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Superhydrophobic aluminum alloy surfaces prepared by chemical etching process and their corrosion resistance properties

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Highlights

1. Fabrication of superhydrophobic aluminum alloy surfaces by chemical etching followed by organic molecule passivation.

2. The formation of flake-like micro-nanostructure morphology of the low surface energy aluminum stearate on aluminum.

3. The complementary corrosion studies by polarization resistance and electrochemical impedance spectroscopy (EIS).

4. The modulus of impedance is found to be 70 times larger for the superhydrophobic surfaces compared to the as-received aluminum alloy surface.
ABSTRACT

Superhydrophobic aluminum alloy surfaces are obtained by chemical etching using 1 M NaOH solution followed by passivation using 0.01 M ethanolic stearic acid (SA) solution. The formation of low surface energy aluminum stearate takes place during the passivation process between stearic acid and hydroxyl group terminated aluminum alloy surfaces. A schematic model of the SA passivation process on the –OH terminated Al-surfaces is presented in this work. The flake-like micro-nanostructure morphology of the low surface energy aluminum stearate increases the water contact angle by more than 150°, demonstrating the superhydrophobic properties. The corrosion current density reduces and polarization resistance increase systematically with increasing passivation time. The polarization resistance, calculated from the Tafel curve of the superhydrophobic surfaces prepared by stearic acid passivation for 60 min, is determined to be 137 times larger than that of the as-received aluminum alloy substrate. Similarly, the modulus of impedance, as determined from electrochemical impedance spectroscopy (EIS), is found be 70 times larger for the superhydrophobic surfaces compared to the as-received aluminum alloy surface. These results demonstrate that the superhydrophobic aluminum alloy surfaces created by chemical etching followed by passivation have superior corrosion resistance properties than the as-received aluminum alloy substrate.

Keywords: Corrosion resistance, Superhydrophobic aluminum alloy surfaces, Chemical etching,
1. Introduction

Superhydrophobicity is the property that describes the non-wetting characteristics of material surfaces. Superhydrophobic surfaces are attracting ever increasing attention from the scientists and engineers due to wide applications in corrosion resistance and anti-sticking of snow and ice and potential incorporation into eyeglasses, windows, self-cleaning automobile windshields, and other technologies [1-3]. Recently, various fabrication methods for superhydrophobic surfaces have been explored [4-16]. These methods are guided by the common principles of optimizing topography and lowering surface energy. In other words, both the surface geometrical structure and the chemical composition control the wettability of the solid surface.

Chemical etching process is the process of removing a layer on a metal surface through a chemical reaction and is an effective method for obtaining rough surfaces. It has been widely used to fabricate superhydrophobic aluminum alloy surfaces [6, 7, 17-21]. Sarkar et al. obtained superhydrophobic aluminum surfaces by chemical etching followed by coating with an ultrathin rf-sputtered Teflon film [14]. Saleema et al. used a one-step etching process to obtain a superhydrophobic aluminum alloy substrate with a NaOH and fluoroalkylsilane (FAS-17) mixed solution [6, 7]. Ruan et al. utilized HCl mixed with HF as an etchant on an aluminum alloy substrate followed by passivation with different modifiers such as dodecyl mercaptan (DDM), lauric acid, myristic acid and palmitic acid [17]. Similarly, HCl was also used by Escobar et al.
in a chemical etching process, together with passivation employing dodecaneoic acid, to obtain superhydrophobic aluminum alloy substrates [18]. In addition, Liao et al. fabricated superhydrophobic aluminum alloy substrates by copper assisted chemical etching with HCl solution followed by passivation with hexadecyltrimethoxysilane [19].

A number of investigations have been performed on other superhydrophobic surfaces (apart from aluminum alloy substrates) obtained by chemical etching, such as superhydrophobic silicon etched by HF mixed with AgNO₃ followed by passivation with trimethoxysilane [22], superhydrophobic titanium etched by NaCl followed by passivation with tridecafluoroctyltriethoxysilane [23], superhydrophobic zinc (Zn) etched by NaCl/NaNO₃ followed by passivation with fluorinated polymer [24], superhydrophobic magnesium etched by H₂SO₄/H₂O₂ followed by passivation with stearic acid (SA) [25] and superhydrophobic copper etched by HNO₃ followed by passivation with 1H,1H,2H,2H-perfluorodecyltriethoxysilane (FDTES) [26].

