Polyacrylonitrile Infused in a Modified Honeycomb Aluminum Alloy Bipolar Plate and Its Acid Corrosion Resistance

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ABSTRACT: Bipolar plates, accounting for a large proportion of proton exchange membrane fuel cells (PEMFCs), are highly susceptible to corrosion by $H^+$, $SO_4^{2-}$, and so on because of the strong acid-rich and oxygen/hydrogen-rich environments. In this work, the corrosion resistance of aluminum alloy bipolar plates modified in the cathodic environment of PEMFCs has been investigated. A honeycomb structure is constructed by anodizing on an aluminum alloy (AA5052) bipolar plate, and a polyacrylonitrile (PAN) film is prepared by infusing PAN solution on the surface. From scanning electron microscopy and atomic force microscopy, we observe that the porous structure of the aluminum alloy surface is more advantageous for enhancing the mechanical engagement between PAN and the aluminum alloy. Therefore, the PAN film is dense and smooth. Electrochemical tests confirm that the PAN film greatly improves the corrosion resistance of the aluminum alloy bipolar plate under the cathodic environment of the PEMFC. When graphene oxide (GO) is added, the charge-transfer resistance ($R_{ct}$) is not only improved but also the stability under oxygen-rich acidic conditions is prolonged.

1. INTRODUCTION

With the popularity of green and clean energy, fuel cells have a wide application prospect in the fields of transportation, military, and portable power supply because of their high energy-conversion efficiency without pollution.1–3 As a typical representative of fuel cells, a proton exchange membrane fuel cell (PEMFC) has the advantages of high power density, low operating temperature ($60–80 \degree C$),4,5 fast start, long life, and so on. Therefore, it is the most promising alternative in comparison to fossil fuels for the vehicle power source.6,7 Besides the membranes and catalysts,8 bipolar plates are another key element in the PEMFC stack, which not only occupy 70–80% of the battery weight and 35–45% of the total cost of the PEMFC stack but also survive in harsh acidic conditions.9,10 Therefore, it is necessary to reduce the weight, cost, and corrosion rate of the bipolar plate.

In general, bipolar plates are mainly classified into graphite bipolar plates and metal bipolar plates. The earliest bipolar plates are made of nonporous graphite plates,11 which have low thermal expansion coefficient, good thermal conductivity, stable chemical properties, and strong electrical conductivity. However, graphite could be limited to the brittleness and multiple pores formed during the process, which lead to the difficulty in PEMFCs. Based on these unfavorable factors of graphite, polymer-carbon composite bipolar plates with the characteristics of good corrosion resistance and electrical conductivity are selected in the PEMFC.12 Husby et al.13 studied the application of carbon-polymer composite coating on stainless steel (SS) bipolar plates by spraying technology. However, high cost is still a problem we need to consider. At present, metal bipolar plates are mostly used instead of graphite bipolar plates.14 Extensive research studies have been conducted on the treated surfaces of different metal materials including pure metals and alloys. Compared to the use of graphite, metallic bipolar plates in the PEMFC may reduce fuel loss by about 22%.15–17 At present, the materials for studying different types of metal bipolar plates as a substitute for graphite bipolar plates are mainly concentrated in SS,18 nickel-based bipolar plates,19 titanium-based bipolar plates,20 and so forth. Yi et al.21 formed the graphitization of nanothin TiCx/a-C films in SS bipolar plates by magnetron sputtering with good corrosion resistance. Because a passivation oxide film is easily formed on the surfaces of SS and titanium, the film may increase the interfacial contact resistance between the metal plate and the

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gas diffusion layer. In addition, the long-term operation of such a metal plate under such acidic conditions may cause some heavy-metal ions to dissolve, which could cause some catalyst poisoning and failure that affect the fuel cell working efficiency.

Along with these disadvantages, an aluminum alloy also has a unique advantage as bipolar plates. An aluminum bipolar plate reduces 65% weight compared to a SS bipolar plate. Among them, as one of the most promising and widely used alloys, AA5052 has unique advantages, such as lightweight, good moldability, weldability, high strength, good conductivity, and processing performance.\textsuperscript{22-25} Hence, the aluminum alloy is considered as the ideal bipolar plate material. However, considering the working environment of the fuel cell bipolar plate, the aluminum alloy must be modified to enhance its corrosion resistance in the PEMFC environment. At present, common methods for surface modification of aluminum alloys include electrodeposition,\textsuperscript{24} anodization,\textsuperscript{25} chemical/physical vapor deposition,\textsuperscript{26-28} spray coating,\textsuperscript{29} and so forth. The appropriate film coating on the surface modification of aluminum alloy bipolar plates is regarded as the most common and effective method which can provide not only good corrosion resistance but also high electrical conductivity. González-Gutiérrez et al.\textsuperscript{16} investigated the electrochemical characteristics of the fuel cell simulation environment by zinching the aluminum bipolar plate and then depositing the Ni–P coating. The results show that the Ni–P coating is more suitable for the anodic side. Besides, it is also important that the thermal expansion coefficient should be similar to that of the metal matrix. In addition, Au, Pt, and other noble metal coatings can improve the corrosion resistance of the bipolar plate and reduce the interfacial contact resistance, except for their high cost. Therefore, it is difficult to meet the commercial requirements.

