CrN/Cr multilayer coating on 316L stainless steel as bipolar plates for proton exchange membrane fuel cells

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ABSTRACT

CrN/Cr multilayer coating is prepared on 316L stainless steel as bipolar plates for proton exchange membrane fuel cell (PEMFC) by pulsed bias arc ion plating (PBAIP). Interfacial conductivity of the bipolar plate with CrN/Cr multilayer is improved obviously, presenting an interfacial contact resistance (ICR) of $8.4 \, \text{m}\Omega \, \text{cm}^{-2}$ under 1.4 MPa. The results tested by potentiodynamic and potentiostatic measures in simulated PEMFC environments show that the bipolar plate with CrN/Cr multilayer has good anticorrosion performance. The corrosion current density of the bipolar plate with CrN/Cr multilayer is approximately $10^{-8.0} \, \text{A cm}^{-2}$ at 0.6 V (vs. SCE) in a $0.5 \, \text{M} \, \text{H}_2\text{SO}_4 + 5 \, \text{ppm} \, \text{F}^-$ solution at $70 \,^\circ\text{C}$ with pressured air purging. The results of SEM and ICR before and after corrosion tests indicate that the bipolar plate with CrN/Cr multilayer is considerably stable electrochemically. The bipolar plate with CrN/Cr multilayer combined the prominent interfacial conductivity and the excellent corrosion resistance, showing great potential of application in PEMFC.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is an ideal candidate for automotive propulsion application due to fast start-up, near-zero emission and high efficiency of energy conversion [1–3]. As a major part of the PEMFC stack, the bipolar plate accounts for most of the total weight and volume of the stack [3]. The bipolar plate serves as separators and current collectors, distributing reactants uniformly, mechanically supporting the cell stack and managing the heat and water of the cells. The ideal bipolar plate materials should feature excellent corrosion resistance in PEMFC environment, low interfacial contact resistance, low gas permeability, light weight, good mechanical strength and cost effectiveness etc. [4–6].

It is generally considered that the stainless steel is an optimal bipolar plate material for PEMFC as its high bulk electrical and heat conductivity, high strength, low gas permeability and ease of manufacture [4–7]. But the bare stainless steel is not suitable under PEMFC working conditions. The bare stainless steel suffers corrosion attack in the harsh acidic and humid environment. And the corrosion products could contaminate and poison other fuel cell stack components (notably catalyst and membrane) [6,7]. Moreover, the bare stainless steel forms passive layer under PEMFC operating conditions leading to high interfacial contact resistance. Both the corrosion products and the passive layer could result in decreasing in cell performance [4–8]. Thus, surface modification by cost-effective, highly corrosion-resistant and good conductive film is needed.

Transition metal nitrides, carbides and borides are "metallic ceramics" with many desirable characteristics such as high hardness, good resistance to mechanical wear and electrochemical corrosion, prominent electrical conductivity etc. [4–6]. As protective layers, they have been being widely used to improve the performance of the bipolar plates for PEMFC and yield considerable outcomes [9–13]. However, the PVD coatings are almost embedded with defects and impossible to totally avoid the formation of pinholes [14–16]. Consequently, when coated materials exposed to an aqueous solution, the localized galvanic corrosion will occur, leading to accelerated attack at the place of such defects. So, with the developing of new coating materials, reducing and eliminating defects such as pinholes will be among the most crucial issues. As reported by many researchers [16–19], the corrosion attack of coated materials can be reduced considerably by the deposition of multilayered coatings. The improvement of the anticorrosion by multilayered coatings can be ascribed to the reduced through-coating defects.

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Wei-Yu Ho et al. [16] prepared CrN/Ti and TiN/CrN coatings on SUS 304 stainless steel using a cathodic arc deposition system. They confirmed that the corrosion resistance of the multilayer was better than that of single layer coated one. Zhang et al. [17] also found that Ti_2N/TiN multilayer coating exhibited superb corrosion protective layer for stainless steel. Nguyen Dang Nam et al. [18] have shown that the corrosion protection from TiN/CrN multi-coating on 316L stainless steel can be improved by reactive rf-magnetron sputtering. Wang et al. [19] studied the performance of TiN-, TiAlN- and CrN-coated 316L SS bipolar plates by EBPVD in simulated PEMFC environments. They suggested that multilayered coatings may disconnect the pinholes and prevent through-coating pinholes.

