

Short communication

Sodium silicate/graphite conductive composite bipolar plates for proton exchange membrane fuel cells

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Abstract

The flexural strength, pore size distribution, resistance to acid corrosion and thermal properties of sodium silicate/graphite composite bipolar plates for proton exchange membrane fuel cells (PEMFC) were investigated in this paper. The experiment results show that when the graphite content is greater than 40 wt.%, the flexural strength of composite bipolar plate can attain 15 MPa and this composite bipolar plate was not broken during machining the flow fields. The large amount of porosity in this composite bipolar plate is from the silica gel capillary pores because of the solidification of sodium silicate, which makes it possess a humidifying function during PEMFC operation. The corrosion current is about $10^{-4.5}$ A cm^{-2} from the polarization curves for this composite bipolar plate, which shows that this composite bipolar plate is acid-resistant. Na^+ ions leached from this composite bipolar plate is only a small percentage of the total Na^+ ion content in the composite bipolar plate after 1 M H_2SO_4 solution corrosion at 30 °C for 1 h. Na^+ ions in the acidic corrosion solution increased a little with temperature from 30 to 80 °C. In addition, this composite bipolar plate was thermally stable from room temperature to 400 °C.

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1. Introduction

Perfluorosulfonic proton exchange membranes such as Nafion membranes from the DUPONT Company are used widely as the electrolyte in a PEMFC, because of excellent performance. But the proton conductivity decreases with the decrease of the water content in the membrane [1], for example, when the temperature of the PEMFC is >80 °C. So it is essential to humidify the membrane during the course of operating the PEMFC, which is a key problem to be resolved in the PEMFC system [2]. In addition, if the water produced at the cathode during the PEMFC operation cannot be removed, the pores of the gas diffusion layer (GDL) may be blocked, which may prevent oxygen (O_2) from entering the catalyst layers.

Humidifying the membrane through external equipment is generally adopted at present in PEMFC systems, which increases the volume and the cost of the fuel cell stack [3]. So, it is desirable

to humidify the NAFION membrane internally. In recent years, worldwide research efforts have addressed external humidification by endowing the membrane electrode assembly (MEA) or GDL with self-humidifying capabilities [4,5]. The Institute of Gas Technology and International Fuel Cells provide the bipolar plate with a self-humidifying function by changing the materials or structure of the bipolar plate [6]. In this way, the volume and weight of the fuel cell stack can be reduced.

In our laboratory, a sodium silicate/graphite conductive composite, which will be used as the bipolar plate of a PEMFC, was prepared by mold pressing at room temperature [7]. This conductive composite bipolar plate has hydrophilicity. So, it can absorb water from the surface of the GDL and accelerate water removal during PEMFC operation [8], which can prevent the accumulation of water on the cathode side thereby flooding the catalyst. In addition, the water content of this conductive composite bipolar plate can reach 9 wt.%. Water may be released from this composite bipolar plate to humidify the incoming reactant gases (H_2). The conductivity of the Sodium silicate/graphite composite bipolar plates have been reported in previous papers [7]. When the graphite content is greater than 40 wt.%, the conduc-

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tivity of the composite bipolar plate is greater than 100 S cm^{-1} and can usually meet the requirement of performance of the bipolar plate in a PEMFC. In this paper, other performances of this composite bipolar plate were studied.

2. Experimental

2.1. Materials preparation

Graphite and fluorine sodium silicate (Na_2SiF_6) were mixed evenly in the beaker. Then a sodium silicate solution ($\text{Na}_2\text{O}\cdot n\text{SiO}_2$) was added. The slurry was stirred for 30 min and held for 12–24 h. The mixture was then mould pressed using a suitable mould in a simple pressure machine at room temperature. Finally, the sample was pulled off the mould and was dried at 50°C for 24 h.

2.2. Measurements of flexural strength

The flexural strength of the composite bipolar plates was investigated by 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} .

2.3. Porosity analysis

The pore size in the composite bipolar plates was also measured by a PM-33 mercury intrusion porosimeter from Quantachrome Instruments.

2.4. Acid corrosion test

The corrosion resistance of the composite bipolar plates was examined by a potentiostat/galvanostat from Autolab of Eco Chemie Inc. in The Netherlands. Plots of the voltage versus current density were recorded. Tafel plots were used to determine the corrosion current.