At present, there are many reports on the anodizing of aluminum alloy surfaces. Common electrolytes for preparing porous anodized aluminum include oxalic acid, sulfuric acid, and so on.\textsuperscript{30} Most anodized aluminum is used in simulated seawater. Zhang et al.\textsuperscript{31} constructed a superhydrophobic film on the surface of AA5083 by anodization, which indicated that the inhibition efficiency in simulated seawater was as high as 99.99%. In this study, we simulate the cathodic environment of proton exchange fuel cells. Honeycomb micro–nanostructures were successfully constructed by anodization on the surface of AA5052. Different concentrations of polyacrylonitrile (PAN) solution were applied to penetrate the porous aluminum alloy surface to enhance the better bonding of the PAN solution to the aluminum alloy. We chose to perform electrochemical tests in the cathode environment of a proton exchange fuel cell. The results show that the aluminum alloy coated with the PAN film can greatly improve the corrosion resistance under the condition of strong acid oxygen enrichment, and the corrosion resistance rate is as high as 90% or more. However, in order to enhance the stability, different concentrations of graphene oxide (GO) are added to the PAN solution. The experimental results show that under the severe conditions, the ac impedance value is greatly improved. After immersion in an oxygen-rich solution for 1 and 5 days, the corrosion resistance rate is still over 90%.

2. RESULT AND DISCUSSION

2.1. Surface Morphology Analysis of Coating. As is well-known, aluminum is anodized to form a porous micro–nanostructure on its surface. From the SEM images in Figure 1, the surface topography of the aluminum alloy after different treatments is examined, in which Figure 1a,c,e shows the low multiple images of the treated/untreated aluminum alloy, and Figure 1b,d,f shows the high multiple images correspondingly. Figure 1a,b displays the SEM images of the blank AA5052 under different multiples, from which the entire aluminum alloy surface is evenly scratched by the sanding of the aluminum alloy. The surface topographies of different magnifications of two processes of aluminum alloys undergoing anodization are shown in Figure 1c–f. Among them, Figure 1c,d shows the surfaces after electrochemical polishing. It could be seen that the entire surface is much smoother than the blank aluminum alloy without scratches. However, after oxidation of the phosphoric acid solution, the surface becomes rough, forming a honeycomb-like structure with each cavity of about 100 nm. After oxidation of the phosphoric acid solution at 30 V, the surface of the aluminum alloy became rough. At high-magnification observation, it is seen from Figure 1f that the surface forms a honeycomb-like micro–nanostructure. At the same time, compared to the second step, it is apparent from the illustration of Figure 1d that the polished aluminum alloy surface is like a mirror, which can clearly reflect characters. Figure 1g shows the SEM images of the sample coated with the PAN film layer. According to Figure 1, it can be seen that the PAN film is evenly laid in the gap of the
aluminum alloy bipolar plate. The honeycomb shape from the cross-sectional view is covered by the PAN solution as shown in Figure 1h, and the thickness of the oxide layer is about 80 μm, and the thickness of the PAN coating is about 100 μm.

In fact, throughout the anodizing process (including electrochemical polishing and oxidation), the dissolution of aluminum alloy is accompanied by the formation of a new barrier layer. Eventually, the metal surface reaches an equilibrium between dissolution and film forming. In the phosphoric acid solution, the dissolution of the barrier layer forms a cavity similar to a honeycomb. It is concluded that the electric field strength between the anode and cathode causes the ion migration rate to accelerate the chemical reaction at a higher reaction rate level during the entire process, thereby forming an aperture like a honeycomb. The principle is as follows:

$$\begin{align}\text{Al}_2\text{O}_3 + n\text{H}_2\text{O} & = 2\text{Al}^\text{3+} + (3 + n - x)\text{O}_2^- + x\text{OH}^- \\
& + (2n - x)\text{H}^+ \end{align} \quad (1)$$

The growth reaction of the oxide layer at the metal/oxide interface is as follows:

$$2\text{Al} + 3\text{O}_2^- = 2\text{Al}_2\text{O}_3 + 6\text{e}^- \quad (2)$$

2.2. AFM Analysis. AFM images (scan range 20 μm × 20 μm) of bare AA5052, electrochemically polished AA5052, and anodized AA5052 are shown in Figure 2. On the left and right sides of Figure 2, there are two-dimensional (2D) surface images of the substrate and three-dimensional (3D) structure images. As can be seen from Figure 2a,b, the surface of AA5052 has some scratches due to sanding. Figure 2c,d shows the AFM pattern of electrochemical polishing, and it is apparent that the surface is relatively smooth, which corresponds to the SEM image. Figure 2e,f shows the AFM characterization of the anodized aluminum alloy with a regular surface. In addition, the surface roughness (Ra), the maximum height of the surface (St), and the height change (Hc) from A to B in the 3D diagram have been analyzed. Compared with AA5052, the roughness of the electrochemically polished aluminum alloy is reduced by 66.4%, and the roughness of the anodized aluminum alloy is reduced by 63.5%. At the same time, it is seen from Table 1 that the St and Hc data of the maximum height of the treated aluminum alloy surface are reduced. It can be seen from the 3D Hc data that the difference
of the surface of the treated aluminum alloy is small, which means that the surface is uniform.

