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Conductive amorphous carbon-coated 316L stainless steel as bipolar plates in polymer electrolyte membrane fuel cells

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Amorphous carbon (a-C) film about 3 μm in thickness is coated on 316L stainless steel by close field unbalanced magnetron sputter ion plating (CFUBMSIP). The AFM and Raman results reveal that the a-C coating is dense and compact with a small size of graphitic crystallite and large number of disordered band. Interfacial contact resistance (ICR) results show that the surface conductivity of the bare SS316L is significantly increased by the a-C coating, with values of 8.3–5.2 mΩcm² under 120–210 N/cm². The corrosion potential (Ecorr) shifts from about −0.3 V vs SCE to about 0.2 V vs SCE in both the simulated anode and cathode environments. The passivation current density is reduced from 11.26 to 3.56 μA/cm² with the aid of the a-C coating in the simulated cathode environment. The a-C coated SS316L is cathodically protected in the simulated anode environment thereby exhibiting a stable and lower current density compared to the uncoated one in the simulated anode environment as demonstrated by the potentiostatic results. © 2009 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Bipolar plates are a key multifunctional component in polymer electrolyte membrane fuel cells (PEMFC) and account for the large portion of the mass and volume of a typical fuel cell stack [1–3]. The bipolar plates collect the current of the fuel cells and separate individual fuel cells. They serve as a collector connecting the cathode side of one cell to the anode side of the other one with good conductivity and supply the reactive gases to the anode side (hydrogen gas) and cathode side (oxygen gas) via the flow channels while removing the heat and reaction products (water) [3–6]. Therefore, high corrosion resistance, low interfacial contact resistance, high gas impermeability, high mechanical strength, and low cost are required for the practical application of the bipolar plate materials [7,8].
Much effort has been made to develop commercial bipolar plate materials. At present, two types of materials are used in bipolar plates, namely graphite and metal [4,9]. With respect to corrosion resistance and electrical conductivity, graphite is preferred [7,10–14]. However, the fabrication costs of graphite bipolar plates incorporating gas flow channels are high, subsequently limiting its application in bipolar plates. In addition, the graphite bipolar plates are typically several millimeters thick in fuel cell stacks due to its poor mechanical strength and brittle nature and so such PEMFC stacks are heavier and bulkier [15]. The alternative is to use metallic materials in bipolar plates. Metals have advantages such as good mechanical strength, high electrical conductivity, high gas impermeability, low cost, and ease of manufacturing [16–19]. In addition, the gas flow channels can be easily fabricated in thin metal plates by pressing, but the corrosion resistance and passivation must be considered. Stainless steel is one of the suitable materials in this respect capable of providing satisfactory performance for several thousand hours without obvious power density decline [20]. Due to its self-passivating ability, stainless steel is usually covered by a passive film in the cathode environment and this surface layer prevents the bulk from further corrosion [21]. Although the passive film can decrease the corrosion rate of stainless steel, it will significantly increase the interfacial contact resistance (ICR) between the bipolar plate and back electrode thereby compromising the cell performance due to ohmic loss [17]. On the anode side, metal ions in the stainless steel can leach out into the membrane blocking the sulfonic acid sites and poisoning the catalytic process [2,22,23]. The corrosion resistance and electrical conductivity appear to be mutually exclusive in stainless steel, but it is possible to achieve both by coating technology [24–26].

