

Short communication

Aluminate cement/graphite conductive composite bipolar plate for proton exchange membrane fuel cells

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Abstract

Aluminate cement/graphite conductive composite bipolar plate for proton exchange membrane fuel cells (PEMFC) was prepared by mold pressing at room temperature. The effect of size of graphite particles on the conductivity and the flexural strength of composite bipolar plate were discussed. Resistance to acid corrosion, thermal property and pore size distribution of this composite bipolar plate were also investigated in this paper. The experiment results show that the conductivity and the flexural strength of this composite bipolar plate can be improved by choosing uniform size graphite as conductive fillers. The corrosion current is about $10^{-4.5}$ A cm⁻² from polarization curves of this composite bipolar plate, which shows that this composite bipolar plate is acid corrosion-resistant. Al and Ca ions may leach from this composite bipolar plate after 1 M H₂SO₄ acid corrosion. But Al and Ca ions leaching from this composite bipolar plate are only a little percentage of the total Al and Ca ions content in the composite bipolar plate after acid corrosion at 30 °C. This composite bipolar plate is also thermally stable from room temperature to 400 °C. The large amount of pore in this composite bipolar plate is gel capillary pores because of the hydration and solidification of aluminate cement, which make it possess humidifying function during the PEMFC operating.

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1. Introduction

The performance of machined graphite bipolar plate is excellent and it is adopted extensively in the construction of proton exchange membrane fuel cell (PEMFC). However, its manufacturing technology is relatively complicated and, especially, its flow channels can be only machined, so its cost is very high and account for about 45% of fuel cell stack cost [1]. The US Department of Energy (DOE) requires that the cost of a fuel cell stack system must be reduced from US\$ 800 to US\$ 35 kW⁻¹ to become a commercial success in automobile use. Other stack designs consider the use of metal hardware such as stainless steel [2]. However, a number of disadvantages are also associated with stainless steel, including high cost of machining and especially possible corrosion in the fuel cell environment, which is very difficult to be resolved at present.

In the light of these difficulties, much of the recent work on fuel cell bipolar plate materials has concentrated on a molded composite graphite bipolar plate [3–7], which offer the potential advantages of lower cost, lower weight and greater ease of manufacture than traditional graphite bipolar plates, for instance, flow fields can be molded directly into these composites. So, a molded composite graphite bipolar plate is inexpensive and performs as well as machined graphite bipolar plates.

In addition, because NAFION membrane of DUPONT Company is used in PEMFC extensively, it is very essential to humidify the membrane in the course of operating the PEMFC. Humidifying through external equipment is generally adopted at present, which increase the volume and the cost of the fuel cell stack directly [8]. So, it is a considerable direction to humidify the NAFION membrane through internal equipment. In recent years, world wide research efforts have been addressed to remove the externally humidifying unit from the PEMFC system by endowing the membrane electrode assembly (MEA) with self-humidifying ability [9]. Differently, Institute of Gas

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Technology and International Fuel Cells give bipolar plate self-humidifying function by changing the materials or structure of bipolar plate [10,11]. In this way, the volume and weight of the fuel cell stack can be reduced and it is favorable to be integrated.

So, aluminate cement/graphite composite bipolar plate, which has self-humidifying function, have been developed in our laboratory.

2. Experimental

2.1. Materials

Aluminate cement/graphite composite bipolar plates were prepared according to literatures [12]. The flow fields were carved using numerical control (NC) machine tool of Beijing Carving Technological Co. Ltd. The sample pictures are shown in Fig. 1. All the conductive composite bipolar plates were not broken during machining flow fields. The flow channels are very clear and the ridges of flow fields don't collapse.

2.2. Measurements of conductivity

The electrical resistance (R) of composite samples was measured using a TH 2512 type testing apparatus of 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: $\rho = RWT/L$ and the conductivity (σ) was calculated as: $\sigma = 1/\rho = L/WTR$, where L , W and T are length, width and thickness of the sample, respectively. The contact resistance between bipolar plates and gas diffusion layer (GDL) in PEM fuel cells is also very crucial, which will be tested in the future experiments.

