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Short communication

Arc ion plated Cr/CrN/Cr multilayers on 316L stainless steel as bipolar plates for polymer electrolyte membrane fuel cells

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ABSTRACT

Arc ion plating (AIP) is applied to coat sandwich-like Cr/CrN/Cr multilayers on stainless steel 316L (SS316L) as bipolar plates for polymer electrolyte membrane fuel cell (PEMFC). Phase structure, hardness, adhesion property, interfacial contact resistance (ICR) between bipolar plates and carbon papers, and electrochemical corrosion property in the simulated PEMFC conditions are investigated. Cr phase with crystal plane of (1 1 0), (2 1 1), (3 2 2), and CrN phase with (3 2 1) are observed in the multilayer. The coating is found smooth, continuous and dense in cross-sectional observation by SEM, and the sandwiched structure of the coating is also confirmed by EDX results. Scratch tests show that the multilayer exhibits strong adhesion strength with steel substrate, which is beneficial to prevent layers from peeling off mechanically. After the coating treatment, the performance of the bipolar plate is greatly improved. Knoop hardness of the bipolar plates increases from 324 HK to 692 HK. The ICR decreases by one order of magnitude; furthermore, the corrosion resistance was also enhanced. Our analysis indicates that the improvement is attributed to high adhesion force of the smooth and dense coating and the synergistic function of Cr/CrN/Cr multilayer structure.

1. Introduction

A polymer electrolyte membrane fuel cell has attracted increasing interests due to its high efficiency and near-zero emissions as a power source. Currently, the major challenges for the commercial application of PEMFC systems include reducing the cost and weight of the fuel cell stack. One of the key components of the fuel cell stack is the bipolar plate which has the main functions of distributing and separating the cathodic and anodic reactant gases, and collecting and transmitting electric current [1]. Good conductivity, high corrosion resistance, high mechanical strength, and low gas permeability, low cost and easy machining are highly desirable characteristics for ideal bipolar plates [2]. Stainless steel 316L exhibits most of the characteristics and is widely considered as a promising bipolar plate material [3]. However, its corrosion resistance is still far from satisfaction in the acidic environment of PEMFC operation. The corrosion products, such as Fe ions, tend to contaminate the catalysts and poison the proton exchange membrane, reducing the overall efficiency of the cell [4]. Meanwhile, the corrosion finally causes the formation of a passivating layer on the stainless steel surface, which leads to an increase in ICR and a decrease in cell performance [5]. Additionally, the corrosion can deteriorate water management in the fuel cell, leading to increased mass transport losses. These effects cause the durability of the fuel cells degrade quickly, resulting in a poor lifetime [6].

How to impart SS316L bipolar plates with sufficient corrosion resistance and contact conductivity inexpensively is currently a hot issue. Forming a protective film on the plates by surface modification is proven to be an effective method and has been extensively studied. Fu et al. reported that both CrN [7] and Cr_xN gradient films [8] on SS316L by arc ion plating show high interfacial conductivity and good corrosion resistance in 0.5 M H_2SO_4 + 5 ppm F^- solution. Subsequently, Carbon-based films coated SS316L bipolar plates were reported by Fu to enhance corrosion resistance and interfacial conductivity in simulated PEMFC conditions [9]. Good initial performance of PEMFC stacks assembled with $Cr_{0.5}N_{0.5}$ film coated bipolar plates was close to that of the cell assembled with the Ag-plated ones [10]. Lee and co-workers investigated the ICR and corrosion resistance of TiCrN and titanium oxynitride films on SS316L bipolar plates by magnetron sputtering [11]. The bipolar plates were also coated with Ni [12] and Cr [13] by electroplating. Wang conducted plasma nitriding on SS316L plates and found that the treated plates exhibit good corrosion resistance, however poor interfacial conductivity [14]. Brady used thermal nitridation to form

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a pin-hole free nitride layer on metallic bipolar plates, including Ni–Cr based alloys [15,16], Fe–Cr based alloys [17], AISI446 [18], and 349^{TM} [19]. It was found that dense Cr nitride layer formed on Ni–Cr based alloys and exhibited improved corrosion resistance and low ICR under simulated PEMFC conditions, while thermal nitrided 349^{TM} showed poor corrosion resistance because of the lack of continuity of the Cr-rich nitride layer [19]. Additionally, thermal nitrification generally requires a high-temperature process (>1000 °C) that can cause undesirable deformation of the machined metal bipolar plate [20] and a decrease of corrosion resistance [21]. Further, the process typically entails a high manufacturing cost.

More recently, Wang et al. [22] investigated the performance of TiN-, TiAlN- and CrN-coated SS316L bipolar plates by EBPVD under simulated PEMFC environments. It was found that CrN-coated SS316L showed a significantly lower ICR and better corrosion resistance. They suggested that multilayered coatings may disconnect the pinholes, or prevent through-coating pinholes and block corrosion channels. Zhang et al. [23] also deduced that a Ti_2N/TiN multilayer coating can provide superb corrosion protective layer for stainless steel. Despite of this, few reports have been presented on the possibility of the multilayer used for PEM fuel cell bipolar plates, maybe due to complicated process and poor cost efficiency.