It is well known that the contact of metals with water triggers corrosion; therefore, one may consider using superhydrophobic surfaces to repel water and thus prevent corrosion. The corrosion resistance properties of superhydrophobic aluminum alloy substrates have been studied in the literature [3, 27-29]. He et al. investigated the corrosion resistance of superhydrophobic aluminum alloy substrates, prepared by anodizing followed by passivation with myristic acid, via potentiodynamic polarization experiments as well as electrochemical impedance spectroscopy (EIS) [3]. A similar method for preparing superhydrophobic aluminum alloy substrates has also been used by Liu et al., and the reduced microbiologically influenced corrosion of superhydrophobic
aluminum alloy substrates was investigated using EIS, polarization as well as scanning electron microscopy (SEM) [28]. Furthermore, Liang et al. developed a facile sol–gel method, with tetraethylorthosilicate (TEOS) and vinyltriethoxysilane (VTES) as co-precursors at room temperature, to create a superhydrophobic aluminum alloy substrate [27], the authors then characterized the corrosion resistance and durability of the superhydrophobic silica-based surface formed on the aluminum substrate in a corrosive NaCl solution via EIS measurements [27]. In another study by Liu et al. [29], the corrosion resistance properties of a superhydrophobic aluminum alloy substrate, fabricated by graphene spin-coated on the surface, were investigated and compared with those of the as-received aluminum alloy substrate.

In our previous study, superhydrophobic copper surfaces were fabricated by a one-step electrochemical modification process with ethanolic stearic acid solution using a DC voltage [13]. Furthermore, the corrosion resistance of the superhydrophobic copper substrates was investigated by potentiodynamic polarization experiments [30]. The decrease of corrosion current density ($I_{corr}$) as well as the increase of polarization resistance ($R_p$) obtained from the polarization curves revealed that the superhydrophobic film on the copper surfaces improved the corrosion resistance of the copper substrate. In a recent study from our group, anti-corrosion and anti-icing superhydrophobic steel coatings were achieved by electrodeposition of Zn on steel followed by functionalization of Zn using an ultra-thin film of commercial silicone polymer [31].

In the present study, superhydrophobic aluminum alloy substrates were prepared by chemical etching using alkaline NaOH solution followed by passivation with ethanolic stearic acid (SA) solution. Chemical etching has the technological advantages of being both cost-effective and easy to
scale up. The fabricated superhydrophobic aluminum alloy substrates were analyzed using both potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) to evaluate their corrosion properties.

2. Experiments

As starting materials, rolled sheets of AA 6061 aluminum alloy were chemically etched using 1 M alkaline NaOH solution (pH of 14) in an ultrasonic bath. After cleaning with distilled water, the etched aluminum alloy substrate was dried at 70 °C in a closed oven for more than 10 hr. The passivation process was performed by immersing the etched aluminum alloy substrate at room temperature in 0.01 M ethanolic SA solution for a range of passivation times. The morphological analyses of the samples were performed using a scanning electron microscope (SEM, JEOL JSM-6480 LV). The chemical composition of surfaces was analyzed by X-ray diffraction (XRD, D8 discover with Cu K$_\alpha$ wavelength 0.154 nm), Fourier Transform Infrared spectroscopy (FTIR, Perkins Elmer Spectrum One) and x-ray photoelectron spectroscopy (XPS, VG ESCALAB 220iXL). The XPS spectra were collected using an Al K$_\alpha$ (1486.6 eV) x-ray source. The wetting characterization of the sample surfaces was carried out by measuring static and dynamic contact angles using a First Ten Angstrom contact angle goniometer (the static contact angle has been abbreviated as CA and the dynamic contact angle has been abbreviated as contact angle hysteresis (CAH)). The adhesion of the superhydrophobic aluminum alloy substrates was carried out according to the ASTM D3359 standard test method using a Cross Hatch Cutter, model Elcometer.
107. The corrosion resistance properties of the samples were investigated via both potentiodynamic polarization experiments as well as electrochemical impedance spectroscopy (EIS). Electrochemical experiments were performed using a PGZ100 potentiostat and a 300 cm$^2$ EG&G PAR flat cell (London Scientific, London, ON, Canada), equipped with a standard three-electrode system with an Ag/AgCl reference electrode, a platinum (Pt) mesh as the counter electrode (CE), and the sample as the working electrode (WE) [6]. For the potentiodynamic polarization experiments, the open-circuit potential was scanned from -250 mV to +1000 mV in a 3.5 wt.% NaCl solution. An attempt was made to perform EIS measurements using 3 wt.% NaCl, as 3.5 wt.% was more reactive, in the frequency ranges between 0.01 Hz and 100 kHz with a sine-wave amplitude of 10 mV at room temperature.

