Performance of Nb_{0.8}Zr_{0.2} Layer-Modified AISI430 Stainless Steel as Bipolar Plates for Direct Formic Acid Fuel Cells

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Abstract

To improve the interfacial conductivity and corrosion resistance of AISI430 stainless steel (430SS) as bipolar plates for direct formic acid fuel cells (DFAFCs), a Nb_{0.8}Zr_{0.2} layer has been successfully synthesized via the pulsed laser deposition (PLD) technique on the surface of 430SS. This Nb_{0.8}Zr_{0.2} layer is smooth, uniform, and comparatively compact without any surface flaw and micropore. Investigation under the simulated anodic environment of DFAFCs (0.05 M H₂SO₄ + 2 ppm HF + 10 M HCOOH at 70 °C) shows that the corrosion resistance of 430SS is obviously ameliorated after the PLD modification. In addition, the interfacial contact resistance of Nb_{0.8}Zr_{0.2}-430SS (6.0 mΩ cm²) is much smaller than that of bare 430SS (151.3 mΩ cm²) at the clamping force of 140 N cm⁻². Besides, different from the highly increased interfacial contact resistance of bare 430SS, the Nb_{0.8}Zr_{0.2}-430SS shows a minor increase resistance after potentiostatic tests in simulated anodic environment of DFAFCs.

Keywords Corrosion resistance · Nb_{0.8}Zr_{0.2} layer · Direct formic acid fuel cell · Interfacial contact resistance · Bipolar plates

1 Introduction

At present, environmental degradation, fossil fuel scarcity, and increasing energy depletion have coerced investigators to seek much cleaner and better electrochemical energy systems [1, 2]. Proton exchange membrane fuel cells (PEMFCs), as a new generation of energy conversion device, can convert chemical energy into electric power via catalytically

electrochemical reactions [3]. Owing to relatively simple operating mechanisms, high efficiency, zero pollution emission, and mild operating temperature (less than 100 °C), these PEMFCs have the prospect of becoming a main power source for electric vehicles (EVs) [4, 5]. Nevertheless, hydrogen storage technology seriously restricts the commercial application of PEMFCs [6]. HCOOH is a low toxic and non-flammable liquid at ambient temperature and a relatively strong electrolyte, which can accelerate H⁺ transfer in the anode of PEMFCs [7, 8]. Moreover, direct formic acid fuel cells (DFAFCs) have a high theoretical open-circuit voltage (1.45 V), lower fuel crossover, and reasonable power densities at ambient temperature [9], so they have recently drawn many investigators' and countries' attentions [10] and are regarded as a close to commercial utilization technology [11].

Like PEMFCs, DFAFCs comprise an anode, a perfluoro-sulfonic acid membrane electrolyte, and a cathode [12]. Generally, the electrodes (anode and cathode) of DFAFCs consisted of three key components: bipolar plates, a diffusion media, and a catalyst layer [13, 14]. Among these components of DFAFCs, the bipolar plates, as backbone of the DFAFCs stacks, not only distribute air (oxidant) and HCOOH uniformly to the reaction surface, but also connect

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the individual cells within the stack in turn [15]. In addition, the bipolar plates, which occupy 29–45% of the total cost and 60–80% of the total weight in the fuel cell stacks, bring electric current away from each cell [16] and facilitate water and heat management [17]. Last but not least, bipolar plates are always immersed in the high acid solution containing the cations of F^- , SO_3^{2-} , SO_4^{2-} , HSO_4^- , HSO_3^- , CO_3^{2-} , and HCO_3^- , etc., in the PEMFCs [18, 19]. Nevertheless, except the inevitable harsh corrosion environment of PEMFCs, the anode plates, that are used in DFAFCs stacks, have to confront additional higher concentration of HCOOH [20, 21]. Consequently, the anode plates applied in DFAFCs should possess higher mechanical strength, better surface electrical conductivity in DFAFCs environment, stronger corrosion resistance, as well as lower cost [22, 23].

