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

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Microbiological corrosion induced by sulfate reducing bacteria (SRB) is one of the main threats 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.

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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 infiltration 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
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 \( \times \) 2 cm x 0.1 cm) was electrochemically polished in a mixture of perchloric acid and ethanol (HClO\(_4\)):C\(_2\)H\(_5\)OH = 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 \( \sim 20^\circ \) 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 \( 1 \times 10^{-2} \) Hz at open circuit potential with amplitude of perturbation voltage \( \pm 20 \) 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\(_2\)PO\(_4\), 1 g of NH\(_4\)Cl, 0.1 g of CaCl\(_2\), 2 g of MgSO\(_4\), 0.5 g of Na\(_2\)SO\(_4\), 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.
circle of SRB, SRB present high activity after inoculation for 3 days [23]. Thus, sterilized bare aluminum sample and SLIPS sample were vertically immersed into a 3-days-old culture solution to start the experiments, including analyzing the bacterial adhesion, corrosion behavior on test samples. During these experiments process, a 50 ml inoculated culture solution with SRB was replaced by the equivalent volume of fresh culture solution every 2 days, to maintain the high activity of SRB.

2.4.2. Toxicity test of the lubricant

The impact of lubricant PFPE on bacterial suspensions was analyzed by comparing the growth curves of SRB in culture solution with and without addition of lubricant. The procedure for monitoring SRB growth curve in culture solution with lubricant is as follows: after sterilization process as mentioned in Section 2.4.1, 100 mL culture solution was inoculated with the bacteria sample, and added with 2 mL lubricant at room temperature and subsequently sealed. To facilitate the full contact between SRB and lubricant, SRB were inoculated in an orbital shaker at 30 °C at 200 rpm. Different with the bacteria adherence experiment mentioned above, no fresh culture was added to replace the inoculated culture solution every 2 days, to maintain the high activity of SRB.

2.4.3. Imaging and analysis

SRB adhesion was observed by a fluorescence microscopy (Olympus BX-51 with an image software of Cellsens) after staining with AO. Briefly, samples after adhesion experiments were transferred into the AO solution (10 μg/mL) for 30 min, and washed slightly with sterile sea water for 3 times. Subsequently, the samples were mounted on a slide and covered by a coverslip. A glycerinum/sea water solution (1:1 in volume) was added in the gap between the sample and coverslip to keep the sample wet. These samples were then observed on fluorescence microscopy utilizing an exciter filter of 490 nm and barrier filter of 530 nm.

3. Results and discussion

3.1. Fabrication of SLIPS

SLIPS on aluminum were designed based on three important criteria [18]: (1) the solid surface should preferably have roughened nanostructures to provide increased surface area for the adhesion and the retention of the infused lubricating fluid; (II) the chemical affinity between the lubricating fluid and the solid should be higher than that between the repellent fluid and the solid; and (III) the lubricating fluid and the repellent fluid have to be immiscible. According to these criteria, SLIPS were fabricated on Al substrate by constructing rough anodic aluminum oxide layer followed by fluorination of the rough layer and infiltration with lubricant. It was widely reported that anodization can finely
control the morphology of aluminum oxide layer, which can be achieved by varying the anodic current density and temperature [24]. Herein, it is utilized to fabricate rough structure on aluminum surface, which can satisfy the first condition of criteria. As shown in the morphology of aluminum oxide layer after anodization (Fig. 1), it can be observed that aluminum oxide layer presents composite structure with a thin nano-wire-like layer (around a couple of micrometers) on thick nano-pore-like layer (around 15 μm). Both nano-pore-like and nano-wire-like structures provide increased surface area for lubricant infusion and retention [18].

For the application in MIC inhibition in water, SLIPS should be designed based on the criterion that they can repel water effectively. In this research, the anodic aluminum oxide layer is modified with fluorocarbon, which presents strong repellent to water. As shown in XPS spectra of aluminum foil after anodization and surface modification with PFDS (Fig. 2), it reveals the presence of C, O, Al and F elements on the sample surface (Fig. 2a). The binding energy of Al2p peak is found to be 74.2 eV (Fig. 2b), which is assigned to O–Al–O (Al₂O₃) bonding [25]. It is proven that the aluminum foil...
surface after anodization is mainly composed of Al$_2$O$_3$. The high resolution C1s core level spectrum (Fig. 2c) can be resolved into several components, including –CF$_3$ (293.8 eV), –CF$_2$ (291.2 eV), –CH$_2$–CF$_2$ (288.8 eV), –C–O (286.2 eV), and –C–C (284.6 eV) [25]. The main F1s peak can be found around 688.5 eV (Fig. 2d), which is attributed to F–C covalent bond [26]. Furthermore, the atomic percentage of element F is 36.03%, which is much higher than that of element Al (16.38%). It is indicated that the low-surface energy –CF$_3$ and –CF$_2$– groups comprise the outermost surface.