A promising approach is to deposit a carbon film on the stainless steel substrate. This process combines the advantages of graphite and stainless steel. Show et al. [27,28] have prepared amorphous carbon film on titanium bipolar plates at different temperature and their results show that the a-C film deposited at 600 °C possesses a low resistivity of 10^{-3} \Omega \cdot cm, and the fuel cell assembled from the a-C coated Ti bipolar plate has an output power of 1.4 times higher than that of a bare Ti bipolar plate fuel cell. Chung et al. [29] have coated carbon film on stainless steel 304 by thermal chemical vapor deposition (CVD) at 680 °C using a mixture of C_2H_2/H_2. Both the corrosion tests and PEMFC operation indicate that the carbon film has excellent chemical stability similar to that offered by high purity graphite plate. Fukutsuka et al. [6] have deposited stainless steel 304 with a carbon coating by plasma-assisted chemical vapor deposition. The carbon-coated SS304 exhibits high electrical conductivity and improved corrosion resistance in spite of the absence of a passive film. Fu et al. [9] have prepared a C-Cr composite film on stainless steel by pulsed bias arc ion plating. The results show that the interfacial conductivity and corrosion resistance are improved by the C-Cr film and the C-Cr film coated sample has high surface energy as well.

When the PEMFC is in operation, corrosion of the bipolar plate in the fuel cell system takes place potentiostatically. The anode and cathode environments are at about −0.1 V vs SCE with aerated H_2 and 0.6 V vs SCE with air, respectively [30,31]. Therefore, the bipolar plates in the anode and cathode undergo corrosion at an applied potential which is different from the free potential corrosion. To gauge the corrosion resistance for long-term operation in the simulated PEMFC anode and cathode environments, the potentiostatic test is necessary. However, not much work about carbon coating has been carried out in this respect. In the present study, SS316L is coated with amorphous carbon (a-C) by close field unbalanced magnetron sputter ion plating (CFUBMSIP) [22] and the corresponding effects on the electrical conductivity and corrosion resistance are investigated.

2. Experimental details

Austenitic stainless steel 316L (SS316L) coupons with size of 15 mm \times 15 mm \times 5 mm were used in bipolar plates. They were polished with No. 2000 SiC waterproof abrasive paper and No. 5 diamond paste polisher, cleaned with acetone and distilled water in an ultrasonic cleaner, and dried. The a-C film was deposited onto the samples using a close field unbalanced magnetron sputter ion plating (CFUBMSIP) system consisting of two targets of 99.99% pure graphite and two targets of 99.99% Cr. High purity argon (99.99%) and helium (99.99%) were used as the sputtering gases. The chamber was evacuated to a base pressure below 3.0 \times 10^{-3} Pa using a turbo molecular pump and a rotary pump. Prior to deposition, the substrates were sputtered by Ar ions to clean and remove the native passive film on the surface at a bias voltage of −500 V. A Cr transition layer was first deposited, followed by deposition of the amorphous carbon (a-C) film using both targets operated synchronously. The surface morphology of a-C coating was observed by atomic force microscopy (AFM, Multimode Nanoscope IIIa in the Instrumental Analysis Center of SJTU) and the internal structure was characterized by Raman spectroscopy (inVia + Reflex).

The interfacial contact resistance (ICR) of the uncoated and a-C coated SS316L samples was determined according to the method of Davies et al. [23], Wang et al. [30] and Lee et al. [15,33]. Briefly, two pieces of conductive carbon paper (Toray TGP-H-090) were sandwiched between the sample and two copper plates. A constant current (0.1 A) was applied via the two copper plates, and the variation in the total voltage was recorded with respect to the compaction force that was steadily increased. The ICR value between the carbon paper and copper plate was corrected by calibration. Thus, the ICR results shown here are the corrected values between the sample and carbon paper. Further details of this method can be found elsewhere in the literature [30]. For comparison, the ICR of commercial graphite was also measured.