Most importantly, in combination with SEM, when the PAN solution is dropped on the anodized aluminum alloy bipolar plate, these honeycomb-like uneven structures promote the PAN solution to fall into these ‘honeycombs’. Therefore, it increases the effective adhesion area between the coating and the aluminum substrate and also enhances the mechanical meshing between the two; PAN is better attached to the aluminum substrate.

2.3. Surface Component Analysis. Figure 3 shows the Raman spectra of the PAN-GO film, from which the characteristic peaks of the D band and G band (representing the in-plane vibration of the sp² carbon atom) (representing defect) are located at ~1333.2 and ~1599 cm⁻¹, respectively. As shown in the Raman spectra of the PAN-GO films, the intensity ratio of \( I_D/I_G \) is about 1.18, which represents a higher degree of GO defects in the coating than the in-plane vibration of the sp² carbon atom) (representing defect) are located at ~1333.2 and ~1599 cm⁻¹, respectively. As shown in the Raman spectra of the PAN-GO films, the intensity ratio of \( I_D/I_G \) is about 1.18, which represents a higher degree of GO defects in the coating than the blank aluminum alloy.

2.4. Electrochemical Characterization of the Coating.

Generally, as one of the basic parameters for studying metal corrosion, the open-circuit voltage is of great significance for studying metal corrosion behavior and analyzing corrosion processes. It is the fact that low open-circuit potential means a higher tendency to corrode. The potentiodynamic polarization behaviors of the bare AA5052 alloy and the PAN-coated AA5052 alloy samples are investigated. Typically, the lower corrosion current density \( (i_{corr}) \) and the higher corrosion potential \( (E_{corr}) \) in the potential polarization curve represent better corrosion resistance.

Figure 4a,b shows the open-circuit voltage and the potentiodynamic polarization tested on the surface of the aluminum alloy coated with different concentrations of PAN solution under an oxygen-rich condition of 0.5 M H₂SO₄ + 2 ppm HF, respectively. The simulated solution is aerated for 30 min, in order to ensure that the oxygen in the solution reaches saturation. In order to stabilize the entire coating in the simulated solution, different samples are immersed in the saturated oxygen solution for 20 min. Then, the open-circuit voltage is tested within 400 s. The specific experimental results are shown in Figure 4. It can be seen from Figure 4a and the inset picture that the open-circuit voltage of the aluminum alloy coated with the PAN coating is relatively positively shifted than the open-circuit voltage of the blank.

The open-circuit voltage of the coated aluminum alloy is more stable than that of the blank aluminum alloy, indicating that the coated aluminum alloy is more stable in the oxygen-rich acidic solution and has more excellent corrosion resistance than the blank aluminum alloy. At the same time, at the range of different concentrations of the coating, the value of the open-circuit voltage increases (0.1-PAN—0.5-PAN) at first and then decreases (0.5-PAN—1-PAN), as shown in Figure 4a. When the sample was labeled as 0.5-PAN, the corrosion tendency gets lower, which is due to the passivation effect of the aluminum alloy surface in the cathode environment.

Table 2 shows the potentiodynamic polarization curves of bare and PAN-coated AA5052 alloys in the simulated PEMFC cathode environment. The values of \( E_{corr} \) (vs SCE) and \( i_{corr} \) are obtained by the Tafel linear extrapolation method. The electrochemical parameters of potentiodynamic polarization curves are summarized in Table 2. It can be seen from Figure 4 and Table 2 that the PAN-treated surface has a higher corrosion potential and lower corrosion current density compared to bare AA5052. At the range of different concentrations of the coating, the corrosion potential of the

Table 1. AFM Parameter of Bare AA5052, Electrochemically Polished Surface, and Anodized Surface

| sample                  | Ra/µm        | St/µm        | Hc/µm        |
|-------------------------|--------------|--------------|--------------|
| AA5052                  | 1.46 × 10⁻¹  | 9.08 × 10⁻¹  | 8.41 × 10⁻²  |
| electrochemically polished AA5052 | 4.9 × 10⁻²  | 7.22 × 10⁻²  | 3.54 × 10⁻²  |
| anodized AA5052         | 5.32 × 10⁻²  | 3.59 × 10⁻²  | 1.19 × 10⁻²  |

Table 2. Electrochemical Parameters of the Polarization Curve of the Bare Aluminum Alloy and PAN Film-Modified Aluminum Alloy in the Cathode Environment of the PEMFC

| sample                  | \( E_{corr} \) (mV vs SCE) | \( i_{corr} \) (A·cm⁻²) | \( \eta \) % |
|-------------------------|----------------------------|--------------------------|--------------|
| bare AA5052             | -692                       | 1.341 × 10⁻⁴             |              |
| 0.1 PAN                 | -634                       | 3.526 × 10⁻⁶             | 97.3         |
| 0.25 PAN                | -647                       | 2.367 × 10⁻⁶             | 98.2         |
| 0.5 PAN                 | -678                       | 4.868 × 10⁻⁵             | 99.9         |
| 0.75 PAN                | -562                       | 9.753 × 10⁻⁷             | 99.2         |
| 1 PAN                   | -409                       | 6.393 × 10⁻⁷             | 99.5         |

Figure 4. (a) Open-circuit voltage and (b) potentiodynamic polarization curves for different concentrations of PAN-coated AA5052 alloy samples in the cathode environment of the PEMFC.
0.5-PAN-coated AA5052 alloy has the most positive corrosion voltage and the smallest current density. These results suggest that the 0.5-PAN-coated AA5052 alloy can show a better corrosion resistance.

