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Technical communication

Carbon-based films coated 316L stainless steel as bipolar plate for proton exchange membrane fuel cells

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ABSTRACT

Carbon-based films on 316L stainless steel were prepared as bipolar plates for proton exchange membrane fuel cells (PEMFCs) by pulsed bias arc ion plating. Three kinds of films were formed including the pure C film, the C–Cr composite film and the C–Cr–N composite film. Interfacial conductivity of the bipolar plate with C–Cr film was the highest, which showed great potential of application. Corrosion tests in simulated PEMFC environments revealed that the C–Cr film coated sample always showed better anticorrosive performance than 316L stainless steel either in reducing or oxidizing environments. The C–Cr film coated bipolar plate sample also had high surface energy. The contact angle of the C–Cr film coated sample with water was 92°, which is beneficial for water management in a fuel cell.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is an ideal candidate for automotive propulsion applications due to its high efficiency and near-zero emissions [1–3]. As a major part of the PEMFC stack, the bipolar plate accounts for most of the total weight and cost of the stack [4]. The bipolar plate serves as the following functions such as distributing reactants uniformly over the active areas, removing heat from the active areas, carrying current from cells, preventing leakage of reactants and coolant etc. So the bipolar plate material should have the characteristics as follows: 1) high corrosion resistance in PEMFC environment; 2) low interfacial contact resistance; 3) high surface tension with water; 4) lightweight; 5) high mechanical strength; 6) high volume cost-effective manufacturability etc.

Two types of bipolar plate material are commercially available: graphite and metal [5]. Graphite is an ideal bipolar plate material due to its high chemical stability and good electrical conductivity, but it is fragile to impact. What is more, forming gas channels on graphite bipolar plate is usually a high cost course. So graphite is not suitable for commercialization application directly. Metal such as the stainless steel is considered to be a good candidate material because of its high bulk electrical and heat conductivity, high strength, low gas permeability, and ease of manufacture. However, the corrosion resistance and interfacial contact resistance of metal material should be considered. Forming

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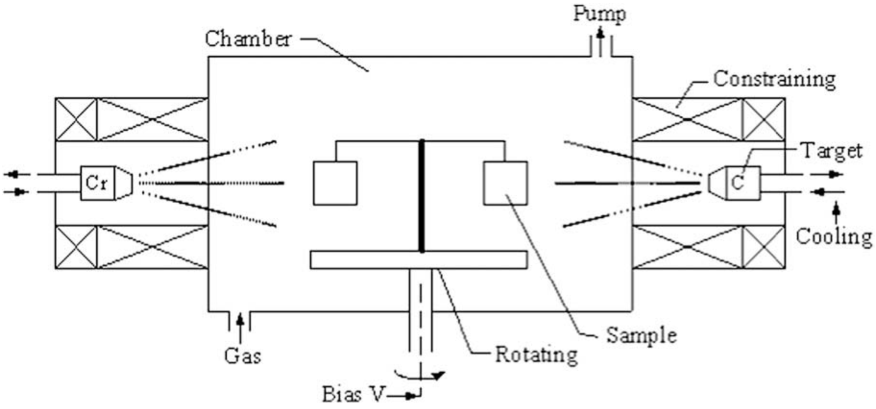

Fig. 1 – Diagram of the PBAIP experimental setup.

a protecting film with good corrosion resistance and high interfacial conductivity on stainless steel through surface treatment is one of the possible solutions [6–10].

Some researches have been conducted on forming carbon material film on metal bipolar plate. This kind of bipolar plate could combine the advantages of the two materials. Show et al. [11,12] coated amorphous carbon film on Ti bipolar plate at various growth temperatures. They found that the bipolar plate showed a low contact resistance when the growth temperature increased up to 600 °C, and the fuel cell assembled with this kind of bipolar plate showed an output power of 1.4 times higher than that assembled with the bare Ti bipolar plates. Fukutsuka et al. [13] prepared carbon coating on SUS304 using plasma-assisted chemical vapor deposition. The corrosion resistance of the bipolar plates was improved in simulated PEMFC conditions, and the interfacial contact resistance was also greatly reduced. Similar study was also conducted by Chung et al. [14]. In addition, some patents are also associated with the technology of metal base/carbon coating bipolar plates [15–17].