It is known that the theoretical water contact angle on a flat surface modified with PFDS is around 119° [27], and the contact angle of lubricant PFPE on its surface modified with PFDS is around 27°, indicating that the substrate modified with PFDS shows much stronger affinity to lubricant PFPE in comparison with that to water. Thus, PFPE is an appropriate lubricating fluid for SLIPS in our research, because this kind of design can satisfy the second condition of criteria. Furthermore, the lubricant used in this research is immiscible with water, and this characteristic satisfies the third condition for stable SLIPS design. As we expected, the aluminum oxide layer after modification with PFDS shows superhydrophobic property with contact angle of 160.1°. It is indicated that the modified aluminum oxide layer shows highly repellent property to water for the low surface energy of C–F groups and rough micro-structure. In contrast with that, the lubricant PFPE can easily spread on the surface after it is dropped on modified aluminum oxide layer, and finally it will spread out over surface (the results are not shown here). It is proven that the surface presents high affinity to lubricant in comparison with water. For the capillary effect, the lubricant can easily infuse into rough structure, and finally, stable SLIPS in air environment can form.

It can be found that a water droplet can easily move on the as-fabricated SLIPS with a low titled angle (<10°) (Fig. 3). The surface is stable in the presence of water droplet over it. It provides experimental evidence to support that the underlying rough aluminum oxide layer with high surface area could effectively assist the infusion and stabilization of the hydrophobic lubricant. Finally, a smooth and nearly defect-free surface forms, which shows extremely low pinning effect to the water droplet over its surface [15].

3.2. Inhibition of SRB adhesion on SLIPS

To study the inhibition effect of SLIPS to the adhesion of SRB, both bare aluminum and SLIP-coated aluminum samples are immersed into 200 mL 3-days-old culture solution with SRB, in
which, the growth of SRB is in vigorous growth period with approximately $10^7$ CFU ml$^{-1}$ [23]. During the entire test period, a 50 ml freshly sterile culture solution is utilized to replace an equivalent volume of inoculated culture solution every 2 days, to provide sufficient energy for the growth of SRB. After immersion, staining is performed to the samples, and fluorescence microscopy is used to observe the colony adhered on samples surface. As shown in Fig. 4a, after 1 day of immersion, many bright green-colored points disperse on bare aluminum surface. Every single point represents a SRB cell adhered on surface. After 4 days of immersion, the coverage area by green-colored points increases, and some aggregate colonies can be observed obviously (Fig. 4c). After 7 days of immersion, the colonies density further increases, and the aggregation phenomenon gets more obvious, implying that mature SRB-biofilm forms over bare aluminum surface (Fig. 4e). In contrast, SRB colonies are seldom found on SLIPS after a short period of immersion (Fig. 4b and d). Even after immersion of 7 days, only very few colonies can be observed on SLIPS (Fig. 4f). It is demonstrated that the SRB is effectively inhibited to adhere and grow on SLIPS.

3.3. Toxicity test of lubricant

To confirm that the inhibition effect to growth of biofilm on SLIPS is not a result of the toxicity of lubricant, the effect of lubricant to the growth of SRB under shaking environment is tested. The OD value at the wavelength of 550 nm is used as a parameter to determine the growth of SRB. The displayed OD values in Fig. 5 are the average of five replicates with the error bars representing the standard deviations. Similar with SRB growth in static environment, its growth under shaking environment can be also divided into three periods including growing, death and residual phases, according to the variation tendency of OD value [23]. Noticeably, the SRB in culture solution with 2 vol.% lubricant shows almost the same growth kinetics as in control culture solution without lubricant. It is implied that lubricant shows null toxicity to the growth of SRB. The small deviation between the two growth curves in culture solution with and without lubricant can be attributed to the unavoidable experiment error, such as the difference of inoculative SRB amount, and so forth.

