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Polylaminate TaN/Ta coating modified ferritic stainless steel bipolar plate for high temperature proton exchange membrane fuel cell

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HIGHLIGHTS

- Electrochemical behaviour of 430 SS is firstly investigated in HT-PEMFC environment.
- A polylaminate coating with intersecting Ta and TaN had been prepared on 430 SS.
- Corrosion resistance in HT-PEMFC conditions and the ICR are evaluated.
- PL-TaN/Ta-430 shows greatly improved surface conductivity and corrosion resistance.

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ABSTRACT

A polylaminate coating with intersecting tantalum and tantalum nitride (TaN/Ta/TaN/Ta/TaN/Ta, TaN is the outermost layer) is deposited on surface of 430 stainless steel bipolar plate for high temperature proton exchange membrane fuel cell by a reactive magnetron sputtering method. Electrochemical tests including potentiodynamic, potentiostatic polarisation and electrochemical impedance spectroscopy, are carried out to evaluate the corrosion resistance and stability of the polylaminate TaN/Ta coating in simulating high temperature proton exchange membrane fuel cell environments (85% H_3PO_4 solution at 80 °C and 130 °C). Results show that the polylaminate TaN/Ta coating greatly improve the corrosion resistance of 430 stainless steel, which can provide almost 100% protection of the substrate in both high temperature proton exchange membrane fuel cell anode and cathode environment. Besides, the interfacial contact resistance of coated 430 stainless steel (9.03 mΩ cm^2) is much lower than that of bare substrate (106.74 mΩ cm^2). Furthermore, different from the highly increased interfacial contact resistance of bare specimen, the coated 430 stainless steel shows a minor increase resistance after potentiostatic tests in 85% H_3PO_4 solution at 130 °C.

1. Introduction

High temperature proton exchange membrane fuel cell (HT-PEMFC) (above 100 °C) based on phosphoric acid doped polybenzimidazole (PBI) membrane has drawn extensive attention due to its excessive advantages over the low temperature PEMFC (LT-PEMFC, typically below 80 °C). Operating beyond 100 °C can enhance the electrochemical kinetics of electrode reactions, simplify water and heat management, increase the tolerance to carbon monoxide (CO) and sulphur, which is able to simplify the fuel cell system and adopt reformed hydrogen with lower quality. The tolerance of CO contained in reformed hydrogen is ascended from 10 ppm to 1000 ppm when the operation temperature increases from 80 °C to 130 °C [1]. Besides, when PEMFC stacks operate at temperature above 100 °C, it is possible to use the non-precious metal material as catalyst, such as Co, Ni and their oxides etc, to further reduce the cost of HT-PEMFC.

Like LT-PEMFC, the major components of HT-PEMFC stacks are proton exchange membrane, catalyst, gas diffusion layers and bipolar plates etc. Bipolar plates not only serve as backbone of the stacks, but also play a critical role in connecting individual cells, providing flow channels for reactant gases, collecting and conducting current as well as facilitating thermal management. Besides, bipolar plates account for the majority of total weight and 29–45% cost of fuel cell stack [2,3]. Therefore, high corrosion resistance, good mechanical strength, low

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electrical resistance and cost-effective materials are crucial for fuel cell stack.

Unlike LT-PEMFC, the proton exchange membrane for HT-PEMFC is PBI doped with 85% H_3PO_4 and the operating temperature is usually higher than 120 °C [4]. Therefore, the operating environment of HT-PEMFC is more harsh and corrosive than that of LT-PEMFC. Obviously, traditional machined graphite used in LP-PEMFC is unsuitable for the HT-PEMFC and rare alternatives have been discussed in details. By far only carbon composite materials were proposed as bipolar plate for HT-PEMFC [5–11].

Coated stainless steels have received considerable attention as bipolar plate materials for LT-PEMFC, due to their comprehensive properties especially high strength and easy machining [12–14]. Among various protective coatings, refractory metal tantalum has been proposed to protect the austenitic stainless steel bipolar plate owing to its excellent corrosion resistance [15], which is not attacked by common acids, such as HCl, H_2SO_4, HNO_3 and their mixtures, even aqua regia. However, the high corrosion resistance of Ta coating will sacrifice surface conductivity since the formation of Ta_2O_5 passive film in fuel cell operating environment, which severely affects the power output of fuel cell stack. Tantalum nitride (TaN), as a refractory ceramic, possesses high chemical stability and metallic-like electrical conductivity [16]. Recently, tantalum nitrides coating was deposited on austenitic stainless steel bipolar plate for LT-PEMFC [17,18]. Nevertheless, it is necessary to verify whether the tantalum nitride is able to protect stainless steel in highly corrosive HT-PEMFC environment. Besides, the protecting characteristics of a coating, especially the corrosion resistance, rely on not only the nature of composition but also the structure of coating (i.e. whether the coating is compact and defects-free). With a dense and stable protective coating, the metal materials having relatively lower-cost and worse corrosion resistance, such as ferritic stainless steel even plain steel, may be utilized to produce bipolar plates for further reducing the cost of HT-PEMFC. In this paper, a relatively low cost ferritic stainless steel 430 SS has been applied as bipolar plate for HT-PEMFC.

