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Full Length Article

Corrosion protection application of slippery liquid-infused porous surface based on aluminum foil

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ABSTRACT

Corrosion is a major problem for metal in marine systems. In this research, we fabricated a slippery liquid-infused porous surface (SLIPS) on the aluminum foil to protect the underneath metal. The as-fabricated samples were characterized with EDS, XRD, SEM, and contact angle meter. And the anti-corrosion property was evaluated by electrochemical measurements. The corrosion current density of SLIPS is ca.2 orders of magnitude lower than that of the untreated aluminum and superhydrophobic surface. And the impedance spectra of the SLIPS shows a large impedance semicircle with a diameter of several hundred k$\Omega\cdot$cm^2. The SLIPS exhibits an outstanding corrosion protection capability, thus it has a broad application prospect in marine.

1. Introduction

Metal corrosion is an eternal enemy in the industrial fields, especially in marine applications. In recent years, it has been found that superhydrophobic film has an anti-corrosion capability to protect the underneath metal [1–4]. When the superhydrophobic surface is immersed in seawater, air layer trapped in the gap of the superhydrophobic film can block the contact of seawater and metal substrate [5–7]. It has been proved that air layer trapped in superhydrophobic film is the essential contributor to the enhancement of barrier performance [8]. Due to capillary effect, at the interface between liquid and air, the capillary pressure prevents seawater from penetrating the superhydrophobic film [9]. As the immersion time increases, unfortunately, the trapped air layer will be slowly dissolved by seawater. The increase of contact area between seawater and metal substrate will cause the collapse of corrosion resistance. Owing to the temporary durability, the application of superhydrophobic surface has been hindered greatly in water phase [10–12]. This forces researchers to explore alternatives instead of the superhydrophobic surface.

Nepenthes pitcher, which survives in tropical rainforests, uses micro-structure to lock in an intermediary liquid to obtain repellent surface [13]. It offers a compelling idea to acquire a stable anti-corrosion surface. Slippery liquid-infused porous surfaces (SLIPS) inspired by *Nepenthes* can catch a thin film of lubricant immiscible with water phase by porous structures [14,15]. Therefore, it can work as an effective self-protective layer to prevent the invasion of water and corrosive ions [16–18]. Besides, the lubricant film is insoluble in seawater, allowing it to be stored in a rough surface for a longer time than air layer. Thus, replacing the air layer with lubricant film is a promising option to acquire a stable anti-corrosion surface. In process of constructing SLIPS, three criteria should be met [19,20]. First, a rough hydrophobic surface is needed to lock in lubricant film, which can form a continuous, homogenous and smooth liquid-solid interface. Second, lubricant and external medium should be immiscible. Third, the affinity between lubricant and rough structure should be well matched.

Fouling and corrosion are the two recognized problems in shortening metal life in marine environments. In previous study, SLIPS shows an excellent anti-fouling performance [21–24]. If SLIPS has admirable corrosion resistance, it will be widely applied in marine. Yang et al. have proven that the SLIPS fabricated on the low alloy steel can afford an effective self-standing layer to protect the steel substrate [20]. Slippery anodic aluminum oxide surfaces fabricated by Song et al. have excellent anticorrosion property [25]. In this study, we use a facile method to fabricate LDHs (LDHs are a class of synthetic anionic clays that consist of positively charged layers containing alternatively distributed divalent and trivalent cations in the sheets and charge balancing anions between the layers [26–28]) superhydrophobic surface on aluminum foil, then impregnate lubricant on it to form stable SLIPS. The lubricant can match well with the superhydrophobic surface, so the lubricant

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film can't be replaced by external seawater automatically. It is reasonable to infer that slippery LDHs surface can protect aluminum substrate from corrosion in seawater for a long time, but it should be proven. Electrochemical experiments were carried out in simulated seawater (3.5% sodium chloride aqueous solution) to evaluate the corrosion resistance of SLIPS and superhydrophobic surface. Results showed that the anti-corrosion property of SLIPS was better than the superhydrophobic surface in simulated seawater. Therefore, the SLIPS is a promising candidate to protect metal in marine applications. Moreover, the stabilities of SLIPS and superhydrophobic surface were tested under acidic and alkaline environments. We can conclude that the SLIPS doesn't always have better corrosion resistance than the superhydrophobic surface. While the lubricant working as self-standing layer can protect aluminum substrate from corrosion in alkaline environment, SLIPS will be severely corroded in acidic condition. For the superhydrophobic surface, it's just the opposite, which has a better anti-corrosion property in acidic corrosion. We believe this study will be meaningful in the research of corrosion resistance in different conditions.