Different types of bipolar plate materials, such as non-porous graphite [24, 25], carbon–polymer composite [26, 27], and metal [15, 28], have been investigated to achieve the above-mentioned stringent target properties. At present, the technology of preparing graphite bipolar plates is basically mature and has intrinsic high electrical conductivity and remarkable corrosion resistance in the DFAFCs environments [29]. However, the brittleness of graphite leads to the increase in the volume and cost of bipolar plate. Hence, graphite is gradually replaced by metal and composite materials in DFAFCs [30]. The carbon–polymer composite bipolar plates overcome the problems such as poor mechanical and difficult processing of graphite bipolar plates, and poor corrosion resistance of metal bipolar plates [31]. However, the electrical conductivity and thermal conductivity of them are lower than those of pure graphite and metal bipolar plates, so it is still difficult to meet the requirements of DFAFCs [32]. Metallic bipolar plates, particularly stainless steels, have the characteristics of good mechanical properties [33], high electrical conductivity [34], high air tightness [35], low cost, and easy processing [36], as well as very thin form (<0.1 mm) [37]. Unfortunately, the bare stainless steels are prone to corrosion and passivation, and the precipitation of metal ions causes catalyst poisoning in the fuel cell membrane electrode assembly [38]. At the same time, the passivation layer produced on the surface of stainless steel bipolar plates increases the surface contact resistance and affects the working life of the DFAFCs stacks [39]. Hence, a staunch protective layer has to be prepared on the surface of bare stainless steels to lengthen their service life in DFAFCs stacks.

In the previous papers, many investigators have synthesized transition metals and their carbides or nitrides protecting coatings, such as W [40], Nb [37], Mo [41, 42], NbC [39], NbN [43], CrN [44, 45], TiN [46], and MoN [47], on the surface of stainless steels to improve their corrosion resistance in the PEMFCs or DMFCs working condition. Nevertheless, few people use two metal alloy protective

films to enhance the corrosion resistance and contact resistance of stainless steel bipolar plates in DFAFCs stacks. The corrosion resistance of Zr is superior to Nb in acidic environment [37]. While, the electrical conductivity of Nb is higher than that of Zr, that is to say, the contact resistance of Nb is lower than that of Zr under the same mechanical pressure [44]. Therefore, the alloy protective layer of these two elements can better adapt to the harsh acidic environment of DFAFCs and has a lower contact resistance. In this work, we have fabricated $Nb_{0.8}Zr_{0.2}$ layer on the surface of AISI 430SS to be bipolar plates of DFAFCs stacks via pulsed laser deposition technology. The characteristics of the thin $Nb_{0.8}Zr_{0.2}$ layer have been examined and evaluated under the simulated anodic environment of DFAFCs (0.05 M H_2SO_4 + 2 ppm HF + 10 M HCOOH at 70 °C).

2 Experimental

2.1 Preparation of $Nb_{0.8}Zr_{0.2}$ Layer

The commercial AISI 430SS sheet (thickness of 1.5 mm) was cut in 10 mm × 10 mm as the substrate via electric discharge machining. The composition of 430SS (wt.%) is 0.079 C, 16.42 Cr, Ni < 1, 0.272 Si, 0.331 Mn, 0.025 P, and Fe balanced. Each sample was ground with SiC paper of 320-grit to 2000-grit and polished, then cleaned in an ultrasound acetone bath and dried in room temperature. The Nb_4Zr target material was purchased from Kejing group, and PLD-450 pulsed laser deposition sputtering and COMPex-Pro201 pulsed laser excimer was used to form the $Nb_{0.8}Zr_{0.2}$ layer. The distance between the 430SS substrate and Nb_4Zr target material is adjusted for 5 cm. The temperature of the 430SS substrate is 973 K and the pressure of the vacuum chamber is 6.0×10^{-5} Pa. The operation mode of the laser for constant pressure is 27 kV with 450 MJ laser power and 5 Hz laser sputtering frequency.