2.3. Measurements of flexural strength

The flexural strength of composite bipolar plates was investigated by Instron 5548 micro tester. The width and thickness

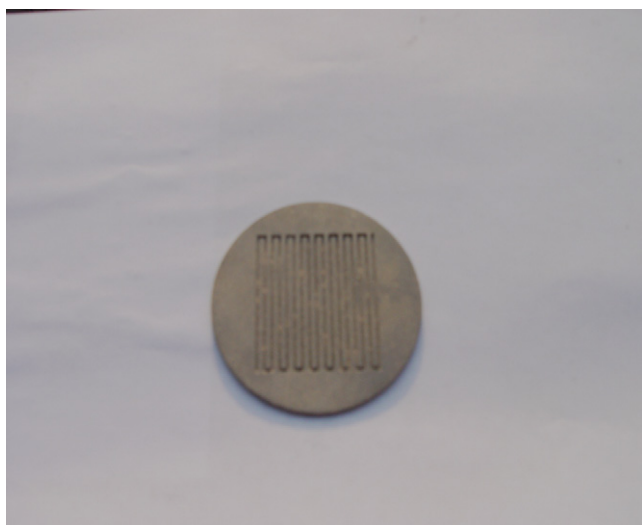


Fig. 1. The picture of aluminate cement/graphite composite bipolar plate.

of sample are 5 and 2.5 mm, respectively. The adjusted span is 22 mm. The rate of displacement is 0.5 mm min^{-1} .

2.4. Characterizations of resistance to acid corrosion

The resistance to acid corrosion of composite bipolar plate samples was examined with Potentiostat Galvostat, Autolab of Eco Chemie Inc., Netherlands. A conventional three-electrode system was used in the electrochemical measurements, in which a platinum sheet acted as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and the composite bipolar plate sample as the working electrode. A scanning rate of 1 mV s^{-1} was selected for linear sweep voltammetry measurements. Plots of voltage versus current were recorded. Tafel plots were used to determine the corrosion current density.

In addition, metal ions possibly leach from this composite bipolar plate, which is will significantly reduce the conductivity of the proton exchange membrane. So, metal ions content in corrosion solution also need to be measured. The composite bipolar plate sample is immersed in 1 M H_2SO_4 solution. After 1 h, metal ions content in the solution was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) of Perkin-Elmer Inc., US.

2.5. Thermogravimetric analysis (TGA)

Thermal degradation of composite bipolar plates was measured by DSC–TG instrument (NETZSCH STA 449C) from room temperature to 400°C with a heating rate of $10^\circ\text{C min}^{-1}$.

2.6. Porosity analysis

The pore size in the composite bipolar plates was also measured by PM 33 Mercury Intrusion Porosimeter from Quantachrome Instruments.

3. Results and discussion

3.1. The effect of graphite size on the conductivity and the flexural strength of composite bipolar plate

Four kinds of graphite powder with size of <45 , 45–65, 65–90 and $>90 \mu\text{m}$ were divided using sample sifter and the effect of graphite size on the conductivity and the flexural strength of composite bipolar plate were investigated. The experimental result is shown in Tables 1 and 2.

Table 1

The effect of graphite size on the conductivity of composite bipolar plate with 60 wt% graphite content

Graphite powder size (μm)	The conductivity of composite bipolar plate (S cm^{-1})
<45	367.54
45–65	386.98
65–90	428.17
>90	467.61

Table 2

The effect of graphite size on the flexural strength of composite bipolar plate with 60 wt% graphite content

Graphite powder size (μm)	The flexural strength of composite bipolar plate (MPa)
<45	49.08
45–65	38.54
65–90	38.11
>90	34.31

It can be seen from Tables 1 and 2 that when the graphite content is certain (60 wt%), the conductivity and the flexural strength of composite bipolar plate with uniform graphite size are all higher than that of composite bipolar plate with mixed graphite size (shown in Ref. [12]). The possible reason is that when graphite size is uniform, the piling up of the graphite powder is near to the most closely accumulation and the compactness of composite bipolar plate was also improved. At the same time, the adhesion between hydration product of aluminate cement and graphite is near same and the defect of composite bipolar plate is reduced. Consequently, the conductivity and the flexural strength of composite bipolar plate were all improved.

It can also be seen from Table 1 that the larger the graphite size is, the higher the conductivity of composite bipolar plate is. The main reason of this phenomenon is that, in the same content of the graphite, the larger the graphite size is, the fewer the number of graphite particle is, namely, the contact dot between the graphite particles will be reduced, at the same time, the contact area between the particles increases. These all make the contact resistance among graphite particles reduce. For composites containing a large quantity of conductive filler, the contact resistance of particle greatly influences the conductivity of composite, so the larger the particle size is, the higher the conductivity is.

