Corrosion behavior and electrical conductivity of niobium implanted 316L stainless steel used as bipolar plates in polymer electrolyte membrane fuel cells

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A R T I C L E   I N F O
Article history:
Received 11 January 2010
Accepted in revised form 2 June 2010
Available online 9 June 2010

Keywords:
Polymer electrolyte membrane fuel cells
Bipolar plates
Ion implantation
Corrosion resistance
316L stainless steel
Niobium

A B S T R A C T
The corrosion behavior and interfacial contact resistance (ICR) of niobium implanted SS316L used as the bipolar plate in a polymer electrolyte membrane fuel cell (PEMFC) are investigated. The ICR values of the bare and niobium implanted SS316L are measured to evaluate the electrical conductivity. The effects of ion implantation on the corrosion behavior are investigated by potentiodynamic and potentiostatic tests in the simulated PEMFC anode and cathode environments. The solutions after the potentiostatic test are analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES). The surface topography of the samples before and after the potentiostatic test is monitored by SEM in order to investigate the mechanism and degree of corrosion. The XPS results indicate that the composition on the surface is altered by ion implantation. The electrochemical results reveal that the passivation current density of the Nb implanted SS316L decreases and has higher chemical stability in the simulated PEMFC environment. However, the ion implantation influence affects the current density. The ICP results are in agreement with those of the electrochemical test disclosing that the bare SS316L has the highest dissolution rate in both the cathode and anode environments and niobium implantation reduces the dissolution rate significantly. SEM shows that the bare SS316L undergoes serious corrosion whereas after Nb implantation, corrosion is greatly retarded. The XPS depth profiles indicate that a passive film with a new composition consisting mainly of niobium oxide is formed after the potentiostatic test. Our results suggest that niobium implantation with proper ion fluences can significantly improve the corrosion resistance and the electric conductivity of SS316L in the simulated PEMFC environments.

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1. Introduction

Although stainless steels were discovered about a century ago by Monnartz [1], their usage is still increasing at about 5% per annum. Stainless steels are being investigated as potential materials in bipolar plates in polymer electrolyte membrane fuel cells (PEMFC) because of their good mechanical strength, high electrical conductivity, high gas impermeability, low cost, and well understood manufacturing processes [2–6]. However, stainless steels have certain disadvantages such as the relatively poor corrosion resistance in the PEMFC environment that is weakly acidic containing ions such as \( \text{SO}_4^{2-}, \text{Cl}^-, \text{F}^-, \text{SO}_3^{2-}, \text{HSO}_3^-, \text{HCO}_3^- \), etc. [7]. Therefore, the durability and lifetime of stainless steels are not adequate. Corrosion releases metallic ions from the materials and they can leach into the membrane blocking the sulfonic acid sites and poisoning the catalytic process. Consequently, the fuel cell performance is degraded [2,8].

Ion implantation is widely adopted to modify surface properties such as the corrosion resistance as well as mechanical and tribological properties. Unlike thermodynamically limited processes such as diffusion and phase transformation, the quantity of elements that can be ion implanted is not restricted by solubility and phase diagrams [9]. Ion implantation has thus been utilized to improve the surface properties of many types of materials [10,11]. It is known that the corrosion resistance of stainless steels can be drastically improved by means of alloying. This is possible because the composition and properties of the passive films depend on the alloy composition. Niobium exhibits good corrosion resistance in an acidic environment and belongs to the class of “valve metals" that show very small anodic currents [12]. It has been reported that niobium exhibits high corrosion resistance to sulfuric acid which is the main constituent in the liquid medium in the PEMFC stack. The reported rate of metal loss in 1 M boiling H\( \text{H}_2\text{SO}_4 \) is less than 0.2 \( \mu \text{m/a} \) [13]. Weil et al. [14] have evaluated niobium cladded metals in 1 M H\( \text{H}_2\text{SO}_4 \) with 2 ppm HF at 80 °C and observed no measurable weight loss even after 2000 h of exposure. The electrochemical behavior of niobium is comparable to that of platinum. Pozio et al. [15] have determined the ICR and...
corrosion resistance of niobium-coated 430 stainless steel (SS430/Nb) in a typical PEMFC environment. Their results show that SS430/Nb has low ICR values and very good corrosion resistance in comparison with commercial steels and Ni-based alloys. In the work described in this paper, stainless steel 316L is implanted with niobium to alter the surface composition and enhance the surface properties. The electrochemical behavior of the bare and niobium implanted SS316L samples is evaluated by potentiodynamic and potentiostatic tests in a simulated PEMFC environment (0.5 M H2SO4 with 2 ppm HF) at 80 °C.