According to the analysis above, it is suggested that the inhibition effect to SRB adherence only originates from some special properties of SLIPS. It is widely accepted that the “fluid” property is the main mechanism that inhibit the attachment of biofilm on the SLIPS, and hence, it is reasonable to infer that SRB are hard to anchor to the mobile interface [20]. In our opinion, the low surface roughness of SLIPS should also be considered as another possible reason for the low coverage of SRB on its surface. Roughness is proven to be an important factor that determines the initial bacterial contamination attachment to solid surface and the subsequent formation of bio-film [28-30]. Awad research group [31] has proposed electropolishing method to decrease the roughness of immersion, the coverage area by green-colored points increases, and some aggregate colonies can be observed obviously (Fig. 4c). After 7 days of immersion, the colonies density further increases, and the aggregation phenomenon gets more obvious, implying that mature SRB-biofilm forms over bare aluminum surface (Fig. 4e). In contrast, SRB colonies are seldom found on SLIPS after a short period of immersion (Fig. 4b and d). Even after immersion of 7 days, only very few colonies can be observed on SLIPS (Fig. 4f). It is demonstrated that the SRB is effectively inhibited to adhere and grow on SLIPS.

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Table 2

Electrochemical parameters of SLIPS-coated aluminum samples after immersion in SRB medium for 1 and 7 days. (These parameters are EIS simulation results with equivalent circuit in Fig. 9b. Each data is mean ± standard deviation of at least five replicates.)

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$Q_o$ Y (F/cm$^2$)</th>
<th>$R_i$ (Ω cm$^2$)</th>
<th>$Q_i$ Y (F/cm$^2$)</th>
<th>$R_w$ (Ω cm$^2$)</th>
<th>$Q_w$ Y (F/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 day</td>
<td>11.3 ± 3.1</td>
<td>$(2.48 ± 0.13) \times 10^{-10}$</td>
<td>1</td>
<td>$(8.42 ± 0.41) \times 10^8$</td>
<td>$(5.85 ± 0.32) \times 10^{-8}$</td>
<td>$(2.23 ± 0.18) \times 10^8$</td>
</tr>
<tr>
<td>7 days</td>
<td>10.4 ± 2.5</td>
<td>$(3.35 ± 0.11) \times 10^{-10}$</td>
<td>1</td>
<td>$(5.47 ± 0.35) \times 10^8$</td>
<td>$(7.57 ± 0.28) \times 10^{-8}$</td>
<td>$(2.42 ± 0.30) \times 10^8$</td>
</tr>
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</table>

Fig. 10. Schematic of SLIPS-coated aluminum sample immersed in SRB medium.

Aluminum oxide film and the barrier layer properties. The properties of each part can be characterized by resistance and capacitance, in parallel and in series, describing their electronic and dielectric behaviors [33]. The equivalent circuit for aluminum oxide film [33], is utilized to model the electrochemical behavior of SLIPS in SRB medium. In this model, $R_e$ represents the electrolyte resistance, $R_t$ represents the resistance of layer on aluminum, $R_w$ represents the charge-transfer resistance, and $Q_w$ and $Q_i$ are constant phase elements that model capacitance of double-layer and film formed over aluminum, respectively. The impedance of constant phase element is given by:

$$Z_Q = \frac{1}{Y_0(\omega)^n}$$

where $j$ is the imaginary number, $\omega$ is angular frequency, $Y_0$ is the frequency-independent real constant, and $n$ is the constant phase element exponent. To confirm that the circuit proposed is proper to simulate the EIS plots of bare aluminum, a preliminary simulation is carried out to analyse the EIS plots with circuit in Fig. 7a. It is found that the $R_e$ value got from simulation is very small (the results are not shown here), indicating the film formed over aluminum shows very weak affection to the electrochemical performance of substrate. Hence, the equivalent circuit in Fig. 7a can be simplified to equivalent circuit in Fig. 7b. Table 1 shows the electrochemical parameters of bare aluminum after immersion in SRB medium for 1 and 7 days. It can be found that the $R_w$ value increases with immersion time, which might be attributed to the accumulation of corrosion product over aluminum sample during immersion.