All samples for electrochemical measurements were embedded in epoxy resin with an exposed surface of 10 mm^2 \times 10 mm^2 and the backside connected to a soldered copper wire. The open circuit potential (OCP) measurements as well as potentiodynamic and potentiostatic tests were conducted to evaluate the electrochemical behavior of the uncoated and a-C coated samples. A CHI 606C electrochemical analyzer with computer control was used in the electrochemical experiments. A conventional three-electrode system was used for the electrochemical measurements. A platinum
sheet served as the counter electrode, a saturated calomel electrode (SCE) was the reference electrode, and the samples were the working electrode. All the electrochemical measurements were conducted in a 0.5 M H₂SO₄ solution with 2 ppm HF at 80 °C to simulate the PEMFC environment. The solution was aerated with either hydrogen (to simulate the anode environment) or air (to simulate the cathode environment) prior to and during the electrochemical test. The open circuit potential (OCP) vs time relationship was recorded for 30 min before potentiodynamic polarization and the potentiodynamic polarization was measured with a potential scanning rate of 1 mv/s. The potentiostatic test was carried out to investigate the performance and stability of the uncoated and the a-C coated samples in the simulated PEMFC environment. The potentiostatic test was conducted for 8.9 h at the potential of −0.1 V vs SCE while aerated with H₂ and 0.6 V vs SCE with air in order to simulate the anode and cathode operating environment in PEMFC, respectively.

3. Results and discussion

3.1. Surface morphology and structure

Fig. 1 depicts the AFM images showing the surface morphology of the amorphous carbon (a-C) coating on the SS316L sample. The a-C coating prepared by CFUBMSIP is dense and a continuous and compact film is observed, indicating that the a-C coating can block the substrate from direct corrosion. The Raman spectrum acquired from the a-C coated SS316L sample shown in Fig. 2 can be deconvoluted into two Gaussian curves, namely the G-band and D-band corresponding to the graphite band (originating from the graphite lattice) and disordered band (originating from the defects in the graphite crystal). The intensity of the D-band around 1390 cm⁻¹ is higher than that of the G-band around 1568 cm⁻¹, indicating that the size of the graphitic crystallites is small and the number of disordered band is large.

3.2. Interfacial contact resistance (ICR)

The interfacial contact resistance (ICR) between the a-C coated SS316L and carbon paper is investigated as a function of compaction force (Fig. 3), with the graphite (Fig. 3(a)) and the uncoated SS316L (Fig. 3(b)) measured as a reference. In general, the ICR values decrease with increasing compaction force due to the increasing contact areas between the carbon paper and stainless steel [34]. The ICR determined from the a-C coated SS316L is lower than that from graphite throughout almost the entire range of applied compaction force. In particular, the ICR value of the a-C coated SS316L is 8.3–5.2 mΩ cm² under 120–210 N/cm², and that of graphite is 10.4–5.4 mΩ cm² under 120–210 N/cm². Fig. 3(b) gives the ICR values of the uncoated SS316L and a-C coated SS316L samples. The uncoated SS316L sample exhibits much higher ICR values than the a-C coated one due to the surface passive film. At compaction forces from 120 to 210 N/cm², the ICR values vary between 477 and 255.4 mΩ cm². The results indicate that the a-C coating prepared by CFUBMSIP is highly electrically conductive.

