Corrosion inhibition by a superhydrophobic surface on aluminum that was prepared with a facile electrochemical route

X Q Du\textsuperscript{1} and Y Chen\textsuperscript{2} \textsuperscript{a}

\textsuperscript{1} School of Materials Science and Energy Engineering, Foshan University, Foshan, Guangdong 256600, People’s Republic of China
\textsuperscript{2} Department of Chemical Engineering and Safety, Binzhou University, Binzhou, Shandong 256600, People’s Republic of China

Keywords: corrosion, aluminum, superhydrophobic surface, electrodeposition

Abstract

A superhydrophobic surface featuring high roughness and low surface energy is designed for effective corrosion protection on aluminum via a facile and cost-effective electrochemical route. The effects of the electrolyte composition and electrodeposition time on the surface wettability were investigated. Moreover, the corrosion resistance performance of the as-prepared superhydrophobic aluminum surface was studied using electrochemical impedance spectroscopy and electrochemical noise techniques. The results show that the superhydrophobic aluminum surface obtained at 2 V for 20 min has a high static water contact angle of 155.8°. Both the average corrosion rate and pitting intensity are remarkably inhibited by the as-prepared superhydrophobic surface on aluminum. Moreover, the static water contact angle for the obtained superhydrophobic surface remains above 150° after exposure to 3.5 wt% NaCl solution for 30 days. This facile and economical superhydrophobic surface, with its excellent anti-corrosion property and stability, shows significant potential for use in industrial applications.

1. Introduction

Because of the excellent physical and mechanical properties, aluminum and its alloys have been widely used as construction materials in recent years. However, when exposed to aggressive media, especially chloride in the environment, aluminum and its alloys inevitably undergo serious corrosion, which considerably hinders their number of applications. Numerous efforts have been made to inhibit metal corrosion, including organic coatings [1–3], inhibitors [4, 5], cathodic protection [6] and surface modification [7]. Inspired by lotus leaves, a superhydrophobic surface with a water contact angle greater than 150° and rolling angle smaller than 10°, has attracted great attention over the past decades, because it presents significant potential in the fields of self-cleaning [8, 9], corrosion resistance [10–12], oil-water separation [13] and energy conservation [14].

Generally, the fabrication of superhydrophobic surfaces is based on two aspects. One is the presence of a rough surface at the micro/nano level, and the other is having a low surface energy. To date, various methods including chemical etching [15], sol-gel [16], electrodeposition [17–19] and chemical vapor deposition [20], have been explored to prepare superhydrophobic surfaces. Huang \textit{et al} [21] obtained superhydrophobic surfaces on an aluminum alloy through a chemical etching mechanism using 1 M NaOH solution and then passivated in a 0.01 M ethanolic stearic acid solution. Rezayi \textit{et al} [22] fabricated a superhydrophobic glass from a facile sol-gel-dip-coating method and the obtained superhydrophobic glass shows high transparency. Lu \textit{et al} [23] prepared a superhydrophobic film on aluminum with a simple anodization procedure followed by a fluorination treatment and the inhibition efficiency of this layer was 99.99%. Compared with these methods, the electrodeposition method exhibits some superiority, such as low cost, ease of realization without special equipment and easy reproducibility [24]. Liu \textit{et al} [18] created a superhydrophobic surface on AZ91D magnesium alloy by a nickel plating process and the contact angle reached 160.8°. Liu \textit{et al} [25] combined etching and calcination treatment processes to prepare superhydrophobic surfaces on copper and the synthesized superhydrophobic surface owned a contact angle of 157.6°. The superhydrophobic copper surface...
exhibited a persistent anti-corrosion performance in a 3.5 wt% NaCl solution. However, to the best of our knowledge, the electrodeposition voltages are usually as high as 20 V and the electrodeposition times are as long as 12 h, which inevitably causes serious waste of energy.

When placed in a chloride containing environment, aluminum and its alloys are apt to suffer serious localized corrosion. The localized corrosion behavior of aluminum and its alloys has been investigated for decades [26, 27]. Unfortunately, the pitting resistance performance of superhydrophobic aluminum surfaces is rarely reported. In the present work, a superhydrophobic aluminum surface is prepared with a facile one-step electrochemical method at a relatively low voltage (2 V). Scanning electron microscopy (SEM) and x-ray photoelectron spectroscopy (XPS) were used to characterize the superhydrophobic surface morphology and composition. Meanwhile, the anti-corrosion performance was evaluated using electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques. The results indicate the prepared superhydrophobic surface on aluminum has excellent anti-corrosion properties.

