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Slippery liquid-infused porous surfaces fabricated on aluminum as a barrier to corrosion induced by sulfate reducing bacteria

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ABSTRACT

Microbiological corrosion induced by sulfate reducing bacteria (SRB) is one of the main threatens to the safety of marine structure. To reduce microbiological corrosion, slippery liquid infused porous surfaces (SLIPS) were designed and fabricated on aluminum substrate by constructing rough aluminum oxide layer, followed by fluorination of the rough layer and infiltration with lubricant. The as-fabricated SLIPS were characterized with wettability measurement, SEM and XPS. Their resistances to microbiological corrosion induced by SRB were evaluated with fluorescence microscopy and electrochemical measurement. It was demonstrated that they present high resistance to bacteria adherence and the resultant microbiological corrosion in static seawater.

1. Introduction

Corrosion is one of the main factors for the degradation of engineering structure in ocean. Metabolic activity of micro-organism can be involved in corrosion process in aqueous environment [1]. The loss for microbiological corrosion occupies about 20% of the total corrosion loss in ocean.

Sulfate reducing bacteria (SRB), the chief culprits among causative organisms of corrosion, instigate half of all the instances of bio-corrosion failures [2]. The complex SRB colonies attach to surfaces by self-produced extracellular polymeric substance (EPS), and form biofilm finally [3]. Cathodic depolarization theory is a classical theory about the SRB corrosion mechanism. It was proposed that the hydrogenase produced by SRB can help to consume the cathodic hydrogen, thereby accelerating the oxidation of metal [4]. It was also reported that EPS produced by SRB has the ability to accelerate corrosion by binding with metal ions [5]. Thus, it is extremely desirable to design an effective coating for preventing SRB-biofilm formation.

Recently, bio-inspired coatings have attracted much attention from researchers for their potential application value in a wide industrial area [6–14]. *Nepenthes* is a kind of plant that can “catch” insects and digest them as nutrient. They can use porous structures on their peristome to lock-in an intermediary liquid film, which causes insects to slide from the wetted pitcher rim into the digestive juices at the bottom by repelling the oils on their feet [15,16]. Inspired by this idea, a new type of materials called slippery liquid-infused porous surfaces (SLIPS) have been introduced to exhibit non-wetting behavior to almost all fluids [17–19]. In the case of SLIPS, a thin layer of liquid lubricant is injected into porous structure to form a continuous, smooth, and chemically homogenous liquid interface, which presents low-hysteresis and non-wetting property. It has been reported that SLIPS prevent 99.6% of *Pseudomonas aeruginosa* biofilm attachment over a 7-day period [20]. Levkin research group further proved the great potential of SLIPS for anti-biofouling application in marine and wastewater [21,22]. It is reasonable to infer that SLIPS can inhibit the adherence of SRB and the resultant corrosion, but it should be proven.

In this work, SLIPS were designed and fabricated on a model metallic material aluminum by constructing rough aluminum oxide layer, followed by fluorination of the rough layer and infusion with lubricant. It was proven that the as-fabricated SLIPS can effectively inhibit the adherence of SRB and the resultant MIC in static seawater. This research provides a novel and effective strategy for inhibiting microbiological corrosion of metallic material in seawater.

2. Experimental

2.1. Materials and reagents

Aluminum (⩾99.99 wt.%) foil with thickness of 0.1 cm was purchased from Beijing Cuibolin Nin-ferrous Technology Developing

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Co., Ltd. The chemical reagents were used as received, including 1H,1H,2H,2H-perfluorodecyltriethoxysilane (PFDS) (97%, Aldrich Inc.), Acridine orange (AO) (Aldrich Inc.), and Perfluoropolyether (PFPE) (Nascent™ FX-5200, Switzerland). Other chemical reagents were purchased from Sinopharm Chemical Reagent Co., Ltd., which were analytical grade and used as received. Water used in all experiments was Milli-Q water (Milli Q, USA).

2.2. Fabrication of SLIPS

2.2.1. Electropolishing

Aluminum foil (1.2 cm × 2 cm × 0.1 cm) was electrochemically polished in a mixture of perchloric acid and ethanol ($HClO_4$:C_2H_5OH = 1:4 in volumetric ratio) at 5 °C. The electropolishing process was carried out under an applied voltage of 20 V for 3 min in a two-electrode cell, in which, aluminum foil is a working electrode, and stainless steel electrode is a counter electrode. The electrolyte was vigorously stirred during electropolishing process.

2.2.2. Anodization of aluminum

The aluminum foil after electropolishing was applied to anodization in two-electrode cell, in which, aluminum substrate was used as a working electrode, and a stainless steel electrode was employed as a counter electrode. The aluminum substrate was anodized in aqueous solution of 0.3 M oxalic acid under anodizing voltage of 120 V for 150 s. The initial anodization temperature is set as 25 °C.

