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Short communication

Ag–polytetrafluoroethylene composite coating on stainless steel as bipolar plate of proton exchange membrane fuel cell

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ABSTRACT

Forming a coating on metals by surface treatment is a good way to get high performance bipolar plate of proton exchange membrane fuel cell (PEMFC). In our research, Ag–polytetrafluoroethylene (PTFE) composite film was electrodeposited with silver-gilt solution of nicotinic acid by a bi-pulse electroplating power supply on 316 L stainless steel bipolar plate of PEMFC. Surface topography, contact angle, interfacial conductivity and corrosion resistance of the bipolar plate samples were investigated. Results showed that the defects on the Ag–PTFE composite coating are greatly reduced compared with those on the pure Ag coating fabricated under the same condition; and the contact angle of the Ag–PTFE composite coating with water is 114°, which is much bigger than that of the pure Ag coating (73°). In addition, the interfacial contact resistance of the composite coating stays as low as the pure Ag coating; and the bipolar plate sample with composite coating shows a close corrosion resistance to the pure Ag coating sample in potentiodynamic and potentiostatic tests. Coated 316 L stainless steel plate with Ag–PTFE composite coating exhibits well hydrophobic characteristic, less defects, high interfacial conductivity and good corrosion resistance, which shows a great potential of the application in PEMFC.

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]. An ideal bipolar plate material should be cost-effective, corrosion-resistant and electricity conductive. In addition, its hydrophobic characteristic is also very important.

Forming a protecting film with good corrosion resistance and high interfacial conductivity on stainless steel by surface treatment is one of the possible solutions to obtain high performance bipolar plate of PEMFC. There are mainly two kinds of materials used for the coatings. One is carbon-based material and another is metal-based material [5]. Carbon-based coatings [6–13] include graphite, conductive polymer, and diamond-like carbon, etc.; metal-based coatings include noble metals, metal nitrides [14–19] and metal carbides [20]. The techniques of carbon-based coatings are far from the practical applications. Further investigations are needed for the carbon-based coatings. In recent years, most of the researches are focused on metal-based coatings, especially for the metal nitrides and metal carbides.

However, noble metals are still the most suitable coating materials by considering the corrosion resistance and conductivity. Some researches have been conducted by forming noble metal coatings on metal bipolar plate. Wind et al. [21] measured the current–voltage curve of a single cell assembled with gold-coated 316 L stainless steel bipolar plates and found that there was no difference between the gold-coated plates and the graphite plates. The fuel cell was operated for 1000 h and no obvious deterioration of the cell voltage was observed. Hentall et al. [22] and Wang et al. [23] coated gold on aluminium and titanium bipolar plate, respectively. The performances of both bipolar plates were very similar or even better than that of graphite plates. Wang et al. [24] also formed iridium oxide and platinum coatings on titanium bipolar plates and good fuel cell performances were obtained. Yoon et al. [25] deposited zirconium nitride with a gold top layer on stainless steel substrates. The results indicated that very thin gold coating (2 nm) can significantly decrease the contact resistance, but a relatively thick gold coating (>10 nm) is necessary for adequate corrosion

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resistance. In addition, some patents are also associated with the noble metal coatings on metal bipolar plates [26–28]. However, the high cost of noble metal limits the application of this kind of bipolar plate.

Silver is a kind of noble metal with low material cost, so it is suitable for PEMFC bipolar plate coating. Electrodeposition of Ag on stainless steel is a conventional technology for surface treatment, but defects on the coating which are prone to corrosion are unavoidable and thus destroying the whole protecting film.

In our research the composite coating of Ag–polytetrafluoroethylene (PTFE) was developed. The PTFE particles were used to reduce the defects, which can also increase the contact angle of bipolar plate material and benefit for water removal in PEMFC. Surface topography, contact angle, interfacial conductivity and corrosion resistance of the bipolar plate samples with Ag–PTFE composite coating were investigated.