In our previous work [20], a sandwich-like Cr/CrN/Cr tri-layer was coated on 316L stainless steel, yielding relatively good performance but still far from satisfaction for PEMFC. In this study, CrN/Cr multilayer (six chemical modulation periods, twelve layers in total) was coated on 316L stainless steel by pulsed bias arc ion plating (PBAIP) [11] as bipolar plates for PEMFC to further improve performance. The "metallic ceramics" CrN was assigned as the outmost layer to improve interfacial conductivity and corrosion resistance. The soft Cr layer was assigned as the interlayer to enhance the bonding strength. Most of all, the structure of multilayer coating was designed to improve the anticorrosion. In short, it was anticipated that the modified bipolar plate could further improve the corrosion resistance and yield prominent interfacial conductivity, satisfying the requirements of application for PEMFC. The microstructure characterization, corrosion properties, interfacial conductivity and electrochemical stability of the bipolar plate samples were investigated in simulated PEMFC environments. The bare 316L stainless steel was used as the counter material.

2. Experimental

316L stainless steel was chosen as the base metal of bipolar plate. The stainless steel substrates with the size of $100\,mm \times 100\,mm \times 0.1\,mm$ were ultrasonically cleaned in ethyl ethanol for 30 min. After washing with deionized water, they were blown dry and put on holders. The CrN/Cr multilayer was deposited on 316L stainless steel in PBAIP system [10]. The multilayer was obtained by repeating the same process for six multiple runs, so it consisted of six consecutive "single layer" depositions. During each "single layer" treatment, Cr interlayer was prepared for 3 min before the CrN layer deposition (7 min). The total deposition time is 1 h and the thickness of the multilayer is about 400 nm. The pure metal chromium (99.9%) was used as the target. The Cr deposition took place in an atmosphere of Ar (99.99%) and the CrN deposition took place in a gas mixture of Ar (99.99%) and N_2 (99.99%). Prior to the deposition, the substrates were sputtered by Ar ions for 10 min to remove the passive film on the 316L stainless steel surface.

Thickness of the CrN/Cr multilayer was measured with New View 5022 Surface Profiler by protecting some area of the substrate. Morphology of cross-section was observed with a field emission scanning electron microscope (FESEM; Hitachi, S-4800). The phase structure of the multilayer was analyzed by grazing-angle incidence X-ray diffraction (XRD). Surface characterizations of coated samples before and after electrochemical measurements were studied with JSM6360-LV scanning electron microscopy (SEM).

The interfacial contact resistance between the sample and the bare Toray® carbon paper was measured by Wang's method [21]. Two pieces of Toray® carbon paper were sandwiched between the bipolar plate sample and two copper plates which were plated with gold on both sides to enhance conductivity. An increasing compaction force was controlled by a WDW Electromechanical Universal Testing Machine with a step of $5\,N\,s^{-1}$. A constant electrical current of 5.0 A, sourced by a PSP-2010 Programmable power
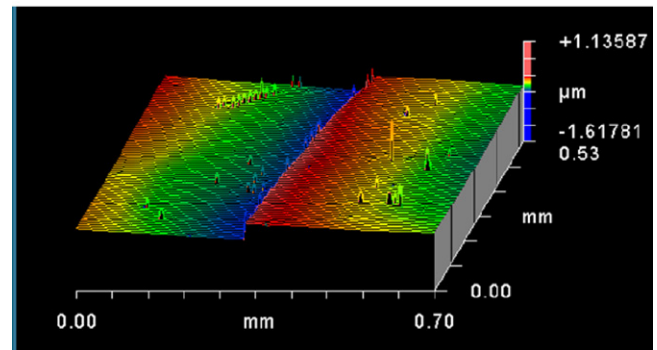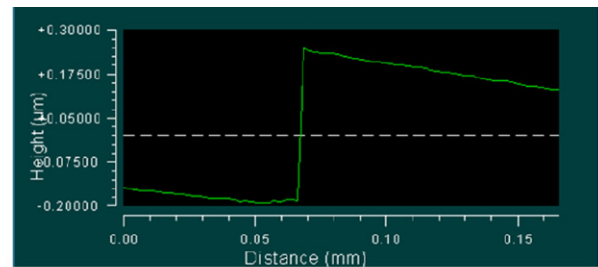

Fig. 1. Thickness of the bipolar plate sample with CrN/Cr multilayer.

supply, was provided via the two plated copper plates during the tests. Both the sample and the carbon paper were wafers with the diameter of 60 mm which are the same size as the copper plates.

