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Short communication

Research progress of aluminium alloy endplates for PEMFCs

Yu Fu [a,b], Ming Hou [a,*], Xiqiang Yan [a], Junbo Hou [a,b], Xiaokuan Luo [a], Zhigang Shao [a], Baolian Yi [a]

[a] *Fuel Cell system and Engineering Laboratory, Dalian Institute of Chemical & Physics, Chinese Academy of Sciences, Dalian 116023, China*
[b] *Graduate University of Chinese Academy of Sciences, Beijing 100049, China*

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Abstract

The endplate is a crucial component in a proton exchange membrane fuel cell (PEMFC) stack. It can provide the necessary rigidity and strength for the stack. An aluminium alloy is one of the ideal materials for PEMFC endplates because of its low density and high rigidity. But it does not meet the requirements of corrosion resistance and electrical insulation in PEMFC environments. In this work, methods of sealing treatments and the conditions of aluminium alloy anodization were investigated. Corrosion resistances of the samples prepared by different technologies were evaluated in simulated PEMFC environments. The results showed that the corrosion resistance of the samples sealed by epoxy resin was greatly improved compared with those sealed in boiling water, and the samples anodized at a constant current density performed better than those anodized at a constant voltage. By insulation measurements, all of the samples showed good electrical insulation. The aluminium alloy endplate anodized at a constant current density and sealed with thermosetting bisphenol-A epoxy resin exhibited promising potential for practical applications by assembling it in a PEMFC stack and applying a life test.

Keywords: PEMFCs; Endplates; Aluminium alloy; Surface treatments

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) as power generators have been paid much attention recently due to their high efficiency and near-zero emissions [1–3]. Commonly, a PEMFC stack (Fig. 1) consists of plurality of single cells, current collectors, endplates, tightening components, etc. When a stack is assembled, the tightening force is often applied to the endplates to obtain low contact resistance and good sealing. So, the materials for the endplates should have enough rigidity and strength in the operational temperature, pressure and humidity ranges. Since there are passages for inlets and outlets for the fuel, the oxidant and the coolant in the endplates, the chemical and electrochemical stabilities are also very crucial. To prevent the membrane from dehydrating, the inlet gases need to be humidified and the exhausts are often mixed with the resultant water. So the endplates are prone to corrosion in the two-phase flows, especially for acidic media. Moreover, the metal ions from the endplates could pollute the membrane resulting in the output power decreasing [4]. In addition, to ensure startup from freezing, glycol antifreeze is often added to the cooling water. The endplates should exhibit high chemical stability in glycol solution, too. Furthermore, the high-power PEMFC stacks consisting of over 100 single cells have a very high output voltage. Accordingly, the endplates should have good electrical insulation to ensure safety. Also, to increase the gravimetric specific power and the volumetric specific power of the PEMFCs, the density of the endplates material should be as low as possible. For these reasons, ideal materials for the endplates should possess all of the following properties: low-density, high-rigidity, good chemical and electrochemical stabilities as well as high electrical insulation.

Currently, most of the research is focused on bipolar plates [5–8] and there are very few papers on PEMFC endplates. Pozio et al. [9] investigated the possibility of SS316L as a PEMFC endplate material, but found that iron cations from the SS316L endplates led to Nafion degradation, and assessed the degradation by a massive fluoride loss. Except for this paper, almost

* Corresponding author. Tel.: +86 411 84379051; fax: +86 411 84379185.
E-mail address: houming@dicp.ac.cn (M. Hou).