2. Experimental

2.1. Preparation of a superhydrophobic surface on aluminum
A superhydrophobic aluminum surface was fabricated through a DC electrodeposition method and the fabrication process is illustrated in figure 1. Briefly, aluminum samples (purity >99.9%, Shandong Kaiser Aluminum CO., Ltd) embedded in epoxy resin with working areas of 0.50 cm² were used as working electrodes. Prior to electrodeposition, the working surface was polished with SiC papers and alumina powder, degreased using acetone, rinsed with double distilled water, and finally dried with N₂. The electrodeposition electrolyte was composed of 0.05 M stearic acid and different concentrations of HCl. The conductivity of the as-prepared electrolyte was measured using a commercial conductivity meter (S230K, METTLER TOLEDO). The distance between the aluminum working electrode and Pt electrode was maintained 20 mm during the electrodeposition process.

2.2. Surface characterization
Contact angles (CAs) of the modified aluminum surface were measured using a JC2000A CA system at a room temperature of 20 °C with a 5.0 μl deionized water droplet. During the measurements, three different positions on the same sample were chosen, and each of the positions was tested at least five times to calculate the average value of the contact angle. Scanning electron microscopy (SU-8010) was employed to observe the surface morphologies of the modified aluminum samples. X-ray photoelectron spectra were recorded to study the aluminum surface composition using a VG ESCALAB MARK II spectrometer with the monochromatized Mg Kα radiation (1253.6 eV) at an operating energy of 50 eV. The characteristic peaks were all adjusted by fixing the C 1s band at 284.6 eV.

2.3. Anti-corrosion properties
Both the EIS and EN measurements were conducted using a classical three-electrode cell. The bare and superhydrophobic aluminum surface were used as the working electrodes. A platinum foil with large area and a saturated calomel electrode (SCE) connected through a salt bridge were used as the auxiliary and the reference electrode, respectively. Certain amount of analytical grade NaCl was dissolved into double distilled water to prepare the aggressive media of 3.5 wt% NaCl solution. EIS measurements were taken out using an impedance measurement unit (PARSTAT 2273) in a frequency range from 100 kHz to 10 mHz at the open circuit potential ($E_{ocp}$) and the sine amplitude perturbation was set at 5 mV. Prior to the EIS measurements, the aluminum
electrodes were immersed into 3.5 wt% NaCl solution for about 1 h to obtain a steady $E_{ocp}$. EIS data were fitted by the Z-View software. A commercial PowerLab coupled with GP Amp (ADInstruments Pty Ltd, Australia) was used to record the EN data with a sampling rate of 4 Hz. All the electrochemical tests were taken out in a quiescent solution and the experimental device was shielded in a Faradic cage. Each electrochemical measurement was repeated at least three times in parallel.

3. Results and discussion

Figure 2 depicts the dependence of the water contact angle and electrolyte conductivity on the HCl concentration at 2 V for 20 min. It is clear that the electrolyte composition has a significant effect on the water contact angle and electrolyte conductivity. With increasing HCl concentration from 0 to 0.025 M, the electrolyte conductivity increases from 0.8 to 1207 $\mu$S cm$^{-1}$. The high electrolyte conductivity will facilitate the ion transfer process and consequently increase the electrochemical reaction rate. The contact angle initially increases from 87.5° to 155.8° with the addition of HCl concentration from 0 to 0.015 M, and then decreases gradually with increasing HCl concentration from 0.015 M to 0.025 M. Xu prepared a superhydrophobic aluminum alloy film at 20 V in a mixture of ethanoic stearic acid and nickel nitrate hexahydrate [28]. The high voltage was also applied by Liu to fabricate a superhydrophobic copper surface in an electrolyte composed of ethanoic myristic acid and cerium chloride [29]. The superiority of employing a much lower voltage in this electrochemical process can be related to the addition of HCl in the electrolyte, which results in fast surface etching and a low potential drop between the aluminum and Pt electrodes. In most of the previous studies, chemical etching by an HCl solution has been explored as a pretreatment to create a micro-nano scale rough surface [12], whereas surface etching and electrochemical modification occur simultaneously in this work. Therefore, the contact angle reaches the highest value of 155.8° when 0.05 M stearic acid and 0.015 M HCl are mixed in the electrolyte.