However, compared to pristine bare AA5052, the corrosion potential is shifted to positive, and current density of the PAN-coated AA5052 alloy is reduced by 2−4 orders of magnitude. In generally, combined with higher corrosion voltage (\(E_{\text{corr}}\)) and lower corrosion current density (\(i_{\text{corr}}\)), the sample has better corrosion resistance.35 These results suggest that the PAN-coated AA5052 alloy can show a better corrosion resistance. The corrosion inhibition efficiency (\(\eta\)) is calculated as follows:23,36

\[
\eta\% = \left(\frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0}\right) \times 100
\]

where \(i_{\text{corr}}^0\) and \(i_{\text{corr}}\) are the corrosion current densities without and with the film, respectively. The high \(\eta\) (99.9%) of the 0.5-PAN-coated AA5052 alloy surface indicates that it can significantly inhibit the corrosion progress.

At the same time, the ac impedance test was performed. Electrochemical impedance spectroscopy (EIS) provides a powerful method to interpret the dynamical process of corrosion in the cathode environment of the proton exchange fuel cell.36−38 Furthermore, the EIS experiments of PAN with different concentrations after immersion in oxygen-rich acidic solution for 20 min were done at the steady-state corrosion potential, and the results are shown in Figure 5, which presents the Nyquist and Bode plots of the bare AA5052 alloys and different concentrations of samples. They were conducted in a solution of 0.5 M H\(_2\)SO\(_4\) + 2 ppm HF by bubbling oxygen at room temperature. As shown in the illustration of Figure 5b, the Nyquist impedance of the bare aluminum alloy consists of three parts: (1) capacitance caused by charge-transfer resistance in the high-frequency region, (2) the film capacitor loop caused by the corrosion product (MgAl\(_2\)(SO\(_4\))\(_4\)·2H\(_2\)O), and (3) the inductive loop caused by the metastable Mg\(^+\) and Al\(^+\) in the low-frequency region including electric double-layer capacitance. The Nyquist plots of the coated aluminum alloy are shown in Figure 5a,b. Figure 5c,d shows the Bode plots of the bare aluminum alloy and PAN film-modified aluminum alloy, respectively. Obviously, the total impedance modulus of the bare sample from high frequency to low frequency is smaller than that of any one of the PAN coatings in Figure 5c. In the high-frequency region, the total impedance of the 0.5-PAN film-modified aluminum alloy apparently is larger than that of other concentration film-modified aluminum alloys, while in the low-frequency region, the total impedance of them are similar. According to Figure 5d, the bare aluminum alloy has two time constants, and the aluminum alloy with the PAN coating is composed of three time constants. The appearance of an extra time constant may be due to the PAN film.

The equivalent circuits are used to calculate the fitting parameters of the circuit elements, which are of great significance for further investigating the corrosion process of the coating.39 The circuits of bare AA5052 and the samples with different concentrations are shown in Figure 6. Equivalent circuits of bare AA5052 are shown in Figure 6a. In the equivalent circuit, the anodized layer is due to the formation of an oxide layer on the surface of the aluminum alloy under oxygen-rich conditions. Furthermore, \(R_s\) represents solution resistance, and \(C_1\) and \(R_2\) represent film (corrosion products and oxidation film) capacitance and resistance within the...
systems by using the impedance modulus. The protection is typically used to characterize coating/metal after immersion for 1 and 5 days, respectively. Figure 8a,b and the other relevant electrochemical parameters of each circuit element are shown in Table 3. Compared to the different circuits of the bare aluminum alloy, the substrate with different concentrations of coatings becomes complicated, as shown in Figure 6b and Table 3. It can be seen from Table 3 that the transfer resistance ($R_2$) of the coated sample is significantly higher than that of the blank aluminum alloy, and when the sample is 0.5-PAN, the transfer resistance gets maximized. With increased concentrations of PAN, the observed significantly reduced magnitude of CPE ($Y_0$) slightly increased, as shown in Table 3, which reveals the displacement and migration of molecules and ions in aqueous solution. It increases 2−4 orders of magnitude compared to other coatings. However, because of the presence of corrosive ions such as $\mathrm{F}^−$, $\mathrm{H}^+$, and so forth in the solution, it is easy to break the PAN film and eventually reach and corrode the substrate for a long time.