2. Experimental details

Stainless steel 316L samples containing 16.4 at.% Cr, 8.2 at.% Ni, and 2.0 at.% Mo (balance being Fe) were used in our experiments. The steel plates were cut into 10 mm × 10 mm coupons for ion implantation and subsequent tests. Before ion implantation, the samples were polished with SiC waterproof abrasive paper up to #1200, degreased with acetone, cleaned with alcohol in an ultrasonic cleaner, and dried. Ion implantation was carried out in a custom-designed multifunctional ion implantation apparatus and a MEVVA (Metal Vapor Vacuum Arc) source. The vacuum in the implantation chamber was 3.0 × 10−3 Pa and the acceleration voltage was 20 kV. The samples were implanted for 0.5 h (designated as Nb0.5), 2 h (Nb2), or 5 h (Nb5).

X-ray photoelectron spectroscopy (XPS) was conducted on the Kratos AXIS Ultra to determine the Fe, Ni, Cr, O and Nb depth profiles and concentrations. The oxidation states of Nb were also determined by analyzing the binding energy calibrated to that of carbon at 284.8 eV. The ICR of the bare and niobium implanted SS316L was evaluated using a sandwiched structure with two pieces of conductive carbon paper (Toray TCP-H-090) that were sandwiched between the sample and two copper plates. A constant current (0.1 A) was applied via two copper plates and the variations in the resulting voltage drop were recorded as a function of 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 plotted in the figure represent the corrected ICR values between the sample and carbon paper. With regard to the niobium implanted SS316L samples, the ICR between the Nb implanted surface and carbon paper was measured by the same procedures with the ICR between the bare backside and carbon paper being the same as that of the bare SS316L sample.

The electrochemical tests were carried out on the CHI 606C Electrochemical Analyzer. The potentiodynamic and potentiostatic tests were conducted in a 0.5 M H2SO4 solution containing 2 ppm HF at 80 °C to evaluate the electrochemical behavior of the bare and niobium implanted samples in the aggressive environment typical of that in a fuel cell. The solution was aspirated thoroughly by either hydrogen gas (to simulate anode environment) or air (to simulate cathode environment) prior to and during the electrochemical test. Before the potentiodynamic polarization measurement, the sample was measured by open circuit potential (OCP) for 1 h to ensure stability. The scanning rate used in the potentiodynamic test was 1 mV/s and the scanning direction was from negative to positive potential. The potentiostatic test was performed to investigate the performance and stability of the bare and Nb implanted samples in the simulated PEMFC environment. The potentiostatic test was conducted for 8.9 h at a potential of −0.1 V vs SCE while aspirated with H2 and 0.6 V vs SCE aspirated with air to simulate the anode and cathode operating environment in the PEMFC, respectively [6,16–18]. After the potentiostatic test, the solutions (100 ml) were collected and analyzed by inductively-coupled plasma atomic emission spectrometry (ICP–AES) to determine the concentrations of Fe, Cr, Ni, Mo and Nb in the solutions. A solution containing 1 ppm of each of the metal ions in 0.5 M H2SO4 was purchased from SPEX CertiPrep Inc as the standard solution. The error in the ICP is estimated to be ±5%. The surface topography of the samples before and after the electrochemical tests was monitored by an FEI SIRION 200 scanning electron microscope.

3. Results and discussion

3.1. XPS analysis

Fig. 1 shows the XPS depth profiles of the bare control and niobium implanted SS316L sample (Nb2). The Fe and Cr contents are high, but Ni is not a major component in the native passive film on the bare SS316L as shown in Fig. 1(a), indicating that this passive film is basically composed of iron and chromium oxides. A niobium-rich layer with a thickness of about 60 nm is formed in the near-surface region as shown in Fig. 1(b) and the peak atomic fraction of Nb is about 40% at a depth of approximately 8 nm. The oxygen content in the niobium implanted SS316L sample is significantly reduced compared to that in the bare sample. The results indicate that the composition of the passive film is altered by ion implantation.

The chemical state of Nb in the niobium-rich layer after ion implantation is determined by high resolution XPS spectra acquired at different sputtered depths and the results are displayed in Fig. 2. The montages, which illustrate the changes in the XPS peak shape and position at different depths, reveal that niobium near the surface exists as Nb5+, suggesting the existence of predominantly Nb2O5. The Nb peak moves towards a lower binding energy upon further...
sputtering indicating the chemical state of niobium is smaller towards the bulk and finally becomes metallic Nb.