3. Results and Discussion

3.1 Superhydrophobic aluminum alloy surfaces prepared by chemical etching followed by SA passivation

Figure 1(a) shows the SEM image of the surface of an as-received aluminum rolled sheet, which had a surface root-mean-square (rms) roughness of 0.45 µm and water contact angle (CA) of 87 ± 3° (inset of the Figure). The surface of rolled aluminum sheets generally exhibits the rolled lines and therefore will have a certain inherent roughness [32]. The CA of the SA passivated aluminum alloy substrate was found to be only 110 ± 1°. Therefore, a pretreatment of chemical etching using a 1 M alkaline NaOH solution was performed to modify the surface of the as-received aluminum alloy substrate. The morphology of the etched aluminum alloy substrate is shown in
Figure 1(b). The NaOH etched aluminum alloy substrate (Figure 1(b)) was found to be rougher compared with the as-received aluminum alloy substrate (Figure 1(a)). Consequently, the surface roughness of the etched aluminum alloy substrate was increased to $1.38 \pm 0.17 \, \mu m$ from $0.45 \pm 0.03 \, \mu m$ of the as-received aluminum alloy substrate. The CA on the NaOH etched aluminum alloy substrate was decreased to $34 \pm 4^\circ$, which can be attributed to the increase of surface area as well as the possible change of surface composition. The Wenzel model and its mathematical equation (Equation (1)) [33] can be used to explain the decrease of CA assuming no change of surface composition due to chemical etching.

$$\cos \theta^* = R_w \cos \theta$$

(Equation 1)

where $\theta^*$ is the CA of a smooth surface and $\theta^*$ is the CA of a rough surface without any alteration of surface composition, the roughness factor $R_w$ is the ratio of the true to the apparent surface areas. It is evident that $R_w$ is always more than 1 as true surface area is larger than the apparent surface area due to the presence of roughness; therefore, as the CA of the as-received aluminum alloy substrate (assumed to be smooth) is $87 \pm 3^\circ$, the CA of the etched rough surface would be smaller than $87 \pm 3^\circ$. As the CA of the NaOH etched aluminum alloy substrate was $34 \pm 4^\circ$, the $R_w$ associated with the roughness of the etched substrate was calculated to be 15.84. However, it was not evident from the surface morphology that the surface area of the etched substrate could be 15 times more than that of as-received aluminum alloy. Therefore, the change of chemical composition due to the chemical etching process also played a role in the change of CA on the etched aluminum
alloy substrate. We will see further that the SA passivation can modify the morphology of the NaOH etched aluminum alloy substrate but is unable to modify the as-received aluminum alloy substrate, which may due to the surface composition of the latter.
Figure 1 SEM images of the surface of (a) as-received aluminum alloy substrate; (b) NaOH etched aluminum alloy substrate; (c-e) 5 s-, 1 min- and 24 min-SA passivated NaOH etched aluminum alloy substrates. The insets of Figure 1(a-e) show the water drops and CA on the respective surfaces.

The NaOH etched aluminum alloy substrate was then passivated by SA for a range of passivation times varying from couple of seconds to a maximum of an hour. Figure 1(c-e) shows the morphologies of the NaOH etched aluminum alloy substrates followed by SA passivation for 5 s, 1 min and 24 min. The flake-like micro-nanostructure features appeared on the etched surface after SA passivation for 5 s as shown in Figure 1(c). The inset of Figure 1(c) shows the image of a water drop with a CA of $145 \pm 2^\circ$. The enhancement of the CA was due to the formation of low surface energy aluminum stearate (AlSA). The chemical analysis of these flake-like molecules is given in Figure 2(a). The number density of these flake-like micro-nanostructures increased by increasing the SA passivation time to 1 min, as shown in Figure 1(d). Consequently, the surface of etched substrate is nearly covered with these flake-like structures just after 1 min of SA passivation. In this
situation, the CA of this surface further increased to 154 ± 2°, as shown in the inset of Figure 1(d).

