

Short communication

Coated 316L stainless steel with Cr_xN film as bipolar plate for PEMFC prepared by pulsed bias arc ion plating

Yu Fu^{a,b}, Ming Hou^{a,*}, Guoqiang Lin^c, Junbo Hou^{a,b},
Zhigang Shao^a, Baolian Yi^a

^a Fuel Cell System and Engineering Laboratory, Dalian Institute of Chemical & Physics,
Chinese Academy of Sciences, Dalian 116023, PR China

^b Graduate University of Chinese Academy of Sciences, Beijing 100049, PR China

^c Dalian University of Technology, Dalian 116024, PR China

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Abstract

Three different kinds of Cr_xN films on 316L stainless steels were prepared by pulsed bias arc ion plating as bipolar plates for proton exchange membrane fuel cell (PEMFC). The interfacial contact resistance, corrosion resistance and surface energy of the bipolar plate samples were investigated. Among the three samples, the 316L stainless steel coated with $\text{Cr}_{0.49}\text{N}_{0.51} \rightarrow \text{Cr}_{0.43}\text{N}_{0.57}$ gradient film (sample 2) exhibited the best-integrated performance. The contact resistance between sample 2 and Toray carbon paper was 6.9–10.0 m Ω cm² under 0.8–1.2 MPa. The bipolar plate sample also showed improved corrosion resistance in simulated PEMFC environments. Either in the reduction environment or in the oxidation environment 25 °C and 70 °C, the corrosion current densities of sample 2 were about one to two orders of magnitude lower than those of the base metal. In addition, the open circuit corrosion potential of sample 2 was also the highest in 0.5 M H_2SO_4 + 5 ppm F^- solution at 25 °C. The treated bipolar plate had high surface energy; and the contact angle of sample 2 with water was about 90°, which is beneficial for water management in fuel cell.

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1. Introduction

The stainless steel is considered to be the best candidate material for the bipolar plate (BPP) of proton exchange membrane fuel cell (PEMFC) because of its good bulk electrical and heat conductivity, high strength, low gas permeability, and ease of manufacture. However, the corrosion resistance and interfacial contact resistance should be considered. As the stainless steel is prone to be corroded in PEMFC environment at its natural state, the metal ions most likely result in membrane pollution [1], and the passive film on the stainless steel surface often leads to a high interfacial contact resistance. Forming a protecting film with a good corrosion resistance and a low interfacial contact

resistance on stainless steel by surface treatment is one of the possible solutions.

The metal nitrides have good corrosion resistance and high conductivity, so they are ideal surface materials for metal BPP. Cho et al. [2] manufactured a 1 kW class stack using TiN-coated BPPs, no obvious performance degradation was found after 1000 h operation at a constant load. Furthermore Wang and Northwood [3,4] studied the corrosion behaviors of the TiN-coated stainless steel, and found the corrosion resistance of samples was improved compared with the base metal except for occurrence of pitting. In recent years Cr_xN have been the focus of the research. Bertrand et al. [5] coated Cr_2N and CrN on AISI 304 stainless steel by using an industrial magnetron reactive sputtering device. They found the Cr_2N coatings or CrN coatings had an inert intrinsic behaviour either in acidic or in chloride solutions. Brady et al. [6–10] conducted a series of experiments by the thermal nitridation. At first, they formed

* Corresponding author. Tel.: +86 411 84379051; fax: +86 411 84379185.
E-mail address: houming@dicp.ac.cn (M. Hou).

the films of nitrides of Cr, including CrN and Cr₂N, on Ni50Cr alloy, and each sample showed a high corrosion resistance and surface conductivity. Then, they treated 349TM, AISI446, Ni–Cr based and Fe–Cr based commercial alloys using the same technology, and all the samples showed improvement in corrosion resistance and conductivity.