2.2 Characterizations

The compositions of 430SS were obtained via an optical emission spectrometer. The crystalline structure of $Nb_{0.8}Zr_{0.2}$ layer was analyzed by X-ray diffraction (XRD). The surface and cross section of $Nb_{0.8}Zr_{0.2}$ layer were observed by a scanning electron microscope (SEM) combined with an energy-dispersive X-ray analysis spectrometer (EDS). The surface contact angles with water for bare 430SS and $Nb_{0.8}Zr_{0.2}$ -430SS were also determined via a contact angle system. Interfacial contact resistance (ICR) values of bare 430SS and $Nb_{0.8}Zr_{0.2}$ -430SS were measured with the methods depicted in our previous paper before and after potentiostatic polarization tests [48].

2.3 Electrochemical Measurements

The untreated side of the sample was connected with a copper wire by means of soldering. The soldered side and edges of the sample were covered with insulating epoxy and only one side was exposed for electrochemical tests. A solution (0.05 M H₂SO₄ + 2 ppm HF + 10 M HCOOH) at 70 °C was used as an electrolyte to simulate the aggressive anodic environment of DFAFCs. Before each test, the samples were cleansed with acetone and then immersed in the simulated solutions. The electrochemical tests were executed in an electrochemical workstation (CHI760E). A typical three-electrode system was applied for the electrochemical tests, with a saturated calomel electrode (SCE) as the reference electrode, a platinum sheet as the counter electrode and the samples acted as the working electrode. All samples were stabilized at the open-circuit voltages for 30 min before electrochemical tests. The potentiodynamic polarization curves were obtained at a scanning range from a specific voltage (a 0.2 V shift below the open-circuit voltage) to 1.2 V with a sweep speed of 1 mV s⁻¹. The potentiostatic polarization tests were carried out at 0.1 V (vs. SCE) potential in the simulated anodic environment of DFAFCs for 4 h. After 4 h potentiostatic tests, the surface morphologies of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS were observed via SEM. After permeated in the simulated solution for 0.5 h at open-circuit voltage, the electrochemical impedance spectroscopy (EIS) tests were executed between 0.01 Hz and 100 kHz. The amplitude of input sine-wave voltage was 10 mV.

3 Results and Discussion

3.1 Characterization of Nb_{0.8}Zr_{0.2} Layer

The X-ray diffraction patterns of the Nb_{0.8}Zr_{0.2}-430SS and bare 430SS are displayed in Fig. 1. It is an obvious crystal structure both Nb_{0.8}Zr_{0.2}-430SS and bare 430SS, indicating that the modified coating has been successfully fabricated on 430SS substrate via the pulsed laser deposition (PLD) technology. The diffraction peaks at 35.8°, 41.2°, 60.3°, 72.1°, 76.1°, 102.2°, 105.3°, and 120.1° can be ascribed to (111), (200), (220), (311), (222), (331), (420), and (422) crystal planes of Nb_{0.8}Zr_{0.2}-430SS, respectively [49].

The surface morphology plays a vital role in the corrosion process of materials. The surface morphology and cross-sectional images were obtained to comprehend the corrosion resistance of Nb_{0.8}Zr_{0.2}-430SS. As shown in Fig. 2a, the surface morphology of Nb_{0.8}Zr_{0.2}-430SS is smooth, homogeneous and comparatively compact without surface flaw and micropore. This exquisite surface morphology would contribute to improve the corrosion resistance of materials in the simulated anodic DFAFCs environment [47]. Scanning

Fig. 1 X-ray diffraction patterns for Nb_{0.8}Zr_{0.2}-430SS and bare 430SS

cross section morphology of Nb_{0.8}Zr_{0.2}-430SS is displayed in Fig. 2b. This modified coating with a thickness of about 100 nm is uniform and continuous in micro-morphology without micro-cracks and micro-holes. As shown in Fig. 2c, the composition of Nb_{0.8}Zr_{0.2}-layer is relatively uniform and consistent. Furthermore, the modified coating is bonded to the 430SS matrix with commendable tightness and continuity, which would enhance durability of 430SS as bipolar plates for DFAFCs [48].