### 3.2. Interfacial contact resistance (ICR)

The ICR between the niobium implanted SS316L and carbon paper is shown in Fig. 3 as a function of compaction force compared to the bare SS316L as a reference. The ICR decreases with compaction force exponentially, indicating that the compaction force is dominant in the low compaction force region whereas the surface composition is predominant in the high region. The ICR of the niobium implanted sample is different from that of the bare SS316L due to the altered surface as shown in Fig. 1. After implantation for 0.5 h, the ICR increases relative to the bare SS316L and that of Nb2 is lower than that of the bare SS316L, the current density of Nb2 diminishes significantly from about 10 μA/cm² (bare SS316L) to 5.4 μA/cm². Additionally, Nb2 exhibits a much lower passivation current peak at −0.2 V compared to the bare SS316L, indicating that Nb2 is more prone to passivation.

### 3.3. Potentiodynamic test

The potentiodynamic polarization behavior of the bare and niobium implanted SS316L in 0.5 M H₂SO₄ with 2 ppm HF at 80 °C is presented in Fig. 3. Fig. 4(a) and (b) shows the potentiodynamic polarization results in the simulated anode (purged with H₂) and cathode (purged with air) environments, respectively. In general, the bare and Nb implanted SS316L samples exhibit a typical polarization curve consisting of three regions, namely the active region, passivation region, and transpassive region. The corrosion potential ($E_{corr}$) of the bare SS316L is close to $-0.3$ V vs SCE in the simulated anode environment and the anode operation potential (about $-0.1$ V) is in the passive region as shown in Fig. 4(a). After niobium ion implantation, the corrosion potential does not increase significantly, but the passivation current density is affected. Although the current densities obtained from Nb0.5 and Nb5 are higher than that of the bare SS316L, the current density of Nb2 diminishes significantly from about 10 μA/cm² (bare SS316L) to 5.4 μA/cm². Additionally, Nb2 exhibits a much lower passivation current peak at $-0.2$ V compared to the bare SS316L, indicating that Nb2 is more prone to passivation.

Fig. 4(b) illustrates the corrosion behavior of the bare and niobium implanted SS316L samples in the simulated cathode environment. The PEMFC cathode operation potential (0.6 V vs SCE) is in the passivation region in which a stable passive film is formed on the surface. The passivation current density of the bare SS316L at the cathode operation potential (0.6 V vs SCE) is 10.7 μA/cm². In comparison, the current densities of Nb0.5 and Nb2 at 0.6 V vs SCE which decrease with increasing niobium ion implantation fluences are 12.0 μA/cm² and 6.3 μA/cm², respectively. The current density measured from the SS316L niobium implanted for 2 h is reduced by
about one fold compared to that of the bare sample. It implies that Nb ion implantation effectively decreases the corrosion rate of the passive film due to niobium incorporation. However, when SS316L is implanted for 5 h, the current density increases to 8.2 μA/cm². It is believed that high-fluence ion implantation introduces too much damage and defects that can accelerate corrosion.

### 3.4. Potentiostatic test and ICP-AES measurements

In the simulated anode environment, −0.1 V vs SCE is applied during the potentiostatic test while purging with H₂ whereas in the cathode environment 0.6 V vs SCE, air is bubbled. The current density as a function of time is plotted in Fig. 5. Fig. 5(a) presents the potentiostatic curves at −0.1 V vs SCE acquired from the bare and Nb implanted SS316L samples in the anode environment. The current densities of all samples diminish rapidly in the beginning but gradually stabilize. The change in the current density indicates the formation of a passive film on the surface. With regard to the bare SS316L, the current densities decay very fast in the beginning exhibiting a positive-negative switch and then gradually stabilize in the positive direction undergoing a negative-positive switch. When the potentiostatic test is continued to 16,000 s, the current densities drop suddenly towards the negative direction. In comparison, much lower current densities are measured from the Nb implanted samples, namely 0.06 to −0.07 μA/cm², 0.03 to −0.07 μA/cm² and −0.20 to −0.40 μA/cm² for Nb0.5, Nb2 and Nb5, respectively. However, the cathodic current density does not mean that the samples are free of corrosion. Actually, the samples are cathodically protected and the active dissolution rate is relatively low in the anode environment, since the measured current is the sum of the anodic and cathodic reactions.