Because the small size graphite possesses more surface area and the number of graphite particle, the combining dot between the small size graphite and hydration product of aluminate cement increases. As a result, the adhesion between small size graphite and hydration product of aluminate cement in the composite bipolar plate become stronger. The porosity and number of voids decreases with decreasing graphite size. Hence, the flexural strength of composite bipolar plate increases with decreasing graphite size, which is shown in Table 2.

In addition, before the graphite size is chosen, we must also consider the exquisiteness of flow field of mold pressing composite bipolar plate.

3.2. Resistance to acid corrosion of composite bipolar plate

During running PEMFC system, firstly, acid concentration of water discharging from PEMFC is pH 1–4, lastly, pH is 6–7. Thus, in the present experiment, 1 M H_2SO_4 solution is chosen as accelerating corrosion solution, which simulated the direct contact of bipolar plate with strong acidic polymer electrolyte

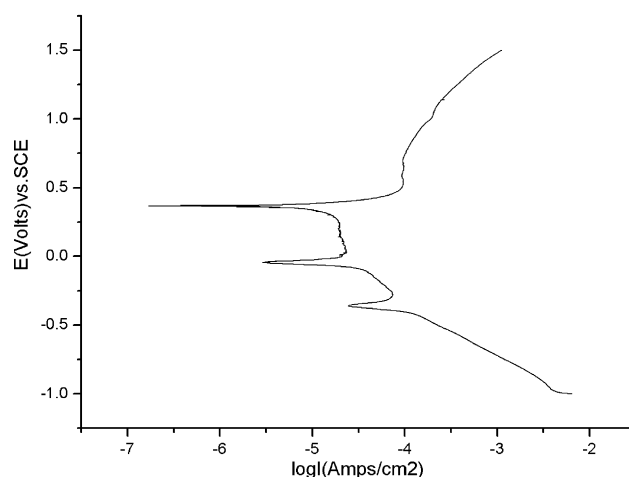


Fig. 2. Polarization curve for aluminate cement/graphite composite bipolar plate with 60 wt% graphite content in 1 M H_2SO_4 solution at R.T.

and represented an aggressive environment for a relatively short test time.

3.2.1. Polarization curve

The primary hydration products of aluminate cement at room temperature are crystals: $\text{CAH}_{10}(\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O})$, $\text{C}_2\text{AH}_8(2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 8\text{H}_2\text{O})$ and alumina hydrate $\text{AH}_3(\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O})$ fill into pores of crystal frameworks. Because this experiment sample were immersed in water of 80 °C for an hour during measuring the water content of sample, hydration products may change from CAH_{10} , C_2AH_8 to $\text{C}_3\text{AH}_6(3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O})$. Thus, there is a great deal C_3AH_6 in the sample. Fig. 2 gives polarization curve for aluminate cement/graphite composite bipolar plate with 60 wt% graphite content in 1 M H_2SO_4 solution at room temperature. It can be seen that the polarization curve displayed definitely three current peaks with increasing electrode potential from the corrosion potential. The first current peak was caused by the AH_3 dissolution, $\text{AH}_3(\text{Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}) + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 6\text{H}_2\text{O}$ and the corrosion current is about $10^{-6} \text{ A cm}^{-2}$. The second current peak was caused by the CAH_{10} or C_2AH_8 dissolution and the corrosion current is about $10^{-5.5} \text{ A cm}^{-2}$. The third current peak was caused by the C_3AH_6 dissolution, $\text{C}_3\text{AH}_6(3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}) + 6\text{H}^+ \rightarrow 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3 \downarrow + 6\text{H}_2\text{O}$ and the corrosion current is about $10^{-4.5} \text{ A cm}^{-2}$. American Department of Energy requires that the corrosion current of bipolar plate in PEMFC should be less than $16 \mu\text{A cm}^{-2}$ and leachants from bipolar plate do not contaminate MEA.