Interfacial contact resistance between bipolar plate and diffusion layer (carbon paper) is one of the key limitations of power output DFAFCs stack. Therefore, the power output of DFAFCs can be substantially ameliorated by lowering the ICR. The ICR values of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS under different clamping forces are shown in Fig. 3. The ICR of two specimens drops rapidly in the beginning and then gradually becomes stable after the clamping forces more than 140 N cm⁻². The reason for this phenomenon is that more contact points between the bipolar plate and carbon paper can be generated with increasing clamping force, which ensures advantageous electrical current distribution [50, 51]. In addition, when the clamping force exceeds 120 N cm⁻², the effective contact points could not increase further and thus the ICR would not increase evidently [52]. In more details, the ICR of Nb_{0.8}Zr_{0.2}-430SS is much lower than that of bare 430SS at the same clamping force. Especially, the ICR of Nb_{0.8}Zr_{0.2}-430SS is 6.0 mΩ cm² at the clamping force of 140 N cm⁻², which is prominently smaller than that of bare 430SS (151.3 mΩ cm²). This surface modifying technology could extremely ameliorate the surface conductivity of 430SS to raise the power output efficiency of DFAFCs.

With the introduction of HCOOH, a large amount of water is transferred into DFAFCs. Additionally, carbon dioxide (CO₂) and water are generated from the complete

Fig. 2 **a** Surface morphology, **b** SEM image, **c** composition analysis of the cross section of Nb_{0.8}Zr_{0.2}-430SS

Fig. 3 ICRs of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS under different clamping forces

combustion of HCOOH during DFAFCs operation. Liquid water can effectively avoid the dehydration of the proton exchange membrane and obviously enhance membrane ionic conductivity. Nevertheless, excess liquid water spurs water flooding in gas diffusion layer and channel clogging and accelerates the corrosion of the metallic bipolar plates. Therefore, water management strategies are critical to

enhancing DFAFCs operation [53]. The preferable hydrophobicity of bipolar plates could contribute to water removal from the stack timely and help to simplify water management [53]. The contact angle is generally used to describe the hydrophobicity of materials. As shown in Fig. 4, the Nb_{0.8}Zr_{0.2}-430SS delivers super hydrophobicity (104.9°), much larger than bare 430SS (68.6°), revealing that the hydrophobicity can be considerably improved by this surface modifying technology. Hence, the Nb_{0.8}Zr_{0.2}-430SS can optimize the electrochemical reaction environment and enhance corrosion resistance of 430SS as bipolar plates for DFAFCs.

3.2 Potentiodynamic and Potentiostatic Polarization

Corrosion potential and corrosion current density are approximate indicators to assess the corrosion resistance of materials [54]. A higher corrosion potential and lower corrosion current density typically reflect a better corrosion resistance [55]. The potentiodynamic polarization curves of Nb_{0.8}Zr_{0.2}-430SS and bare 430SS are presented in Fig. 5(a). Both of these two potentiodynamic polarization curves manifest a passive behavior, and the anode

Fig. 4 Contact angles of **a** bare 430SS, **b** Nb_{0.8}Zr_{0.2}-430SS with water

Fig. 5 Potentiodynamic polarization curves **a** and current–time curves **b** for bare 430SS and Nb_{0.8}Zr_{0.2}-430SS measured in the simulated anodic DFAFCs environment

Table 1 Corrosion potential and current density of samples polarized in the simulated DFAFCs environment