The effect of electrodeposition time on the contact angle in the electrolyte containing 0.05 M stearic acid and 0.015 M HCl at 2 V was also investigated, and the results are shown in figure 3. It is apparent that the static water contact angles are only 115.6° and 129.2° when the electrodeposition times are 5 min and 10 min, respectively. The low contact angles at a short electrodeposition time may be related to insufficient surface etching on the aluminum. When prolonging the electrodeposition time to over 20 min, the contact angles exceed 150°, showing a good superhydrophobic property. The superhydrophobic aluminum surface in the following text no otherwise specified referred to the surface fabricated in the electrolyte containing 0.05 M stearic acid and 0.015 M HCl at 2 V for 20 min.

Figures 4(a) and (b) shows the morphologies of the bare and superhydrophobic aluminum surfaces. As seen, only some scratches that originate from the polishing process can be observed on the bare sample, whereas the superhydrophobic surface is much rougher and covered by leaf-like sheets of different sizes. The compact micro- and nanosheets adhered on the aluminum surface can gather considerable amounts of air and thus possess a superhydrophobic nature [30]. The chemical composition of the bare and superhydrophobic aluminum surface is depicted in figures 4(c) and (d). Compared with the bare sample, new characteristic peaks...
for C and O appear on the superhydrophobic surface. The existence of C and O may be related to the formation of $[\text{CH}_3(\text{CH}_2)_{16}\text{COO}]_3\text{Al}$ on the aluminum surface [31], suggesting the successful modification of the aluminum surface by stearic acid.

Figure 3 presents the XPS spectra of the superhydrophobic aluminum surface. From figure 5(a), two strong O 1s and C 1s peaks and another small Al 2p peak can be detected on the superhydrophobic aluminum surface. Two distinct peaks in the Al 2p spectra in figure 5(b) which are centered at 74.6 eV and 77.6 eV, are ascribed to

Figure 3. Contact angle as a function of electrodeposition time.

Figure 4. Surface microstructure of aluminum (a) Bare surface (b) Superhydrophobic surface and the EDS results of aluminum (c) Bare surface (d) Superhydrophobic surface.
The presence of Al–O and Al–OH, respectively [31]. The O 1s spectrum in figure 5(c) can be decomposed into three peaks. Two peaks located at 530.7 eV and 531.8 eV correspond to Al–O and Al–OH, respectively, which confirms the analysis of figure 5(b). Another peak at 532.5 eV corresponds to the adsorbed H2O and/or oxygen on the aluminum surface [32]. The main peak at 284.8 eV in figure 5(d) maybe due to the functional groups of C–C and C–H [33]. The other weak peak located at 288.4 eV is ascribed to the presence of C–O and C=O groups [33]. The above observations imply the formation of a thin film on the aluminum surface by stearic acid.

The corrosion resistance performance of the as-prepared superhydrophobic aluminum was first investigated using EIS. Bode and Nyquist plots for the corrosion of bare and superhydrophobic aluminum in a 3.5 wt% NaCl solution are shown in figure 6. The superhydrophobic modification of the aluminum surface has a remarkable effect on the corrosion resistance of aluminum in a 3.5 wt% NaCl solution. Apparently, both the impedance and radius of the Nyquist circle for the superhydrophobic aluminum surface increase significantly compared to that of the bare surface, suggesting that the corrosion of aluminum in a 3.5 wt% NaCl solution is strongly inhibited due to the superhydrophobic nature. It is worth noting that the centers of the Nyquist loops are all below the real axis, indicating a non-ideal electrochemical behavior at the aluminum/solution interface [34]. This phenomenon may be originated from the roughness and inhomogeneity of the aluminum surface [35]. From the method explored by Wit [36], the time-constant numbers in the EIS diagrams for the corrosion of both the bare and superhydrophobic aluminum in a 3.5 wt% NaCl solution can be determined. It is inferred that two capacitive loops and one inductive loop exist in the EIS diagrams. Briefly, one capacitive loop appearing in the high frequency domain is related to the charge transfer process [37]. The other semicircle located in the middle frequency domain is ascribed to the surface film capacitance. The inductive loop appearing in the low frequency domain can be related to the relaxation process of Clads or Hads on the aluminum surface [38]. Additionally, the shapes of the EIS diagrams for both the bare and superhydrophobic aluminum corrosion in a 3.5 wt% NaCl solution are similar, which means that the corrosion mechanism is not changed after the superhydrophobic modification of the aluminum surface [39].