2. Experimental

2.1. Fabrication of metal bipolar plate sample

To prepare metal bipolar plate sample, 316 L stainless steel plate with the dimension of 100 mm × 100 mm × 0.1 mm was used as the base metal. Ag–PTFE composite coating was electrodeposited with silver-gilt solution of nicotinic acid by a bi-pulse electroplating power supply, which is an environment-friendly cyanide-free plating method. Pure Ag film was also coated on 316 L stainless steel under the same condition for comparison.

2.2. Experimental

Surface topography of the bipolar plate sample was conducted with JMS-5600LV SEM and VK-8550 Super Depth Surface Profile Measurement Microscope. The contact angle of bipolar plate sample with water was measured with JC2000A Contact Angle Measurement. In addition, the interfacial contact resistance between the bipolar plate sample and Toray carbon paper was measured. The measurement was described in our previous paper [29]. At last, potentiodynamic and potentiostatic tests were utilized to analyze the corrosion characteristics of the bipolar plate samples. A conventional three-electrode system was used with a working electrode, a platinum sheet as the counter electrode and a saturated calomel electrode (SCE, sat'd KCl) as the reference electrode. All the electrochemical tests were conducted using a potentiostat Model 2273 A by EG&G Princeton Applied Research. Before corrosion tests, all the samples were stabilized at open circuit potential for 30 min. In the potentiodynamic tests, the scan rate was 2 mV s^{-1}. In order to simulate the working conditions of PEMFC, potentiostatic tests were conducted at the anode, the applied potential was −0.1 V versus SCE purged with H_2 and at the cathode, the applied potential was 0.6 V versus SCE purged with air. The potentiodynamic and potentiostatic tests were conducted at 70 °C. The electrolyte was 0.5 M H_2SO_4 + 5 ppm F^-.

3. Results and discussion

3.1. Surface topography

SEM micrographs of the coatings on 316 L stainless steel are shown in Figs. 1 and 2. There are about 40 defects per square millimeter on the pure Ag coating; the number of defects on the Ag–PTFE composite coating is greatly reduced to about 20 per square millimeter. The size of defects on the pure Ag coating obtained is about several microns, whereas the size of PTFE particles is only 0.5 μm, so the PTFE particles can be embedded in the defects of Ag coating thus reducing the defects and smoothing the coating.

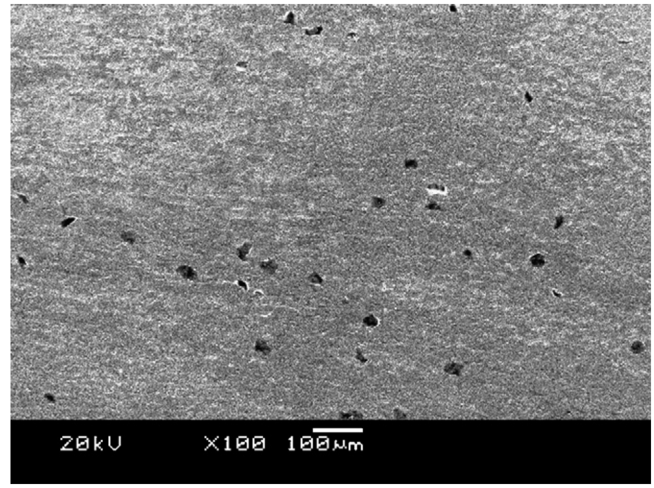

Fig. 1. SEM micrograph of the Ag–PTFE composite coating on 316 L stainless steel.

Three-dimensional micrographs of the samples by Super Depth Surface Profile Measurement Microscope are shown in Figs. 3 and 4. The planeness of the Ag–PTFE composite coating is 3 μm, and that of the pure Ag coating is about 6 μm. Obviously the composite coating is smoother than the pure Ag coating, which is in accordance with the above analysis.