The corrosion behaviors of the bipolar plate samples were investigated by electrochemical tests in a $0.5\,M\,H_2SO_4 + 5\,ppm$ F^- solution to simulate the PEMFC environments. A conventional three-electrode system was used with a working electrode, a platinum sheet as the assistant electrode and a saturated calomel electrode (SCE, saturated KCl) as the reference electrode. The dimensions of the working electrodes were $15\,mm \times 15\,mm \times 0.1\,mm$. The edges were protected by epoxy resin exposing $10\,mm \times 10\,mm$ surface to the electrolyte. The experiments were performed at 70 °C to simulate the environment when the cell power was on. The corrosion solution was bubbled thoroughly with either hydrogen gas (for simulating a PEMFC anodic environment) or pressured air (for simulating a PEMFC cathodic environment) prior to and during the electrochemical measurements. The potential was swept in the range from $-0.25\,V$ to $0.85\,V$ vs. SCE at a scanning rate of $2\,mV\,s^{-1}$. Potentiostatic tests were performed at 0.6 V vs. SCE purged with air at the anode and at $-0.1\,V$ vs. SCE purged with hydrogen at the cathode both for 7.5 h to simulate the working conditions of PEMFC.

3. Results and discussion

3.1. Characterization of the multilayer

Before depositing the multilayer, some area of the substrate was protected. After the multilayer was prepared, the thickness difference between the coated area and the uncoated area could be considered as the thickness of the multilayer. As we can see from the Fig. 1, the thickness of the multilayer is about 0.4 μm. Cross-section FESEM image of CrN/Cr multilayer is shown in Fig. 2. It is indeed multilayer consisting of Cr and CrN layers alternately, which conforms well to our design. The multilayer is fine, dense and uniform, while the interface between layers is distinct. The thickness of the multilayer is about 400 nm from the cross-section FESEM image, which is consistent with Fig. 1. The CrN phase with crystal planes of (1 1 1), (2 0 0), (2 2 0) and Cr (1 1 0), (2 0 0) were observed
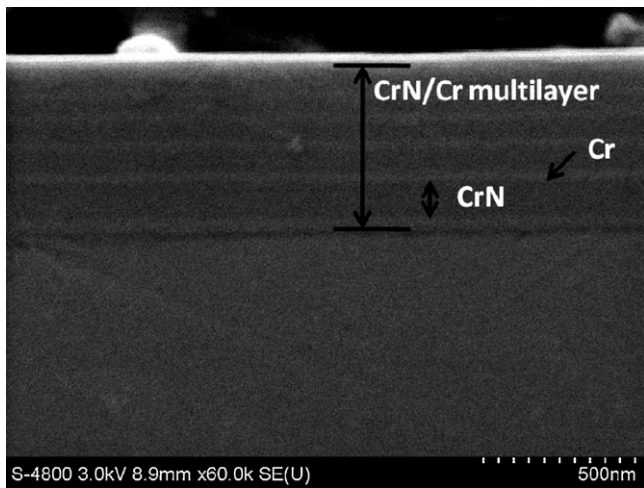
Fig. 2. Cross-section FESEM image of the bipolar plate sample with CrN/Cr multilayer.

from the XRD pattern of the multilayer, as shown in Fig. 3. It can be concluded that the multilayer consist of CrN and Cr phases.

