Optimized Cr-nitride film on 316L stainless steel as proton exchange membrane fuel cell bipolar plate

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Abstract
Pulsed bias arc ion plating was used to form Cr-nitride films on stainless steel as bipolar plate of proton exchange membrane fuel cell. Surface micrograph, film thickness, film composition, corrosion resistance, interfacial conductivity and contact angle with water of the sample obtained at the optimal flow rate of N₂ were investigated. The atomic ratio of Cr to N was close to 2:1 and the CrN phase with crystal planes of (111), (200), (220) and (311) was found in the film. Potentiodynamic and potentiostatic tests showed that the corrosion resistance of the bipolar plate sample was greatly enhanced. The contact resistance between the bipolar plate sample and Toray carbon paper was about two orders of magnitude lower than that of 316L stainless steel. The contact angle of the sample with water was 95°, which is beneficial for water management in fuel cells.

1. Introduction
Bipolar plate is an important component of proton exchange membrane fuel cell (PEMFC), and it accounts for most of the total weight. The bipolar plate serves as the functions of distributing reactants uniformly over the active areas, removing heat from the active areas, collecting currents from cells, preventing leakage of reactants and coolant. An ideal bipolar plate material should have the characteristics as follows: (1) high corrosion resistance in PEMFC environment; (2) low interfacial contact resistance; (3) big contact angle with water; (4) lightweight; (5) high mechanical strength; and (6) cost-effective etc.

Forming a film with good corrosion resistance and high interfacial conductivity on stainless steel is one of the possible solutions. Metal nitrides are the promising surface modification materials for metal bipolar plate owing to their good corrosion resistance and high conductivity. Many of the researches have been focused on Cr-nitrides in recent years [1–10]. In our previous work [11], Cr-nitride gradient films were coated on 316L stainless steel by pulsed bias arc ion plating (PBAIP) as bipolar plate for PEMFC. The composition of film varied with the flow rates of N₂. Films obtained at N₂ gas flow rates from 25 to 100 sccm exhibited high interfacial conductivity, good corrosion resistance and big contact angle, which showed great potential in the application of PEMFC.

The aim of the present work was to optimize the flow rate of N₂ and obtain bipolar plate with better performance. Surface micrograph, film thickness, film composition, corrosion resistance, interfacial conductivity and contact angle with water of the bipolar plate sample prepared at the optimal flow rate of N₂ were investigated.
2. Experimental

The 316L stainless steel (bright annealed) with the size of $100 \times 100 \times 0.1 \text{mm}^3$ was chosen as the base metal of bipolar plate. Details of forming the Cr-nitride films are described in our previous paper [10]. By changing the flow rate of N$_2$, film with different composition could be obtained. However, the total pressure in the chamber, which is a sum of the N$_2$ pressure and the Ar pressure, was kept constant at $5.0 \times 10^{-3} \text{Pa}$. The flow rates of N$_2$ conducted in this study are listed in Table 1. In this study, duration of the treatment for all the samples was 100 min. And the temperature of the samples during the treatment was round about 200°C.

Surface topography of the bipolar plate sample was performed with VK-8550 Super Depth Surface Profile Measurement Microscope. Thickness of the film was also measured by protecting some area of the substrate. X-ray energy dispersive spectrometer was used to characterize the composition of the film and the phase was identified by X-ray diffraction. The corrosion characteristics of the bipolar plate samples were analyzed by potentiodynamic and potentiostatic tests in 0.5 M H$_2$SO$_4 + 5 \text{ppm} \text{ F}^{-}$ solution. The tests were performed at 25°C and 70°C. The corrosion solution was bubbled with either air (simulating the PEMFC cathodic environment) or hydrogen gas (simulating the PEMFC anodic environment) prior to and during the electrochemical measurements. The initial contact resistances between the bipolar plate sample and bare TGP-H-060 Toray carbon paper were also measured. During the tests, the compacting force was increased with a step of 5 N s$^{-1}$. In addition, the contact angles of the samples with water were measured by a JC2000A Contact Angle Measurement system for investigating the surface energy.