The technology of surface treatment used in this study is pulsed bias arc ion plating (PBAIP). PBAIP was first introduced by Olbrich et al. [11] in 1991, and great development has been made on PBAIP in recent years. The successful applications of PBAIP in machining, surface ornamentation, solar cell and so on have promoted the development in the industries. It 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. However, up to now, forming films synchronously processing high conductivity and corrosion resistance using PBAIP has not been reported yet.

In this paper, we fabricated the film of Cr_xN on 316L stainless steel by PBAIP. Then the electrochemical performance, the interfacial conductivity and surface energy of the samples were investigated to evaluate the potential application as BPP for PEMFCs.

2. Experimental

The PBAIP system used in this study is shown in Fig. 1. The cylindrical deposition chamber (diameter 800 mm and length 1000 mm) is fabricated using stainless steel. Two 99.9% pure chromium targets, 58 mm in diameter, are mounted at the end of linear ducts that are connected with the vertical chamber. Both ducts consist of a two-step magnetic coil. The first-step coil is used to stabilize the burning arc, and the second-step one is used to constrain the plasma and remove some droplets. Stainless steel holders lying in the middle of the plasma beams can rotate and turn simultaneously. The distance between the centre of the holder and the arcs is 600 mm. A pulsed bias is applied on the holders through the axis.



Fig. 1. The PBAIP experimental setup used in this study.

Table 1
Composition of 316L stainless steel in this study

Elements	316L stainless steel (wt.%)
C	≤0.030
Si	≤1.00
Mn	≤2.00
P	≤0.035
S	≤0.030
Cr	16.00–18.00
Ni	12.00–15.00
Mo	2.00–3.00
Fe	Balance

316L stainless steel was chosen as the base metal of BPP and its composition is given in Table 1. The 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 for 10 min with a pulsed bias –500 V in ambient Ar at 2.0 Pa.

The deposition took place in an atmosphere of Ar (99.99%) and N₂ (99.99%). The Ar/N₂ gas pressure ratio, determined by pressure control regulators, was maintained at 0.4. Meanwhile the N₂ gas flow, determined by mass flow meter, was changed to obtain different composite films. Both arc currents were maintained at 80 A and the deposition time was 100 min. By adjusting the flow of N₂, coating with different composition could be obtained. Three different coatings were conducted in this study. The flow of N₂ for sample 1 was increased from 25 sccm to 100 sccm; the flow of N₂ for sample 2 was decreased from 100 sccm to 25 sccm; and the flow of N₂ for sample 3 was kept still at 100 sccm. Composition of the samples was analyzed by EPMA. And the details are listed in Table 2.

Wang's method [12] of measuring the contact resistance between stainless steel and carbon paper was modified. In the setup (Fig. 2), two pieces of Toray carbon paper were sandwiched between the bipolar plate sample and two copper plates. The copper plates were plated with gold on both sides to enhance conductivity. An electrical current of 5.00 A, sourced by a PSP-2010 Programmable power supply, was provided via the two plated copper plates. During the tests, the compacting force was increased with a step of 5 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 as big as the copper plates.

The corrosion behaviors of the samples were investigated in simulated PEMFC environments ($0.5 \text{ M H}_2\text{SO}_4 + 5 \text{ ppm F}^-$)

Table 2
Composition of the coatings formed by PBAIP with different technologies

Code	Flow of N ₂ (sccm)	Film composition
1#	100 → 25	Cr _{0.43} N _{0.57} → Cr _{0.49} N _{0.51}
2#	25 → 100	Cr _{0.49} N _{0.51} → Cr _{0.43} N _{0.57}
3#	100	Cr _{0.43} N _{0.57}