Metal ion content in the corrosion solution leached from the novel composite bipolar plates was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.5. Thermogravimetric analysis (TGA)

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

3. Results and discussion

3.1. Study on the flexural strength of sodium silicate/graphite composite bipolar plates

PEMFC bipolar plates, which are support materials for the PEMFC stack, must have sufficient mechanical strength. So, the

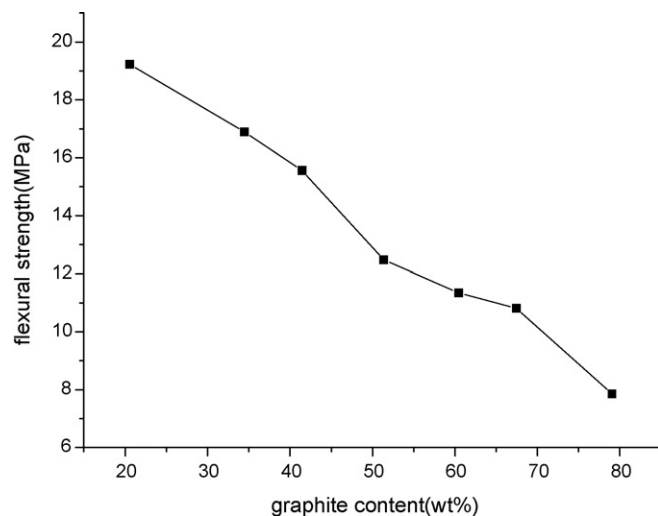
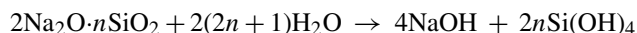


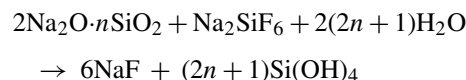
Fig. 1. Effect of graphite content on flexural strength of Sodium silicate/graphite composite bipolar plate.

effect of graphite content on the flexural strength of composite bipolar plate was investigated (Fig. 1).

A sodium silicate ($\text{Na}_2\text{O}\cdot n\text{SiO}_2$) solidifying reaction using fluorine sodium silicate (Na_2SiF_6) is shown below:



Overall the solidifying reaction is shown in below equation:



Silica acid gel produced by the solidification of sodium silicate may be transformed into silica gel particles with further dehydration. Silica gel particles agglomerate and form a three-dimensional framework, in which the graphite is packaged. So, this composite bipolar plate has good mechanical strength.

It can be seen from Fig. 2 that the flexural strength of composite bipolar plate decreases with the increase in graphite content.

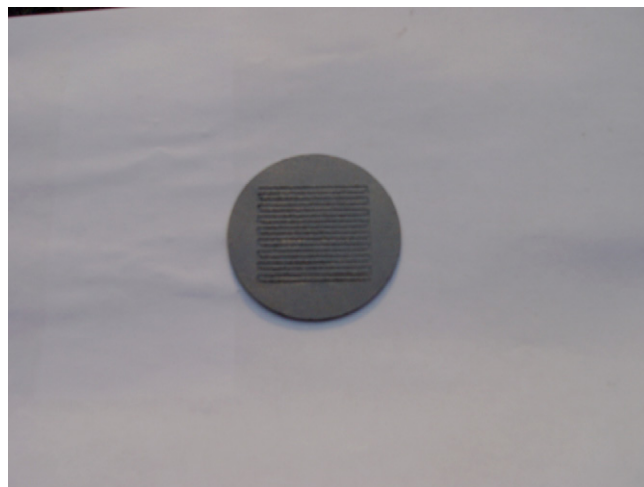


Fig. 2. The picture of sodium silicate/graphite composite bipolar plate.

When the graphite content is greater than 40 wt.%, the flexural strength of composite bipolar plate can attain 15 MPa. However, the flexural strength of Poco™ graphite bipolar plate can attain 45 MPa.

The flow fields were carved using a numerical control (NC) machine tool of the Beijing carving technological Co. Ltd. This composite bipolar plate was not broken during machining flow fields. The flow channels are very clear and the ridges of the flow fields do not collapse. A sample picture is shown in Fig. 2. The width and depth of flow channels are 0.75 and 0.5 mm, respectively. The width of ridges is 0.75 mm.

3.2. Pore size distribution in the composite bipolar plate

The pore size in the composite bipolar plate was also measured for the composite bipolar plate with 60 wt.% graphite content. The experimental results are shown in Fig. 3. It can be seen from Fig. 3 that the smallest and the biggest pore size is 0.008–0.01 and 5–6 μm , respectively and the volume percent of >1 μm pore size is <15 vol.%, which could be possibly caused by the pileup of graphite particles. The large amount of porosity is due to the silica gel capillary pores after solidification of the sodium silicate. The total porosity in the composite bipolar plate is about 13.8 vol.%. So, the basic reason why this composite bipolar plate has internal water content is that the sodium silicate can form gel capillary pores during solidification.