Sample	$E_{\text{corr}}/\text{mV}$	$I_{0.1 \text{ V}}/\mu\text{A cm}^{-1}$
Bare 430 SS	– 441	227.51
Zr-430 SS	– 263	1.06

potential ($0.1 \text{ V}_{\text{SCE}}$) of DFAFCs operation also appears in the passivation zone. Evidently, Nb_{0.8}Zr_{0.2}-430SS possesses a higher corrosion potential and a lower corrosion current density compared with bare 430SS. After surface modification, the corrosion potential (E_{corr}) shifted from – 0.441 to – 0.263 V and the corrosion current density at the anode potential ($0.1 \text{ V}_{\text{SCE}}$) ($I_{0.1 \text{ V}}$) migrated from 227.51 to 1.06 $\mu\text{A cm}^{-1}$ (Table 1), illustrating that the corrosion resistance of 430SS as bipolar plates has been considerably ameliorated after coated with Nb_{0.8}Zr_{0.2} layer. Unlike bare 430SS, the potentiodynamic polarization curve of Nb_{0.8}Zr_{0.2}-430SS has a smaller peak of active–passive transition, indicating that the Nb_{0.8}Zr_{0.2}-430SS is more easily passivated under the simulated anodic environment of DFAFC.

For comprehensive acquaintance with the effect of this surface modification technology on the electrochemical behavior of bare 430SS, the stability of Nb_{0.8}Zr_{0.2}-430SS was determined by potentiostatic polarization in the simulated DFAFCs environment for 4 h (Fig. 5b). As mentioned above, the anode working potential ($0.1 \text{ V}_{\text{SCE}}$) for DFAFCs is just in the passivation zone, so a passive film can be generated on the surface of the samples under the simulated anodic DFAFCs condition. From the survey current–time curves, the current density drops quickly at first and then becomes gradually stable (Fig. 5b). That may be because the formation of passivation film affects the change of current density. When the passivation film covers the whole surface

of the sample, the current would tend to be stable [3]. It is obvious that the current density of Nb_{0.8}Zr_{0.2}-430SS is three orders of magnitude lower than that of bare 430SS, demonstrating that the corrosion resistance is greatly improved after surface modification. The surface morphologies of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS after the potentiostatic polarization tests in the simulated anodic environment of DFAFCs are displayed in Fig. 6. It is obvious to see that serious corrosion occurs on the surface of bare 430SS, and the original surface is corroded away leaving etching pits abounded (Fig. 6a). At the other extreme, the corroded surface of Nb_{0.8}Zr_{0.2}-430SS was relatively smooth without any obvious pitting (Fig. 6b), suggesting that the passive film formed on the Nb_{0.8}Zr_{0.2} layer is relatively dense and tough and provides excellent corrosion resistance in the simulated anodic environment of DFAFCs.

After potentiostatic polarization tests in the simulated anodic DFAFCs environment, ICRs for both bare 430SS and Nb_{0.8}Zr_{0.2}-430SS enhance as shown in Fig. 7. Unlike the substantial increases of ICRs for bare 430SS, the Nb_{0.8}Zr_{0.2}-430SS exhibits a slight change of the value. As described above, bare 430SS was corroded severely with a damaged surface during the potentiostatic tests, which causes a low conductivity owing to the greatly decrease in contact area with carbon paper. ICR (at the clamping force of 140 N cm^{-2}) of bare 430SS is up to $1250.5 \text{ m}\Omega \text{ cm}^2$ after tested in the simulated anodic DFAFCs environment. However, ICR of Nb_{0.8}Zr_{0.2}-430SS is only $13.2 \text{ m}\Omega \text{ cm}^2$ under the same test condition due to the stable and high electrical conductivity of Nb_{0.8}Zr_{0.2} layer.

3.3 Electrochemical Impedance Spectroscopy

EIS was explored to learn more detailed processes of corrosion kinetics. Figure 8 presents the Nyquist plots of bare 430SS and

Fig. 6 Surface morphologies of **a** bare 430SS **b** Nb_{0.8}Zr_{0.2}-430SS after potentiostatic polarization tests for 4 h in the simulated anodic DFAFCs environment

Fig. 7 ICRs of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS under different clamping forces after 4 h potentiostatic polarization tests in the simulated anodic DFAFCs environment