3. Results and discussion

3.1. Optimization of the flow rate of N$_2$

The corrosion resistance and interfacial conductivity are the two main properties of metal bipolar plate materials. The parameters of passive current density (the current density under passivation potential) and interfacial contact resistance were used to evaluate these properties. All the bipolar plate samples were prepared at different flow rates of N$_2$ by PBAIP. Passive current density in 0.5 M H$_2$SO$_4 + 5 \text{ppm} \text{ F}^{-}$ solution at 25°C and initial contact resistance with carbon paper under 1.2 MPa of all the samples are shown in Fig. 1. The corrosion resistance of the samples increased with the flow rate of N$_2$ and came to a head at 20–25 sccm. Then the corrosion resistance of the samples decreased with the flow rate of N$_2$. As for the interfacial contact resistance, it decreased with the increment of N$_2$ flow rate when the flow rates of N$_2$ was lower than 20 sccm; then it increased evidently to a high level at
25 sccm; when the flow rates of N₂ was over 50 sccm, the ICR stayed a relatively low level. As a whole, the sample obtained at 20 sccm N₂ exhibited the best corrosion resistance and the highest interfacial conductivity simultaneously. Other characteristics of the bipolar plate sample obtained at the optimal flow rate were analyzed in detail as follows.

3.2. Characterization of the film

Fig. 2 shows the micrograph of the sample prepared at 20 sccm nitrogen flow. The picture shows a uniform, homogeneous film with regular stripes and a few protuberances on the 316L stainless steel base metal. These regular stripes were induced by the base metal which could also be seen on the surface of the untreated 316L stainless steel (Fig. 3). Although the pulsed bias arc is helpful to reduce droplets on the surface, there are still minor quantities of Cr droplets on the film. During the process of forming the film, N₂ can also react with the Cr droplets. Thus the protuberances in the film are a kind of defects but not pinholes, so the influence of protuberances can be negligible.

Before preparing the film, some area of the substrate was protected. After the film was formed, the thickness difference between the coated area and the uncoated area could be considered as the thickness of the film. Usually, the “Maximum depth” in Fig. 4 is regarded as thickness of the film. Thickness of the films obtained at the optimal N₂ flow rate at three different points are 0.768 μm, 0.81 μm and 0.81 μm, respectively. So the average thickness of the film obtained at 20 sccm N₂ was 0.80 μm.

![Thickness of the film obtained at 20 sccm N₂ flow.](image)
To eliminate the effect of the Cr in 316L stainless steel, pure Fe was used as the base metal for composition analysis of the film. X-ray energy dispersive spectrometer analysis of the film obtained at 20 sccm N₂ flow on pure Fe plate shows that the final composition of the film was 11.8 wt.% N and 88.2 wt.% Cr, and the atomic ratio of Cr to N is very close to 2:1 (Table 2). Further analysis by X-ray diffraction (Fig. 5) indicates that there was CrN phase with crystal planes of (111), (200), (220) and (311) on the film. As we know, the coating material obtained by PBAIP is of metastable state. So the film obtained at 20 sccm N₂ might be with CrN structure, which is a kind of structure with high chemical stability; what is more, there is almost one more Cr atom in the face-centered cubic CrN and the additional Cr enhances the conductivity greatly.

### 3.3. Corrosion resistance

Potentiodynamic tests were conducted in 0.5 M H₂SO₄ + 5 ppm F⁻ solution bubbled with air at 70 °C to investigate the corrosion resistance of the bipolar plate sample. The two potentiodynamic curves of the bipolar plate sample and 316L stainless steel are shown in Fig. 6. From the slopes of the anodic curve and the cathodic curve, the corresponding corrosion current can be determined. The corrosion current density of the bipolar plate sample was about 10⁻⁶ A cm⁻². As the applied potential increases from 0 to 0.75 V versus SCE, the corrosion current increased from 10⁻⁶ to 10⁻⁵ A cm⁻² accordingly. As for the 316L stainless steel, the corrosion current density was about 10⁻³.⁵ A cm⁻², over two orders of magnitude higher than that of the coated sample. What is more, it could be passivated spontaneously under the test conditions and the passive current density of 316L stainless steel was 10⁻⁴.⁵ A cm⁻². The potentiodynamic curves of the bipolar plate sample and 316L stainless steel in 0.5 M H₂SO₄ + 5 ppm F⁻ solution at 70 °C bubbled with H₂ are shown in Fig. 7. The bipolar plate sample was in passive state under test condition with a passive current density of 10⁻⁵ A cm⁻², which shows an obvious anticorrosion characteristic compared with 316L stainless steel.

In order to study the corrosion behaviors of the bipolar plate sample in the actual working conditions of PEMFC, potentiostatic tests were conducted at 0.6 V versus SCE bubbled with air to simulate the cathode working condition and at 0.1 V versus SCE bubbled with H₂ to simulate the anode working condition. In the simulated cathode condition (Fig. 8), the current density of the sample with Cr-nitride film obtained at 20 sccm N₂ stabilized within 3 min and stayed in the range of 10⁻⁷.⁰–10⁻⁸.⁰ A cm⁻². The current density of the

### Table 2 – Elementary composition of the film obtained at 20 sccm N₂ on pure Fe plate.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>11.8</td>
<td>33.2</td>
</tr>
<tr>
<td>Cr</td>
<td>88.2</td>
<td>66.8</td>
</tr>
</tbody>
</table>

![Fig. 5](image5.png) Displays the X-ray diffraction pattern of the film obtained at 20 sccm N₂ flow on Fe.

