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Molybdenum nitride modified AISI 304 stainless steel bipolar plate for proton exchange membrane fuel cell

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ABSTRACT

A molybdenum nitride diffusion coating has been prepared on the surface of AISI 304 stainless steel (304 SS) by plasma surface diffusion alloying method as bipolar plate for proton exchange membrane fuel cell (PEMFC). X-ray diffraction data shows that the molybdenum nitride is face-centered-cubic Mo_2N phase. The results of scanning electron microscopy in combination with energy-dispersive X-ray analysis spectrometer indicate that the as-prepared molybdenum nitride diffusion coating consists of a ~3.5 μm surface layer (molybdenum nitride) and a ~0.5 μm subsurface layer (Mo and N solid solution). In addition, the average contact angle with water for modified 304 SS is 91°, demonstrating the better hydrophobic property of the surface modified 304 SS as compared to the untreated ones with average contact angle of 68°. Potentiodynamic and potentiostatic testing in simulated PEFMC operating conditions (0.05 M H_2SO_4 + 2 ppm F^- solution at 70 °C purged with either hydrogen or air) as well as interfacial contact resistance (ICR) measurement imply that the molybdenum nitride modified 304 SS exhibits improved corrosion resistance and promising ICR.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is expected to be promising substitutes for the traditional fossil fuel, and major power sources for electrical vehicle and portable applications owing to the following merits: high efficiency, operating at low temperature (about 60 °C), faster startups at room temperature, environment friendliness, noiselessness, etc. [1,2]. To put the PEMFC into commercialization, the cost needs to be decreased and the performances to be improved. As one of the most important components in PEMFC, bipolar plates, a multifunctional component, account for the dominant share of the total stack weight and cost [3]. Typically, a bipolar plate is used to electrically connect the anode of one single cell to the cathode of another adjacent single cell, provides flow fields of reactive gases (hydrogen and oxygen) as well as facilitates water management within the cell in PEMFC stack. Meanwhile, the PEMFC operating environments contain ions such as F^-, SO_4^{2-}, SO_3^{2-}, HSO_4^-, HSO_3^-, CO_3^{2-}, HCO_3^-, and voltage difference between cathode and anode is up to 1 V while starting the PEMFC system. Therefore, an ideal bipolar plate material should possess excellent electrochemical corrosion resistance, high electrical conductivity, relatively low cost, high strength and small volume as well as good hydrophobicity [4–6].

A variety of materials have been chosen and evaluated to serve as PEMFC bipolar plates. Non-porous graphite has been at first chosen for the bipolar plates for its high conductivity

and excellent corrosion resistance. However, graphite's high cost, poor machining property with brittleness and large percent of mass and volume in PEMFC stack are the fatal obstacles in commercialization of transportation and portable application. Metallic bipolar plates, especially stainless steels (SS), have been drawn more and more attention due to the low prices, easy stamping manufacture, good physical and mechanical properties and thin plate use [7–9]. As afore-mentioned, the operating conditions of PEMFC are so harsh acidic and humid that the bare stainless steels can not be successfully applied into a commercial PEMFC stack in terms of corrosion resistance and interfacial contact resistance (ICR). In order to improve the performances of stainless steel bipolar plates, many efforts have been made by employing different surface modification techniques and methods on various types of stainless steels [10–15]. Among the many developed coatings, transition metal nitrides fabricated by several coating techniques have been widely investigated and evaluated in PEMFC conditions. Multi-arc ion plating TiN was prepared on the surface of 316L by Tian and Sun [16]. Both the corrosion resistance and ICR of TiN coated 316L are improved. Jeon et al. [17] synthesized TiN coatings on 316L by closed-field unbalanced magnetron sputtering and they found that TiN coating prepared with N_2 partial pressure of 0.4 mTorr showed good corrosion resistance due to the low porosity. Cho et al. [18] prepared TiN coating on AISI 316 stainless steel with chemically etched flow channels using hollow cathode discharge ion plating method. The TiN-coated 316 bipolar plates were applied in a 1 kW class PEMFC stack and the life-time was significantly improved in comparison with that using bare 316 as bipolar plates. The above mentioned TiN obtained by physical vapor deposition (PVD) inevitably has inherent coating defects, pin-hole and micro porosity, which evidently decrease the coating durability in the aggressive PEMFC conditions. Wang et al. [19] evaluated TiN, CrN and TiAlN electron beam physical vapor deposition coatings on 316L and found that all the TiN-, CrN- and TiAlN-coated 316L showed a lower ICR than the uncoated ones, however only the CrN coated 316 could be potentially be used as a bipolar plate in terms of the corrosion resistance. Pozio et al. [20] indicated that the properties of chromium nitride (CrN)-coated SS304, fabricated by PVD technology, were superior to those of CrN-coated SS316. Larijani et al. [21] deposited zirconium nitride (ZrN) films on AISI 304 substrates through ion beam sputtering technique and concluded that films with higher (111) texture coefficient present better corrosion protection against destructive agents. Brady et al. [22] obtained a CrN surface layer in Ni−50Cr alloy by gas nitridation at 1100 °C and showed excellent performances in corrosion resistance, ICR and durability. Nam et al. [23] nitrided the electroplated Cr on the surface of AISI 316L and obtained a more preferable Cr_2N film than $CrN + Cr_2N$ blended coating through controlling the nitriding conditions. Nitrogen plasma immersion ion implantation (PIII) has been conducted on the surface of pure titanium sheets by Feng et al. [24] and titanium oxy-nitride layers were formed in the Ti specimens. In our previous work, Nb nitride diffusion coating on AISI 304 was fabricated by plasma surface diffusion alloying method [25]. The various schemes using protective coating are adopting transition metal nitrides to enhance the corrosion resistance and reduce the interfacial contact resistance of stainless steel bipolar plate and the results seem promising.