Fig. 5(b) shows the potentiostatic curves at 0.6 V vs SCE obtained from the samples in the simulated PEMFC cathode environment. The current densities measured from both the bare and Nb implanted samples decrease rapidly initially and then gradually stabilize. The fast decay in the current density can be attributed to the formation of a 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 is not stable in the simulated PEMFC environment. It quickly dissolves and then a passive film with a different composition is formed. The stabilized current densities are 0.31 μA/cm², 0.23 μA/cm², 0.07 μA/cm², and 1.16 μA/cm² for the bare SS316L, Nb0.5, Nb2 and Nb5, respectively. It is noted that the stable current density measured by the potentiostatic test is much lower than that by the potentiodynamic test. This is actually reasonable because the cathode operation potential is in the middle of the passive region and the passive film formed on the surface prevents the substrate from further corrosion.

The US Department of Energy (DOE) has suggested that a corrosion current density of 1 nA/cm² or less is preferred for the satisfactory performance of metallic bipolar plates in fuel cells presuming that all corrosion product ions remain as ionomers [20]. However, the DOE target does not sufficiently specify the potential and environment. We consider that the corrosion current density in the potentiostatic test is more representative because the actual working environment is polarized at −0.1 V and 0.6 V in the anode and cathode environments. It is generally considered that for most of the metallic ions accounting for corrosion of the metallic bipolar plate, about 95%, will leave the cell stack along with the by-product, water [21,22]. Therefore, a corrosion current density below 0.02 μA/cm² is required to satisfy the corrosion resistance target proposed by DOE. It can be seen that the stabilized current density of SS316L in the cathode environment is reduced by more than four times after implantation for 2 h. Nevertheless, this is still higher than the desired corrosion current density. On the other hand, the corrosion current density cannot directly represent the released metal ions because usually the current density comprises all the chemical reactions occurring on the surface. On the bare SS316L, the major reactions are: Fe → Fe²⁺ + 2e⁻ and Cr → Cr³⁺ + 3e⁻ since the top surface (passive film) is mainly comprised of Fe and Cr. With regard to sample Nb2, the additional reaction is Nb → Nb⁵⁺ + 5e⁻ or Nb → Nb⁵⁺ + 5e⁻ due to the formation of a niobium-rich layer. This means that Nb2 will release less metal ions assuming that the corrosion current density is the same as that of the bare SS316L. Therefore, the quantity of metal ions released from Nb2 is more close to the technical target stipulated by DOE. However, the accurate amount of released metal ions is

<table>
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<tr>
<th>Sample</th>
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<th>Ion concentration in PEMFC</th>
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<td>anode environment after 10 h (ppm)</td>
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<td>Ni</td>
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<td>Nb2</td>
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</tr>
<tr>
<td>Nb5</td>
<td>4.08</td>
<td>0.20</td>
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</table>

Fig. 5. Potentiostatic curves obtained from the bare and Nb implanted SS316L in the (a) simulated anode (−0.1 V vs SCE purged with H₂) and (b) cathode environment (0.6 V vs SCE purged with air).
difficult to calculate based on the corrosion current density determined from the potentiostatic test. The ICP-AES measurement is necessary to more accurately determine the amount of released metal ions.

The solutions after the potentiostatic test for 32,000 s are analyzed by ICP-AES and the results are summarized in Table 1. Before and after niobium implantation, more metal ions are generally released in the cathode environment than in the anode environment, indicating that the cathode environment is more aggressive. This is reasonable since the negative current in the simulated PEMFC anode environment should provide partial cathodic protection. Fe is found to have the highest concentration in all cases due to its high concentration in the SS316L and selective dissolution. This can be attributed to higher mobility of iron cations compared to chromium cations in the passive

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**Fig. 6.** SEM images of: (a) Nb2, (b) bare SS316L in the anode environment, (c) bare SS316L in cathode environment, (d) Nb2 in the anode environment, and (e) Nb2 in the cathode environment.
film [23,24]. The bare SS316L sample has the highest concentrations of Fe, Ni, Cr and Mo in the solution, whereas niobium ion implantation reduces the concentrations of these elements in the solution. The greatest reduction of the ion concentrations is obtained after 2 h of ion implantation. In more details, the metal concentrations determined from Nb2 in the simulated PEMFC cathode environment are Fe 2.13 ppm, Cr 0.10 ppm, Ni 0.06 ppm, Mo 0.03 ppm, and Nb 0.02 ppm. These values are lower by over 4 times than those determined from the bare SS316L. In the simulated anode PEMFC environment, the greatest reduction in the ion concentrations is also observed from Nb2. The Fe ions are reduced by 5 times, Cr 13 times, Ni 5 times, and Mo 6 times, compared to the bare SS316L. The ICP-AES results show that surface alloying with niobium can greatly retard metal ion release from the stainless steel. It also confirms the slight increase in the current density of Nb5. The reason is probably defects and damage introduced by ion implantation. Nonetheless, the electrochemical tests and ICP-AES measurement reveal that Nb ion implantation at a suitable fluence can greatly improve the corrosion resistance of SS316L in the simulated PEMFC environment.