Fig. 8 shows the EIS plots and their fitting results of SLIPS-coated aluminum after immersion in SRB medium for 1 and 7 days. As shown in Fig. 8a, Nyquist plots are characterized by the presence of loop at high frequency and capacitive behavior at lower frequencies. The high frequency loop increases (Fig. 8a), and there is a shift of the minimum phase angle to lower frequencies (Fig. 8c) as immersion time increases. This phenomenon can be attributed to the change of aluminum oxide film structure in corrosive medium [32]. Noticeably, the impedance of SLIPS (Fig. 8b) is much higher than that of bare aluminum (Fig. 6b), indicating that the presence of SLIPS can improve the resistance of substrate to microbiological corrosion. It is widely reported that the aluminum oxide film consists of a very thin compact part and a thick porous part [33]. To describe the electrochemical behavior of aluminum oxide film, both oxide parts are considered independent and separated into two oxide phases: porous and barrier parts [33]. Similar with that, SLIPS is composed with two phase (Fig. 9a): the barrier layer at the bottom of aluminum oxide layer, and the porous aluminum oxide layer infused with lubricant. The high and medium frequency ranges of EIS results reflect the properties of porous layer infused with lubricant, and the low frequency range corresponds to the barrier layer properties. The properties of each part can be characterized by resistances and capacitances, in parallel and in series, describing their electronic and dielectric behaviors [33]. The equivalent circuit (Fig. 9a), which is proposed on the basis of equivalent circuit for aluminum oxide film [33], is utilized to model the electrochemical behavior of SLIPS in SRB medium. In this model, $R_e$ represents the electrolyte resistance, a parallel branch with resistance $R_w$ and the associate capacitance $C_w$ characterizes the walls of the porous aluminum oxide film, a parallel branch with resistance $R_t$ and the capacitance $C_t$ characterizes the lubricant infused in the porous aluminum oxide film, and a parallel branch with resistance $R_b$ and the associate capacitance $C_b$ characterizes the barrier layer of aluminum oxide film. To confirm that the circuit proposed is proper to simulate the EIS plots of SLIPS-coated aluminum, a preliminary simulation is carried out to analyse the EIS plots with circuit in Fig. 9a. Our primary analysis results (not shown here) indicate that the value of $R_w$ is extremely high because the thick walls of aluminum oxide layer prevent the passage of current [32]. Thus, equivalent circuit in Fig. 9a can be reduced to that shown in Fig. 9b. Considering the possible non-ideal capacitive behavior, constant phase element $Q$ is used to replace the all capacitances in Fig. 9a.

Table 2 shows the electrochemical parameters of SLIPS-coated aluminum after immersion in SRB medium for 1 and 7 days. The high resistance values of both barrier layer ($R_b$) and lubricant ($R_l$) indicate that the SLIPS can protect the underlying aluminum effectively. The resistance value of lubricant ($R_l$) slightly decreases from $8.42 \times 10^8$ Ω cm$^2$ to $5.47 \times 10^8$ Ω cm$^2$ with the increase of immersion time from 1 day to 7 days, but its value after immersion of 7 days ($5.47 \times 10^8$ Ω cm$^2$) is still much higher in comparison with charge-transfer resistance of bare aluminum ($3.33 \times 10^8$ Ω cm$^2$ in Table 1). It is indicated that the SLIPS present high stability in...
SRB medium. As shown in schematic diagram (Fig. 10), SLIPS are composed of aluminum oxide layer infused with stable lubricant layer. The lubricant with low surface energy can inhibit the penetration of water into the film. Furthermore, resistance of barrier layer to electrolyte penetration is also widely reported in the references about anodic aluminum oxide layer [33]. Thus, both barrier layer of aluminum oxide film and lubricant infused can effectively separate the aluminum substrate and corrosive medium, and the synergistic effect of the two layers are believed to intensify the barrier effect of SLIPS to the microbiological corrosion of aluminum substrate.

4. Conclusions

In our research, SLIPS fabricated on model engineering metal aluminum are demonstrated their great potential for inhibition of corrosion induced by SRB in marine environment. The SLIPS on aluminum are fabricated with three-step procedure, including construction of pillar-on-pore structure with anodization method, modification with fluorocarbon, and the subsequent infusion of fluorocarbon lubricants into the porous microstructure. The as-fabricated SLIPS not only depress the adherence of SRB, but also inhibit the erosion of corrosive medium to the underlying substrate. The special advantage of SLIPS for inhibition of SRB adherence is expected to originate from their “fluid” property and the low surface roughness. The synergistic effect of barrier layer of aluminum oxide film and the lubricant infused can intensify the barrier effect of SLIPS to the microbiological corrosion of aluminum substrate. It is believed that this research provides a novel and effective strategy for microbiological corrosion protection of metallic material in ocean.

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