In our study 316L stainless steel substrates were coated with carbon-based films by pulsed bias arc ion plating (PBAIP) to obtain protecting layers. PBAIP inherits the advantages of arc ion plating and brings in new features such as reduced droplets, dense films and low-temperature deposition. As a result, films with excellent performance can most likely be obtained. What is more, forming film by PBAIP is an environment-friendly process. Compared with the Cr–nitride films formed by PBAIP in our previous work [10], deposition of the carbon-based film can be greatly accelerated, which is appropriate for commercial production. This is because that the carbon source can be induced by the carbon target and not from the atmosphere. In addition, the economical price of the carbon target is helpful to lower the bipolar plate cost.

2. Experimental

The PBAIP system used in this study is shown in Fig. 1. The 316L stainless steel substrates with size of 100 mm × 100 mm × 0.1 mm were ultrasonically cleaned in acetone, ethyl ethanol and deionized water for 15 min. Then they were blown dry and put on holders. The chamber was evacuated to a base pressure below 5.0×10^{-3} Pa using a turbo molecular pump and a rotary pump. Prior to the deposition, the substrates were sputtered by Ar ions to remove the passive film on the stainless steel surface. Then the carbon-based films were deposited with the two targets work synchronously. Three kinds of films were formed in our study (Table 1). When forming the pure carbon film, two carbon targets were used in a vacuum. As for the carbon-based films, a chromium target and a carbon target were used; the deposition processes were in a high vacuum and in a N_2 atmosphere, respectively.

In our setup (Fig. 2) for measuring the contact resistance, two pieces of Toray carbon paper were sandwiched between the bipolar plate sample and two copper plates which are plated with gold on both sides to enhance conductivity. An electrical current of 5.0 A, sourced by a PSP-2010 Programmable power supply, was provided through the copper plates. During the tests, the compacting force was increased with $5\ \mathrm{N\,s^{-1}}$ controlled by a WDW Electromechanical Universal Testing Machine. All the samples (including the bipolar plate samples and the carbon papers) were wafers with diameter of 60 mm which is the same size as the copper plates.

X-ray photoelectron spectrometer (XPS) was used to characterize the coating.

The corrosion behaviors of the bipolar plate samples were investigated in simulated PEMFC environments (0.5 M H_2SO_4 + 5 ppm F^-) by electrochemical tests. The experiments were performed at 25 °C to simulate the environment when the stack power was off and at 70 °C to simulate the environment when the stack power was on. The corrosion solution was bubbled thoroughly with either hydrogen gas (for

Table 1 – Technologies of forming the carbon-based films with PBAIP.

Film type	Target material	Flow rate of N_2 (sccm)
C	Carbon	0
C–Cr	Carbon and Cr	0
C–Cr–N	Carbon and Cr	20

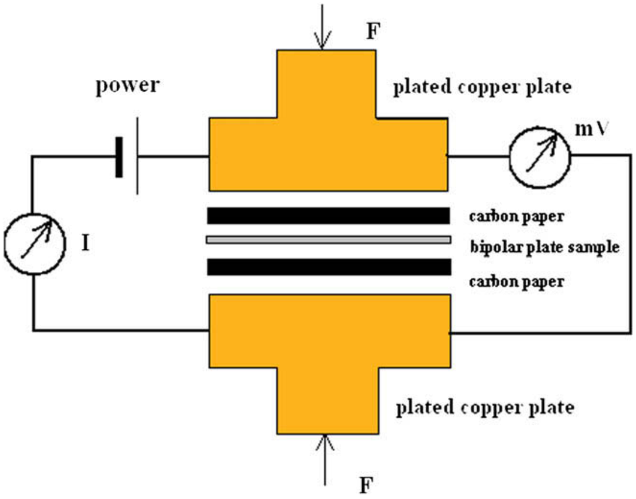

Fig. 2 – Diagram of the setup for measuring the interfacial contact resistance.

simulating a PEMFC anodic environment) or pressured air (for simulating a PEMFC cathodic environment) prior to and during the electrochemical measurements. The samples were stabilized at open circuit potential for 30 min, then the potential was swept at a scanning rate of 2 mV s^{-1}.