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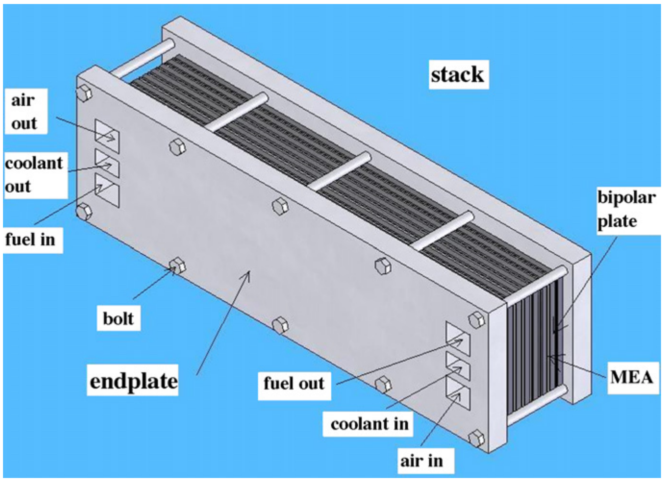

Fig. 1. Structural representation of a PEMFC stack.

no other articles have been published. Similarly, only several patents on endplates [10,11] have been applied for, and the materials mentioned are only resin mixtures. However, there are many materials used for endplates currently, which can be classified as two types. One is a non-metal, including engineering plastics, polysulfone, etc. But the thermal stabilities of engineering plastics and polysulfone are not satisfactory. They tend to degenerate under PEMFC operating temperatures. Another kind of endplate material is metal, such as aluminium alloy, titanium, stainless steel, and so on. Metals have a high mechanical strength, but their corrosion-resistance and electrical insulation should be considered. There are two ways to achieve the desired properties: one is to put an additional insulating plate between the current collector and the endplate, which makes the stack more complicated, another is to make a surface modification, however, its effectiveness is still an open issue. Aluminium alloy is an ideal material for the PEMFC endplate because of its low-density and high-rigidity. Anodization is considered to be the technology for aluminium alloy surface treatment, which can greatly improve the corrosion resistance and provide insulation [12,13]. But anodized aluminium alloy is often used in atmosphere environment and its performances in the complex PEMFC corrosion conditions needs to be investigated. On the other hand, epoxy resin has been widely used as a surface protection against corrosion because of its good dielectric property and high stability in chemical media. Müller and Fischer [14] found that proxy resin was an excellent corrosion inhibitor both for aluminium and zinc pigments. And Du et al. [15] studied the protective coatings for aircraft aluminium alloy substrates and found the sol–gel/epoxy resin hybrid coating showed enhanced mechanical strength and enhanced corrosion resistance.

In our research, the surface treatments of aluminium alloy for PEMFC endplates were investigated. Aluminium alloy samples were sealed with epoxy resin after anodization in two different conditions: anodization at a constant current density and at a constant voltage. The conventional method of sealing in boiling water was also conducted for comparison. Behavior of the samples prepared by different technologies were characterized in simulated PEMFC environments. Electrical insulation of the samples was also evaluated. Two endplates prepared by different methods were also used to assemble a PEMFC stack and the endplate surfaces after an aging test were observed.

2. The experimental

2.1. Fabrication of the aluminium alloy samples

LY12 aluminium alloy was selected in this study and its composition is given in Table 1. Firstly, the samples were degreased with organic solvent and rinsed with ethanol. Then they were washed with distilled water, and dried. After cleaning, the samples were put into 50 g L^{-1} NaOH solution at 70 °C for 2 min to remove the oxide film on the surfaces. Then the samples were immersed in 10% (v/v) nitric acid solution for 30 s to clean the surfaces. After that, the samples were anodized and the electrolyte was 10% (v/v) sulfuric acid solution prepared in distilled water. The aluminium alloy samples were used as the anode and a lead sheet with the same area was used as the cathode. The temperature of the electrolyte solution was controlled at 8–15 °C. Two different methods for anodization were adopted. One was holding the voltage constant at 15 V and another was holding the current density constant at 2 A dm^{-2}. The samples were immediately withdrawn, then washed with distilled water after treatment of 30 min anodization. Also, two sealing methods were used. One was to seal the sample with epoxy resin. A film of bisphenol-A epoxy resin was smeared on the dried samples after anodization, and the loading was 4–8 mg cm^{-2}. Then the samples were put into a heating furnace. After which they were heated at 220 °C for 6 h, then the heating furnace was turned off. The samples cooled to room temperature and after 12 h were ready for further characterization. Another sealing method was to immerse the samples in boiling distilled water for 30 min after they were anodized. The samples with different anodization methods and different sealing methods are listed in Table 2.