3.2. Contact angle

The contact angles of the bipolar plate samples with water are shown in Figs. 5 and 6. The contact angles with water for the Ag–PTFE composite coating and the pure Ag coating are 114° and 73°, respectively. The former shows more hydrophobic than the latter. The inlet gases in PEMFC need to be humidified to prevent the membrane from dehydration, and the exhausts are often mixed with the resultant water, so two-phase fluids exist in PEMFC. If the liquid water was not removed in time, the electrode flooding could occur and the power of the stack would decrease rapidly. Bipolar plate with well hydrophobic characteristic is helpful for water removal and beneficial for the water management. In addition, the water with weak acid adhering on the surface of metal bipolar plate

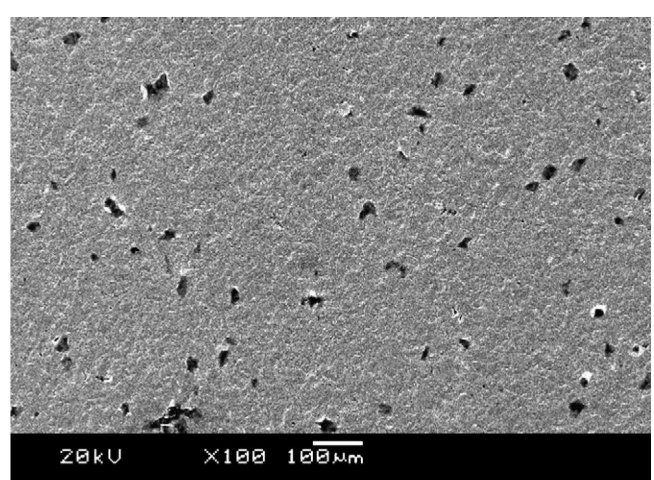

Fig. 2. SEM micrograph of the Ag coating on 316 L stainless steel.

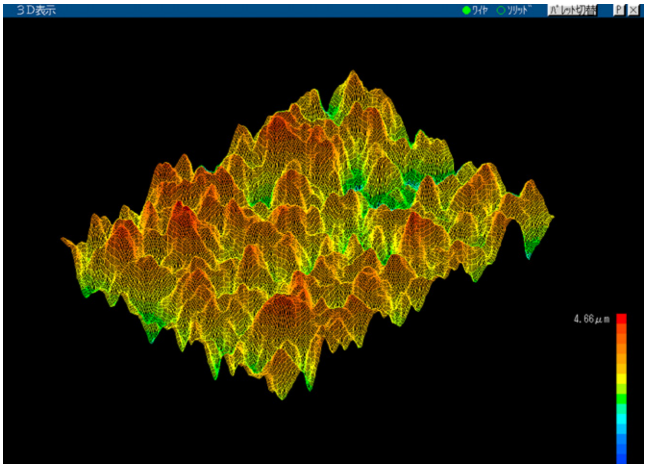

Fig. 3. Picture of 2000× three-dimensional micrograph of the Ag–PTFE composite coating on 316 L stainless steel.

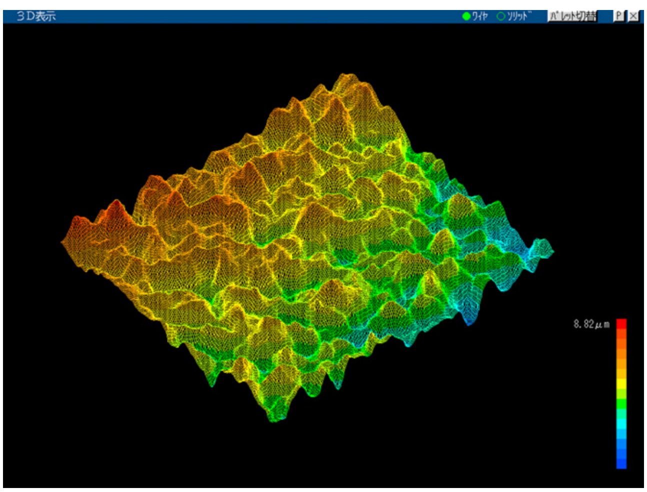

Fig. 4. Picture of 2000× three-dimensional micrograph of the Ag coating on 316 L stainless steel.

