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Investigations on reducing microbiologically-influenced corrosion of aluminum by using super-hydrophobic surfaces

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ABSTRACT

Electrochemical impedance spectroscopy, potentiodynamic polarization and scanning electron microscopy were carried out to determine the effect of super-hydrophobic surfaces on the marine bacterium *Vibrio natriegens* (*V. natriegens*) adhesion. Four different samples were prepared in order to investigate the anti-biocorrosion mechanism of super-hydrophobic surfaces. Potentiodynamic polarization suggested that the *V. natriegens* attached on the surface mainly enhanced the reaction kinetics of the anodic reaction and accelerated the dissolution of aluminum. EIS results were interpreted with different equivalent circuits to model the physicoelectric characteristics of the electrode/biofilm/solution interface. The results showed that neither anodization nor chemical modification could decrease the bacterial adhesion and corrosion rate individually. *V. natriegens* showed only weak attachment to the super-hydrophobic surface, and the biocorrosion mechanism was closely associated with surface energy and surface topography.

1. Introduction

Reports on cellular responses to topographical cues on both the nanometer and micrometer scales have increased in the past few decades [1–3]. Appropriately scaled nanotopographies have been shown to prevent cell attachment by prohibiting the formation of focal contacts [4]. Alternatively, cells can respond to microscale features by altering their shape, such as elongating along grooves [5,6]. The change in wettability of a surface that results from surface roughness, i.e., topography, is likely to be a contributing factor to these responses. Previous studies have focused on understanding the role of these cues in the attachment of algae and invertebrate shells to hydrophobic surfaces [7–9]. However, there is little known about bacterial adhesion. Bacterial adhesion and biofilm formation are commonly encountered in both natural environments and industrial processes, and microbially-influenced corrosion (MIC) is a serious problem due to safety and economic concerns. Therefore, it is very important to study the relation between hydrophobic surfaces and bioadhesion. In this study, *V. natriegens* was used due to its ubiquity in marine and estuarine environments and its strong vitality in both aerobic and anaerobic environments [10].

In our earlier work [11], the use of super-hydrophobic surfaces (hydrophobic surface with a water contact angle above ∼150° [12,13]) was proven to be a successful method for protecting against corrosion in sterile seawater. Inspired by that finding, the present work investigated the role of super-hydrophobic surfaces in bacterial adhesion and corrosion.

2. Experimental

2.1. Preparation of coupons

Pretreatment: The samples were annealed at 500 °C for 3 h to remove mechanical stress and then spontaneously cooled. Samples were sealed using a phenolic material before the experiments, leaving an exposed area of 10 mm × 10 mm on the material surface, which was polished with silicon carbide papers (from 400 to 1600 grade) and then degreased with acetone, washed with distilled water and dried. The natural oxide film on the aluminum sheet was dissolved in 1 mol/L sodium hydroxide for 2 min at 25 °C, followed by immersion in 1 mol/L nitric acid for 10 s to counteract remnant sodium hydroxide and washing in deionized water.

Anodization: The samples were anodized under a constant current of 0.32 A/cm^2 in 15 wt% sulfuric acid while the temperature was kept constant at 25 °C for 7 min. During this process, the electrolyte was vigorously stirred.

Chemical modification: Samples were chemically modified in 100 wt% melting myristic acid for 30 min at 70 °C, washed in ethanol at 70 °C, deionized in water and dried in an oven at 80 °C for 1 h.

In order to investigate effect of aluminum with a super-hydrophobic surface on marine bacterial adhesion, four different samples were used in our experiments:

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S_1: pretreatment
S_2: pretreatment + anodization
S_3: pretreatment + chemical modification
S_4: pretreatment + anodization + chemical modification

2.2. Bacterium isolation and incubation

A *V. natriegens* strain was isolated from plates of aluminum immersed in local seawater for 15 days. The marine isolate was scraped into sterile seawater from a layer of deposit on the metal surface. It was then incubated in Marine Postgate medium E for enrichment and subsequently purified in sterile agar plates by selecting several single colonies with a sterile inoculation loop. The isolated bacterium was characterized on the basis of 16S rRNA. The bacterium was cultured at 37 °C in a modified Postgate's C medium used for enrichment, which contained 35 g NaCl, 0.5 g KH_2PO_4, 0.06 g $CaCl_2{\cdot}6H_2O$, 2 g $MgSO_4{\cdot}7H_2O$, 1 g yeast extract, 0.004 g $FeSO_4{\cdot}7H_2O$ and 0.3 g sodium citrate in 1 L of deionized water. The medium was autoclaved at 121 °C and 20 psi for 15 min. After 4 days of incubation, the polished aluminum coupons were hung in the medium for the biocorrosion experiments.