2.2. Electric insulation

A variac, a fuse (0.5 A) and the sample constituted a circuit (Fig. 2), and the voltage applied was increased continuously from zero to the puncture voltage. When the insulation film of the sample was broken down, the current in the circuit would

Table 1
Composition of LY12 aluminium alloy in this study (wt.%)

Elements	LY12
Cu	3.8–4.9
Mg	1.2–1.8
Mn	0.3–0.9
Fe	0.5
Si	0.5
Zn	0.3
Ni	0.1
Ti	0.05
Others	0.1
Al	Balance

Table 2
Samples with different anodization conditions and sealing methods

Code	Technologies			
	Anodization conditions		Sealing methods	
	Constant voltage	Constant current density	Boiling water	Epoxy resin
A	O		O	
B		O	O	
C	O			O
D		O		O

jump momentarily to a very high level and the fuse would be melt. The largest voltage before the circuit turned off was the puncture voltage.

2.3. Corrosion tests under simulated PEMFC conditions

The corrosion behavior of the samples was investigated in the simulated PEMFC conditions (0.5 M H_2SO_4 + 5 ppm F^-) by electrochemical experiments. A conventional three-electrode system was used for the electrochemical measurements, with a working electrode, a platinum sheet as the counter electrode and a saturated calomel electrode (SCE, sat'd KCl) as the reference electrode. The tests were conducted using a potentiostat Model 2273 A by EG&G Princeton Applied Research and analyzed with the corrosion software of EG&G Version 2.43.0. The dimensions of the working electrodes prepared were 15 mm × 15 mm × 0.2 mm. The edges were protected by paraffin exposing 10 mm × 10 mm surfaces to the electrolyte. The tests were performed at 26 ± 0.5 °C. Dynamic polarization technique was used to compare the general electrochemical behaviors of the samples. In these tests, the samples were stabilized at an open circuit potential (OCP) for 30 min. The potential was then swept from −0.3 V versus OCP to +0.3 V versus OCP with a scanning rate of 2 mV s^{-1}, and the scan increment was set at 0.5 mV. Potentiostatic polarization experiments were also conducted to investigate the corrosion resistance and the stability of the samples under simulated PEMFC conditions. In the measurements, the samples were stabilized at OCP for 30 min, then a specific potential was applied and the current versus time curve was recorded. The potential of 1 V was chosen for the tests, and the tests were performed at 26 ± 0.5 °C. The behaviors of the samples in the coolant were also investigated. The samples with dimensions of 100 mm × 100 mm × 0.2 mm were immerged in 1 L 50% (v/v) glycol solution at 26 ± 0.5 °C, and mass changes of the samples were measured.

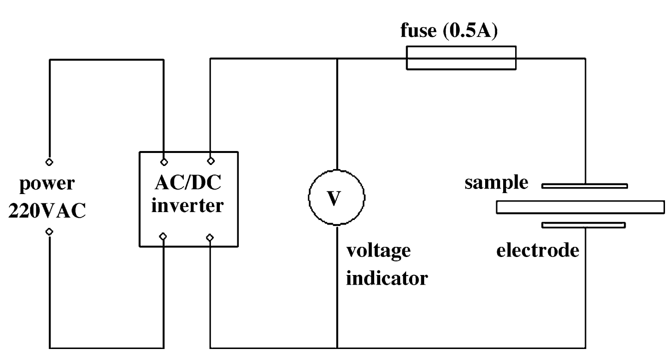

Fig. 2. Sketch of measuring the puncture voltages.