3.2. Interfacial contact resistance (ICR)

Among all the requirements for the surface-modified metal bipolar plates, the interfacial conductivity is the most important one. If the conductivity of the bipolar plate material is not satisfied, the high performance of the cell would not be obtained. Thus, the interfacial contact resistance of the bipolar plate sample with the untreated Toray® carbon paper was used to evaluate the interfacial conductivity of the modified material. The changes in the interfacial contact resistance with compaction force for bipolar plate samples are given in Fig. 4. As we can see, the ICR of the 316L stainless steel is rather high, ranging from 95.5 to 1340.7 mΩ cm^{-2} under 0.1–1.5 MPa. Compared to the bare stainless steel, the ICR of the modified 316L stainless steel with CrN/Cr multilayer decreased dramatically. The value of the sample with CrN/Cr multilayer coating in ICR is 12.8–8.4 mΩ cm^{-2} under 0.8–1.4 MPa, far lower than that of our previous work (Cr/CrN/Cr tri-layer) [20]. The modified 316L stainless steel with CrN/Cr multilayer presents excellent interfacial conductivity as anticipated, which can be attributed to the good electrical conductivity of the outmost layer CrN as reported [10].
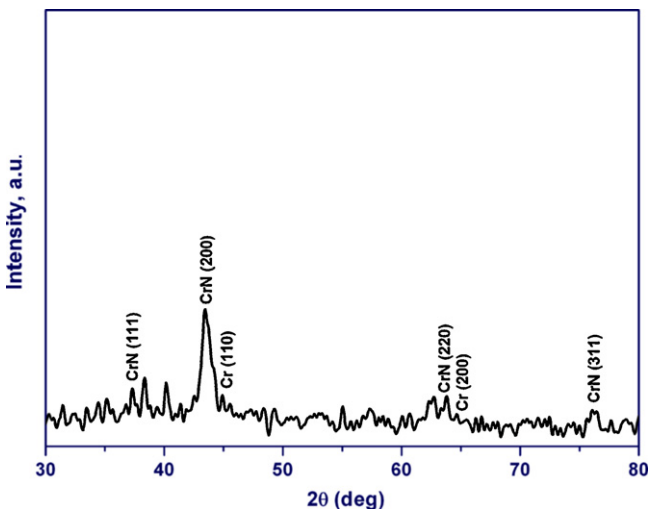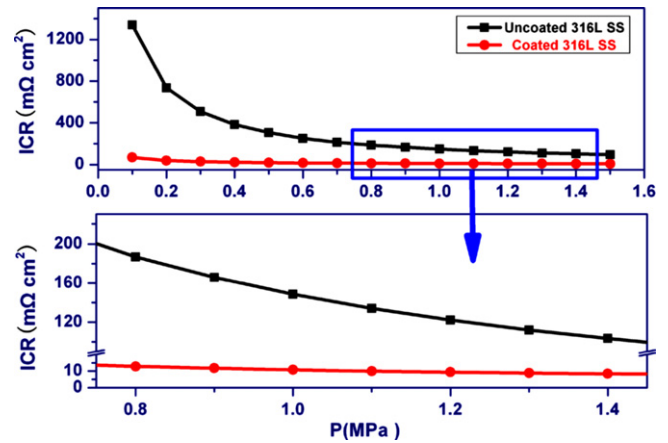

Fig. 4. Interfacial contact resistance between the bipolar plate samples and carbon paper.

3.3. Corrosion resistance

Potentiodynamic and potentiostatic tests were used to evaluate electrochemical behavior of the bipolar plate with CrN/Cr multilayered coating.

Potentiodynamic polarization behaviors of bipolar plate samples conducted in 0.5 M H$_2$SO$_4$ + 5 ppm F$^-$ solution at 70 °C bubbled with pressured air (to simulate a PEMFC cathodic environment) are shown in Fig. 5. Compared with 316L stainless steel, the modified 316L stainless steel bipolar plate with Cr/CrN multilayer presents a distinctly passive region from 0 to 0.3 V vs. SCE. The corrosion current can be determined from the corresponding slopes of the anodic curve and the cathodic curve. The corrosion current density of the 316L stainless steel substrate is about 10$^{-5.5}$ A cm^{-2}, and that of the modified bipolar plate with CrN/Cr multilayer is about 10^{-7} A cm^{-2}. Moreover, further increase in the potential results in remarkable increase in the anodic current density beyond corrosion potential for 316L stainless steel substrate. Potentiodynamic polarization behaviors of bipolar plate samples conducted in 0.5 M H$_2$SO$_4$ + 5 ppm F$^-$ solution at 70 °C bubbled with hydrogen (to simulate a PEMFC anodic environment) are shown in Fig. 6. The modified 316L stainless steel bipolar plate with Cr/CrN multilayer is in a passive region from 0 V to 0.4 V vs. SCE under test condition. And the corrosion current density of the coated sample is 10$^{-7.5}$ A cm^{-2}, more than two orders of magnitude lower than
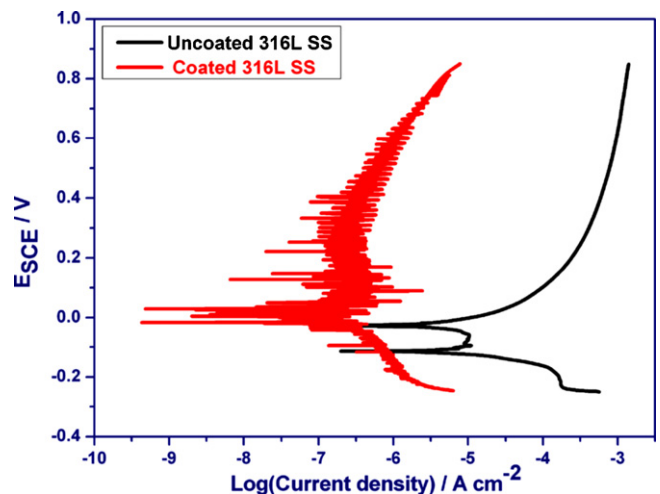

