table 1
Testing result of H_2 permeability of composite bipolar plate

Graphite content of sample (wt.%)	H_2 pressure (Psi)	H_2 flux (no sample) ($\text{cm}^3 \text{ min}^{-1}$)	H_2 flux (sample) ($\text{cm}^3 \text{ min}^{-1}$)	H_2 permeability ($10^{-5} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$)
50	10	6.37	6.40	7.08
60	10	6.35	6.37	4.72
50	25	13.45	13.56	25.95
60	25	13.34	13.44	23.60

the reactant gases across the bipolar plate can be ignored. The single cell performance with this composite bipolar plate will be reported in the future.

4. Conclusions

With an aluminate cement as the adhesive and graphite as the conductive filler, aluminate cement/graphite conductive composite bipolar plates were prepared by a mould pressing method at room temperature. The conductivity of the composite bipolar plate can reach 100 S cm^{-1} and meet the requirement for conductivity of the bipolar plate in a PEMFC when the graphite content is greater than 60 wt.%. The flexural strength of the composite bipolar plate with 60 wt.% graphite content is 20 MPa and is lower than that of a PocoTM graphite bipolar plate (45 MPa). The electrical conductivity and the flexural strength of this composite bipolar plate can all be improved by optimizing the mould pressing conditions, especially the mould pressing time.

This composite bipolar plate has hydrophilicity and contains capillary pores, which is different from other composite bipolar plates. The water content can reach 6 wt.%. On the one hand, it can save water produced at the cathode, which can prevent the accumulation of water on the cathode side and flooding of the catalyst. On the other hand, it possesses an inner humidifying function. That is to say that the water in the capillary pores of the bipolar plate can release from this composite bipolar plate and humidify the reactant gases while the PEMFC operates.

References

- [1] S. Srinivasan, Fuel cells for extraterrestrial and terrestrial applications, *J. Electrochem. Soc.* 136 (1989) 41.
- [2] K.S. Dhathathreyan, P. Sridhar, G. Sasikumar, Development of polymer electrolyte membrane fuel cell stack, *Int. J. Hydrogen Energy* 24 (11) (1999) 1107–1115.
- [3] Hsu-Chiang Kuan, Chen-Chi M. Ma, Ke Hong Chen, Preparation, electrical, mechanical and thermal properties of composite bipolar plate for a fuel cell, *J. Power Sources* 134 (2004) 7–17.
- [4] E.A. Cho, U.-S. Jeon, H.Y. Ha, et al., Characteristics of composite bipolar plates for polymer electrolyte membrane fuel cells, *J. Power Sources* 125 (2004) 178–182.
- [5] A. Heinzl, F. Mahlendorf, O. Niemi, C. Kreuz, Injection moulded low cost bipolar plates for PEM fuel cells, *J. Power Sources* 131 (2004) 35–40.
- [6] Allen Hermann, Tapas Chaudhuri, Priscila Spagnol, Bipolar plates for PEM fuel cells: A review, *Int. J. Hydrogen Energy* 30 (2005) 1297–1302.
- [7] F. Barbir, J. Braun, J. Neutzler, Properties of molded graphite bipolar plates for PEM fuel cell stacks, *J. New Mater. Electrochem. Syst.* 2 (1999) 197–200.
- [8] J. Braun, J.E. Zabriskie Jr., J.K. Neutzler, M. Fuchs, R.C. Gustafson, Fuel Cell Collector Plate and Method of Fabrication, US 6,180,275 (30 January 2001).
- [9] Buchifn, S. Srinivasan, Operating proton exchange membrane fuel cells without external humidification of the reactant gases: fundamental aspects, *J. Electrochem. Soc.* 144 (8) (1997) 2767–2772.
- [10] Gerald J. Koncar, Leonard G. Marianowski, Proton exchange membrane fuel cell separator plate, US 5,942,347 (24 August 1999).
- [11] S. Miachon, P. Aldebert, Internal hydration H_2/O_2 100 cm² polymer electrolyte membrane fuel cell, *J. Power Sources* 56 (1995) 31–36.
- [12] Li Li-yin, Characteristics and application of aluminate cements, *J. Luoyang Technol. College*, PR China 11 (1) (2001) 9–11.
- [13] Zhou Mei, Liu Ceng-dan, Zhao Jia-zhen, Research of the application of alumina cement and concrete, *J. Fuxin Mining Inst.*, PR China 14 (4) (1995) 94–98.
- [14] Carl Reiser, Glastonbury, conn. Ion exchange membrane fuel cell power plant with water management pressure differentials, US 5,853,909 (29 December 1998).