Table 3
FEMFC stack operating conditions

PEMFC stack parameters	Parameter values
Hydrogen pressure (inlet) (psi(gauge))	40
Oxygen pressure (inlet) (psi(gauge))	30
Cell temperature (°C)	55
Single cell potential range (V)	0.5–0.95
Humidification	Yes

2.4. Fuel cell test

Two endplates prepared by techniques A and D were used to assemble a 1 kW (16 single cells) PEMFC stack with expanded graphite bipolar plates [16], and the MEAs were fabricated as described in Ref. [17]. The performance of the stack was tested on PEMFC testing equipment (FCATS-H36000, Hydrogenics, Canada), and the experimental parameters are listed in Table 3. The accumulative life time of the stack was 1100 h, including the 200 h operation time and 900 h idle time. Finally, changes of the endplates were observed with Super Depth Surface Profile Measurement Microscope VK-8550 (Keyence Corporation, Japan).

3. Results and discussion

3.1. Electric Insulation

The puncture voltages of the samples prepared by different technologies were measured and the results are listed in Table 4. The puncture voltages of all the samples were over 220 V. Considering most of PEMFC stacks with less than 200 single cells nowadays, the maximum voltage for one stack is often lower than 200 V. So the electric insulation of the samples is high enough for practical applications.

3.2. Corrosion-resistant abilities under simulated PEMFC conditions

In 0.5 M H_2SO_4 + 5 ppm F^- solution at 26 ± 0.5 °C, dynamic polarization curves of the samples are shown in Fig. 3. From the slopes of the anodic curve and the cathode curve, the corresponding corrosion current and corrosion voltage can be determined. Polarization curves of samples A and B are very close, and the corrosion current densities (I_{corr}) of samples A and B are $10^{-7.5}$ to $10^{-8.5}$ A cm^{-2}, about two orders of magnitude higher

Table 4
The puncture voltages of the samples

Samples	A	B	C	D
Puncture voltage (V)	>220	>220	>220	>220

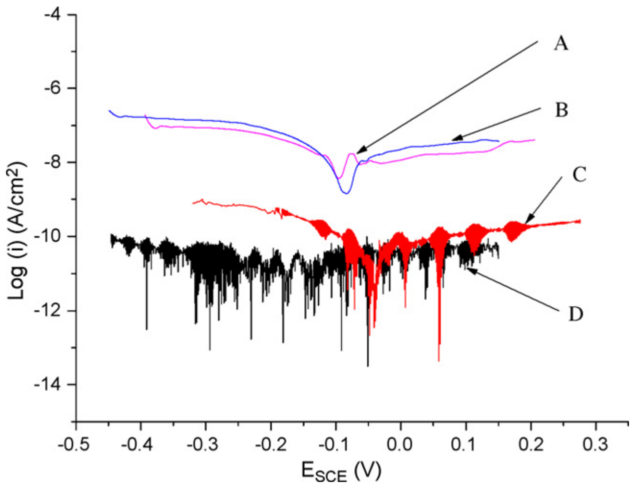

Fig. 3. Potentiodynamic behaviors of the samples in simulated PEMFC environments at 26 ± 0.5 °C.

than those of samples C and D, which illustrates that sealing conditions have significant effects on the corrosion resistance. Samples sealed with epoxy resin show better corrosion resistance than those sealed in boiling water under the test conditions. Although the I_{corr} of sample B is approximately equal to that of sample A, but the corrosion voltage (E_{corr}) value for sample B is a little more positive than that of sample B, which elucidates that sample B has a better corrosion resistance. Compared with samples C and D, the sample anodized at a constant current density has a higher corrosion resistance than that anodized at a constant voltage. Furthermore, in the case of sample D, a passive region wider than 600 mV is observed and it indicates the best corrosion-resistant ability.