3.3. Electrochemical characteristics

The open circuit potential (OCP) vs time relationship is determined from the uncoated and a-C coated SS316L samples in the simulated PEMFC anode (H₂) and cathode (air) environments before the potentiodynamic test. The results are displayed in Fig. 4. The OCP of the uncoated SS316L sample shows a dramatic decrease in both the simulated PEMFC anode and cathode environments at the beginning of exposure. The sharp decrease in the OCP is related to the dissolution of the native surface oxide during immersion. When the passive film is dissolved and the surface is wholly covered by a passive film with a different composition, the OCP becomes stable indicating that a steady state. The OCP of the uncoated SS316L sample stabilizes at −307 mV vs SCE and −286 mV vs SCE in the anode and cathode environments, respectively. The a-C coated SS316L sample exhibits a more stable and noble OCP of 255 mV vs SCE and 257 mV vs SCE, in the simulated anode and cathode environments, respectively. The data indicate that the a-C coating renders better corrosion resistance.
Fig. 5 shows the potentiodynamic polarization behavior of the uncoated and a-C coated SS316L samples in the 0.5 M H_2SO_4 solution with 2 ppm HF at 80 °C. The uncoated SS316L yields a polarization curve typical of austenitic stainless steel that can be divided into three regions, the active region, passive region, and transpassive region. The polarization behavior observed from the uncoated sample is similar in the simulated PEMFC anode and cathode environments, both showing a very high peak passivating current of about 1 mA/cm² caused by the active dissolution [35]. However, the uncoated SS316L sample shows a corrosion potential of \(-0.293\) V vs SCE and passivation potential at around \(-0.07\) V vs SCE in the anode environment, and corrosion potential of \(-0.292\) V vs SCE and passivation potential at around \(-0.10\) V vs SCE in the cathode environment. It indicates that a stable passive film is more difficult to be established in the simulated PEMFC anode environment. The major difference in the polarization curve obtained from the coated sample is the absence of a passive region. Fig. 5(a) shows the potentiodynamic polarization results in the simulated anode (H_2 bubbled) environment. The corrosion potential of the a-C coated SS316L sample shifts towards the positive direction reaching about 0.2 V vs SCE more positive than the operation potential in the PEMFC anode environment (around \(-0.1\) V vs SCE). It implies that the anode operation potential is cathodic to the a-C coated SS316L sample and corrosion in the
simulated anode environment is retarded by the a-C coating. Fig. 5(b) shows the potentiodynamic polarization results when the solution is bubbled with air to simulate the PEMFC cathode environment. The cathode operation potential is around 0.6 V vs SCE and in the passive region of the bare SS316L. The passivation current density determined from the uncoated sample at the cathode operation potential is 11.26 μA/cm². The corrosion potential of the coated sample also moves to about 0.2 V vs SCE. Although there is no apparent passive region as indicated by the a-C coated sample, the current density determined from the coated sample diminishes significantly to 3.56 μA/cm². Based on the linear polarization data, we can calculate the corrosion parameter of the two samples in the PEMFC environments and the results are given in Table 1. The polarization resistance can be calculated by the following equation:

\[ R_p = \frac{\beta_a \beta_c}{23i_{corr}(\beta_a + \beta_c)} \]

where \( \beta_a \) and \( \beta_c \) are the Tafel slopes of the anodic and cathodic reactions, \( i_{corr} \) is the corrosion current density, and \( R_p \) is the polarization resistance [36].

The polarization resistance in the simulated anode environment increases by about 626 times and the corrosion current density decreases by about 718 times with the a-C coating. The polarization resistance and corrosion current density of the uncoated SS316L sample in the cathode environment are about 541 Ω cm² and 21.0 μA cm⁻², respectively. In contrast, the polarization resistance and corrosion current density of the a-C coated SS316L sample are 173,611 Ω cm² and 0.06 μA cm⁻², respectively. These results unequivocally indicate that the polarization resistance is significantly increased by the a-C coating.

In the simulated anode environment, −0.1 V vs SCE is applied during the potentiostatic test while aerated with H₂ whereas in the cathode environment 0.6 V vs SCE, air is bubbled. The current density as a function of time is recorded and plotted in Fig. 6. Fig. 6(a) presents the potentiostatic curves at −0.1 V vs SCE determined from the two samples in the anode environment. The current density determined from the uncoated sample decays very fast in the beginning and then the current exhibits a positive–negative switch gradually stabilizing to a relatively low level. The fast decay in the current density can be attributed to the formation of the new passive film. As soon as the surface is covered by the passive film, the current density needed to maintain passivation is relatively low. This result indicates that the native passive film on the uncoated SS316L sample is not stable in the simulated PEMFC anode environment. It quickly dissolves and then a passive film with a different composition is formed. In comparison, the current measured from the coated sample does not exhibit such a switch. It increases in the beginning and gradually stabilizes at a lower current density. A cathodic current indicates that the sample is cathodically protected and the active dissolution rate is low in the anode environment. As shown by the measured current being the sum of the anodic and cathodic reactions, there is still dissolution (anodic current) even with an external cathodic current.