At last, contact angle of the bipolar plate sample with water was measured by a JC2000A Contact Angle Measurement to investigate the surface energy. The contact angle of untreated 316L stainless steel plate with water was also measured for comparison.

3. Results and discussion

3.1. *Interfacial contact resistance*

Among all the requirements for the surface-treated metal bipolar plates, the interfacial conductivity is the most important one. If the conductivity of bipolar plate material is not satisfied, high performance would not be obtained. For this reason, interfacial contact resistances of the bipolar plate samples with bare Toray carbon paper were used to screen the deposition technology. The interfacial contact resistances of the bipolar plate samples with Toray carbon paper are shown in Fig. 3. Among all the samples interfacial contact resistance of the pure C film was 330–2160 mΩ cm^2 under 0.2–1.5 MPa, which was the highest. The C–Cr–N film showed a better interfacial conductivity and the interfacial contact resistance was 107–555 mΩ cm^2 under 0.2–1.5 MPa. But the bipolar plate with C–Cr–N film could not satisfy the fuel cell application, too. As for the C–Cr film, it exhibited the best conductivity, which was far lower than the other two. And the interfacial contact resistance of the C–Cr film was only 6.86–8.72 mΩ cm^2 under 0.2–1.5 MPa. So the 316L stainless steel plate with C–Cr film was chosen as candidate of bipolar plate for PEMFC.

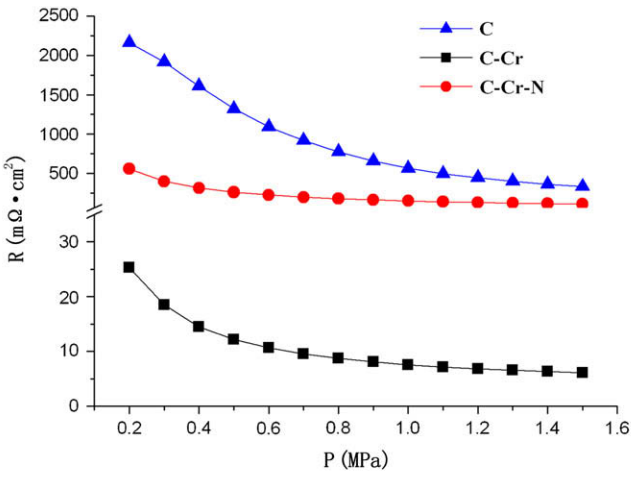

Fig. 3 – Contact resistance between the bipolar plate samples with carbon-based films formed by BPAIP with Toray carbon paper.

Table 2 – Composition of the composite coating by PABIP on 316L stainless steel.

Element	Content (At, %)
C	68.2
Cr	17.1
O	14.7

3.2. *Characterization of the coating*

The XPS analysis result of the bipolar plate with C–Cr film is shown in Table 2. Over 68% C atom was found in the coating, and the proportion of Cr and O is 17.1% and 14.7%, respectively. Obviously, the coating is mainly composed of carbon. As the coating process was conducted under high vacuum, the oxygen was very probably induced by surface adsorption when the sample was exposed to the atmospheric environment.

3.3. *Corrosion resistance*

Potentiodynamic and potentiostatic tests were used to characterize corrosion resistance of the bipolar plate with C–Cr