Because it is difficult for the entire coating to maintain good stability in acidic solution, in order to improve the stability of the coating, GO is added to the optimum PAN solution. The Nyquist and Bode plots of the substrate containing different concentrations of GO are shown in Figure 7. The corrosion protection is typically used to characterize coating/metal systems by using the impedance modulus $|Z_{\text{BDBE}}|$. After the addition of GO, the impedance modulus increases significantly, and the capacitive reactance loop in the low-frequency region is significantly increased. It is worth noting that after the addition of GO, the low-frequency region with the low capacitive reactance arc originally caused by the inductive reactance is controlled by Weber impedance. It is seen from Figure 7b that the impedance modulus increases significantly after the addition of GO. At the same time after adding GO, the time constant is unchanged, but the phase angle in the low-frequency region is improved in Figure 7c. Therefore, the addition of GO increases the membrane resistance, which may be due to the defect of GO prolonging the path of corrosive ions reaching the substrate.

In addition, we conducted the stability test on this basis. The sample after the addition of GO was immersed in an oxygen-rich acidic condition, and electrochemical tests were performed after immersion for 1 and 5 days, respectively. Figure 8a,b represents the potentiodynamic polarization curves of 1 and 5 days of immersion. Because the PAN film fell from the aluminum alloy after immersion for 2 days, there was no related potentiodynamic polarization curve of the PAN film after 5 days of immersion. The other relevant electrochemical parameters are shown in Table 4. When the mass of GO is 4
mg, the stability shows the best after 5 days of immersion from the potentiodynamic polarization curve and related electrochemical parameters. The corrosion current density is reduced by 2 orders of magnitude compared with that of the blank aluminum alloy. The corrosion inhibition efficiency reaches over 90%.

Potentiostatic curves are obtained at a potential of 0.6 V/SCE in the cathodic environment (under O2 bubbling). The results are presented in Figure 9. After testing for 5400 s in acidic solution (enriched oxygen), the current density is $7.67 \times 10^{-7} \text{A}\cdot\text{cm}^{-2}$ which meets the Department of Energy of the United States (DOE) target.

2.5. Film Wear Resistance Measurement. The mechanical stability is characterized by a friction test in Figure 10. The specimen is loaded by a weight of 100 g and rubbed by a 1000 grade SiC sandpaper at a constant speed. The single trip of abrasion distance is 25 cm. A round trip of 50 cm is defined as a cycle. The sample is subjected to 25 cycles. According to Figure 11, the open-circuit potential reaches the most positive in 0.5 M H2SO4 + 2 ppm HF when the abrasion is for 1250 cm under 1 N pressure. As the pressure increases, the open-circuit potential decreases.

2.6. Corrosion Protection Mechanism of Multilayer Coatings. As shown in Figure 12, in order to prevent the corrosion of the metal bipolar plate, it is very important to block F\textsuperscript{−}, O\textsubscript{2}, and aggressive ions from reaching the metal substrate. The reason for the corrosion of the coated metal substrate is that the corrosive medium such as H\textsuperscript{+}, F\textsuperscript{−}, and so on destroys the film, and the corrosive medium penetrates into the coating/substrate interface through the defects on the coating. From the above test results, although the corrosion resistance of the PAN film is very good, it is difficult for the PAN film to guarantee the stability of the cathode environment of the proton exchange fuel cell because of the F\textsuperscript{−} effect. When

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GO is added, the composite coating can be improved. The composite coatings have a very high protective effect and long-term stability on the aluminum alloy substrate compared to PAN coatings. Because the sample is ultrasonicated in phytic acid to make phytic acid as a bridge, the GO and the substrate are connected to ensure the stability of the composite membrane. However, the doping of large immobile functional groups of GO in PAN is difficult to exchange with the anions from the electrolyte, and the negatively charged functional groups repel the corrosive anions (SO$_4^{2-}$) because of cation permselectivity. At the same time, the reason is that GO nanosheets are a good barrier to prevent penetration of the corrosive medium and increase the diffusion path of the corrosion medium.

3. CONCLUSIONS

The micro-nanohoneycomb structure is constructed on the surface of the aluminum alloy by anodizing, which is beneficial to the penetration of the PAN solution into these honeycombs. It effectively increases the contact area between PAN and the aluminum alloy substrate to enhance the binding force. In the cathodic environment of the simulated proton exchange membrane fuel cell, the PAN membrane has a good protection effect, which can increase the load resistance with 2–3 orders of magnitude and the protection efficiency over 95%. In addition, after the addition of GO, the resistance value of the composite coating can be effectively improved, showing better corrosion resistance. Significantly, when adding GO, the stability is clearly improved. After 5 days of immersion in the addition of GO, the protection efficiency is still above 90%.

4. EXPERIMENT METHODOLOGY

4.1. Materials. The material studied herein is aluminum alloy 5052 (purchased from Jieguan industrial cleaning water treatment technology Co., LTD, Hangzhou, China). The AA5052 alloy is mainly composed of Mg and Al, and other ingredients include Fe, Cr, Cu, Mn, Zn, and Si. All chemical reagents such as perchloric acid, ethanol, polyacrylonitrile (M = 3 × 10$^4$), dimethylformamide (DMF), and phytic acid are purchased from Aladdin Chemical Reagent Co., Ltd and used as received. GO was prepared according to modified Hummer’s method from pristine graphite powder.