Arc ion plating has been widely used to form efficiently protective coatings on cutting tools, dies, and bearings, etc. It is one of the most cost-efficient and economic deposition processes among PVD techniques. According to our previous study [8,24,25], arc ion plating, applying a pulsed substrate bias, PBAIP in short, inherits the advantages of arc ion plating, such as high ionized degree, high deposition rate and strong bonging strength, etc. More importantly, a pulsed bias brings new features in this conventional PVD technique, such as reduced droplets, dense films and low-temperature deposition. As a result, films with excellent performance can most likely be obtained. In addition, PBAIP is an environment-friendly process.

In this study, a sandwich-like Cr/CrN/Cr multilayer was designed and deposited on SS316L substrates as bipolar plates in PEMFCs by pulsed bias arc ion plating (PBAIP). Coating quality was evaluated by morphology, phase structure, film hardness, adhesion strength using XRD, SEM, micro-hardness and scratch tests. The interfacial contact resistance (ICR) and anti-corrosion property in the simulated PEMFC environments was presented as well.

2. Design of materials and coating structure

Cr is a kind of inexpensive and abundant metal with a good electrical conductivity and chemical stability. Cr-based coatings can help reduce the production cost. Bare Cr coating has poor mechanical and anti-corrosion properties, while CrN is a conductive nitride with good mechanical and anti-corrosion properties. The combination of Cr and CrN is of great potential to exhibit the synergistic functions. It was found in many reports [11,22,23,26–28] that the ICR decreases with increase in the compaction force. Choi et al. pointed out that this influence of the compaction force is due to an enlargement of the actual contact area under an increasing compaction force [11], and Lee et al. [29] also stated that an increase in the contact areas acts as electrical junctions, leading to an decline of ICR. Soft metal, like Cr, will help increase contact area when pressed, so Cr layer was selected as the outmost layer. Then CrN was assigned as the underneath layer to enhance the mechanical and anti-corrosion property. Accounting for higher internal stress usually caused by the big dismatch of physical properties between hard ceramic CrN and relative soft metallic SS316L [30,31], an interlayer of Cr followed CrN layer to improve the bonding strength. So the designed coating was sandwich-like structure, i.e. Cr/CrN/Cr multilayer.

3. Experimental methods

Bulat-6 arc ion plating system was used in this study. Two opposite Cr targets, 99.9% pure and 55 mm in diameter, were mounted at the end of linear ducts that connect to the chamber. Both ducts consisted of a two-step magnetic coil. The first-step coil was used to stabilize the burning arc, and the second-step one was 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 was 600 mm. A pulsed bias was applied on the holders through the axis.

Stainless steel 316L was chosen as the base metal of bipolar plates. 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 of −800 V in ambient Ar at 2.0 Pa.

When the deposition began, two Cr targets were burnt by the triggers, and both arc currents were kept at 80 A. The partial pressure of Ar was kept at 0.5 Pa. The bias voltage, frequency and duty cycle of the pulsed bias were −300 V, 20 kHz and 40%, respectively. 10 min later, nitrogen gas was introduced in the chamber by mass flow meter and the flow rate was 102 sccm. After 20 min of CrN deposition, the flow rate of N_2 decreased immediately to zero. The deposition process preceded another 10 min, and then halted. According to the deposition rate of our AIP system, the thickness of Cr and CrN layer was controlled to 0.25 and 0.5 μm, consistent with our design.

Phase structure was detected with XRD-6000 X-ray diffractor. Film hardness was measured with a DMH-2LS Knoop hardness tester. Morphology of cross-section and scratch track was observed with scanning electron microscopy (JSM-5600LV). Adhesion strength was evaluated with a CSR-01 scratch tester.

The ICR between uncoated, coated bipolar plates and diffusion layer (carbon paper) was measured with the method similar to that reported by Wang et al. [3]. In the setup, 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 5.0 A, sourced by a PSP-2010 programmable power supply, was provided via the two copper plates. During the tests, the compacting force was increased gradually at a step of 5 N s^{-1} controlled by a WDW electromechanical universal testing machine.

Corrosion behaviors of the samples were investigated by polarization electrochemical experiments using a potentiostat Model 2273A by EG&G Princeton Applied Research and analyzed with the corrosion software of EG&G Version 2.43.0. To simulate an aggressive PEMFC environments, a 0.5 M H_2SO_4 + 2 ppm F^- solution at 70 °C was used, bubbled thoroughly with either hydrogen gas (simulating a PEMFC anodic environment) or pressured air (simulating a PEMFC cathodic environment) prior to and during the electrochemical tests. A conventional three-electrode system was used in the electrochemical measurements, in which a platinum sheet acted as the counter electrode, a saturated calomel electrode (SCE, sat'd KCl) as the reference electrode and the stainless steel sample as the working electrode. The size of the working electrodes prepared was 15 mm × 15 mm × 0.1 mm. The edges were sealed by insulating epoxy resin, only leaving a 10 mm × 10 mm surface exposed to the electrolyte. A copper wire was soldered to the backside of the sample for ohmic contact. As for the potentiodynamic polarizations, the samples were stabilized at open circuit potential (OCP)