The EIS data were quantitatively analyzed using Z-View software with the equivalent circuit shown in figure 7, in which Rs represents the solution resistance, Rf corresponds to the film resistance, Rct is the charge transfer resistance, and CPEf and CPEdl are the constant phase elements of the surface film and electric double layer, respectively. Notably, the constant phase element (CPE) is used in this equivalent circuit to replace the ideal double layer capacitance due to the surface roughness and irregularity of the aluminum. The CPE.

![Figure 5. XPS spectra of superhydrophobic aluminum surface: (a) survey spectrum, (b) Al 2p spectrum, (c) O 1s spectrum, (d) C 1s spectrum.](image-url)
impedance can be calculated using the following equation [40]:

$$Z_{CPE} = [Q(j\omega)^n]^{-1}$$  \hspace{1cm} (1)

where \( \omega \) is the angular frequency, \( Q \) is the modulus of the CPE, and \( n \) is the phase that represents the surface inhomogeneity [41].

The impedance parameters for the bare and superhydrophobic aluminum corrosion in a 3.5 wt% NaCl solution are summarized in Table 1. It is obvious that the values of both \( R_f \) and \( R_{ct} \) increase after the superhydrophobic modification of aluminum. The value of \( R_{ct} \) increases over 15 times than that of the bare surface, which reveals the enhanced corrosion resistance of superhydrophobic aluminum surface. Due to the superior water-repellency of superhydrophobic surface, the diffusion and penetration of \( \text{Cl}^- \) in the 3.5 wt% NaCl solution to the aluminum surface were strongly inhibited, resulting in a much smaller corrosion rate of the aluminum substrate.

EN technique is very powerful for characterizing corrosion types and provides deep insights into localized corrosion behavior. Figure 8 shows the electrochemical potential noise (EEN) data in the time domain for the corrosion of the bare and superhydrophobic aluminum surface in a 3.5 wt% NaCl solution. It is obvious that the different surface states of aluminum present different EEN features during its corrosion process. For the bare sample, the corrosion potential moves in the negative direction during the initial 15 min and then reaches a
relatively stable value. For the superhydrophobic sample, the corrosion potential initially drifts negatively, and then exhibits a positive tendency. The corrosion potential for the superhydrophobic surface always exhibits a positive value compared to that of the bare sample, suggesting the superhydrophobic surface is more thermodynamically stable. Moreover, it can also be seen that the electrochemical potential noise possesses large potential oscillation amplitude for the bare sample, whereas a small noise amplitude can be observed for the superhydrophobic surface. This phenomenon can be explained by the different pitting intensities of these two different surfaces, which will be investigated quantitatively in the following section.

The initial 5120 EN data points were analyzed with wavelet technique using orthogonal Daubechies wavelets (FWT) of the fourth order (db4) [42]; the obtained RP-EDP plot is shown in figure 9, in which different timescales correspond to different types of corrosion events. Generally, large timescales in a low frequency range are assigned to a slow phenomenon (e.g. general corrosion), whereas small timescales correspond to a relatively fast process (e.g. metastable pitting) [43]. The RP-EDP plot can be divided into three types according to previous studies [44–46]: (1) Region A between D1 and D3 in the high frequency domain represents a reasonably fast phenomenon, such as metastable pitting and nucleation process, (2) Region B between D3 and D6 corresponds to the pitting development or nucleus growth process, and (3) Region C between D6 and D8 at a relatively lower frequency range mainly characterizes a slow process, such as adsorption or diffusion process.

From figure 9, it can be seen that the relative energy mainly accumulates at large timescales in the low frequency domain (region C) for both the bare and superhydrophobic aluminum surfaces, indicating a predominance of localized corrosion during the initial immersion period. Rios et al [47] also observed this phenomenon when studying AISI1020 steel corrosion in seawater and found that the corrosion type changed from localized to general as the energy contribution of general corrosion increased with increasing immersion time in the EDP plots. Moreover, the parameters of corrosion active energy [46], which represent the electrochemical reaction rates, are employed to study the pitting behavior of bare and superhydrophobic aluminum surfaces. The corrosion active energy for the corrosion of the bare and superhydrophobic aluminum surfaces in a 3.5 wt% NaCl solution is shown in figure 10. $E_{D_1} + E_{D_2} + E_{D_3}$ is the energy accumulated in region A related to the metastable pitting rate, $E_{D_4} + E_{D_5} + E_{D_6}$ is the energy accumulated in region B corresponding to the pitting growth rate, $E_{D_7} + E_{D_8} + E_{D_9}$ represents the rate of pitting initiation and the