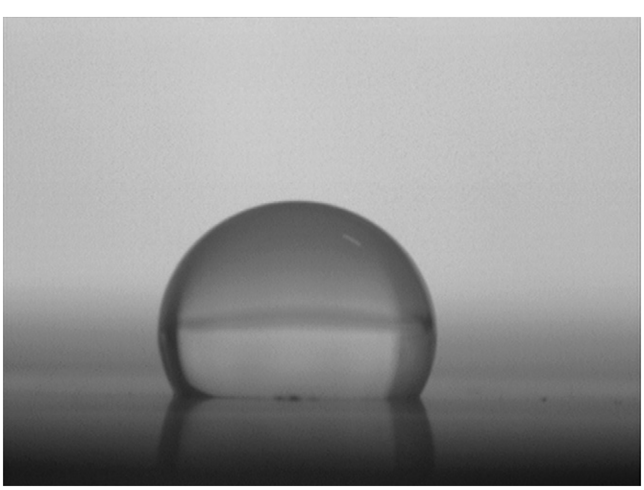

Fig. 5. Contact angle of the Ag–PTFE composite coating on 316 L stainless steel with water.

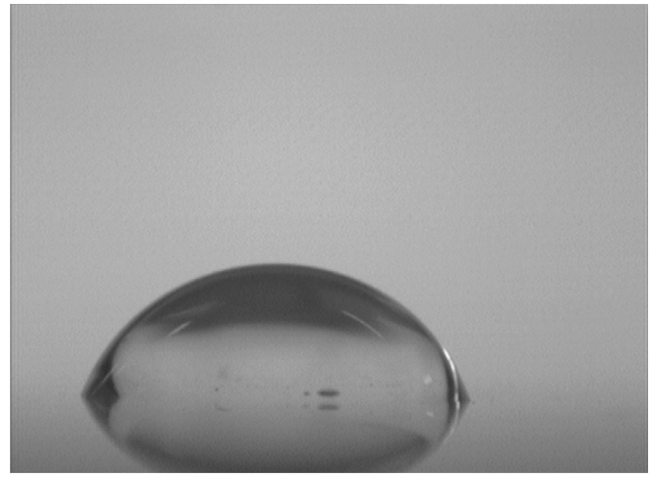

Fig. 6. Contact angle of the Ag coating on 316 L stainless steel with water.

would accelerate up the corrosion. The hydrophobic bipolar plate makes it difficult for water adhering, thus improving the corrosion resistance of the bipolar plate. Obviously, the addition of PTFE particles increases the contact angle of the coating greatly and it is very beneficial to PEMFC.

3.3. Interfacial contact resistance

Interfacial contact resistance of the bipolar plate sample with Toray carbon paper is shown in Fig. 7. The interfacial conductivity of Ag–PTFE composite coating is close to that of the pure Ag coating. The minute quantities of PTFE in Ag coating would not lead to the increment of contact electrical resistance. On the contrary, the contact resistance of the composite coating is a little lower than that of pure Ag coating when the compacting pressure was over 0.3 MPa. It is very probably because that the composite coating is smoother, thus the contact area is larger under high compacting pressure. The larger the contact area is, the lower the resistance is [30]. The compacting pressure applied to the PEMFC stack is often in the range of 0.8–1.2 MPa nowadays. The interfacial contact resistance between the bipolar plate sample with composite coating and carbon paper is in the range of 2.88–3.94 mΩ cm^2 under stack compacting pressure; and the value for the pure Ag coating under the same condition is 3.24–4.54 mΩ cm^2. The higher output power

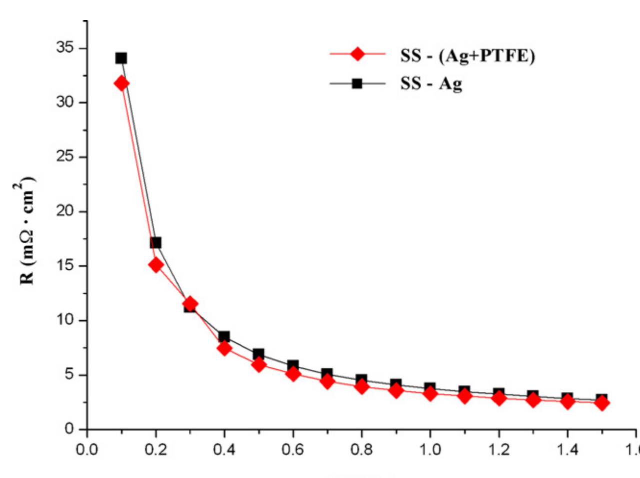

Fig. 7. Interfacial contact resistance of the bipolar plate with Toray carbon paper.