Molybdenum is a very important alloying element to improve the corrosion resistance of stainless steel. Especially when molybdenum exists as nitrides its corrosion resistance is even better. Molybdenum nitrides were initially investigated as diffusion barrier for superconductor and microelectronics application [26] as well as catalyst for hydrotreating reaction [27]. Besides, the mechanical and physical−chemical properties of molybdenum nitrides, such as wear resistance, crack resistance, microhardness and corrosion resistance [28,29] have also been widely researched for mechanical structure applications. In the present research, molybdenum nitride was prepared by plasma surface diffusion alloying method on the surface of AISI 304 stainless steel (304 SS) and expected to improve corrosion resistance and decrease interfacial contact resistance of the 304 SS bipolar plates for PEMFC use. The corrosion resistance and ICR of the molybdenum nitride modified 304 SS (hereinafter referred as Mo−N 304 SS) were tested and evaluated in simulated PEMFC environments.

2. Experimental

2.1. Specimen preparation

Commercial 304 SS sheets with thickness of 1.5 mm were cut into specimens of 10 × 10 mm and ground with SiC papers from #360 up to #1500 grit and polished mechanically with diamond paste and then degreased with acetone in an ultra-sonic cleaner and lastly dried at room temperature.

The molybdenum nitride diffusion coating was formed on the surface of 304 SS in the following consecutive two steps in a double glow plasma alloying furnace, which has three electrodes: an anode, a negative cathode (specimens) and a sputtering source cathode (Mo sinter plate). In step 1: the specimens were firstly heated and sputtering cleaned at 1153 K by work power supply and pure argon ion bombard-ment in the chamber at the pressure of 35−40 Pa and −1 kV voltage. By keeping specimens at 1153 K, then, the source electrode (Mo sinter plate) power supply was loaded and kept at −800 to −900 V, meanwhile the voltage of specimens was decreased to −530 to −580 V, which can allow more metal sputtering elements to move from the source electrode into the surface of specimens. Specimens were treated at 1153 K for 1 h as a molybdenum diffusion process at high tempera-ture. In the meantime, a high molybdenum diffusion alloying layer was formed. And in the consequent step 2, proportional Ar and nitrogen (N_2) mixed gases (Ar:N_2 = 10:1−8:1) were introduced to produce a molybdenum nitride diffusion layer at 1153 K for another 2 h and all the other parameters were kept the same with Step1's. After plasma surface molyb-denum nitride diffusion alloying processing, scanning elec-tron microscopy (SEM) in combination with energy-dispersive X-ray analysis spectrometer (EDS) as well as X-ray diffraction (XRD) were used to observe and analyze the surface modified layer of specimens. In addition, the surface contact angle with water was also measured by a contact angle system SL200B.