4.2. Premodification of the Aluminum Alloy. Before the surface premodification, AA5052 was pretreated by grinding with different grades of sandpaper from 600 to 2000, followed by ultrasonic cleaning in acetone, ethanol, and deionized water for 5 min, respectively. Then, surface premodification of the substrate is performed under the control of a potentiostat which mainly involves two steps: electrochemical polishing and the oxidation process. The sample and platinum plate are connected together with a potentiostat using a conventional two-electrode configuration (anode: AA5052 sample; cathode: Pt sheet). Then, the reaction is carried out by perchloric acid solution at 20 V for 3 min in an ice-water bath. The latter is also the same two-electrode configuration system (V = 30 V). The polished aluminum alloy is anodized in a 0.2 M phosphoric acid solution at 60 °C for 20 min. The experimental process is shown in Figure 13a. Then, the premodified substrate is ultrasonically placed using 1 wt % phytic acid solution for 2 min, followed by drying.

4.3. Preparation of Coating. Different amounts of polyacrylonitrile were dissolved in DMF (labeled as 0.1 PAN/0.2 PAN/~/~/0.5 PAN, respectively) and stirred in a constant-temperature water bath at 60 °C for 2 h and set aside. Next, different amounts of GO were dissolved in PAN solution (referred to as PAN-1 mg GO to PAN-5 mg GO, respectively) and used. A certain amount of the PAN solution and the PAN solution doped with GO were respectively dropped on the surface of the treated aluminum alloy, as shown in Figure 13b. Then, the samples were placed in an oven at 60 °C.

4.4. Sample Characterizations. The surface morphology of the samples was studied by scanning electron microscopy (SEM, JSM-7800F, JEOL, Japan) and atomic force microscopy (AFM, Agilent 5500AFM), and Raman measurements were performed on a LabRAM HR Evolution (λ = 633 nm). The electrochemical properties were tested in 0.5 M H$_2$SO$_4$ + 2 ppm HF aqueous solution-bubbled O$_2$ at room temperature, using the three-electrode system of electrochemical workstations (CHI 660E). The potentiodynamic polarization curves were measured between −250 and 250 mV (vs OCP) with a scanning rate of 1 mV/s. The EIS was tested in the frequency range from 100 kHz to 0.01 Hz at open-circuit potential with an amplitude of 10 mV. All samples were immersed in an oxygen-rich acidic solution for 1 h to obtain a stable open-circuit potential (OCP). In order to further characterize the long-term stability of the composite film, the composite film-modified aluminum alloy was immersed in the simulated liquid under oxygen-rich conditions for different days and then electrochemically tested.
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Notes
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REFERENCES