3.5. SEM observation

In order to investigate the mechanism and degree of corrosion, the samples before and after the potentiostatic tests are inspected by scanning electron microscopy (SEM) and the micrographs are exhibited in Fig. 6. Fig. 6(b) and (c) depicts the topography of the bare SS316L after the potentiostatic test in the simulated PEMFC anode and cathode environments, respectively. The bare SS316L undergoes serious general corrosion forming a porous layer on the surface in the simulated anode environment as shown in Fig. 6(b). Localized corrosion is apparent and there are some corrosion by-products on the surface of the bare SS316L after the potentiostatic test in the simulated cathode environment as shown in Fig. 6(c). On Nb2 [Fig. 6(d) and (e)], little corrosion is evident on the surface but some corrosion by-products can be observed after the potentiostatic test in the simulated anode and cathode environments. A significant increase in the corrosion resistance observed from Nb2 is noticeable in Fig. 6(d) and (e), suggesting that Nb ion implantation can significantly improve the corrosion resistance in the simulated PEMFC environment.

3.6. Depth profiles after potentiostatic test

Fig. 7 shows the depth profiles acquired from the near-surface region of sample Nb2 after the potentiostatic test in the simulated PEMFC anode and cathode environments. In general, the thickness of the passive film increases after the potentiostatic test. The depth profile after potentiostatic test is different from that of the as-implanted sample (Nb2) as shown by Fig. 1(b). This indicates that the composition of the niobium-rich layer is altered by passivation and release of metal ions. The passive film on the as-implanted sample consists of chromium oxides, iron oxides and niobium oxide as indicated by Fig. 1(b) and Fig. 2. After polarization in both the anode and cathode environments, the surface composition basically consists of niobium oxide as shown by Fig. 7 and iron and chromium are depleted during the polarization process resulting in a niobium-rich passive film, especially for iron as verified by ICP-AES results. The passive layer dominated by Nb oxides after the potentiostatic test is expected to have good electrical conductivity since Wei et al. have indicated in Ref. [14] that the contact resistance of niobium cladded stainless steel is still very low after 300 exposure in the simulated PEMFC solution. By carefully inspecting Fig. 7(a) and (b), the depth profiles of Nb after polarization in the anode and cathode environments are almost the same indicating that the passive film is not sensitive to the applied potential and purging gas.

4. Conclusion

316L stainless steel samples implanted with niobium for 0.5 h, 2 h and 5 h to determine the improvement in electrical conductivity and corrosion resistance. A niobium-rich layer about 60 nm thick is formed in the near-surface region of sample Nb2 with a peak atomic fraction of 40% at a depth of approximately 8 nm. The ICR of Nb2 is reduced on account of the formation of the niobium-rich layer. The potentiodynamic and potentiostatic tests conducted at 80 °C in a 0.5 M H2SO4 solution containing 2 ppm HF yield consistent results demonstrating that the corrosion resistance is improved by the formation of this Nb-rich surface layer. Specifically, the corrosion potential of SS316L does not show an apparent change after ion implantation, while the passivation current densities decrease in the both anode and cathode environments, especially for Nb2. However, when the ion implantation time is 5 h, the current densities increase indicating that the damage and defects introduced by high-fluence ion implantation adversely affect the corrosion resistance. The ICP-AES results show that Fe is selectively dissolved in all cases. The bare SS316L sample yields the highest released ion concentrations whereas Nb2 gives the lowest dissolution rate in the simulated PEMFC environment. The SEM results indicate that the bare SS316L undergoes serious corrosion and corrosion is dramatically retarded by Nb ion implantation. The XPS results obtained from sample Nb2 after the potentiostatic test reveal that the composition of the passive film is...
altered due to passivation and dissolution of iron and chromium. However, the composition of the passive film after the potentiostatic test is not sensitive to the applied potential and gases used.

Acknowledgements

Financial support provided by the National Natural Science Foundation of China under contract number 50820125506 and Hong Kong Research Grants Council (RGC) General Research Funds (GRF) No. CityU 112608 is acknowledged.

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