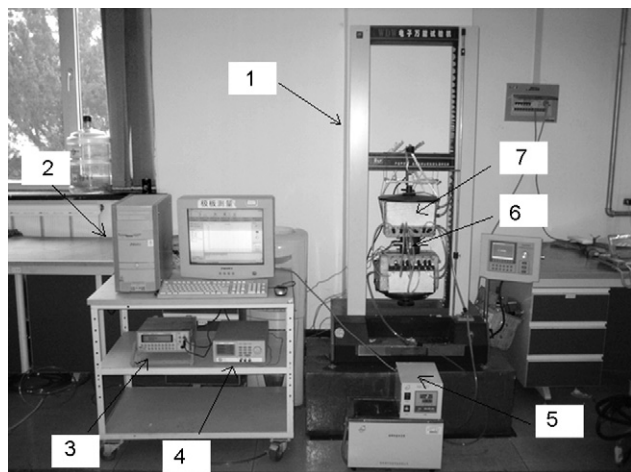


Fig. 2. Experimental configuration for measuring the interfacial contact resistance: (1) WDW Electromechanical Universal Testing Machine, (2) PC, (3) EDM-3150 Multidisplay Multimeter, (4) PSP-2010 Programmable power supply, (5) HH 501 thermostatic water-circulator bath, (6) plated copper plates and samples, and (7) heating elements.

by electrochemical experiments. A conventional three-electrode system was used for the electrochemical measurements with a working electrode, a platinum sheet as the counter electrode and a saturated calomel electrode (SCE, sat'd KCl) as the reference electrode. The tests were conducted using a potentiostat Model 2273 A by EG&G Princeton Applied Research and analyzed with the corrosion software of EG&G Version 2.43.0. The dimensions of the working electrodes prepared were 15 mm × 15 mm × 0.1 mm. The edges were protected by epoxy resin exposing 10 mm × 10 mm surfaces to the electrolyte. The tests were performed at 25 °C to simulate the environment when the stack power was off; as for the tests conducted at 70 °C to simulate the environment when the stack 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 samples were stabilized at open circuit potential for 30 min, then the potential was swept from −0.3 V to +0.8 V at a scanning rate of 2 mV s^{−1}.

At last, the contact angles of sample with water were measured by a JC2000A contact angle measurement to investigate the surface energy.

3. Results and discussion

3.1. Interfacial contact resistance

In Fig. 3, the interfacial contact resistances of the BPP samples with Toray carbon paper are compared. Obviously, the interfacial conductivities of sample 2 and sample 3 were much higher than that of sample 1 in all compacting pressure range. The compacting pressure applied to the stacks is often in the range of 0.8–1.2 MPa nowadays. The interfacial contact resistance between sample 1 and carbon paper was in the

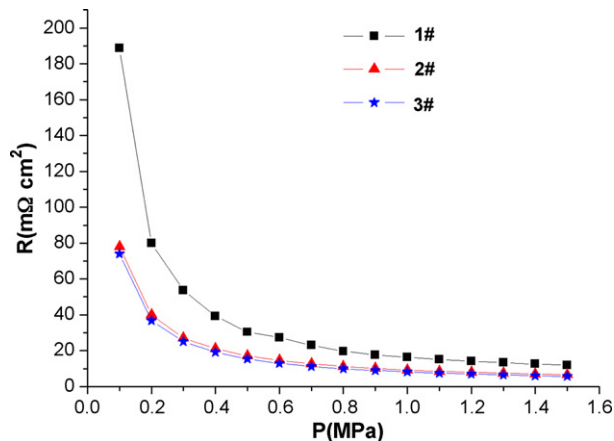


Fig. 3. Interfacial contact resistance of the samples with Toray carbon paper.

range of 14.1–19.6 mΩ cm² under the stack compacting pressure which was the biggest. The interfacial contact resistance of sample 2 was 7.9–11.2 mΩ cm², much lower than that of sample 1. As for sample 3, the interfacial contact resistance was 6.9–10.0 mΩ cm², which is close to that of sample 2. CrN is a semiconductor with face-centred cubic structure. Its band gap is 3.4 eV, and it behaves like an insulator. But when the mol ratio of Cr to N is close to but not equal to 1, the band gap of Cr_xN is not so wide resulting in great enhancement in conductivity. The bigger departure from 1, the higher conductivity of the material is. So Cr_{0.43}N_{0.57} exhibits better conductivity than Cr_{0.49}N_{0.51} in the test. For this reason, the interfacial contact resistances of sample 2 and 3 are much lower than that of sample 1, showing perfect interfacial conductivities as BPP for PEMFC. The coating of sample 2 is composed of Cr_{0.49}N_{0.51} → Cr_{0.43}N_{0.57} gradient film, but the coating of sample 3 consists of a single element of Cr_{0.43}N_{0.57}. So the conductivity of sample 2 is a little lower than that of sample 3.