2.2.3. Surface modification and lubricant infusion

The samples after anodization were modified with self-assembled monolayer of PFDS. Briefly, the samples were immersed into 1 vol.% PFDS/ethanol solution for 5 min, and then taken out and heated at 120 °C in an oven for 10 min. After that, an excess amount of lubricant PFPE is dropped onto the modified porous surface with a pipette. PFPE can penetrate into the porous structure under capillary action. The surface was then tilted at an angle of ~20° for 2 h to let the excess lubricant flow off the sample surface.

2.3. Characterization

2.3.1. Morphology and composition characterizations

The morphology of aluminum oxide layer was characterized with Field-Emission Scanning Electron Microscope (FE-SEM, Hitachi S-3400N). Water dynamic contact angles of SLIPS were measured with a contact-angle meter (JC2000C1, Shanghai Zhongchen Digital Technic Apparatus Co., Ltd.) at room temperature. Chemical composition information about the sample was obtained by X-ray Photoelectron Spectroscopy (XPS). XPS was carried out on a Thermo ESCALAB 250 photoelectron spectrometer equipped with an Al-anode at a total power dissipation of 150 W (15 kV, 10 mA). The experimental data of the relative atomic composition was analyzed using the integrated software of photoelectron spectrometer.

2.3.2. Electrochemical experiments

Electrochemical impedance spectra (EIS) were obtained with a computer-controlled electrochemical system (CHI 760C, CH Instruments Inc.) in SRB medium at 30 °C. They were carried out in a three-electrode cell: a platinum wire was used as counter electrode, and Ag/AgCl (3 M KCl) electrode was as reference electrode. EIS experiments were carried out at frequency range of 10^5 Hz to 1×10^{-2} Hz at open circuit potential with amplitude of perturbation voltage ±20 mV. EIS results were analyzed by fitting data with Zsimpwin software.

2.4. Microorganism cultivation and toxicity test

2.4.1. Microorganism cultivation

Bacterial sample (SRB) was isolated from marine sludge, which was collected from the Bohai Sea of China. The modified Postgate's culture solution was used for growth of SRB. It contains 0.5 g of KH_2PO_4, 1 g of NH_4Cl, 0.1 g of $CaCl_2$, 2 g of $MgSO_4$, 0.5 g of Na_2SO_4, 4 mL of sodium lactate, and 1 g of yeast extract per liter of natural seawater, and its pH value was adjusted to 7.2 ± 0.1 using 1 M NaOH solution.

A 200 mL culture medium was poured into a 250 mL beaker, deoxygenated by N_2 sparging for 1 h, and then autoclaved at 121 °C for 30 min. After cooling, the culture solution was inoculated with the bacteria sample at room temperature (25 ± 2 °C), and subsequently sealed and stored in an incubator at 30 °C. The bare aluminum samples and SLIPS coated samples were sterilized under ultraviolet radiation for 30 min. According to the growth

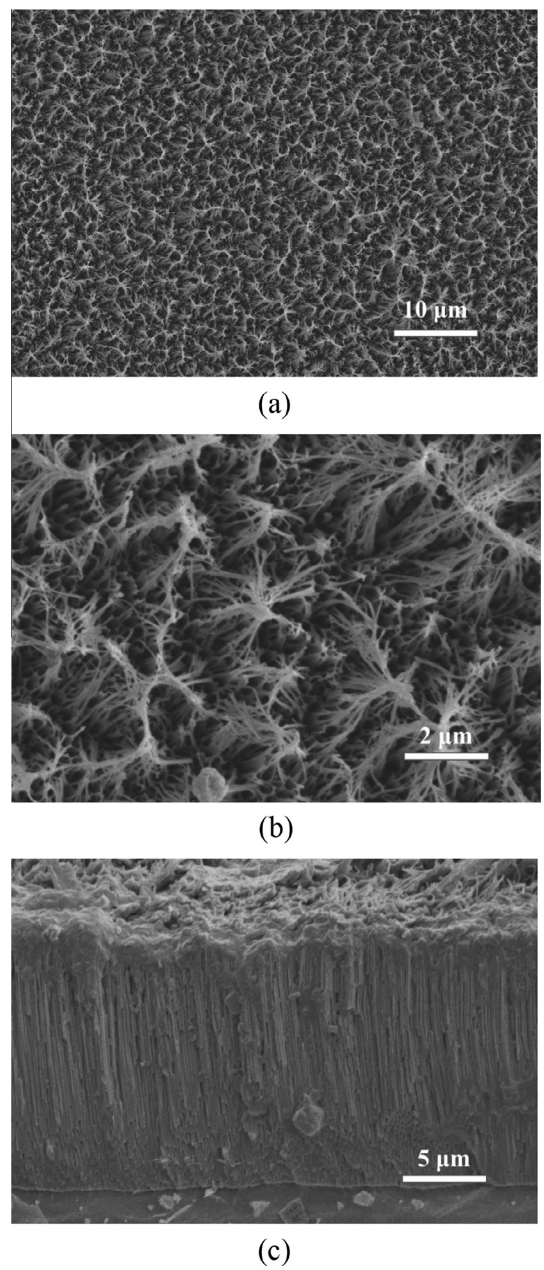

Fig. 1. Top view (a and b) and cross-sectional view (c) of aluminum oxide layer fabricated on aluminum surface after anodization.