Fig. 3. XRD pattern of the bipolar plate sample with CrN/Cr multilayer.

Fig. 5. Potentiodynamic polarization curves of the bipolar plate samples in 0.5 M H$_2$SO$_4$ + 5 ppm F$^-$ solution with a scan rate of 2 mV s^{-1} at 70 °C bubbled with air.

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

Fig. 8. Potentiostatic polarization curves of the bipolar plate samples at −0.1 V versus SCE in 0.5 M H_2SO_4 + 5 ppm F^- solution at 70 °C bubbled with H_2 for 7.5 h.

that of uncoated sample (about 10^5 A cm^{-2}). The potentiodynamic polarization tests show that the corrosion rate of the modified bipolar plate with CrN/Cr multilayer is lower than that of 316L stainless steel substrate sample under test conditions.

In order to study the corrosion properties of the coated sample in the actual operating condition of PEMFC, the potentiostatic polarization tests were investigated.

In the simulated cathode environment conducted at 0.6 V vs. SCE bubbled with pressured air (Fig. 7), the current density of the coated sample stabilized within 15 min and stayed in the range of $10^{-7.4}$–$10^{-7.8}$ A cm^{-2}. The current density of the uncoated sample stabilized within 30 min and stayed in the range of $10^{-6.1}$–$10^{-6.9}$ A cm^{-2}, which is about one order of magnitude higher than that of coated sample. As for the simulated anode environment conducted at −0.1 V vs. SCE bubbled with hydrogen, the polarization curves are shown in Fig. 8. The current densities of the coated and uncoated samples were higher than those in simulated cathode environment. But the current density of coated sample was about two orders of magnitude lower than that of uncoated sample, which is consist with the results in cathode environment.

Both the potentiodynamic polarization and potentiostatic polarization tests show that the modified 316L stainless steel bipolar plate with CrN/Cr multilayer exhibited excellent corrosion
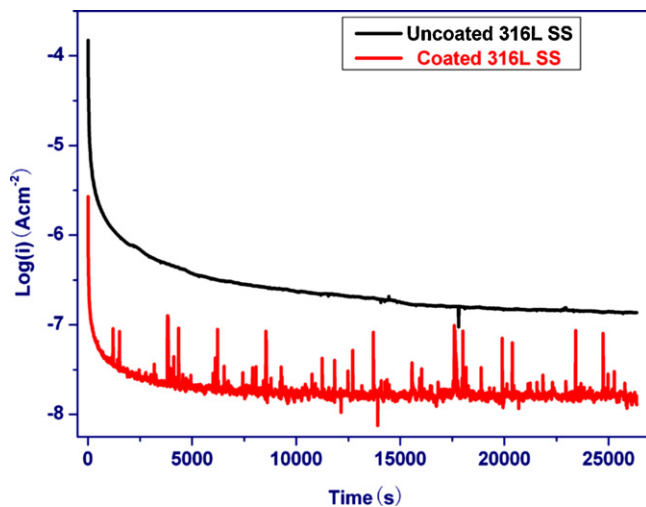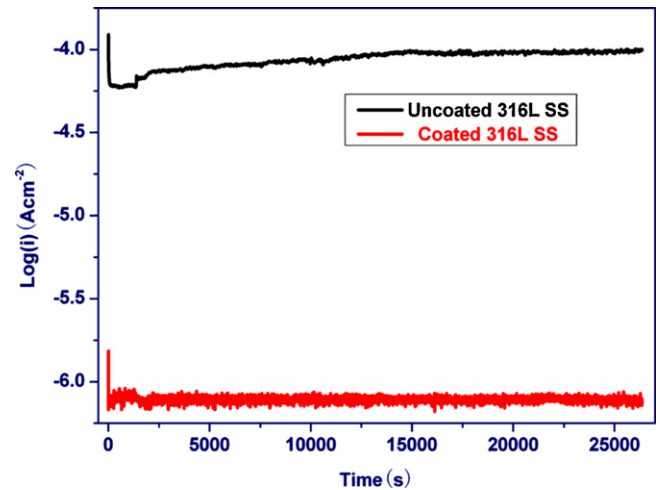
resistance, which is much better than that of our previous work [20]. The improved anticorrosion could be attributed to [15,16]: (1) the reduced possibility of through-coating defects, which can be due to the increase in the coating thickness and the discontinuous crystallite boundaries in the structure; (2) the redirection of the corrosion current flow at the interfaces resulting from alternating interlayers of different compositions.