![Figure 8](image-url) Potential EN for the aluminum corrosion in a 3.5 wt% NaCl solution. (a) bare; (b) superhydrophobic surface.

| Surface       | CPE$_f$ $\mu$F cm$^{-2}$ | R$_f$ $\Omega \cdot$ cm$^2$ | CPE$_dl$ $\mu$F cm$^{-2}$ | R$_{ct}$ $\Omega \cdot$ cm$^2$ | R$_1$ $\Omega \cdot$ cm$^2$ | R$_2$ $\Omega \cdot$ cm$^2$ |
|---------------|---------------------------|-------------------------------|---------------------------|-------------------------------|-------------------------------|-------------------------------|
| Bare          | 10.9 ± 0.3                | 65.1 ± 1.6                    | 396 ± 8                   | 121 ± 4                       | 78 ± 2                        |
| Superhydrophobic | 5.9 ± 0.1                 | 625 ± 14                      | 219 ± 5                   | 1941 ± 35                     | 863 ± 21                      |

Table 1. Impedance parameters for the bare and superhydrophobic aluminum corrosion in a 3.5 wt% NaCl solution.
growth process, and \( E_{D_1} + E_{D_2} + E_{D_3} + E_{D_4} + E_{D_5} + E_{D_6} + E_{D_7} + E_{D_8} \) corresponds to the entire corrosion rate. A remarkable reduction in these corrosion active energies can be found for the superhydrophobic surface compared to those of the bare sample, indicating that the superhydrophobic aluminum surface has an improved pitting resistance. Therefore, from both the macro and micro scales, the average corrosion rate and pitting intensity have both been inhibited by the superhydrophobic structure on the aluminum surface.

The stability of the superhydrophobic aluminum surface is significantly important in practical applications. Thus, the variation in water contact angles of the superhydrophobic aluminum surface was measured when immersed into 3.5 wt% NaCl solution for different times and the results are presented in figure 11. Apparently, the water contact angle decreases gradually to 151.6° when exposed to 3.5 wt% NaCl solution for 20 days. After exposure for 30 days, the water contact angle remains above 150°, suggesting the long-term stability of the as-prepared superhydrophobic aluminum surface. EIS was also used to evaluate the corrosion resistance of the fabricated superhydrophobic aluminum surface when exposed to 3.5 wt% NaCl solution for different times, and the recorded Bode and Nyquist plots are presented in figure 12. It is clear that regardless of the exposure time, the EIS plots consist of two capacitive loops and one inductive loop. This result suggests that the corrosion mechanism on the superhydrophobic aluminum surface in a 3.5 wt% NaCl solution is maintained after exposed to 3.5 wt% NaCl solution for different times. The EIS data were also analyzed using the equivalent circuit shown in figure 7, and the calculated electrochemical parameters are summarized in table 2. The value of \( R_{ct} \) decreases slightly from 1941 \( \Omega \cdot \text{cm}^2 \) to 1496 \( \Omega \cdot \text{cm}^2 \) when immersed into 3.5 wt% NaCl solution from 1 day to 20 days.

Figure 9. RP-EDP generated during aluminum corrosion in a 3.5 wt% NaCl solution. (a) bare; (b) superhydrophobic surface.

Figure 10. The corrosion active energies for bare and superhydrophobic aluminum corrosion in a 3.5 wt% NaCl solution.
After exposure for 30 days, the value of $R_{ct}$ is still 9 times larger than that of the bare sample (Table 1). This phenomenon, from another point of view, demonstrates that the as-prepared superhydrophobic aluminum surface has excellent stability.

Figure 11. Contact angle variations of superhydrophobic aluminum surface in a 3.5 wt% NaCl solution for different exposing times.

Figure 12. Bode and Nyquist plots of superhydrophobic aluminum surface corrosion in a 3.5 wt% NaCl solution for different exposing times.
4. Conclusions

In this work, a superhydrophobic aluminum surface was successfully prepared by a facile and economical electrochemical route. The results suggested that the addition of HCl into the electrolyte had a significant effect on the surface wettability. The static water contact angle reached 155.8° when 0.015 M HCl was added into the electrolyte at 2 V for 20 min. Meanwhile, the results of the electrochemical measurements indicated that both the average corrosion rate and pitting intensity were considerably inhibited by the superhydrophobic structure on the aluminum surface. Moreover, the static water contact angle remained above 150° after exposure to 3.5 wt% NaCl solution for 30 days. Due to its excellent anti-corrosion property and stability, we believe that this simple and economical method for the preparation of superhydrophobic surfaces shows great potential for use in practical applications.