Potentiostatic polarization measurements for samples A, B, C, and D in 0.5 M H_2SO_4 + 5 ppm F^- at 26 ± 0.5 °C with 1 V voltage applied are shown in Fig. 4. In the simulated PEMFC environments, the I_{corr} of sample A increases quickly from $10^{-6.6}$ to $10^{-6.2}$ A cm^{-2} after 20 min corrosion. Similarly, the I_{corr} of sample B increases from $10^{-6.1}$ to $10^{-5.9}$ A cm^{-2} after 35 min corrosion. It is most likely that the films on the surfaces of the samples sealed in boiling water are not dense enough and defects on the surfaces lead to the increasing corrosion currents. And the anodic oxide film obtained at a constant current density was denser than that obtained at a constant voltage, judging from the time when the I_{corr} increases evidently. But for the samples sealed by epoxy resin, the I_{corr} varies gradually. The I_{corr} of sample C increases from $10^{-8.2}$ to $10^{-7.5}$ A cm^{-2} and that of sample D increases from $10^{-9.5}$ to $10^{-8.4}$ A cm^{-2}, two or three orders of magnitude lower than samples A and B, respectively. It can be seen that the corrosion resistance order of the four samples are accordant with that of dynamic polarization, and sample anodized at a constant current and sealed by epoxy resin shows the best corrosion resistance.

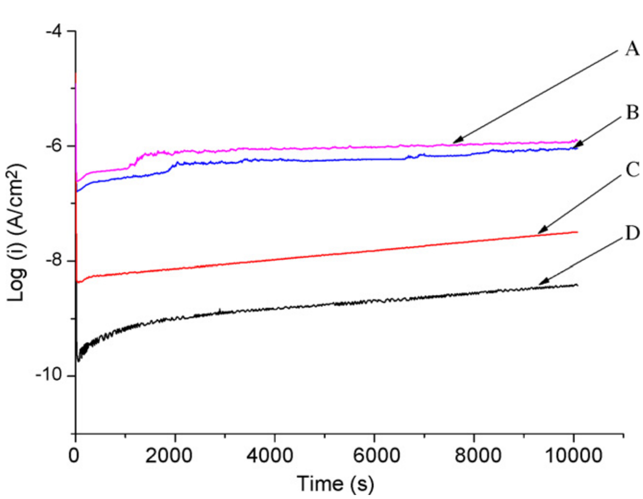

Fig. 4. Transient currents of the samples in simulated PEMFC environments at 26 ± 0.5 °C.

Table 5
Weight losses of the samples in 50% (v/v) glycol solution at 26 ± 0.5

Sample	Corrosion time (h)	Weight loss rate (%)
A	2000	1.810
B	2000	0.194
C	2000	0.005
D	2000	0.000

The corrosion behavior of the samples were also studied in 1 L 50% (v/v) glycol solution to simulate the PEMFC coolant environments. Weight losses of the samples were recorded and the weigh-loss rates are shown in Table 5. The weight loss rate of sample A is 1.81% after 2000 h corrosion, which is the biggest one. The following is that of sample B, which was sealed in boiling water. For the samples sealed by epoxy resin, weight losses are evidently reduced. Especially, no weigh loss is found as for sample D. So it is highly impossible for samples sealed by epoxy resin to produce metal ions causing degradation of stack performance. It can be concluded that the samples anodized at a constant current density perform better than those anodized at a constant voltage in this test.

3.3. Fuel cell test

To evaluate performance of the aluminium alloy endplates for practical applications, a PEMFC stack with 16 single cells was assembled. And two endplates prepared by methods A and D, respectively, were used for comparison. When the PEMFC stack was operated for 200 h, the stack was disassembled and the surface appearances on the endplates were observed with Super Depth Surface Profile Measurement Microscope VK-8550. The 200× micrographs of endplate A are shown in Fig. 5 (as received) and Fig. 6 (after 200 h of operation). It can be seen that there are some defects on endplate A before operation. After 200 h of operation, the internal surfaces of the passages on endplate A suffered severe corrosion. The functional surface film is badly destroyed, and the base metal is in the raw. Similarly, the micrographs of endplate D are shown in Fig. 7 (as received) and Fig. 8 (after 200 h of operation). No defects can be found even through 2000× micrographs, and there is almost no macroscopic corrosion occurred. So the aluminium alloy endplate anodized at a constant current density and then sealed by epoxy resin shows the feasibility for practical applications.