![Fig. 6](image6.png) Potentiodynamic curves of the bipolar plate samples in 0.5 M H₂SO₄ + 5 ppm F⁻ with a scan rate of 2 mV s⁻¹ at 70 °C bubbled with air.

![Fig. 7](image7.png) Potentiodynamic curves of the bipolar plate samples in 0.5 M H₂SO₄ + 5 ppm F⁻ with a scan rate of 2 mV s⁻¹ at 70 °C bubbled with H₂.
316L stainless steel stabilized after 15 min immersing and varied in the range of $10^{-6.0}$–$10^{-6.0}$ A cm$^{-2}$, which is near one order of magnitude higher than that of the coated sample. As for the tests in simulated anode condition, results are shown in Fig. 9. The current densities of the coated sample and 316L stainless steel were higher than that performed in the simulated cathode condition. But the current density of coated sample was also about one order of magnitude lower than that of 316L stainless steel.

As a whole, the bipolar plate with Cr-nitride film obtained at 20 sccm N$_2$ exhibited higher anticorrosion behavior compared with the 316L stainless steel.

### 3.4. Contact resistance

Initial interfacial contact resistance of the bipolar plate sample performed at 20 sccm N$_2$ with Toray carbon paper is shown in Fig. 10. The value of contact resistance decreased with the increasing compact pressure. But the coated sample exhibited excellent interfacial conductivity in all the range of compact pressures. The contact resistance between the coated bipolar plate sample and Toray carbon paper is about two orders of magnitude lower than that of 316L stainless steel. The interfacial contact resistance between the bipolar plate sample and carbon paper is in the range of 8.4–11.8 mΩ cm$^2$ under the common compacting pressure of 0.8–1.2 MPa in PEMFC. The higher output power could be obtained with the lower interfacial contact resistance. So the Cr-nitride film obtained at 20 sccm N$_2$ is helpful to improve the output power.

### 3.5. Contact angle

The contact angles of the bipolar plate sample and untreated 316L stainless steel with water are shown in Fig. 11 and Fig. 12, respectively. Obviously, the coated sample has a bigger contact angle (95°) than 316L stainless steel (73°). As it is
known, the process in fuel cell is always accompanied with water. To prevent the proton exchange membrane from dehydration, the inlet gases need usually to be humidified. In addition, water generated due to the reduction reaction of oxygen in the fuel cell stack also accounts for the hydration of the membrane. So the bipolar plates are often contacted with the mixture of reactant gas and water. Water would block the reactant gases from accessing to the electrode if the liquid water could not be removed in time. The accumulated water induces the electrode flooding phenomenon. Furthermore, the water adhering on the surface of bipolar plate could accelerate up the corrosion of metal bipolar plate. In addition, the bipolar plate with well hydrophobic characteristic is helpful for enhancing heat exchange between coolant and the cell. By considering these reasons, the coated bipolar plate with higher hydrophobic characteristic is helpful for water removal in the stack and beneficial to the water management.

4. Conclusions

Different compositions of Cr-nitride films could be obtained by changing the flow rate of N₂ during PBAIP process. The bipolar plate sample produced at 20 sccm N₂ exhibited the best corrosion resistance and the highest interfacial conductivity simultaneously.

In the film obtained at the optimal flow rate of N₂, the atomic ratio of Cr to N was very close to 2:1 and CrN phase with crystal planes of (111), (200), (220) and (311) was found. Potentiodynamic and potentiostatic tests performed at 70 °C bubbled with either hydrogen gas or air showed that the corrosion resistance of bipolar plate sample was greatly enhanced compared with 316L stainless steel. The initial contact resistance between the bipolar plate sample and Toray carbon paper was 8.4–11.8 mΩ cm² under 0.8–1.2 MPa, which is about two orders of magnitude lower than that of the untreated 316L stainless steel. In addition, the contact angle of the sample with water was 95°, which is beneficial for water management in fuel cell.

Coated 316L stainless steel plate with Cr-nitride film at 20 sccm N₂ shows good corrosion resistance, high interfacial conductivity and well hydrophobic characteristic, so it exhibits great promising in the application of PEMFC. Dura-

bility and performance of this kind of bipolar plate material in actual PEMFC environment is to be studied in the future.

Acknowledgments

This work was financially supported by the National High Technology Research and Development Program of China (863 Program, No. 2007AA032221).

References