This composite bipolar plate can collect water produced at the cathode during the PEMFC operation. Water can diffuse from the cathode side of the bipolar plate to the anode side by capillary action [9] and then release the water from this composite bipolar plate to humidify the incoming reactant gases (H_2). That is to say that this composite bipolar plate possesses a self-humidifying function.

From the experimental results of the pore size distribution in the composite bipolar plate, the H_2 permeability of the composite bipolar plate should be small and the single cell performance with this composite bipolar plate can be measured by FC-Lab of Electro Chem. Inc., USA [10].

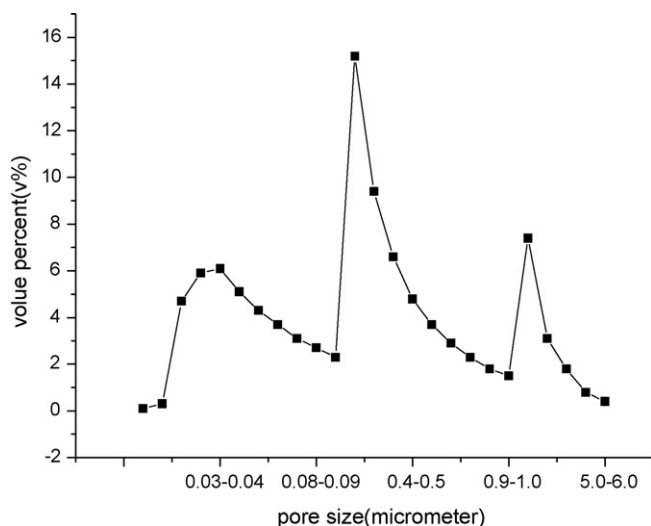


Fig. 3. Pore size distribution in the composite bipolar plate.

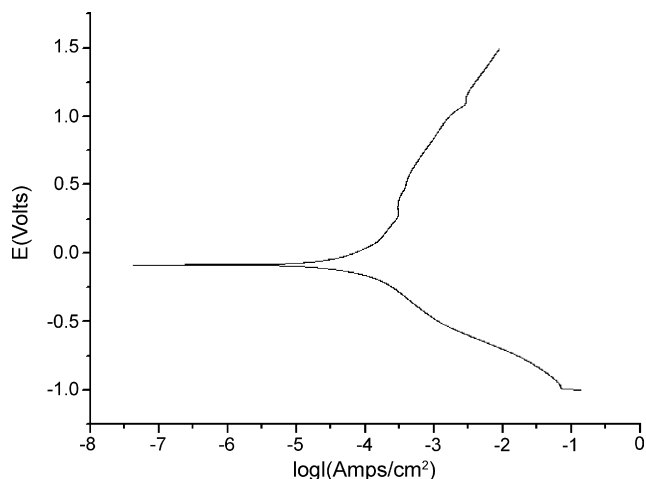


Fig. 4. Polarization curve for sodium silicate/graphite composite bipolar plate with 60 wt.% graphite content in 1 M H_2SO_4 solution at RT.

3.3. Resistance to acid corrosion of sodium silicate/graphite composite bipolar plates

During running a PEMFC system, the acid concentration of water discharging from the PEMFC is pH 1–4. Thus, in the present experiment, a 1 M H_2SO_4 solution is chosen as a corrosion-accelerating solution, which simulated the direct contact of the bipolar plate with a highly acidic polymer electrolyte and represented an aggressive environment for a relatively short test time.

There is residual $\text{Na}_2\text{O}\cdot n\text{SiO}_2$, Na_2SiF_6 or NaF in this composite bipolar plate. So the neutralization reaction can occur between the residual $\text{Na}_2\text{O}\cdot n\text{SiO}_2$, Na_2SiF_6 or NaF and acid when this composite bipolar plate is immersed in 1 M H_2SO_4 solution.

Fig. 4 gives the polarization curve for sodium silicate/graphite composite bipolar plate with a 60 wt.% graphite content in 1 M H_2SO_4 solution at room temperature. It can be seen that the corrosion current is about $10^{-4.5} \text{ A cm}^{-2}$, which shows that this composite bipolar plate is acid corrosion-resistant, because the US Department of Energy (DOE) requires that the corrosion current of bipolar plate in PEMFC is about $10^{-5} \text{ A cm}^{-2}$.