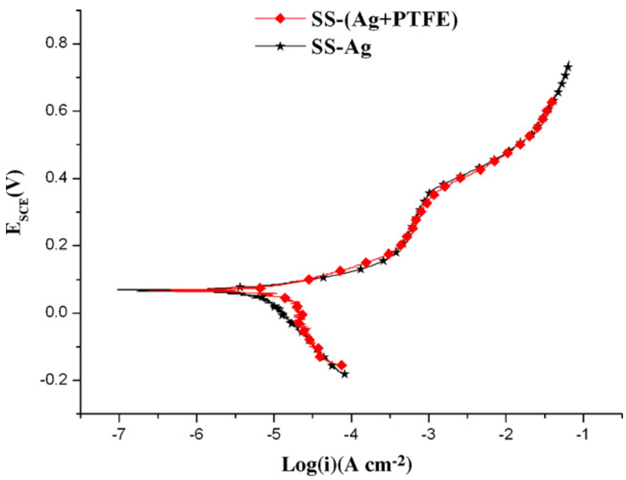

Fig. 8. Potentiodynamic curves of the bipolar plate samples in 0.5 M H_2SO_4 + 5 ppm F^- at 70 °C purged with H_2.

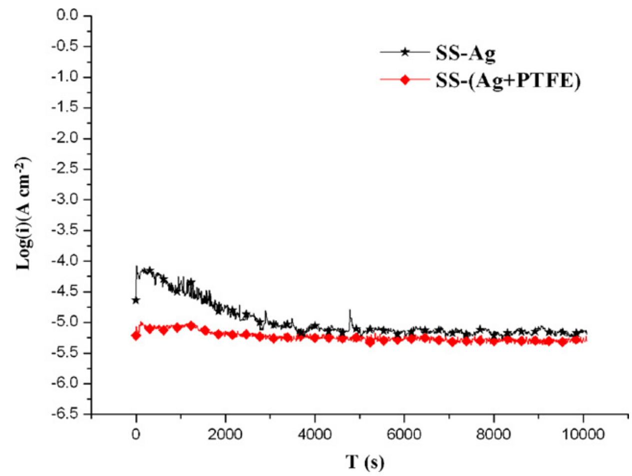

Fig. 10. Transient current of the bipolar plate samples at −0.1 V in 0.5 M H_2SO_4 + 5 ppm F^- at 70 °C purged with H_2.

could be obtained with the lower interfacial contact resistance. So the Ag–PTFE composite coating is helpful to improve the output power.

3.4. Corrosion resistance

Potentiodynamic tests were conducted to investigate the corrosion resistance of the bipolar plate samples with Ag–PTFE composite coating and the pure Ag coating. Fig. 8 presents the potentiodynamic curves of the samples in 0.5 M H_2SO_4 + 5 ppm F^- solution at 70 °C purged with H_2. There are no obvious differences between the two kinds of bipolar plate samples according to their dynamic polarization behaviors. From the slopes of the anodic curve and the cathode curve, the corresponding corrosion current and corrosion voltage can be determined. The corrosion current densities for both of the bipolar plate samples were about 10^{-5} A cm^{-2}, and the corrosion potentials were about 0.08 V versus SCE. The potentiodynamic curves of the samples in 0.5 M H_2SO_4 + 5 ppm F^- solution at 70 °C purged with air are shown in Fig. 9. Corrosion behaviors of the two kinds of bipolar plate samples are also very close, but the corrosion potential of the sample with composite coating was 20 mV more negative than that of the pure Ag coating.