3.2. Corrosion testing

The corrosion potential with time in 0.5 M H₂SO₄ + 5 ppm F[−] solution at 25 °C is shown in Fig. 4. It can be seen

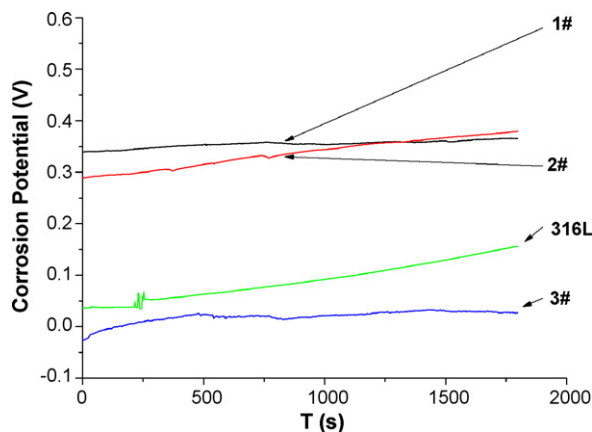


Fig. 4. Corrosion potentials of the BPP samples with time in 0.5 M H₂SO₄ + 5 ppm F[−] solution at 25 °C.

that the noblest open circuit corrosion potential values are for sample 1 and sample 2, which is 200 mV more positive than that of untreated 316L stainless steel. That is because their composition of coatings is the gradient film having different mol ratio of Cr to N, and it includes CrN which is proved to be corrosion resistant in simulated PEMFC environments [6–10]. As for sample 3, its corrosion potential is negative than the base metal attribute to its single element coating of Cr₄₃N₅₇, which is not so corrosion resistant.

Potentiodynamic polarization curves of the samples and untreated 316L stainless steel in 0.5 M H₂SO₄ + 5 ppm F⁻ solution at 25 °C are shown in Fig. 5. The BPP samples coated with Cr_xN were in passive states under test conditions. And the untreated 316L stainless steel could be passivated spontaneously under the same conditions. The corrosion current densities of BPP sample 1, 2, 3 and 316L stainless steel were about 10⁻⁶ A cm⁻², 10⁻⁷ A cm⁻², 10^{-4.5} A cm⁻² and 10⁻⁵ A cm⁻², respectively. In comparison with 316L stainless steel, sample 1 and sample 2 exhibited much lower passive current densities and corrosion current densities. As for sample 3, the corrosion current density was a little higher than that of 316L, although its passive current density was lower than the base metal. Sample 3 did not show obvious advantage compared with stainless steel, in accordance with the result of corrosion potential experiment. As for the experiments conducted in 0.5 M H₂SO₄ + 5 ppm F⁻ solution at 70 °C bubbled with air (Fig. 6) or H₂ (Fig. 7), the corrosion currents were higher than that performed at 25 °C. But the samples showed a same corrosion resistance order: 2# > 1# > 3# > 316L. Obviously, sample 2 exhibited the best corrosion resistance in simulated PEMFC environment among all the samples.