It can be seen from above experiment results that the acid first attack AH_3 , subsequently, the acid further attack CAH_{10} , C_2AH_8 , or C_3AH_6 . Alumina hydrate (AH_3) is stable when acid solution concentration is $\text{pH} > 4$ [13]. Although there is the dissolution of the calcium component of the other hydration product, its dissolution will lead to the formation of additional quantities of AH_3 , which fill into pores, protecting the composite bipolar plate from further attack and generally giving a smoother attacked surface with less aggregate loss. Therefore, aluminate cement/graphite composite bipolar plate is possibly

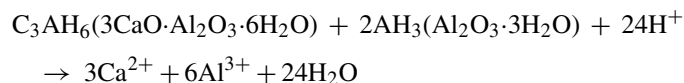
Table 3
Metal ions content in the corrosion solution for aluminate cement/graphite composite bipolar plate

	Metal ions content (mg L ⁻¹)						
	Si	Ti	Al	Ca	Fe	K	Na
Sample 1 (30 °C)	22.34	1.16	92.73	56.04	5.675	4.257	2.002
Sample 2 (80 °C)	47.55	4.49	337.1	220.5	16.82	7.18	2.61
Not sample	0.724	0.008	0.090	1.699	0.128	0.515	1.590

fully acid corrosion-resistant when acid solution concentration is pH > 4.

3.2.2. Metal ions content in acid corrosion solution

The samples 1 and 2 are immersed in 25 mL 1 M H₂SO₄ solution at 30 and 80 °C for 1 h, respectively. The total Al and Ca content in the sample 1 are about 3094 and 2770 mg L⁻¹, respectively. The total Al and Ca content in the sample 2 are about 2150 and 1925 mg L⁻¹, respectively. Metal ions content in the corrosion solution is shown in Table 3. It can be seen from Table 1 that after acid corrosion at 30 °C, Al and Ca ions content in acid corrosion solution increase. But Al and Ca ions leaching from this composite bipolar plate are only 2–3% of the total Al and Ca content in the composite bipolar plate. After acid corrosion at 80 °C, Al and Ca ions leaching from this composite bipolar plate are 12–16% of the total Al and Ca content in the composite bipolar plate. Acid corrosion reaction is shown in below equation:



It can be seen from above experiment results that Al and Ca ions may leach from this composite bipolar plate after 1 M H₂SO₄ acid corrosion. What degree these Al and Ca ions leaching from this composite bipolar plate influence PEMFC performance need to be investigated using *I-V* and *I-P* performance of single cell and stack using this composite bipolar plate in the future experiments. In addition, in order to reduce Al and Ca ions content leaching from this composite bipolar plate, we can choose alu-

minate cement of higher Al₂O₃ content and add polymer, for example, polyvinyl alcohol (PVA) into aluminate cement (MDF cement).

3.3. Thermal property of composite bipolar plate

The DSC–TG curve of this composite bipolar plate is presented in Fig. 3. There is a weak endothermic peak at 112.8 °C, at which the weight loss of plate is about 3.20%. This is release of free water in the hydration products of aluminate cement. There is a strong endothermic peak at 295.2 °C, at which the weight loss of plate is about 9.08%. This is release of gel water in the hydration products of aluminate cement. So, the basic reason why this composite bipolar plate has weight loss is that water can leach from this composite bipolar plate with temperature increasing. Since the working temperature of PEMFC is about 80–100 °C, this composite bipolar plate is thermally stable over this range.

3.4. Pore size distribution in the composite bipolar plate

The pore size in the composite bipolar plate was also measured for composite bipolar plate with 60 wt% graphite content. The experiment result is shown in Fig. 4. It can be seen from Fig. 4 that the smallest and the biggest pore size is 0.01–0.02 and 4–5 μm, respectively, and the large amount of pore is pores with pore size of 0.1–0.4 μm, which be possibly caused by the hydration and solidification of aluminate cement. So, there are gel capillary pores in this composite bipolar plate. The total porosity in the composite bipolar plate is about 17.1 vol.%.