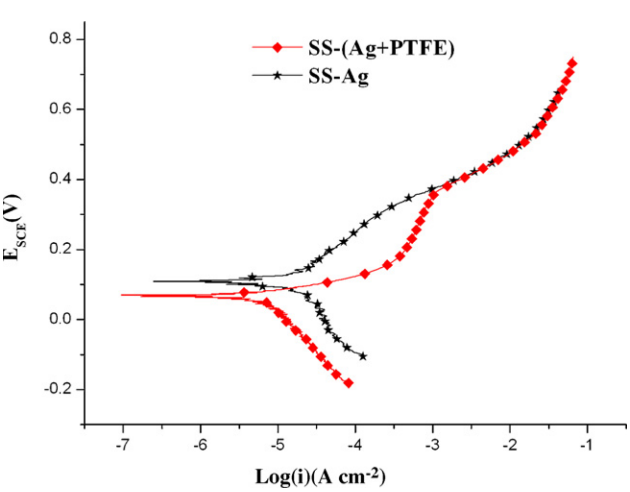

Fig. 9. Potentiodynamic curves of the bipolar plate samples in 0.5 M H_2SO_4 + 5 ppm F^- at 70 °C purged with air.

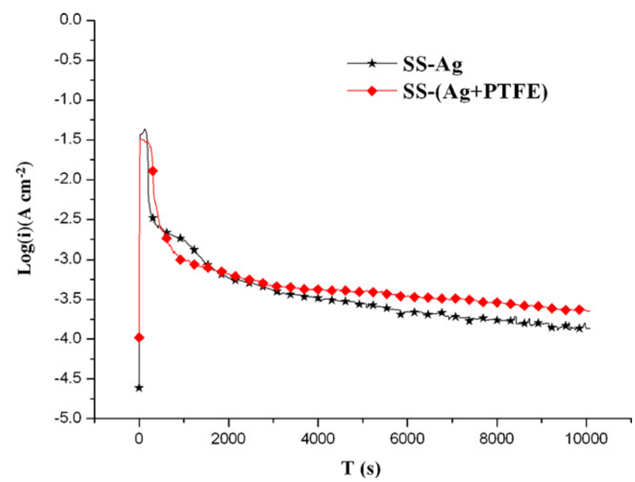

Fig. 11. Transient current of the bipolar plate samples at 0.6 V in 0.5 M H_2SO_4 + 5 ppm F^- at 70 °C purged with air.

In order to study the corrosion behaviors of the bipolar plate samples in actual PEMFC working conditions, potentiostatic tests were conducted at −0.1 V versus SCE purged with H_2 to simulate the anode working condition and at 0.6 V versus SCE purged with air to simulate the cathode working condition. In the simulated anode condition (Fig. 10), the current density of the sample with composite coating stabilized quickly and stayed in the range of $10^{-5.0}$–$10^{-5.3}$ A cm^{-2}. And the current density of the sample with pure Ag coating decreased gradually and varied in the range of $10^{-5.0}$–$10^{-5.2}$ A cm^{-2}, a little higher than the composite coating. As for the tests in simulated cathode condition as shown in Fig. 11, the current density of the sample with Ag–PTFE composite coating was a litter higher than that of the sample with pure Ag coating.

As a whole, the addition of PTFE to Ag coating did not affect the corrosion resistance of the bipolar sample greatly. It seems that the amount of PTFE added needs to be optimized in the coming work.

4. Conclusion

Ag–PTFE composite coating was electrodeposited on 316 L stainless steel as bipolar plate of PEMFC. The PTFE particles can be embedded in the defects of Ag coating, and consequently reducing the defects. The addition of PTFE to Ag coating increases the contact angle of coating greatly, which is beneficial for water management of the stack. In addition, the composite coating is smoother than that of the pure Ag coating, leading to a lower interfacial contact resistance under high compacting pressure due to a bigger contact area. And the addition of minute quantities of PTFE does not have obvious effects on corrosion resistance of the metal bipolar plate samples in electrochemical tests.

Acknowledgements

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