2.3. Surface analysis

The contact angles were measured by a JC2000A CA system at ambient temperature, and the surface morphology measurements were carried out with scanning electron microscopy (SEM) (JEOL JSM-6700F).

2.4. Electrochemical measurements

The working cell was a standard three-electrode cell having a Pt net as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. All the measured potentials presented in the paper were referred to this electrode. The area of the working electrode was 1 cm^2. Prior to potentiodynamic polarization and electrochemical impedance spectroscopy measurements, 1 h of immersion was allowed to ensure steady-state conditions. During the measurements, the open circuit potential (OCP) values of different surfaces were recorded.

For potentiodynamic polarization experiments, the potential was scanned from −1.3 to +0.1 V at a scan rate of 2 $mV\,s^{-1}$.

Electrochemical impedance spectroscopy (EIS) was performed with an IM6 electrochemical workstation under an open circuit potential (OCP). The experimental temperature was kept at 25 °C. EIS measurements were performed in the frequency range between 10^{-2} and 10^5 Hz with a sine-wave amplitude of 10 mV. The experimental EIS spectra were interpreted on the basis of equivalent electrical analogs using the program Zview 2.0 to obtain the fitting parameters.

3. Results and discussion

The SEM and contact angle images of S_1–S_4 are shown in Fig. 1. The contact angles (CA) of S_1, S_2, S_3 and S_4 were 76°, 3°, 123° and 152° respectively. The variation of CA on the four surfaces was due to their different treatments and modifications. When the pretreated surface was only anodized in sulfuric acid, S_2 was super-hydrophilic, as the micro-pores on the anodized surface had an average diameter of 3 μm and could absorb water, causing it to spread on the surface. When the pretreated surface was only chemically modified by melting myristic acid, the CA of S_3 increased from 76° to 123°, clearly indicating that myristic acid may provide an opportunity to control the surface wettability of aluminum films. When the pretreated surface was first anodized and then chemically modified by melting myristic acid, S_4 had a super-hydrophobic

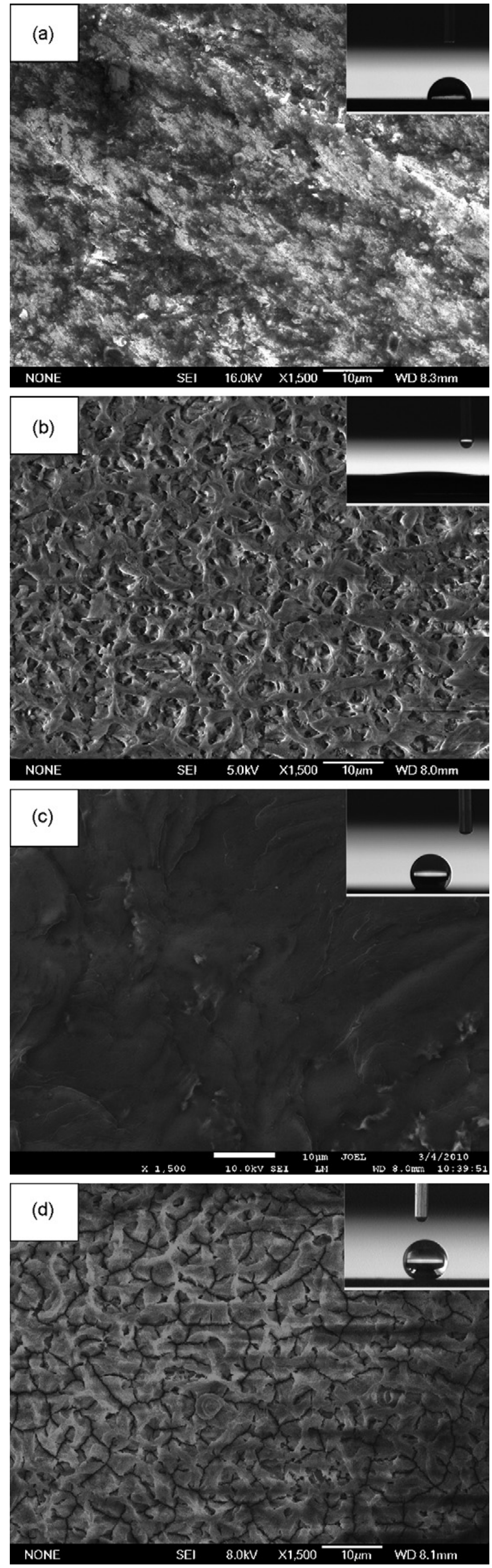

Fig. 1. SEM and contact angle images of: (a) S_1, (b) S_2, (c) S_3 and (d) S_4.