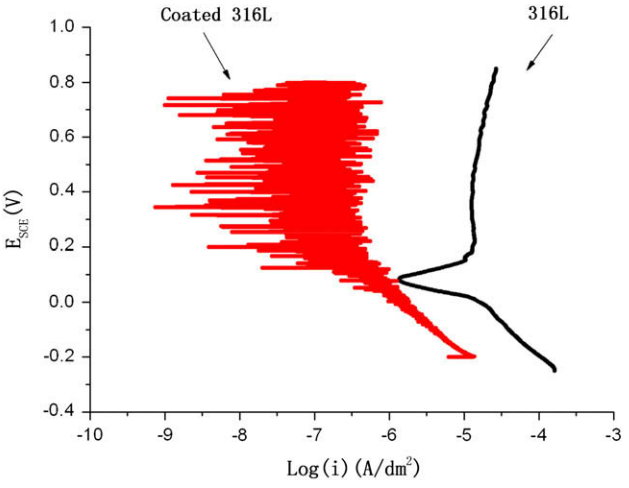

Fig. 4 – Potentiodynamic curves of bipolar plate samples in 0.5 M H_2SO_4 + 5 ppm F^- with a scan rate of 2 mV s^{-1} at 25 °C.

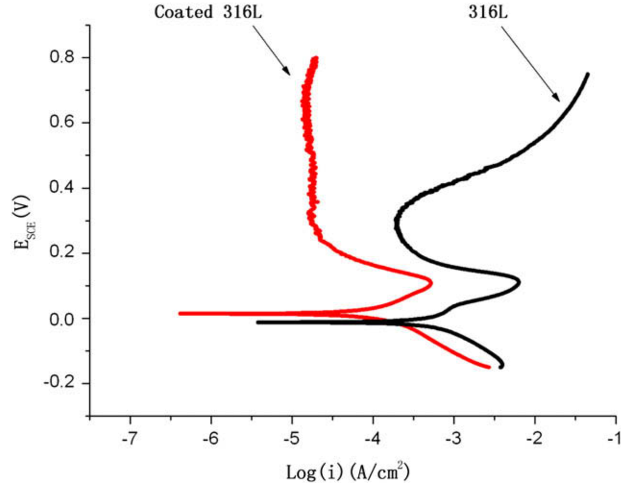

Fig. 5 – Potentiodynamic behaviors of bipolar plate samples in 0.5 M H_2SO_4 + 5 ppm F^- with a scan rate of 2 mV s^{-1} at 70 °C bubbled with air.

film. Potentiodynamic polarization curves of the bipolar plate sample and untreated 316L stainless steel in 0.5 M $H_2SO_4 + 5$ ppm F^- solution at 25 °C (for simulate the environment when the stack power was off) are shown in Fig. 4. The coated bipolar plate sample was in passive state under test condition from 0.1 V to 0.8 V versus SCE. And the untreated 316L stainless steel could be passivated spontaneously under the same condition from 0.2 V to 0.8 V versus SCE. The corrosion current densities of bipolar plate sample and 316L stainless steel were about 10^{-7} A cm^{-2} and 10^{-5} A cm^{-2}, respectively. The coated bipolar plate sample exhibited much better corrosion resistance, in accordance with the result of the corrosion potential experiment. As for the experiments in 0.5 M $H_2SO_4 + 5$ ppm F^- solution at 70 °C (for simulate the environment when the stack power was on) bubbled with air (Fig. 5) or H_2 (Fig. 6), the corrosion currents were higher than that performed at 25 °C. But the bipolar plate sample exhibited a better corrosion resistance than the base metal in all simulated PEMFC environments.

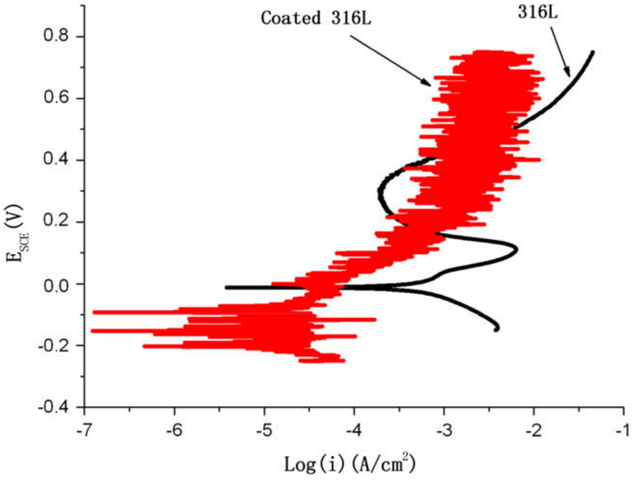

Fig. 6 – Potentiodynamic behaviors of bipolar plate samples in 0.5 M H_2SO_4 + 5 ppm F^- with a scan rate of 2 mV s^{-1} at 70 °C bubbled with H_2.