3.3. Contact angle

The contact angles of the BPP samples with water are shown in Fig. 8(a)–(c) and the values of contact angle are shown in Table 3. Obviously, sample 2 and sample 3 with Cr_{0.43}N_{0.57} surface had bigger contact angles (about 90°) than that of sample 1 (85°) with Cr_{0.49}N_{0.51} surface. To prevent the proton exchange

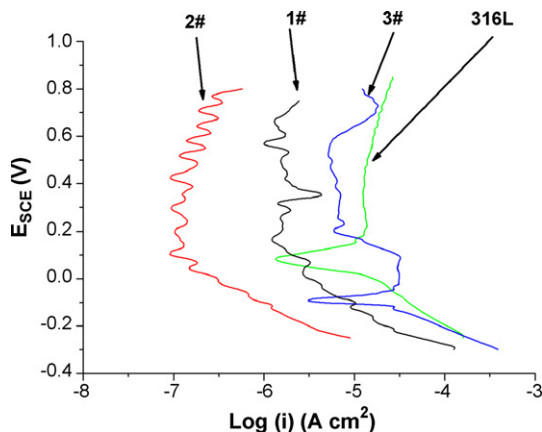


Fig. 5. Potentiodynamic behaviors of the BPP samples and untreated 316L in 0.5 M H₂SO₄ + 5 ppm F⁻ at 25 °C.

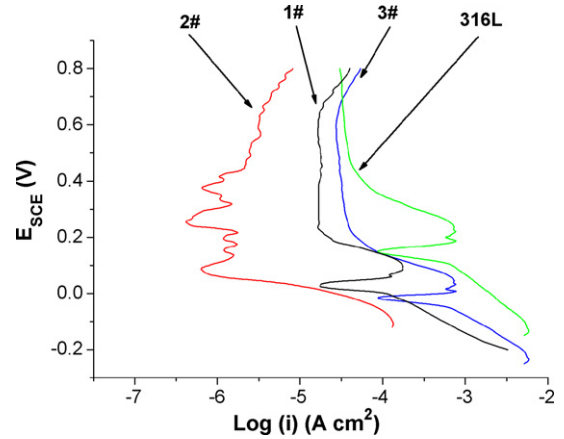


Fig. 6. Potentiodynamic behaviors of the BPP samples and untreated 316L in 0.5 M H₂SO₄ + 5 ppm F⁻ at 70 °C purged with air.

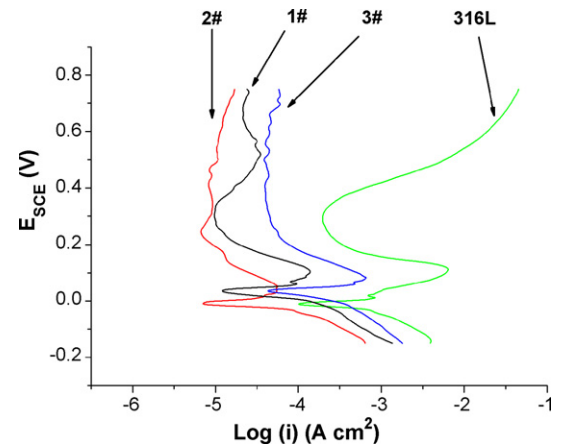


Fig. 7. Potentiodynamic behaviors of the BPP samples and untreated 316L in 0.5 M H₂SO₄ + 5 ppm F⁻ at 70 °C purged with H₂.

membrane from dehydration, the inlet gases need to be humidified and the exhausts are often mixed with the resultant water. In addition, there exists water generated due to oxygen reduction reaction in the fuel cell stack. 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 flooding phenomenon. Furthermore, the water adhering on the surface of BPP accelerates the corrosion of metal BPP. So BPP with high surface energy would be helpful for water removal in the stack and beneficial to the simplification of water management. According to the test data, sample 2 and sample 3 excel sample 1.