3.4. Electrochemical stability (SEM and ICR before and after corrosion tests)

The surface morphology of the coated samples before and after potentiostatic polarization is shown in Fig. 9. Fig. 9a presents initial surface morphology of CrN/Cr multilayer. The surface of CrN/Cr multilayer is relatively dense and uniform but with some droplets. Fig. 9b and c shows the surface morphology of CrN/Cr multilayer after potentiostatic tests in simulated cathodic and anodic environment, respectively. After 7.5 h potentiostatic polarization at −0.1 V vs. SCE purging with hydrogen, the slightly local corrosion took place around the droplets as shown in Fig. 9c. In comparison with anodic polarization, there is no obvious corrosion phenomenon for Cr/CrN multilayer (Fig. 9b) after 7.5 h potentiostatic polarization at 0.6 V vs. SCE purging with pressed air. It can be concluded that the corrosion attack of CrN/Cr multilayer in anode is more severe than that in cathode [13], which is consistent with corrosion tests.

The changes in ICR of CrN/Cr multilayer under 1.4 MPa before and after corrosion tests are shown in Fig. 10. The ICR of CrN/Cr multilayer both increased after anodic and cathodic polarization. After 7.5 h potentiostatic polarization at −0.1 V vs. SCE purging with hydrogen, the ICR of CrN/Cr multilayer under 1.4 MPa increased from 8.4 mΩ cm^{-2} to 23.0 mΩ cm^{-2}. While after 7.5 h potentiostatic polarization at 0.6 V vs. SCE purging with pressed air, it increased from 8.4 mΩ cm^{-2} to 25.2 mΩ cm^{-2}. The variation of ICR is probably induced by different surface conditions before and after corrosion tests. The ICR of CrN/Cr multilayer after cathodic polarization is higher than that of anodic polarization. It can be attributed to the difference between polarization conditions. Compared with anodic condition, the cathode is high potential with oxidize atmosphere. So the bipolar plate in cathode tends to oxidize resulting in high ICR.

Combining the results of SEM with ICR before and after corrosion tests, we can conclude that the bipolar plate with CrN/Cr multilayer is rather stable electrochemically.
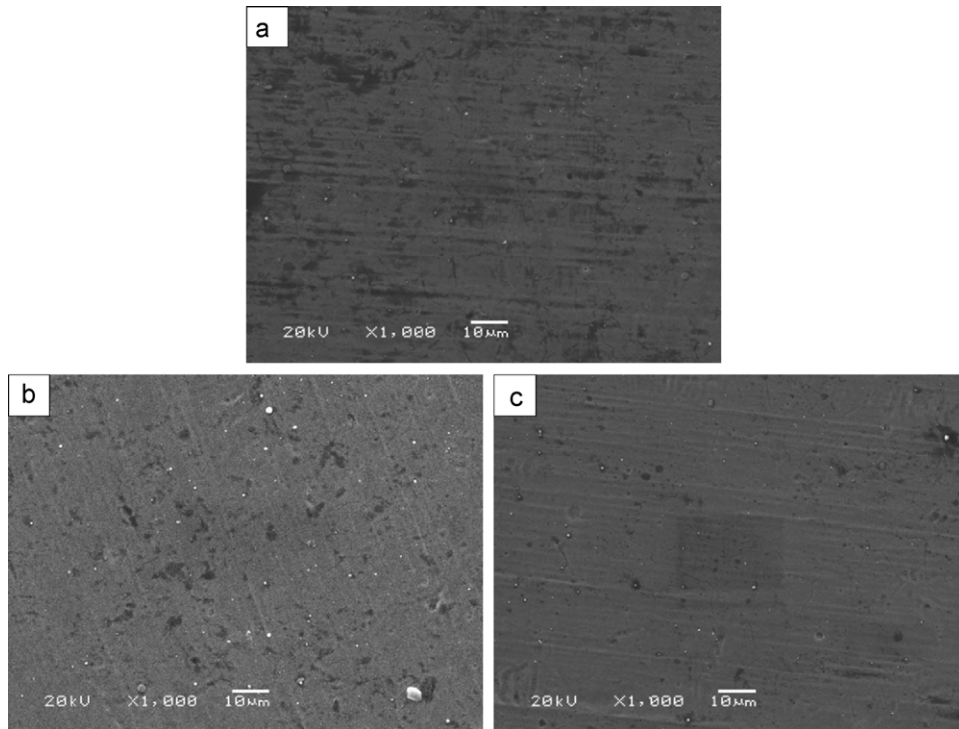