Physical vapor deposition technique (PVD) including magnetron sputtering is usually used to prepare Ta and TaN coating. Typically, protective coatings prepared by PVD inevitably have inherent defects, such as micro-pore and pinhole, which may serve as the direct paths for the corrosive electrolyte to reach the coating/substrate interface, where the localized galvanic corrosion will be initiated due to the difference of corrosion potential between the coating and substrate [19]. In that case, the substrate surface may be corroded severely, even the protective coating may be peeled off during the operation of fuel cell stack. Adopting polylaminate to substitute single coating can effectively reduce the inherent defects [18] because the most defects appeared on single coating may be covered by another adjacent single coating. Report has pointed out that the increase in layers of polylaminate coating can statistically reduce the possibility of through-coating defects [20]. Besides, a polylaminate coating is able to discontinue crystallite boundaries in the columnar structure, which decrease the opportunity of pore formation. And the alternating interlayers of different compositions can redirect the current flow between coating and substrate [20]. Therefore, through-coating defects could be avoided entirely by a proper choice of layers consisting the polylaminate coating. Ho et al. [21] investigated the performance of a double-layer CrN/Ti coated 304 stainless steel in simulated LT-PEMFC environments (10 vol% H_2SO_4). Potentiodynamic polarisation showed that the CrN/Ti coating exhibited better corrosion resistance than that of the CrN single layer. However, due to the inherent pinholes on the coating, the double-layer coating could not provide sufficient protection of the stainless steel substrate in a long term operating LT-PEMFC environment [21]. A sandwich-like Cr/CrN/Cr tri-layer was used as protective coating on 316 L bipolar plate for LT-PEMFC [22]. Although the Cr/CrN/Cr coated 316 L showed improved corrosion resistance, its protective performance was still far from the requirement for bipolar plate. Then Hou et al. [23] prepared CrN/Cr polylaminate coating with twelve intersecting CrN and Cr layers on 316 L stainless steel. The unique coating architecture showed superb corrosion resistance and stability in simulated LT-PEMFC environment. Obviously, the double-layer and tri-layer protective coating prepared by PVD method could not provide sufficient protection for the stainless steel substrate. Liu et al. studied the corrosion resistance of a four-layered TiN polylaminate coating coated mild steel in 0.5 M NaCl solution at room temperature [20]. Result showed that the four-layered TiN coating reduce the corrosion rate of mild steel dramatically, however, there was heavy rust piling up and spreading from the localized corrosion in the immersion test. Hence, four-layered polylaminate coating may not resist the long-term corrosion in PEMFC, especially for HT-PEMFC.

Taking into consideration of more severe corrosive conditions of HT-PEMFC and previous research progress, a polylaminate coating with six intersecting Ta and TaN (TaN/Ta/TaN/Ta/TaN/Ta, TaN was the outermost layer) layers prepared by magnetron sputtering was proposed as the protective coating of 430 SS. The relatively "soft" Ta layer was designed as an interlayer to enhance the conductivity and bonding strength, while the "metallic ceramics" TaN was designed as an outmost layer to improve the interfacial conductivity and corrosion resistance. It is anticipated that the polylaminate TaN/Ta coating is able to undergo a higher temperature and more corrosive environment in HT-PEMFC. The electrochemical behaviour including corrosion resistance and stability as well as surface conductivity of the polylaminate TaN/Ta coating deposited 430 SS (denoted as PL-TaN/Ta-430) were tested and evaluated in simulating HT-PEMFC environment.

2. Experimental

2.1. Preparation of polylaminate TaN/Ta coating

In this work, a ferritic stainless steel (430 SS) was chosen as metal bipolar plates for HT-PEMFC. The stainless steel sheets with thickness of 1.5 mm were cut into specimens of 10 mm × 10 mm (area is 1 cm^2). Bare specimens were ground respectively with series of #360 ~ #1500 grit silicon carbide abrasive papers, polished mechanically with 0.25 μm alumina pastes, rinsed with acetone in an ultrasonic cleaner and lastly dried at room temperature.

The polylaminate coating of intersecting tantalum and tantalum nitride were prepared on 430 SS by a method of direct current reactive magnetron sputtering. The cylindrical Ta target (purity 99.99%) with 60 mm diameter was used and the distance between Ta target and 430 SS substrate was kept constantly at 13 cm for all conditions. Before sputtering, the deposition chamber was vacuumed down to 10^{-4} Pa. During deposition, high purity Ar or Ar/N_2 mixture gases was chosen to maintain the total pressure and gas flow rate at 1 Pa and 50 sccm, respectively. The polylaminate coating with a total thickness of 3 μm was designed as TaN/Ta/TaN/Ta/TaN/Ta/430 SS, where the innermost layer was Ta while the outermost layer was TaN. The thickness of single Ta or TaN layer was about 500 nm. The deposition atmosphere of Ta was in Ar while the TaN was in Ar/N_2 mixture.

The crystalline structure of the PL-TaN/Ta-430 was verified by X-ray diffraction (XRD, D8 Advance). The surface and cross-sectional morphology as well as the thickness of the polylaminate TaN/Ta coating were analysed by a scanning electron microscope (SEM, JEOL JSM-7001 F).

2.2. Electrochemical tests

Since the usage of H_3PO_4/PBI membrane in the operation of HT-PEMFC, the bipolar plates should be set in H_3PO_4 environments. Therefore, in this paper, 85% H_3PO_4 solution at 80 °C and 130 °C, were purposely chosen to simulate the aggressive HT-PEMFC environments. Before electrochemical test, the specimen was weld to a copper wire and the backside edges of the specimen was covered with high