Fig. 6(b) shows the potentiostatic curves at 0.6 V vs SCE obtained from all the samples in the simulated PEMFC cathode environment. The US Department of Energy (DOE) has suggested that a potentiostatic current of 16 μA/cm² or

<table>
<thead>
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<th>Samples</th>
<th>( \beta_a ) (V)</th>
<th>( \beta_c ) (V)</th>
<th>( E_{corr} ) (mV)</th>
<th>( I_{corr} ) (μA/cm²)</th>
<th>( R_p ) (Ω cm²)</th>
</tr>
</thead>
<tbody>
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<td>The anode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The bare SS316L</td>
<td>0.065</td>
<td>0.052</td>
<td>−293</td>
<td>43.1</td>
<td>292</td>
</tr>
<tr>
<td>a-C coated SS316L</td>
<td>0.046</td>
<td>0.056</td>
<td>−206</td>
<td>0.06</td>
<td>183007</td>
</tr>
<tr>
<td>The cathode</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The bare SS316L</td>
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<td>0.113</td>
<td>−292</td>
<td>21.0</td>
<td>541</td>
</tr>
<tr>
<td>a-C coated SS316L</td>
<td>0.046</td>
<td>0.050</td>
<td>−207</td>
<td>0.06</td>
<td>173611</td>
</tr>
</tbody>
</table>

Fig. 5 – Polarization curves of the uncoated and a-C coated SS316L sample in 0.5 M H₂SO₄ solution with 2 ppm HF at 80 °C: (a) aerated with H₂ and (b) bubbled with air.
less is preferred for satisfactory performance of fuel cells up to 5000 h [16,37]. The current densities measured from both the uncoated and a-C coated SS316L samples decrease rapidly initially and then gradually stabilize at 2.8 and 2.4 mA cm$^{-2}$, respectively. Both of these values are below the DOE specified norm. The current density of the uncoated sample measured by the potentiostatic test is much lower than that by potentiodynamic test and it is reasonable to assume that the cathode operation potential is in the middle of the passive region and the passive film formed on the SS316L sample will prevent the substrate from further corrosion. The inset in Fig. 6(b) shows the accumulated charges during the test. A fast increase in the accumulated charges is observed in the beginning followed by a linear relationship between charge and time. The transition occurs at approximately 1 h and it is reasonable to assert that the time needed for the current to stabilize (totally passivated) is about 1 h. In contrast, the charge–time curve derived from the coated sample exhibits a quasilinear relationship during the entire, indicating that the a-C coating prevents the substrate from passivation rendering it stable in the simulated PEMFC cathode environment.

4. Conclusion

316L stainless steel samples were coated with amorphous carbon (a-C) by close field unbalanced magnetron sputter ion plating. The properties of the carbon coating were determined by atomic force microscopy and Raman spectroscopy. The interfacial contact resistance (ICR) and electrochemical behavior were investigated. The results show that the a-C coating is dense, the size of the graphitic crystallites is small, and the number of disordered bands is large. The ICR values determined from the a-C coated SS316L sample show much lower values of being 8.3–5.2 m$\Omega$ cm$^2$ under 120–210 N/cm$^2$. The open circuit potential (OCP), potentiodynamic, and potentiostatic test conducted at 80 °C in a 0.5 M H$_2$SO$_4$ solution with 2 ppm HF demonstrate that the corrosion resistance is improved with the a-C coating. In particular, the corrosion potential ($E_{corr}$) shifts from about −0.3 V vs SCE to about 0.2 V vs SCE in both the simulated anode and cathode environments. The passivation current density is reduced from 11.26 to 3.56 mA/cm$^2$ with the a-C coating in the simulated cathode environment. The potentiostatic test results show that a-C coated SS316L sample is cathodically protected in the simulated anode environment. A stable and lower current density compared to the uncoated samples is observed in the simulated cathode environment. It can be concluded that the SS316L with an a-C coating is suitable for bipolar plates in polymer electrolyte membrane fuel cells.

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