Fig. 7. Potentiostatic polarization curves of the bipolar plate samples at 0.6 V versus SCE in 0.5 M H_2SO_4 + 5 ppm F^- solution at 70 °C bubbled with air for 7.5 h.

Fig. 9. SEM images of coated sample before (a) and after potentiostatic polarization tests in (b) simulated cathode environment and (c) simulated anode environment.
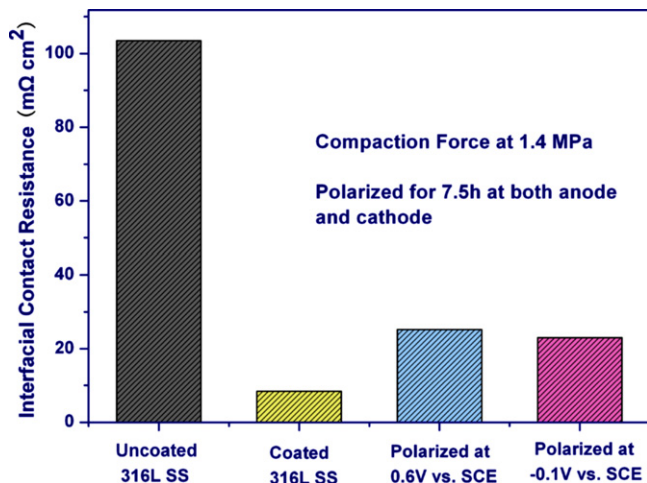

Fig. 10. ICRs under 1.4 MPa before and after polarization tests in the simulated cathode and anode environment for coated sample.

4. Conclusions

CrN/Cr multilayer on 316L stainless steel was formed by PBAIP as bipolar plate material for PEMFC. Interfacial conductivity of the CrN/Cr multilayer coated on 316L stainless steel was 8.4 mΩ cm^{-2} under 1.4 MPa, far lower than that of our previous work (Cr/CrN/Cr tri-layer) [20], showing obvious advantage in actual application for PEMFC. Potentiodynamic and potentiostatic polarization tests in simulated PEMFC environments reveal that the bipolar plate with CrN/Cr multilayer presents superb anticorrosion properties. The corrosion current density of the bipolar plate with CrN/Cr multilayer was approximately $10^{-8.0}$ A cm^{-2}, at 0.6 V (vs. SCE) in a 0.5 M H$_2$SO$_4$ + 5 ppm F$^-$ solution at 70 °C with pressured air purging. Compared with the Cr/CrN/Cr tri-layer [20], both the interfacial conductivity and the corrosion resistance of the sample with CrN/Cr multilayer are improved notably as designed. The results of SEM and ICR before and after corrosion tests indicate that the bipolar plate with CrN/Cr multilayer is considerably stable. What is more, the CrN/Cr multilayer coating is cost-effective, and the modification technology is simple and environmentally benign.

In terms of interfacial conductivity, corrosion resistance, electrochemical stability and material cost, the 316L stainless steel substrate with CrN/Cr multilayer could be a good candidate bipolar plate material for PEMFC. As a potential BPP material for PEMFC, the long-term corrosion property and cell performance of the CrN/Cr multilayer coated bipolar plate need to be investigated in the following work.

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