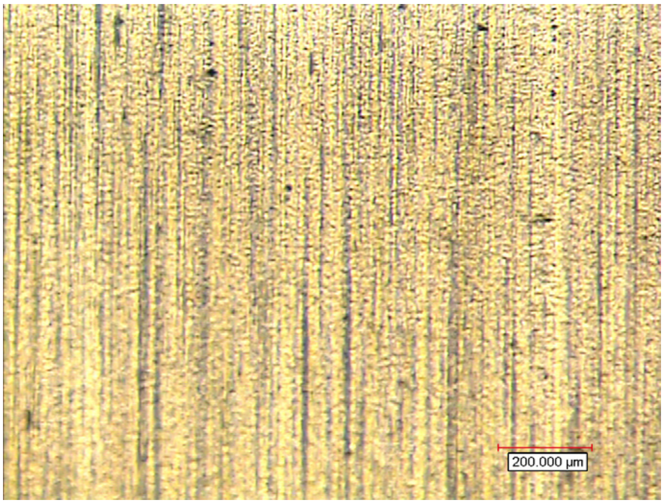

Fig. 5. Picture of 200× micrograph of the endplate prepared by technology A-as received.

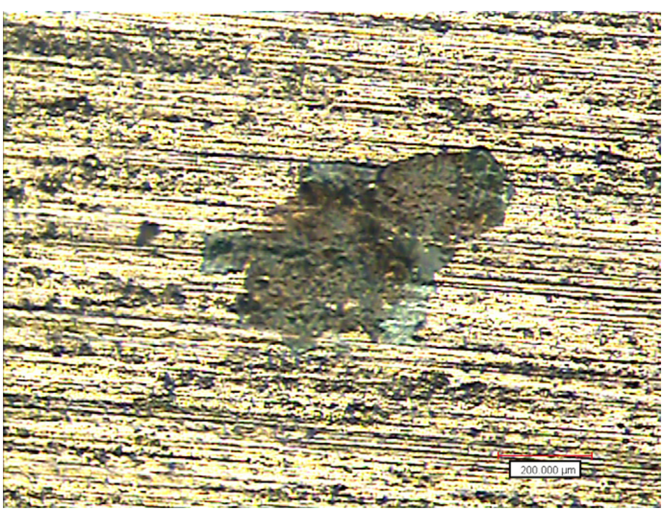

Fig. 6. Picture of 200× micrograph of the endplate prepared by technology A-200 h of operation.

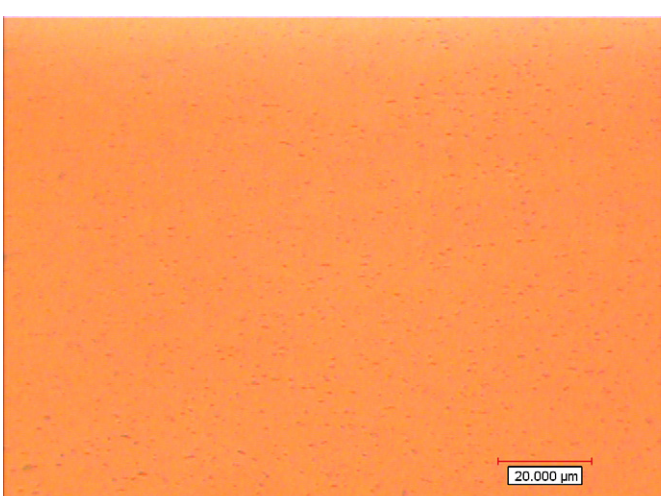

Fig. 7. Picture of 2000× micrograph of the endplate prepared by technology D-as received.

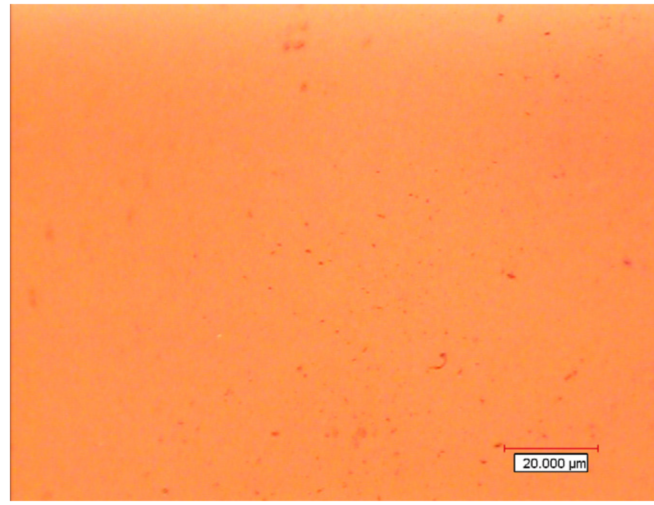

Fig. 8. Picture of 2000× micrograph of the endplate prepared by technology D-200 h of operation.