Acknowledgments

The authors wish to acknowledge the financial supports of the National Natural Science Foundation of China (Project 21403194, 51801013), the Natural Science Foundation of Shandong Province (ZR2019QEM003, 2019JICO20) and the Project of Focus on Research and Development Plan in Shandong Province (2019GSF110148).

ORCID iDs

Y Chen https://orcid.org/0000-0002-4169-039X

References

[1] Cui X, Zhu G, Pan Y, Shao Q, Zhao C, Dong M, Zhang Y and Guo Z 2018 Polydimethylsiloxane-titania nanocomposite coatings: fabrication and corrosion resistance Mat. Res. Express 12 116733
[2] Li M, Liu N, Chen J and Li Q 2019 Simple construction based on epoxy-bonded superhydrophobic anti-corrosion coating J. Taiwan Inst. Chem. E 95 682–91
[3] He Y, Dobryden I, Pan J, Ahmiyaz A, Deltin T, Corkery R W and Claesson P M 2018 Nano-scale mechanical and wear properties of a waterborne hydroxyacrylic-melamine anti corrosion coating Appl. Surf. Sci. 457 546–58
[4] Albini M, Letardia P, Mathys L, Brambilla L, Schröter J, Junier P and Joseph E 2018 Comparison of a bio-based corrosion inhibitor versus benzo triazole on corroded copper surfaces Corros. Sci. 143 84–92
[5] Alvarez P E, Fiori-Bimbi M V, Neske A, Brandán S A and Gervasi C A 2018 Rollinia occidentalis extract as green corrosion inhibitor for carbon steel in HCl solution J. Ind. Eng. Chem. 58 92–9
[6] Dai M, Liu J, Huang F, Zhang Y and Cheng Y F 2018 Effect of cathodic protection potential fluctuations on pitting corrosion of 100 pipeline steel in acidic soil environment Corros. Sci. 143 428–37
[7] González Gutiérrez A G, Sebastian P J, Magallón Cacho L, Berza Arco E, Campos J and Baron A 2018 Surface modification of aluminum alloy 6061 for bipolar plate application: adhesion characteristics and corrosion resistance Int. J. Electrochem. Sci. 13 3958–69
[8] Li S, Page K, Sathasivam S, Heale F, He G, Lu Y, Lai Y, Chen G, Carmalt C J and Parkin I P 2018 Efficiently texturing hierarchical superhydrophobic fluoride-free translucent films by AACVD with excellent durability and self-cleaning ability J. Mater. Chem. A 6 17633–41
[9] Roslizar A, Dottermusch S, Vüllers F, Kavalenka M N, Guttmann M, Schneider M, Paetzold U W, Hölscher H, Richards B S and Klampaftis E 2019 Self-cleaning performance of superhydrophobic hot-embossed fluoropolymer films for solar photovoltaic modules Sol. Energy Mat. Sol. C 188 96
[10] Cheng Y, Wu B, Ma X, Lu S, Xu W, Szunerits S and Boukherroub R 2018 Facile preparation of high density polyethylene superhydrophobic/superoleophilic coatings on glass, copper and polyurethane sponge for self-cleaning, corrosion resistance and efficiency oil/water separation J. Colloid Interf. Sci. 525 76–85
[11] Li D, Wang H, Luo D, Liu Y, Han Z and Ren L 2018 Corrosion resistance controllable of biomimetic superhydrophobic microstructured magnesium alloy by controlled adhesion Surf. Coat. Tech. 347 173–80
[12] Wang H, Di D, Zhao Y, Yuan R and Zhu Y 2019 A multifunctional polymer composite coating assisted with pore-forming agent: preparation, superhydrophobicity and corrosion resistance Prog. Org. Coat. 132 370–8

Table 2. Impedance parameters for superhydrophobic aluminum surface corrosion in a 3.5 wt% NaCl solution for different exposing times.