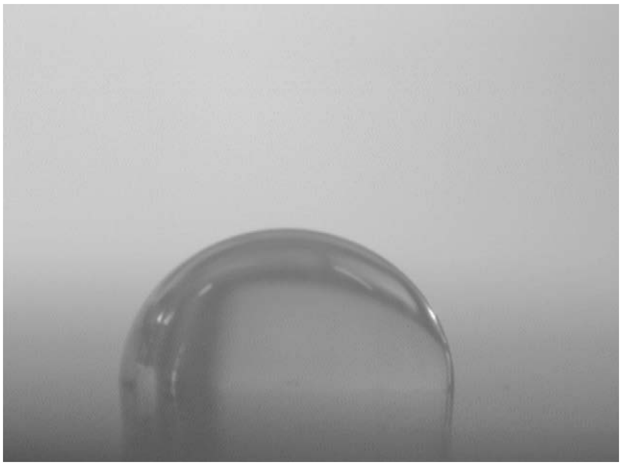

Fig. 7 – Contact angle of the coated bipolar plate with water.

3.4. *Contact angle*

The contact angles of the bipolar plate with C–Cr film and 316L stainless steel with water are shown in Figs. 7 and 8, respectively. Obviously, the bipolar plate sample coated with C–Cr film has a bigger contact angle (91°) than 316L stainless steel (73°). As we know, the process in fuel cell is always accompanied with water. To prevent the proton exchange membrane from dehydration, the inlet gases need to be humidified. In addition, there exists water generated due to oxygen reduction reaction in the fuel cell stack, so the bipolar plates are often contacted with the mixture of reactant gas and water. If the liquid water could not be removed in time, the water would block the reactant gases accessing to the electrode. The accumulated water induces the electrode flooding phenomenon. Furthermore, the water adhering on the surface of bipolar plate accelerates the corrosion of metal bipolar plate. For these reasons, this kind of bipolar plate with

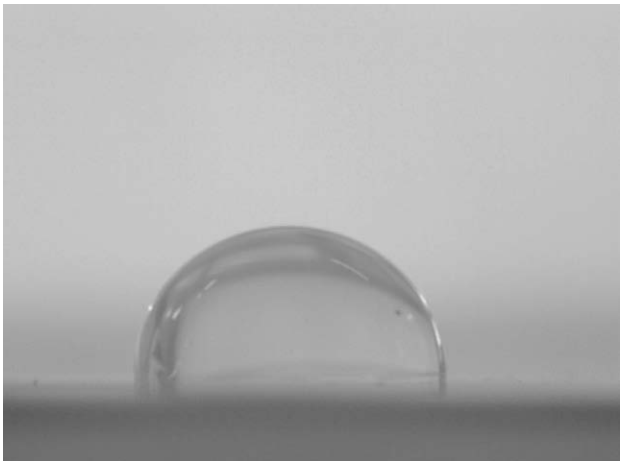

Fig. 8 – Contact angle of the untreated 316L stainless steel plate with water.

high surface energy would be helpful for water removal in the stack and beneficial to the water management.

4. Conclusion

Carbon-based films on 316L stainless steel substrates were prepared by PBAIP as bipolar plate material for PEMFCs. Interfacial conductivity of the bipolar plates with pure C film or with C–Cr–N film is not satisfied, but the bipolar plate with C–Cr film showed very low interfacial contact resistance. Potentiodynamic and potentiostatic tests conducted in simulated PEMFC environments also revealed that the corrosion resistance of bipolar plate sample with C–Cr film was greatly enhanced compared with the substrate. What is more, the contact angle of the sample with water was higher, which is beneficial for water management in fuel cell. It is concluded that the 316L stainless steel substrate with C–Cr film might be a good candidate for bipolar plate for PEMFC.

Acknowledgments

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