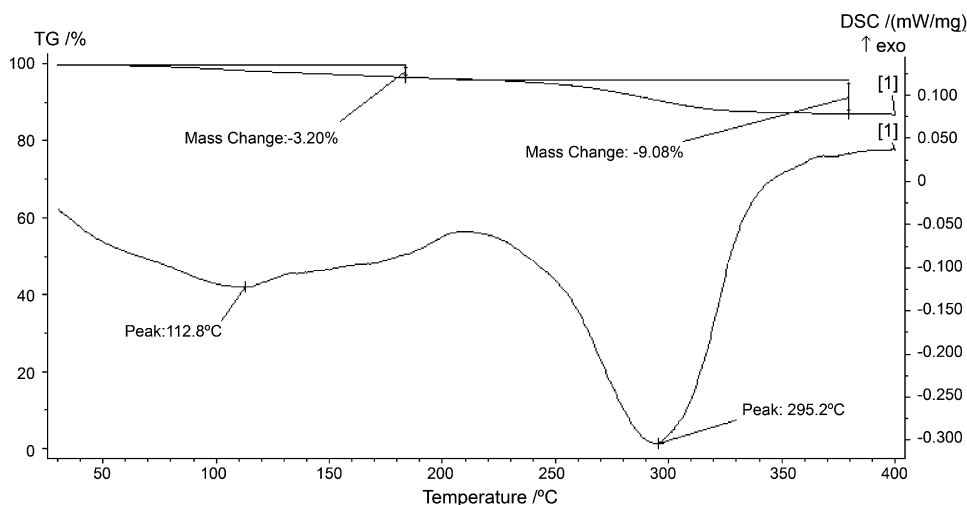


Fig. 3. DSC–TG curves of the aluminate cement/graphite composite bipolar plate with 60 wt% graphite content.

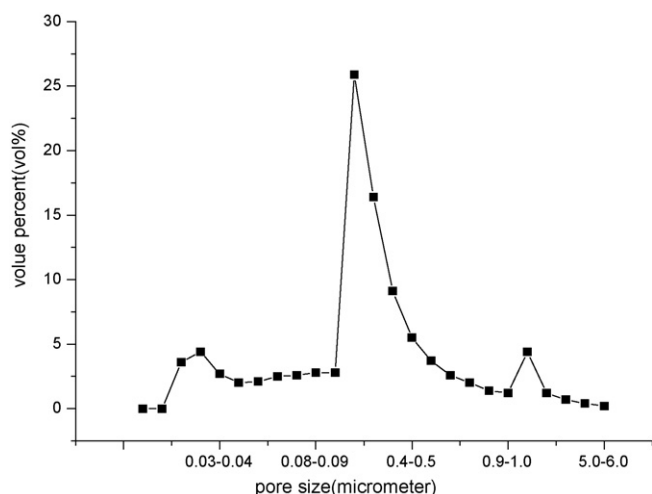


Fig. 4. Pore size distribution in the composite bipolar plate.

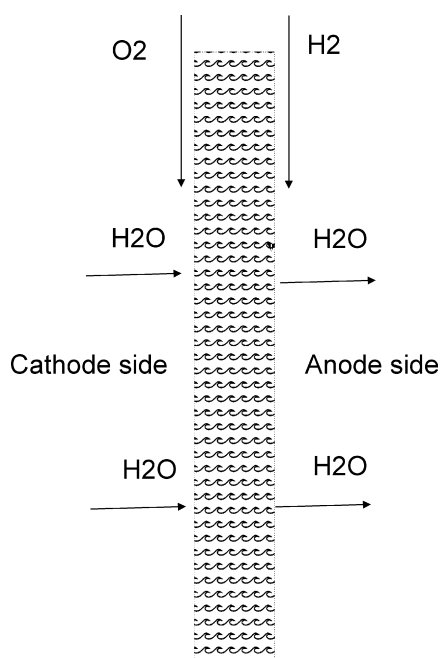


Fig. 5. The schematic drawing of water transport through the composite bipolar plate.

If the pressure difference, which can be obtained by adjusting reactant gases pressure or forming negative pressure in the surface of bipolar plate due to consuming of reactant gases, is well applied across the bipolar plate, water can be transported from the cathode side of the bipolar plate to the anode side by capillarity [14] (shown in Fig. 5), which can humidify the whole proton exchange membrane while the PEMFC operates.

4. Conclusions

The conductivity and the flexural strength of aluminate cement/graphite composite bipolar plate can be improved by

choosing uniform size graphite as conductive fillers. The conductivity and the flexural strength of composite bipolar plate increase and decrease, respectively, with the increase of size of graphite particles.

The polarization curve of aluminate cement/graphite composite bipolar plate displayed definitely three current peaks, corresponding current, of which is 10^{-6} , $10^{-5.5}$ and $10^{-4.5}$ A cm⁻², respectively, in 1 M H₂SO₄ solution at room temperature. This shows that this composite bipolar plate is acid corrosion-resistant and possibly fully acid corrosion-resistant when acid solution concentration is pH > 4. Al and Ca ions leaching from aluminate cement/graphite composite bipolar plate are only 2–3% and 12–16% of the total Al and Ca content in the composite bipolar plate after 1 M H₂SO₄ solution corrosion at 30 and 80 °C, respectively. The experiment on the impact of these Al and Ca ions leaching from this composite bipolar plate on PEMFC performance is underway.

In addition, aluminate cement/graphite composite bipolar plate possesses humidifying function and is also thermally stable while the PEMFC operates.

Acknowledgements

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