The samples 1 and 2 were immersed in 25 mL 1 M H_2SO_4 solution at 30 and 80 $^\circ\text{C}$ for 1 h, respectively. The total Na^+ in samples 1 and 2 are about 4091 and 2214 mg L^{-1} , respectively. The metal ionic content in the corrosion solution is shown in Table 1. It can be seen from Table 1 that after acid corrosion,

Table 1
Metal ions content in the corrosion solution for sodium silicate/graphite composite bipolar plate

	Metal ions content (mg L^{-1})						
	Si	Ti	Al	Ca	Fe	K	Na
Sample 1 (30 $^\circ\text{C}$)	14.64	0.06	1.695	1.66	0.467	1.048	202.0
Sample 2 (80 $^\circ\text{C}$)	31.11	–	1.352	1.685	0.492	0.957	252.4
Not sample	0.724	0.008	0.090	1.699	0.128	0.515	1.590

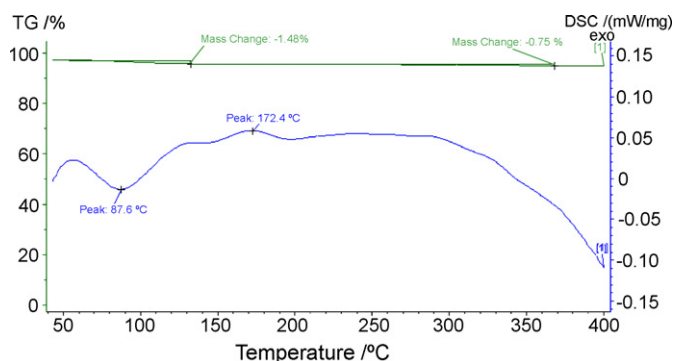


Fig. 5. DSC–TG curves of the composite bipolar plate with 60 wt.% graphite content.

the Na^+ ion content in the acid corrosion solution increases. The Na^+ ions leached from this composite bipolar plate at 30 and 80 °C was 5% and 11.4% of the total Na content in the composite bipolar plate, respectively. Among the silica acid gels, there is a large amount of Na^+ ions, which is stable and can form cation bridges between two silica acid gels [11]. The primary metal ionic content in the corrosion solution is Fe (10250 mg L^{-1}), Cr (2630 mg L^{-1}), Ni (1165 mg L^{-1}) from the austenitic stainless steel in 1 M H_2SO_4 solution at 80 °C for 1 h. So, the metal ionic content leached from the sodium silicate/graphite composite bipolar plate is less than that of austenitic stainless steel.

But, in order to prevent Na ions leaching from this composite bipolar plate, treating with acidification is necessary for this composite bipolar plate before assembling a single cell and stack using this composite bipolar plate.

3.4. Thermal property of sodium silicate/graphite composite bipolar plates

The DSC–TG curve of this composite bipolar plate is presented in Fig. 5. There is an endothermic peak at 87.6 °C, at which the weight loss of plate is about 1.5%. The weight loss of plate is only 2.5% from room temperature to 400 °C. The basic reason why this composite bipolar plate has a weight loss is that water can leach from this composite bipolar plate with the temperature increasing. Since the working temperature of a PEMFC is about 80–100 °C, this composite bipolar plate is thermally stable over this range.

4. Conclusions

Though the flexural strength of sodium silicate/graphite composite bipolar plate is 15 MPa, it was not broken during machining the flow fields. The flow channels were very clear and the

ridges of flow fields did not collapse. The large number of pores in this composite bipolar plate was due to the silica gel capillary pores following solidification of sodium silicate. So, this composite bipolar plate can save water produced at the cathode and water can be released from this composite bipolar plate to humidify the reactant gases (H_2) during PEMFC operation. The corrosion current was about $10^{-4.5} \text{ A cm}^{-2}$ from the polarization curve of this composite bipolar plate. This shows that this composite bipolar plate is essentially acid corrosion-resistant. Na^+ ions leaching from this composite bipolar plate at 30 and 80 °C were 5% and 11.4% of the total Na^+ content in the composite bipolar plate, respectively, after a 1 M H_2SO_4 solution corrosion test for 1 h. The metal ionic content leached from the sodium silicate/graphite composite bipolar plate was less than that from austenitic stainless steel. This composite bipolar plate is thermally stable.

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