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Short communication

Corrosion resistance and electrical properties of carbon/chromium–titanium–nitride multilayer coatings on stainless steel

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HIGHLIGHTS

- C/Cr–Ti–N multilayer coatings with varying Cr:Ti target current is deposited on SS316L.
- Metal ion corroded during 10 h potentiostatic test is reduced by more than 30 times by multilayer.
- Superior conductivity of around 2 and 3 mΩ cm^2 before and after 10 h polarization is achieved.

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ABSTRACT

High electrical conductivity and corrosion resistance are central to advances in wider application of metallic bipolar plates in polymer electrolyte membrane fuel cell (PEMFC). In this study, C/Cr–Ti–N multilayer coatings are deposited by physical vapor deposition and the effect of Cr:Ti ratio on the corrosion resistance and interfacial contact resistance (ICR) are systematically investigated. Scanning electron microscopy (SEM) result shows that the carbon layer is compact and uniform. Excellent corrosion resistance of 0.127 μA cm^{-2} current density at operating voltage in PEMFC cathode environment and low ICR of 2.03 mΩ-cm^2 at compaction force of 150 N cm^{-2} are achieved when Cr:Ti ratio is 2:4 and 3:3, respectively. The significant enhancement in surface conductivity is probably because that the current comes from carbon paper is homogenized by two electrically conductive layers and flows to the passive film with much more contact area. After polarization, ICR increase to 3.07 mΩ-cm^2 and 3.02 mΩ-cm^2 in the simulated PEMFC cathode and anode environment, respectively. However, the Raman spectroscopy results disclose that the bonding type of top carbon film before and after polarization shows little difference. The results indicate that C/Cr–Ti–N multilayer coating with Cr:Ti ratio of 2:4 achieves the optimal composition.

1. Introduction

The bipolar plate is a key multifunctional component in polymer electrolyte membrane fuel cell (PEMFC), which serves to separate individual cells, act as backbone of fuel cell stack, distribute the reactive gases uniformly, collect the electrical current, and remove the heat and water etc. [1,2]. Conventionally, graphite bipolar plate is widely used in PEMFC because of its high electrical conductivity and good corrosion resistance [3]. However, it is neither suitable for transportation applications that demand good structural durability against shock and vibration nor for large-scale manufacturing due to its poor mechanical strength. Currently, the dominating bipolar plate materials can be divided into composites and metals. Stainless steels are considered as one of the promising candidates because they permit properties such as high strength, ease of machining and shaping into thin sheets, low gas permeability and low cost [4,5]. Nevertheless, insufficient surface conductivity and corrosion resistance are two major drawbacks that prevent stainless steel from widely applied as bipolar plate material. Wang et al. [4] studied the electrochemical behavior of stainless steel 316L (SS316L), 317L, and 349TM in 1 M H_2SO_4 with 2 ppm F^- and the potentiodynamic test results showed that the current density of SS316L was as high as 10 μA cm^{-2}, which was one order of magnitude higher than the conventionally acceptable corrosion resistance for metallic bipolar plates as defined by the US Department of Energy (DOE) of ≤1 μA cm^{-2} [6]. Scholta [7] studied SS 316, 316L, and 316Ti in 1 M H_2SO_4 solution and noticed a current

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density, as high as 3 mA cm^{-2} at 0.9 V_{RHE}. Wind et al. [8] also found a high dissolution rate of 316L in the single cell test. Kumagai et al. [9] barely observed corrosion on the anode side of SS304L but discovered substantial corrosion on the cathode side after operation for 1000 h. Therefore, for long term operation and duration concerns, surface modifications are still required in order to improve the surface conductivity and inhibit corrosion during service life of stainless steel bipolar plate in PEMFC [10,11].

Various coatings materials are normally divided into two categories by composition: carbon-based and metal-based [12,13]. Recently, carbon film has attracted extensive attentions because it combines the advantages of graphite and stainless steel with high electrical conductivity and chemical inertness [14,15]. Show et al. [14,16] prepared amorphous carbon film on titanium bipolar plates by chemical vapor deposition technique and their results showed that the fuel cell assembled with the a-C coated Ti bipolar plate has an output power of 1.4 times higher than that of bare Ti bipolar plate fuel cell. Fukutsuka et al. [15] deposited carbon coating on stainless steel 304 by plasma-assisted chemical vapor deposition. The carbon coated SS304 exhibited high electrical conductivity and improved corrosion resistance in spite of the absence of a passive film. Mori et al. [17] deposited a conductive amorphous carbon film on SS316L bipolar plates using electron cyclotron resonance plasma sputtering technique. This carbon film, mainly composed of sp^2 and sp^3 bonding, reduced the contact resistivity between the coated SS316L and carbon paper by two orders of magnitude. Fu et al. [18] prepared a C–Cr composite film on stainless steel by pulsed bias arc ion plating. The results showed that the interfacial conductivity and corrosion resistance were improved by the C–Cr film. In our previous research, amorphous carbon film with high percentage of sp^2 bond has been deposited on stainless steel by using closed field unbalanced magnetron sputtering ion plating (CFUBMSIP) [19–22]. This coating has good corrosion resistance and excellent surface conductivity that is even better than graphite due to the relatively large sp^2 component. With the optimization of deposition parameter, the interfacial contact resistance (ICR) of carbon film coated SS304 is minimized to 4.94 mΩ cm^2 at a compaction force of 135 N cm^{-2}, and the current density at 0.6 V in simulated PEMFC cathode environment is reduced to 2.10 μA cm^{-2} [22]. Yi et al. [23] tested this carbon film coated SS304 bipolar plate and in-situ experiments showed that the peak power density of the single cell using carbon film coated SS304 bipolar plates was twice of that using bare bipolar plates and the performance degradation after 200 h of continuous operation decreased from 28.7% to 3.9%.