4. Conclusions

Aluminium alloy was sealed by anodization, and then was applied to the endplate of a PEMFC stack. Two anodization methods combined with two sealing methods were studied. All the samples exhibited high electrical insulation, and different corrosion resistances were achieved in simulated PEMFC environments. In all of the corrosion tests, the samples showed a corrosion resistance order: $A < B \ll C < D$. After thermosetting, the dense epoxy resin film with an excellent corrosion resistance was obtained on the whole surface of the sample D. Sealing in boiling water could only react to form alumina hydrate where alumina existed and it was not helpful to enhance corrosion resistance where defects existed. So the corrosion resistance of the samples sealed with epoxy resin were better than those sealed in boiling water. In addition, anodization conditions had some impact on the performance of the endplates. Alumina films obtained at a constant current density were denser than those anodized at a constant voltage. So aluminium alloy endplates anodized at a constant current density and sealed with epoxy resin showed the best corrosion resistance, and performed well in a 200 h PEMFC stack operation test. Thus, promising aluminium alloy endplates for PEMFCs were obtained.

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References

[1] B.L. Yi, Fuel Cell-Theory Technology Application, first ed., Beijing, 2003, pp. 160–161.
[2] S.G. Chalk, P.G. Patil, S.R. Venkateswaran, J. Power Sources 61 (1996) 7–13.

[3] D.R. Hodgson, B. May, P.L. Adcock, D.P. Davies, J. Power Sources 96 (2001) 233–235.
[4] M.J. Kelly, G. Fafilek, J.O. Besenhard, H. Kronberger, G.E. Nauer, J. Power Sources 145 (2005) 249–252.
[5] I.E. Paulauskas, M.P. Brady, H.M. Meyer III, R.A. Buchanan, L.R. Walker, Corros. Sci. 48 (2006) 3157–3171.
[6] E.A. Cho, U.S. Jeon, S.A. Hong, I.H. Oh, S.G. Kang, J. Power Sources 142 (2005) 177–183.
[7] S. Joseph, J.C. McClure, R. Chianelli, P. Pich, P.J. Sebastian, Int. J. Hydrogen Energy 30 (2005) 1339–1344.
[8] V.V. Nikam, R.G. Reddy, J. Power Sources 152 (2005) 146–155.
[9] A. Pozio, R.F. Silva, M.D. Francesco, L. Giorgi, Electrochim. Acta 48 (2003) 1543–1549.
[10] A.E. Agizy, D.M. Sheridan, R.G. Hanson, US Patent No. 20,020,182, 470.
[11] M. Takashita, Y. Nakano, S. Fujieda, US Patent No. 20,050,048,347.
[12] G. Patermarakis, N. Papadreadis, Electrochemi. Acta 38 (1993) 1413–1420.
[13] G.E. Thornpson, Thin Solid Films 297 (1997) 192–201.
[14] B. Müller, S. Fischer, Corros. Sci. 48 (2006) 2406–2416.
[15] Y.J. Du, M. Damron, G. Tang, H.X. Zheng, C.J. Chu, Prog. Org. Coat. 41 (2001) 226–232.
[16] H.F. Zhang, Y.F. Fu, M. Hou, Y. Fu, P.W. Ming, B.L. Yi, China Patent No. 200410020905.
[17] X.Q. Yan, M. Hou, H.F. Zhang, F.N. Jing, P.W. Ming, B.L. Yi, J. Power Sources 160 (2006) 252–257.