(1) Antunes, R. A.; Oliveira, M. C. L.; Ett, G.; Ett, V. Corrosion of Metal Bipolar Plates for PEM Fuel Cells: A Review. Int. J. Hydrogen Energy 2010, 35, 3632–3647.
(2) Manohar, M.; Kim, D. Advantageous of Hybrid Fuel Cell Operation under Self-Humidification for Energy Efficient Bipolar Membrane. ACS Sustainable Chem. Eng. 2019, 7, 16493–16500.
(3) He, D.; Tang, H.; Kou, Z.; Pan, M.; Sun, X.; Zhang, J.; Mu, S. Engineered Graphene Materials: Synthesis and Applications for Polymer Electrolyte Membrane Fuel Cells. Adv. Mater. 2017, 29, 1601741.
(4) Wilberforce, T.; El Hassan, Z.; Oungbonghi, E.; Ijaodola, O.; Khattib, F. N.; Durrant, A.; Thompson, J.; Baroutaji, A.; Obali, A. G. A Comprehensive Study of The Effect of Bipolar Plate (BP) Geometry Design on The Performance of Proton Exchange Membrane (PEM) Fuel Cells. Renew. Sustain. Energy Rev. 2019, 111, 236–260.
(5) Yao, K.; Adams, D.; Hao, A.; Zheng, J. P.; Liang, Z.; Nguyen, N. Highly Conductive and Strong Graphite-Phenolic Resin Composite for Bipolar Plate Applications. Energy 2017, 31, 14320–14331.
(6) Ko, T.-J.; Kim, S. H.; Hong, B. K.; Lee, K.-R.; Oh, K. H.; Moon, M.-W. High Performance Gas Diffusion Layer with Hydrophobic Nanolayer under A Supersaturated Operation Condition for Fuel Cells. ACS Appl. Mater. Interfaces 2015, 7, 5506–5513.
(7) Vasile, N. S.; Monteverde Videla, A. H. A.; Specchia, S. Effects of the Current Density Distribution on a Single-Cell DMFC by Tuning the Anode Catalyst in Layers of Gradual Loadings: Modelling and Experimental Approach. Chem. Eng. J. 2017, 322, 722–741.
(8) Lu, J. L.; Abbas, N.; Tang, J. N.; Tang, J.; Zhu, G. M. Synthesis and Characterization of Conductive Ceramic MAX-phase Coatings for Metal Bipolar Plates in Simulated PEMFC Environments. Corros. Sci. 2019, 158, 108106.
(9) Hu, R.; Tang, J.; Zhu, G.; Deng, Q.; Lu, J. The effect of Duty Cycle and Bias Voltage for Graphite-like Carbon Film Coated 304 Stainless Steel as Metallic Bipolar Plate. J. Alloys Compd. 2019, 772, 1067–1078.
(10) Millán, M.; Zamora, H.; Rodrigo, M. A.; Lobato, J. Enhancement of Electrode Stability Using Platinum-Coctal Nanocrystals on a Novel Composite SiC/TiC Support. ACS Appl. Mater. Interfaces 2017, 9, 5927–5936.
(11) Chanda, U. K.; Behera, A.; Roy, S.; Pati, S. Evaluation of Ni-Cr-P Coatings Electrodeposited on Low Carbon Steel Bipolar Plates for Polymer electrolyte Membrane Fuel Cell. Int. J. Hydrogen Energy 2018, 43, 23430–23440.
(12) Ghosh, A.; Goswami, P.; Mahanta, P.; Verma, A. Effect of Carbon Fiber Length and Graphene on Carbon-Polymer Composite Bipolar Plate for PEMFC. J. Solid State Electrochem. 2014, 18, 3427–3436.
(13) Husby, H.; Kongstein, O. E.; Oedegaard, A.; Seland, F. Carbon-Polymer Composite Coatings for PEM Fuel Cell Bipolar Plates. Int. J. Hydrogen Energy 2014, 39, 951–957.
(14) Ren, Z.; Zhang, D.; Wang, Z. Stacks with TiN/titaniu as the Bipolar Plate for PEMFCs. Energy 2012, 48, 577–581.
(15) Tawfik, H.; Hung, Y.; Mahajan, D. Metal bipolar plates for PEM fuel cell-A review. J. Power Sources 2007, 163, 755–767.
(16) González-Gutiérrez, A. G.; Pech-Chanal, M. A.; Chan-Rosado, G.; Sebastian, P. J. Studies on the Physical and Electrochemical Properties of Ni-P Coating on Commercial Aluminum as Bipolar Plate in PEMFC. Fuel 2019, 235, 1361–1367.
(17) Hung, Y.; Tawfik, H.; Mahajan, D. Durability and Characterization Studies of Polymer Electrolyte Membrane Fuel Cell’s Coated Aluminum Bipolar Plates and Membrane Electrode Assembly. J. Power Sources 2009, 186, 123–127.
(18) Kamagai, M.; Myung, S.-T.; Katada, Y.; Yashiro, H. Stability of type 3105 Stainless Steel Bipolar Plates Tested at Various Current Densities in Proton Exchange Membrane Fuel Cells. Electrochim. Acta 2016, 211, 754–760.
(19) El-Enin, S. A. A.; Abdel-Salam, O. E.; El-Abd, H.; Amin, A. M. New Electroplated Aluminum Bipolar Plate for PEM Fuel Cell. J. Power Sources 2008, 177, 131–136.
(20) Wang, J.; Min, L.; Fang, F.; Zhang, W.; Wang, Y. Electrodeposition of Graphene Nano-Thick Coating for Highly Enhanced Performance of Titanium Bipolar Plates in Fuel Cells. Int. J. Hydrogen Energy 2019, 44, 16909–16917.
(21) Yi, P.; Li, X.; Yao, L.; Fan, F.; Peng, L.; Lai, X. A Lifetime Prediction Model for Coated Metallic Bipolar Plates in Proton Exchange Membrane Fuel Cells. Energy Convers. Manage. 2019, 183, 65–72.
(22) Qin, Z.; Zeng, Y.; Hua, Q.; Xu, Q.; Shen, X.; Min, Y. Synergistic Effect of Hydrolyzed Boron Nitride and Silane on Corrosion Resistance of Aluminum Alloy 5052. J. Taiwan Inst. Chem. Eng. 2019, 100, 285–294.
(23) Yang, L.; Wang, Y.; Qin, Z.; Xu, Q.; Min, Y. Fabrication and Corrosion Resistance of a Graphene-Tin Oxide Composite Film on Aluminum Alloy 6061. Corros. Sci. 2018, 130, 85–94.
(24) Wei, D.; Wang, J.; Wang, H.; Liu, Y.; Li, S.; Li, D. Anti-corrosion Behaviour of Superwetting Structured Surfaces on Mg-9Al-1Zn Magnesium Alloy. Appl. Surf. Sci. 2019, 483, 1017–1026.
(25) Gomes, T. C.; Kumar, D.; Fugikawa-Santos, L.; Alves, N.; Kettle, J. Optimization of the Anodization Processing for Aluminum.
Oxide Gate Dielectrics in ZnO Thin Film Transistors by Multivariate Analysis. *ACS Comb. Sci.* **2019**, *21*, 370–379.

(26) Mwema, F. M.; Oladji, O. P.; Akinlabi, S. A.; Akinlabi, E. T. Properties of Physically Deposited Thin Aluminium Film Coatings: A Review. *J. Alloys Compd.* **2018**, *747*, 370–379.

(27) Sun, W.; Wang, L.; Yang, Z.; Li, S.; Wu, T.; Liu, G. Fabrication of Polydimethylsiloxane-derived Superhydrophobic Surface on Aluminium via Chemical Vapour Deposition Technique for Corrosion Protection. *Corros. Sci.* **2017**, *128*, 176–185.