Nb_{0.8}Zr_{0.2}-430SS determined in the simulated anodic DFAFCs environment after 1 h stability at the open-circuit voltage. Within the test frequency range, the Nyquist plots of these two samples show two specific parabolas with different curvature. Based on EIS analysis, two different equivalent circuits were applied to fit the impedance spectra of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS, as displayed in Fig. 8b, c, respectively. In the fitted circuit, R_s represents the solution resistance between working and reference electrode; R_c represents the charge transfer resistance; C_f and R_f represent the capacitance and resistance of the passivation film [22, 56], respectively, and W represents the Warburg impedance. A constant phase element (CPE) was added into the fitting program due to non-ideal capacitive response of the interface between the solution and sample. The impedance of the CPE can be denoted as:

$$Z_{\text{CPE}} = (1/Q)(j\omega)^{-n}, \quad (1)$$

Fig. 8 **a** Nyquist plots measured by EIS in the simulated anodic DFAFCs environment; equivalent circuits of the corrosion system for **b** bare 430SS **c** Nb_{0.8}Zr_{0.2}-430SS

Table 2 Electrochemical parameters for anodic environment of DFAFCs obtained from simulated equivalent circuits

Sample	$R_s/\Omega \text{ cm}^2$	$C_p/\Omega^{-1} \text{ cm}^{-2} \text{ S}^{-1}$	$R_p/\Omega \text{ cm}^2$	$Q_{dl}/\Omega^{-1} \text{ cm}^{-2} \text{ S}^{-n}$	n_{dl}	$R_c/\Omega \text{ cm}^2$	$W/\Omega^{-1} \text{ S}^{-0.5} \text{ cm}^{-2}$
Bare 430SS	1.399	5.081×10^{-7}	10.867	4.531×10^{-4}	0.8757	4.069×10^2	8.273×10^{-3}
Nb _{0.8} Zr _{0.2} -430SS	2.807	9.858×10^{-8}	17.474	5.582×10^{-5}	0.8796	3.038×10^4	2.504×10^{-4}

where ω , Q , and n denote the angular frequency, the admittance magnitude of CPE, and the exponential term [56]. In addition, j^2 equals -1 . A pure capacitor is obtained for $n=1$, while a pure resistor impedance is obtained for $n=0$. In reality, n ranges from 0 to 1, and thus, Q could be approximated as a capacitor [22, 57]. It is clearly noted that these physical models offer accurate fits to the experimental data, especially with regard to the shape of the impedance spectra in the Nyquist plots. Therefore, it was concluded that the models provided a reliable representation of the corrosion system. Matching values for equivalent circuit elements are illustrated in Table 2. R_s of bare 430SS and Nb_{0.8}Zr_{0.2}-430SS are very close in value, illustrating a similar ion conductivity in the test solutions. The charge transfer resistance of Nb_{0.8}Zr_{0.2}-430SS ($30,380 \Omega \text{ cm}^2$) is two orders of magnitude higher than that of bare 430SS ($406.9 \Omega \text{ cm}^2$). The higher charge transfer resistance can represent a lower corrosion rate [4, 58].

4 Conclusion

Two metal alloy protective layer (Nb_{0.8}Zr_{0.2} layer) is successfully deposited on 430SS via a pulsed laser deposition (PLD) technique. The EDS spot scanning exhibits that the Nb_{0.8}Zr_{0.2} layer is composed with the Nb element and Zr element with an atomic ratio of 4:1. The SEM observation shows that the Nb_{0.8}Zr_{0.2} layer has a uniform coverage on the surface of 430SS substrate with good adhesion and defect-free morphology. The corrosion current density of 430SS is smaller in the simulated anodic environment of DFAFCs after PLD modification. The charge transfer resistance of Nb_{0.8}Zr_{0.2}-430SS is much larger than that of bare 430SS in the simulated anodic environment of DFAFCs. After 4 h potentiostatic polarization tests, ICRs of these two samples all increase, but the increasing amplitude of the ICR for Nb_{0.8}Zr_{0.2}-430SS is much smaller than that of bare 430SS.

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