However, due to the defects in the coating such as pinholes and macroparticles generated during PVD process, single layer coatings are usually prone to local corrosion and the current density has been reported to increase dramatically after long time immersion in the simulated PEMFC environment [24,25]. Recently, multilayer coatings have been shown to have improved performance over single layer coatings due to a reduced proportion of pinholes caused by the interruption of through-thickness pinholes [10,26,27]. Therefore, we fabricated a new multilayer coating composed of amorphous carbon as the outer layer and CrN as the inner layer (C/CrN multilayer) [28]. The results showed that the current density of C/CrN multilayer coated SS316L at 0.6 V is decreased to 0.5 μA cm^{-2} and ICR is minimized to 2.6 mΩ cm^2 at compaction force of 150 N cm^{-2} [28]. In this work, chromium target and titanium target are sputtered with different current to fabricated Cr–Ti–N ternary sub-layer with carbon coating on the top (hereafter nominated C/Cr–Ti–N multilayer coatings). It is expected to optimize composition and refine microstructure of sublayer, and subsequently to further improve corrosion resistance and surface conductivity of multilayer coating. The cross-sectional SEM, EDS line scan and bonding type of C/Cr–Ti–N multilayer coatings are studied by scanning electron microscopy (SEM) and dispersive Raman microscope. The electrochemical behavior and ICR are also systematically investigated and discussed.

2. Experimental details

2.1. Substrate materials and coating deposition

Austenitic stainless steel 316L purchased from Trinity Brand Industries, Inc. was used as substrate materials. The chemical composition was shown in Table 1. CFUBMSIP coating system (UDP 650, Teer Coatings, Ltd.) equipped with one chromium target, one titanium target and two graphite targets was used to deposit C/Cr–Ti–N multilayer coatings. After the chamber was depressurized at 3.0×10^{-5} torr, Ar was introduced into the chamber. Meanwhile, bias voltage of −500 V was applied to the substrate and 0.5 A chromium target current was used for 30 min to obtain a clean and active surface by sputtering. A thin Cr metallic seed layer was deposited when 6 A was supplied to Cr target to enhance adhesion. Afterward, a Cr–Ti–N, or CrN, or TiN layer was reactively sputtered in a mixture of argon and nitrogen and the flow rates were controlled to yield the required coating stoichiometry. In this process, the Cr:Ti target current ratio was keep at 6:0, 5:1, 4:2, 3:3, 2:4, 1:5 and 0:6 (hereafter nominated as C/CrN, C/Cr5Ti1N, C/Cr4Ti2N, C/Cr3Ti3N, C/Cr2Ti4N, C/Cr1Ti5N and C/TiN), respectively. Before deposition of the carbon coating, a thin intermediate MC_x layer (M: Cr or Ti) was deposited as an interfacial layer by reducing the current supplied to the chromium or titanium targets, and increasing simultaneously the current supplied to the carbon targets from 0.5 A to 5 A. Finally, the carbon layers were deposited outside. The detail deposition parameters were shown in Table 2.

2.2. Coating characterization

The surface morphology and cross section of the C/Cr–Ti–N multilayer coatings were observed by field-emission scanning electron microscopy (FE-SEM) of HITACHI S-4800. Energy-dispersive X-ray spectroscopy (EDS) was conducted to determine the cross section chemical distribution. In order to explore the change of bonding type and internal structure of carbon coating before and after the potentiostatic test, the Raman spectroscopy of carbon coating on as-received and polarized C/Cr4Ti2N sample was measured by dispersive Raman microscope Senterra R200-L (Bruker Optics).

2.3. Performance test

The electrochemical tests, including potentiodynamic and potentiostatic, were conducted using a Zahner Zennium electrochemical workstation to evaluate the corrosion resistance of the bare and C/Cr–Ti–N multilayer coated SS316L. The electrochemical tests were conducted in 0.5 M H_2SO_4 + 2 ppm HF solution at 70 °C to simulate the aggressive PEMFC environment. The solution was purged with either air (to simulate cathode environment) or hydrogen gas (to simulate anode environment) prior to and during the electrochemical test. A three-electrode system, in which the counter electrode was a platinum sheet, the reference electrode was mercury sulfate electrode (MSE), the working electrode was sample, was employed in this study. MSE, which was suitable for

Table 1
Chemical composition of SS316L (at.%).

Cr	Ni	Mo	C	Mn	Si	P	S	Fe
20.0–21.0	6.0–7.0	1.5	0.03	1.5	1.0	0.04	0.03	Balance