(28) Mu, W.; Fu, Y.; Sun, S.; Edwards, M.; Ye, L.; Jeppson, K.; Liu, J. Controllable and Fast Synthesis of Bilayer Graphene by Chemical Vapor Deposition on Copper Foil using a Cold Wall Reactor. *Chem. Eng. J.* **2016**, *304*, 106–114.

(29) Ngai, S.; Ngai, T.; Vogel, F.; Story, W.; Thompson, G. B.; Brewer, L. N. Saltwater corrosion behavior of cold sprayed AA7075 aluminum alloy coatings. *Corros. Sci.* **2018**, *130*, 231–240.

(30) Gordeeva, E. O.; Roslyakov, I. V.; Napol'skii, K. S. Aluminium Anodizing in Selenic Acid: Electrochemical Behaviour, Porous Structure, and Ordering Regimes. *Electrochim. Acta* **2019**, *307*, 13–19.

(31) Zhang, B.; Xu, W.; Zhu, Q.; Sun, Y.; Li, Y. Mechanically Robust Superhydrophobic Porous Anodized AA5083 for Marine Corrosion Protection. *Corros. Sci.* **2019**, *158*, 108083.

(32) Jiang, F.; Zhao, W.; Wu, Y.; Wu, Y.; Liu, G.; Dong, J.; Zhou, K. A Polyethyleneimine-grafted Graphene Oxide Hybrid Nanomaterial: Synthesis and Anti-corrosion Applications. *Appl. Surf. Sci.* **2019**, *479*, 963–973.

(33) Zhong, F.; He, Y.; Wang, P.; Chen, C.; Lin, Y.; Wu, Y.; Chen, J. Self-assembled Graphene Oxide-Graphene Hybrids for Enhancing the Corrosion Resistance of Waterborne Epoxy Coating. *Appl. Surf. Sci.* **2019**, *488*, 801–812.

(34) Sefer, B.; Virtanen, S. Electrochemical and Corrosion Study of As-cast Ni5Al5 Intermetallic Alloys: Influence of Alloy Composition and Electrolyte pH. *Corros. Sci.* **2019**, *150*, 127–135.

(35) Hwang, M.-J.; Kim, M.-G.; Kim, S.; Kim, Y. C.; Seo, H. W.; Cho, J. K.; Park, I.-K.; Suhr, J.; Moon, H.; Koo, J. C.; Choi, H. R.; Kim, K. J.; Tak, Y.; Nam, J.-D. Cathodic Electrophoretic Deposition (EPD) of Phenylenediamine-modified Graphene Oxide (GO) for Anti-corrosion Protection of Metal Surfaces. *Carbon* **2019**, *142*, 68–77.

(36) Wang, F.; Mao, J. Nacre-like Graphene Oxide/Waterborne Styrene Butadiene Rubber Composite and Its Reusable Anti-corrosion Behavior on Al-2024. *Prog. Org. Coat.* **2019**, *132*, 191–200.

(37) Zhao, W.; Kong, D. Effects of Laser Power on Immersion Corrosion and Electrochemical Corrosion Performances of Laser Thermal Sprayed AlFeSi Coatings. *Appl. Surf. Sci.* **2019**, *481*, 161–173.

(38) Ge, Y.; Wang, Y.; Cui, Y.; Zou, Y.; Guo, L.; Ouyang, J.; Jia, D.; Zhou, Y. Growth of Plasma Electrolytic Oxidation Coatings on Nb and Corresponding Corrosion Resistance. *Appl. Surf. Sci.* **2019**, *491*, 526–534.

(39) Zhang, B.; Hu, X.; Zhu, Q.; Wang, X.; Zhao, X.; Sun, C.; Li, Y.; Hou, B. Controllable Dianthus Caryophyllus-like Superhydrophobic/Superhydrophilic Hierarchical Structure Based on Self-Congregated Nanowires for Corrosion Inhibition and Biofouling Mitigation. *Chem. Eng. J.* **2017**, *312*, 317–327.

(40) Chen, Y.; Li, J.; Yang, W.; Gao, S.; Cao, R. Enhanced Corrosion Protective Performance of Graphene Oxide-Based Composite Films on AZ31 Magnesium Alloys in 3.5 wt% NaCl Solution. *Appl. Surf. Sci.* **2019**, *493*, 1224–1235.

(41) Xiang, T.; Zhang, M.; Sadig, H. R.; Li, Z.; Zhang, M.; Dong, C.; Yang, L.; Chan, W.; Li, C. Slippery Liquid-infused Porous Surface for Corrosion Protection with Self-Healing Property. *Chem. Eng. J.* **2018**, *345*, 147–155.

(42) Tombros, N.; Joza, C.; Popincic, M.; Jonkman, H. T.; van Wees, B. J. Electronic Spin Transport and Spin Precession in Single Graphene Layers at Room Temperature. *Nature* **2007**, *448*, 571–574.

(43) Jiang, L.; Syed, J. A.; Lu, H.; Meng, X. In-situ Electrodeposition of Conductive Polypyrrole-Graphene Oxide Composite Coating for