2. Experimental

2.1. Materials and reagents

The reagents used in this study including copper dichloride ($CuCl_2·6H_2O$), hydrochloric acid (HCl), zinc nitrate ($Zn(NO_3)_2·6H_2O$), hexamethylenetetramine ($C_6H_{12}N_4$), sodium chloride(NaCl), sodium hydroxide (NaOH), fluoroalkylsilane (FAS), lubricant (Krytox100), acetone and ethanol. In the process of the experiment, these regents were used without further purification. The base material was industrial grade aluminum foil which was 1 mm thickness and 99% purity. Deionized water was used in all experiments.

2.2. Fabrication of SLIPS

2.2.1. Chemical etching

The aluminum foil (10mm × 10mm × 1 mm) was polished by #1200 sandpaper and cleaned by acetone, ethanol and deionized water in sequence. Then the aluminum sample was chemically etched in a mixed solution for 4 min at room temperature. In the mixed solution, the concentration of HCl was 1 M and concentration of $CuCl_2$ was 0.2 M.

2.2.2. Hydrothermal synthesis

After chemical etching, the aluminum sample was thoroughly cleaned to remove the copper and dried at 350 °C for 10 min to form hydrogen bonds on the surface. Then the aluminum foil was hydrothermal synthesized in a mixed aqueous solution of $Zn(NO_3)_2$ and $C_6H_{12}N_4$ at 95 °C for 3 h. In the mixed solution, the concentration of $Zn(NO_3)_2$ and $C_6H_{12}N_4$ was 0.05 M.

2.2.3. Surface modification and lubricant impregnation

The sample after hydrothermal synthesis was superhydrophilic, so it must be modified by a functionalization reagent to reduce the surface energy. In this study, the sample was immersed in 0.5% FAS ethanol solution for 1 h at room temperature, then heated at 120 °C for 1 h to obtain a superhydrophobic surface. To form a SLIPS, Krytox100 (20 μL) was applied onto the superhydrophobic surface with a pipette. The surface was tilted at a small angle for several hours to remove the excess lubricant from the sample surface. With the lubricant coating, the SLIPS could repeal various liquids such as water, ethanol, rap oil, etc.

2.3. Characterization

2.3.1. Surface characterization

Contact angle (CA) and sliding angle (SA) was measured by a contact angle meter system (JC2000D2A, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd.) at room temperature. The morphologies of aluminum foil after electrochemical etching and hydrothermal synthesis were observed with a field-emission scanning electron microscope (FE-SEM, TESCAN VEGA). Chemical composition of the as-prepared sample was characterized by energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD).

2.3.2. Electrochemical experiments

Electrochemical tests including polarization curves (Tafel) and electrochemical impedance spectra (EIS) were carried out on a computer-controlled electrochemical system (CHI660D, CH Instruments Inc.) in 3.5% NaCl aqueous solution at room temperature. The tests were carried out in a three-electrode system: a saturated calomel electrode (Ag/AgCl, 3 M KCl) was used as reference electrode, a graphite electrode was used as counter electrode and the as-prepared sample was used as working electrode. The area of the working electrode was 1 cm^2. Tafel curves were obtained with a sweeping range ±0.3 V versus the open circuit potential and with a scanning rate of 1 mV/s. EIS tests were performed at frequencies ranging from 10^5Hz to 1 Hz at open circuit potential with an amplitude of perturbation voltage of 250mV [29].

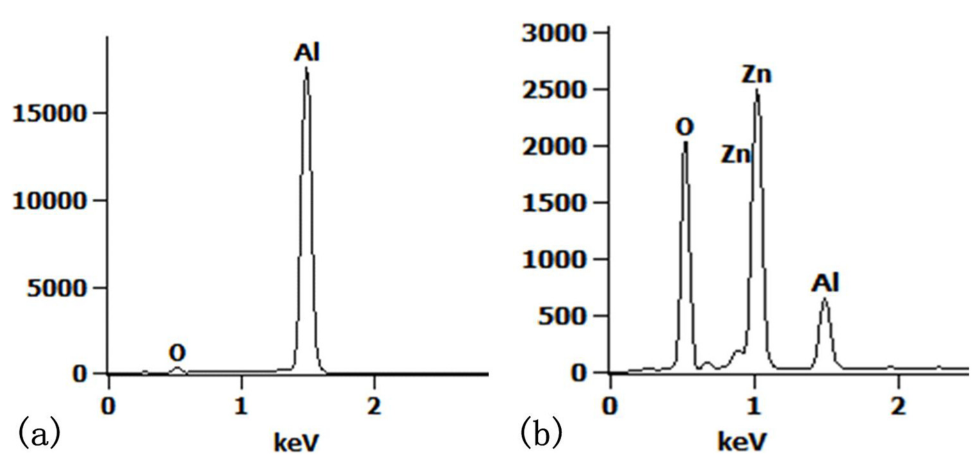

Fig. 1. EDS of the aluminum samples. (a) untreated aluminum. (b) hydrothermal synthesis for 3 h.