



Composition optimization of arc ion plated CrN_x films on 316L stainless steel as bipolar plates for polymer electrolyte membrane fuel cells

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ABSTRACT

Thin films of CrN_x with different nitrogen contents are deposited on 316L stainless steel (SS316L) as bipolar plates for polymer electrolyte membrane fuel cells (PEMFCs) by arc ion plating (AIP) through adjusting nitrogen gas flow rate. The optimal N₂ flow rate and resultant N content in CrN_x films are determined by evaluating the interfacial contact resistance (ICR) between carbon papers and the coated samples, and the corrosion resistance in the simulated PEMFC conditions. After coating CrN_x films, the performance of SS316L bipolar plates is obviously improved, and has a close relationship with N content in the CrN_x films. Compared with the bare SS316L, the CrN_x coated SS316L exhibits a reduced ICR by one order of magnitude and the corrosion resistance increases by two orders of magnitude. The results show that CrN_{0.86} film coated SS316L bipolar plates present best performance, i.e. the ICR of CrN_{0.86} film coated sample reduces to 8.8 mΩ cm² under 1.0 MPa compaction pressure, and the corrosion current density almost reaches 10⁻⁷ A cm⁻². The analysis indicates that the enhanced performance of the coated SS316L bipolar plates is related to the high film density determined by AIP, and the variation of phase structure and film composition.

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1. Introduction

Polymer electrolyte membrane fuel cell is a device that directly and efficiently converts chemical energy into electricity with water as the only by-product. Due to its high efficiency and near-zero emission, PEMFC is of great interest as a clean energy device beyond petroleum [1]. Bipolar plate (BPP) is one of the most important and expensive components in a PEMFC stack and accounts to more than 80% of the total weight of the stack [2]. This multi-functional component not only serves as the backbone of serially connected cells, but also performs several other key functions such as conducting currents between cells, facilitating water and thermal management through the stack, and providing conduits for reactant gases [3]. Therefore, the BPP material must have good mechanical strength, low contact resistance with the backing, low gas permeability, inexpensive massive production and a low cost, be chemically stable,

highly electrical and thermal conductive, and allow uniform reactant gas distribution and product removal.

Stainless steel is considered to be a promising candidate for bipolar plates in PEMFCs because of cost effectiveness, higher mechanical strength, better durability to shock and vibration, no permeability, and superior manufacturability compared to graphite composites [4]. Wang et al. [5] studied the performance of four types of stainless steel BPPs, e.g. 349TM, 904L, 317L and 316L, and proposed that the performance of stainless steel bipolar plates improved with the increase in Cr content in the steels. However, during the operation of PEMFC stacks, BPP is exposed to a highly corrosive environment including F⁻, SO₄²⁻, SO₃²⁻, and HSO₄⁻. Upon the harsh acidic and humid environment inside the PEMFCs, bare metallic bipolar plates undergo the passivation process and a passive oxide film forms on the surface, which will increase the interfacial contact resistance (ICR) between bipolar plate and the adjacent gas diffusion layer (GDL). Furthermore, corrosion leads to a release of metal ions that can contaminate the electrolyte membrane and poison the electrode catalysts [6]. Both conditions can cause considerable degradation of stack performance.

To overcome the formation of surface oxide and the dissolution of metal in PEMFC environments, forming a protective and conductive coating by surface modification is regarded as an effective method and has been studied extensively [7–10]. However, many literatures [11,12] reveal that single modification layer fails

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to effectively protect metallic BPPs from corrosion because the layer, especially by physical vapor deposition (PVD) process, contains some defects like pinholes, pores and droplets, which tend to provide corrosion channels. To avoid this problem, we [13] developed and deposited a Cr/CrN/Cr multilayer with a sandwich-like structure on the SS316L bipolar plates for PEMFCs. The multilayer design introduces the interfaces between layers to block or disconnect the corrosion channels, thereby provides effective protection. The results show that the samples coated with Cr/CrN/Cr exhibit improved corrosion resistance and conductivity compared to bare SS316L samples. But the outmost Cr layer tends to passivate and a few Cr ions will dissolve and poison catalysts, which is unfavorable for PEMFC efficiency and lifetime. Cr/CrN multilayer will be employed in our future work to avoid this problem. Prior to doing this, the optimum of Cr/N content ratio in CrN films should be determined. Although some primary results on optimization of N_2 flow rate were obtained in our previous study [14], the mechanism involved was not discussed from a material and physical point of view.

In this paper, a series of CrN_x films with different nitrogen contents were deposited on 316L stainless steel as bipolar plates for PEMFCs by AIP through adjusting the nitrogen flow rate in order to further investigate the influence of Cr/N ratio on the performance of SS316L bipolar plates, and obtain the optimal value. The physical mechanism involved was discussed as well.