Table 3
Contact angles of the samples with water

Code	Contact angle (°)
1#	85
2#	90.5
3#	90

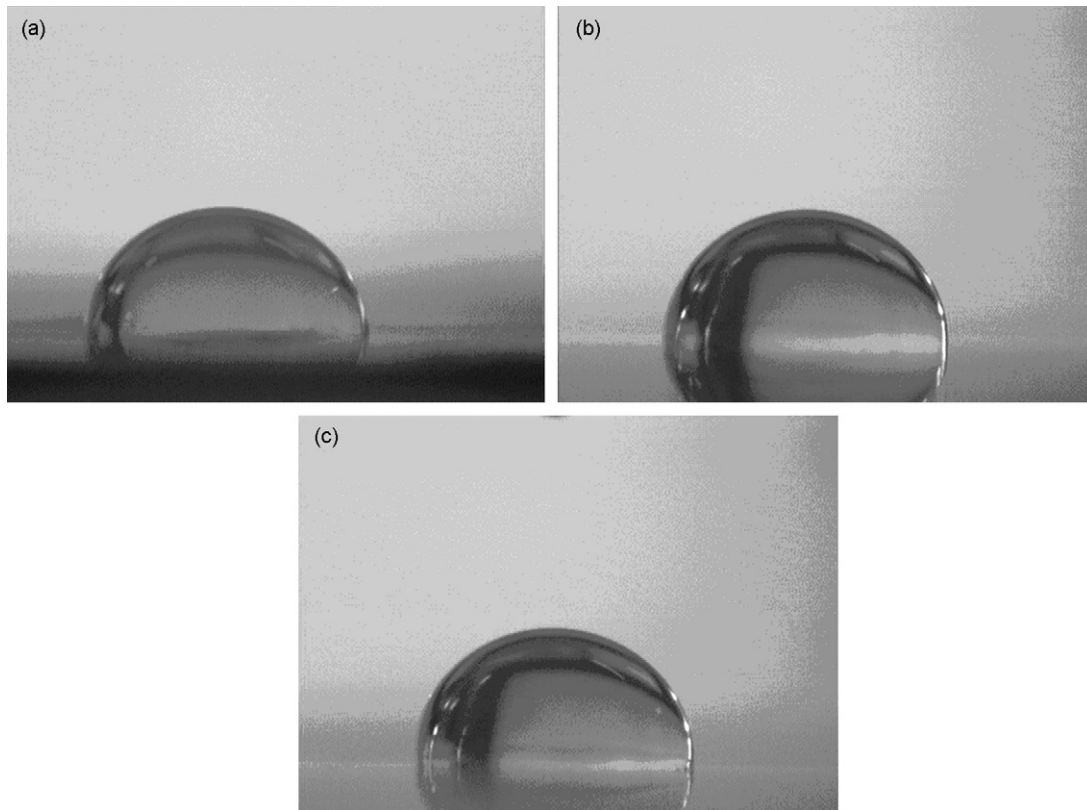


Fig. 8. (a) Contact angle of the sample 1 with water; (b) contact angle of the sample 2 with water; (c) contact angle of the sample 3 with water.

4. Conclusions

The 316L stainless steel was coated with film of Cr_xN by PBAIP as BPP for PEMFCs. Interfacial contact resistance, corrosion resistance and surface energy of the BPP samples were investigated. The samples with $\text{Cr}_{0.43}\text{N}_{0.57}$ surface exhibited better conductivity than those with $\text{Cr}_{0.49}\text{N}_{0.51}$ surface. The corrosion tests were conducted in $0.5 \text{ M H}_2\text{SO}_4 + 5 \text{ ppm F}^-$ solution bubbled with hydrogen gas or pressured air at 25°C and at 70°C . Sample 1 and sample 2 with gradient films showed good corrosion resistances at the open circuit and the corrosion current. And sample 3 did not show obvious advantage compared with the base metal. The samples with $\text{Cr}_{0.43}\text{N}_{0.57}$ surface also had bigger contact angles (about 90°) than those with $\text{Cr}_{0.49}\text{N}_{0.51}$ surface (about 85°).

Coated 316L stainless steel with $\text{Cr}_{0.49}\text{N}_{0.51} \rightarrow \text{Cr}_{0.43}\text{N}_{0.57}$ gradient film as BPP for PEMFCs prepared by PBAIP exhibited high interfacial conductivity, good corrosion resistance and high surface energy, so it shows great potential of application.

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