| Time/day | CPEf $\mu F$ cm$^{-2}$ | $R_1$ $\Omega$ cm$^2$ | CPEdl $\mu F$ cm$^{-2}$ | $R_{ct}$ $\Omega$ cm$^2$ | $R_1$ $\Omega$ cm$^2$ |
|----------|--------------------------|----------------------|--------------------------|----------------|------------------|
| 1        | 5.9 ± 0.1                | 625 ± 14             | 219 ± 5                  | 1941 ± 35    | 863 ± 21         |
| 10       | 8.4 ± 0.2                | 588 ± 7              | 254 ± 6                  | 1692 ± 14    | 752 ± 16         |
| 20       | 6.9 ± 0.1                | 516 ± 9              | 271 ± 4                  | 1496 ± 22    | 689 ± 10         |
| 30       | 9.7 ± 0.2                | 562 ± 11             | 257 ± 8                  | 1359 ± 27    | 625 ± 12         |
[13] Yang Y, Li X, Zheng X, Chen Z, Zhou Q and Chen Y 2018 3D-printed biomimetic super-hydrophobic structure for microdroplet manipulation and oil/water separation Adv. Mater. 30 1704912
[14] Guo X, Lai C, Jiang X, Mi W, Yin Y, Li X and Shu Y 2018 Remarkably facile fabrication of extremely superhydrophobic high-energy binary composite with ultralong lifespan Chem. Eng. J. 335 843–54
[15] Qian B T and Shu Z Q 2005 Fabrication of superhydrophobic surfaces by diocation-selective chemical etching on aluminum, copper and zinc substrates Langmuir 21 9007–9
[16] Wu X, Zheng L and Wu D 2005 Fabrication of superhydrophobic surfaces from microstructured ZnO-based surfaces via a wet-chemical route Langmuir 21 2665–7
[17] Xu X, Zhu L, Li W and Liu H 2011 A variable hydrophobic surface improves corrosion resistance of electroplating copper coating Appl. Surf. Sci. 257 5524–8
[18] Liu Y, Yin X, Zhang J, Yu S, Han Z and Ren L 2014 A electro-deposition process for fabrication of biomimetic super-hydrophobic surface and its corrosion resistance on magnesium alloy Electrochim. Acta 125 395–403
[19] Xiang T, Ding S, Li C, Zheng S, Hu W, Wang J and Liu P 2017 Effect of current density on wettability and corrosion resistance of superhydrophobic nickel coating deposited on low carbon steel Mater. Design 114 65–72
[20] Zhang R, Cai S, Xu G, Zhao H, Li Y, Wang X, Huang K, Ren M G and Wu X D 2014 Crack self-healing of phytic acid conversion coating on AZ31 magnesium alloy by heat treatment and the corrosion resistance Surf. Sci. 631 896–904
[21] Huang Y, Sarkar D K and Chen X G, 2015 Superhydrophobic aluminum alloy surfaces prepared by chemical etching process and their corrosion resistance properties Appl. Surf. Sci. 356 1012–24
[22] Rezayi T and Entezari M H 2015 Achieving to a superhydrophobic glass with high transparency by a simple sol-gel-dip-coating method Surf. Coat. Tech. 276 557–64
[23] Lu Z, Wang P and Zhang D 2015 Super-hydrophobic film fabricated on aluminum surface as a barrier to atmospheric corrosion in a marine environment Corros. Sci. 91 267–96
[24] Wang H, Zhu Y, Hu Z, Zhang X, Wu S, Wang R and Zhu Y 2016 A novel electrodeposition route for fabrication of the superhydrophobic surface with unique self-cleaning, mechanical abrasion and corrosion resistance properties Chem. Eng. J. 303 37–47
[25] Liu W, Xu Q, Han J, Chen X and Min Y 2016 A novel combination approach for the preparation of superhydrophobic surface on copper and the consequent corrosion resistance Corros. Sci. 110 105–13
[26] Solits J 2015 Passivity breakdown, pit initiation and propagation of pits in metallic materials—review Corros. Sci. 90 5–22
[27] Boinovich L B, Emelyanenko A M, Mostovskov A D, Domantowsky A G and Emelyanenko K A 2015 Synergistic effect of superhydrophobicity and oxidized layers on corrosion resistance of aluminum alloy surface textured by nanosecond laser treatment ACS Appl. Mater. Interfaces 7 19500–8
[28] Xu N, Sarkar D K, Chen X-G and Tong W P 2016 Corrosion performance of superhydrophobic nickel stearate/nickel hydroxide thin films on aluminum alloy by a simple one-step electrodeposition process Surf. Coat. Tech. 302 173–84