2. Experimental

The CrN_x films were deposited on the samples using an arc ion plating system, in which two opposite Cr targets of 99.9% pure and 55 mm in diameter were mounted at the end of linear ducts that connect to the chamber. Stainless steel holders lying in the center of the chamber can rotate and turn simultaneously. The distance between the center of the holder and the targets was 600 mm. A pulsed bias was applied on the holders through the axis.

Two kinds of samples are used as substrates, one is pure iron sheet with size of 20 mm × 10 mm × 1 mm, and the other is 316L stainless steel sheet for bipolar plates with size of 80 mm × 80 mm × 0.1 mm. The former is used for the measurement of the film composition and phase structure, and the latter one is for the evaluation of the contact resistance and anti-corrosion property of the coated samples. The substrates were ultrasonically cleaned in acetone, ethyl ethanol and deionized water subsequently for 15 min. Then they were blown dry and hung on the 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 samples 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. A pure chromium thin layer (approximately 30–50 nm) was deposited on the substrates as an interlayer to enhance the adhesion force. Then, nitrogen gas was introduced into the chamber, and reacted with chromium plasma evaporated from the targets, consequently forming CrN_x films on the substrates.

Five groups of CrN_x films with different nitrogen contents were deposited by adjusting the nitrogen gas flow rate, 10 sccm, 15 sccm, 20 sccm, 25 sccm and 50 sccm. The thickness of CrN_x films was controlled at approximately 1 μ m by adjusting the deposition time.

The phase structure of films was identified by X-ray diffraction (XRD), film composition was measured by electron probe microscope analysis (EPMA) and the surface morphology was observed by scanning electron microscopy (SEM, JSM-5600LV).

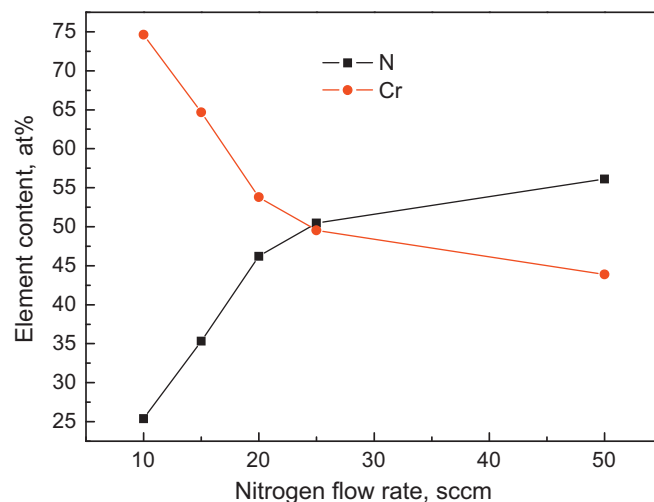


Fig. 1. The N and Cr element contents in the CrN_x films as a function of nitrogen gas flow rate.

The contact resistance between the CrN_x coated samples and gas diffusion layer (carbon paper) was measured with the conventional method extensively used by many researchers [5,15–17]. According to this method, two pieces of Toray carbon paper (TGP-H-060) were sandwiched between the samples and two gold-coated copper plates, on which an electrical current of 5.0 A, sourced by an INSTEK PSP-2010 programmable power supply was applied. 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.

The corrosion resistance of the samples was evaluated at 25 °C 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. A 0.5 M H_2SO_4 with 2 ppm F^- solution was used as the corrosive solution to simulate an aggressive PEMFC operating environment. 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 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. The samples were stabilized at open circuit potential (OCP) for 10 min, and then the potential was swept from the OCP in the anodic direction at a scanning rate of 20 $mV s^{-1}$.

In order to evaluate the stability of the samples in the actual working conditions of PEMFCs, potentiostatic polarizations were performed in 0.5 M H_2SO_4 + 2 ppm F^- solution at 70 °C for over 6.5 h. Either air or H_2 was purged into the solution throughout the test to simulate the cathode or anode environment. During the measurements, the specimens were also stabilized at open circuit potential for 10 min. The current density as a function of time was recorded at applied anode (-0.1 V_{SCE}) and cathode (+0.6 V_{SCE}) potentials for PEMFCs.

3. Results

3.1. Film component

The N and Cr element contents in the CrN_x films as a function of nitrogen gas flow rate are shown in Fig. 1. Nitrogen content increases linearly when the nitrogen gas flow rate is in range of 10–20 sccm, but the increasing trend weakens above 20 sccm, till at 50 sccm, nitrogen content presents a saturation trend. Being the

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