[29] Liu Y, Liu, Zhang J, Liu J, Han Z and Ren L 2015 Corrosion inhibition of biomimetic super-hydrophobic electrodeposition coatings on copper substrate Corros. Sci. 94 190–6
[30] Wang Y, Wang W, Zhong L, Wang J, Jiang Q and Guo X 2010 Superhydrophobic surface on pure magnesium substrate by wet chemical method Appl. Surf. Sci. 256 3837–40
[31] He T, Wang Y, Zhang Y, Lv Q, Xu T and Liu T 2009 Superhydrophobic surface treatment as corrosion protection for aluminum in seawater Corros. Sci. 51 1577–61
[32] Huang X, Li N, Wang H, Sun H, Sun S and Zheng J 2008 Electrodeposited cerium film as chromate replacement for tinplate Thin Solid Films 516 1037–43
[33] QIng Y, Yang C, Zhao Q, Hu C and Liu C 2017 Simple fabrication of superhydrophobic/superoleophobic surfaces on copper substrate by two-step method J. Alloys. Compd. 695 1878–83
[34] Amin M A, Abd El-Rehim S S, El-Sherbini E E and Bayomy R S 2007 The inhibition of low carbon steel corrosion in hydrochloric acid solutions by succinic acid: I. Weight loss, polarization, EIS, PZC, EDX and SEM studies Electrochim. Acta 52 3588–600
[35] Zhang K, Xu B, Yang W, Yin X, Liu Y and Chen Y 2015 Halogen-substituted imidazole derivatives as corrosion inhibitors for mild steel in hydrochloric acid solution Corros. Sci. 90 284–95
[36] Campestrini P, van Westing E P M and de Wit H J H 2001 Influence of surface preparation on performance of chromate conversion coatings on Alclad 2024 aluminium alloy: II. EIS investigation Electrochim. Acta 46 2631–47
[37] Nasser A A and Anvar Salih M 2017 Comparative study of N-[4-(methylamino)phenyl] (methyl-4-yl) acetamide (MMPA) and N-[methyl-4-yl(phenyl)methyl] acetamide (MPA) as corrosion inhibitors for mild steel in sulfuric acid solution Arab. J. Chem. 10 S261–73
[38] Veloz M A and Gonzalez I 2002 Electrochemical study of carbon steel corrosion in buffered acetic acid solutions with chlorides and H2S Electrochim. Acta 48 135–44
[39] Li X, Xie X, Deng S and Du G 2015 Inhibition effect of two mercaptopyrimidine derivatives on cold rolled steel in HCl solution Corros. Sci. 92 136–47
[40] Popova A, Sokolova E, Raicheva S and Christov M 2003 AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives Corros. Sci. 45 33–58
[41] Zarrouk A, Hammouti B, Lakhlit T, Traisnel M, Vezin H and Bentiss F 2015 New 1H-pyrrole-2,5-dione derivatives as efficient organic inhibitors of carbon steel corrosion in hydrochloric acid medium: electrochemical, XPS and DFT studies Corros. Sci. 90 572–84
[42] Huang X, Chen Y, Fu T W, Zhang Z and Zhang J Q 2013 Study of tin electroplating process using electrochemical impedance and noise techniques J. Electrochem. Soc. 160 D530–6
[43] Cao H F, Zhang Z, Su J X and Shi Y Y 2006 Electrochemical noise analysis of LY12–T3 in EXCO solution by discrete wavelet transform technique Electrochim. Acta 51 1359–64
[44] Chen Y, Chen X H, Liu Y W, Zhang X H, Xie Y, Yang Z N and Zhang Z 2018 Evaluation of physical and chemical adsorption using electrochemical noise technique for methylene blue on mild steel J. Chem. Thermodyn. 126 147–59
[45] Liu Y W, Chen Y, Chen X H, Yang Z N, Xie Y and Zhang Z 2018 Study on adsorption behavior of ketocoumaron on Q235 mild steel in 1.0 M HCl solution with electrochemical measurement J. Alloy. Compd. 758 184–93
[46] Chen Y, Chen X H, Yang Z N, Liu Y W, Zhang H H, Yin J Y and Zhang Z 2017 In-situ monitoring the inhibition effect of benzotiazole on copper corrosion by electrochemical noise technique J. Taiwan Inst. Chem. Environ. Sci. 80 908–14
[47] Rios E C, Zimer A M, Pereira E C and Mascaro L H 2014 Analysis of AISI 1020 steel corrosion in seawater by coupling electrochemical noise and optical microscopy Electrochim. Acta 124 211–7