The compactness of these structures was further increased on the surface by increasing the SA passivation time to 24 min, as shown in Figure 1(e). However, the CA did not increase much as shown in the inset of Figure 1(e), yielding a value of 155 ± 1°. Because the surface morphology from 60 min-SA passivation on etched aluminum alloy is very similar to that from 24 min-SA passivation, the SEM image of that surface is not presented.

Figure 2(a) FTIR spectra of (a0) as-received aluminum alloy substrate, (a1) NaOH etched aluminum alloy substrate, and (a2) 5 s-, (a3) 1 min-, (a4) 24 min- and (a5) 60 min-SA passivated NaOH etched aluminum alloy substrates. Figure 2(b) depicts the variation in the area under the hydrocarbon (–CH₂ and -CH₃) peaks as a function of the SA passivation time.

The infrared spectra of the as-received aluminum alloy substrate, the NaOH etched aluminum alloy substrate, and the SA passivated NaOH etched aluminum alloy substrates for a range of passivation times are shown in Figure 2(a). The four main infrared absorption zones were observed in all spectra. These zones are (i) a broad absorption peak between 3000-3500 cm⁻¹, (ii) two sharp
absorption peaks at 2856 and 2917 cm\(^{-1}\), (iii) an absorption zone approximately 1500 cm\(^{-1}\), and (iv) a peak approximately 750 cm\(^{-1}\). The broad absorption peak at 3420 cm\(^{-1}\) in zone (i) is assigned to –OH bonding on the NaOH etched aluminum alloy substrate, as shown in Figure 2(a1). As is evident in comparing with the spectrum of the as-received aluminum alloy substrate (Figure 2(a0)), the presence of –OH bonding at the surface of the NaOH etched aluminum alloy substrate may be due to possible –OH bond formation during the reaction of NaOH with the aluminum alloy substrate, as shown below using Equations (2-5):

\[
2\text{Al} + 2\text{NaOH} + 6\text{H}_2\text{O} \rightarrow 2\text{NaAl}(-\text{OH})_4 + 3\text{H}_2
\]  
\text{(Equation 2)}

\[
\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAlO}_2 + \text{H}_2\text{O}
\]  
\text{(Equation 4)}

\[
\text{NaAlO}_2 + \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NaOH}
\]  
\text{(Equation 5)}

A similar reaction mechanism based on Equations 2 and 3 have been presented by Saleema et al. [6], who studied how to obtain superhydrophobic properties through a one-step process on aluminum alloy substrates using an alkaline NaOH solution containing FAS-17 molecules. However, they did not specify that the sodium aluminate (NaAlO\(_2\)) further hydrolyzed in the continuing reaction to produce Al(OH)\(_3\) and NaOH. Furthermore, the presence of native oxides on aluminum alloy substrates most likely consists of aluminum oxide (Al\(_2\)O\(_3\)). Al\(_2\)O\(_3\) on the surface of the aluminum alloy substrate can react with NaOH and form sodium aluminate (NaAlO\(_2\)), which can then hydrolyze to Al(OH)\(_3\) and NaOH, as presented in Equation 4-5. Therefore, the above
chemical reactions show that the aluminum alloy substrates will be covered with a layer of Al(OH)$_3$ after chemical etching with NaOH. Evidently, the appearance of the –OH peak in the IR spectrum (Figure 2(a1)) of the NaOH etched aluminum alloy substrate is in good agreement with the chemical reactions.

It was observed from the IR spectra of Figure 2(a) that the intensity of the –OH peak increased with the time of SA passivation. The formation of aluminum stearate (AISA) (CH$_3$(CH$_2$)$_{16}$COOAl(OH)$_2$) (in Equation 6) as a reaction product between Al(OH)$_3$, present on the aluminum alloy substrates after NaOH etching, and SA was what led to the enhancement of the –OH peak after SA passivation (Figure 2(a2-a5)). The schematic illustration of the formation of AISA on NaOH etched aluminum alloy substrates, engrafted with Al(OH)$_3$, is shown in Figure 3.

$$\text{Al(OH)}_3 + \text{CH}_3\text{(CH}_2\text{)}_{16}\text{COOH} \rightarrow \text{CH}_3\text{(CH}_2\text{)}_{16}\text{COOAl(OH)}_2 + \text{H}_2\text{O} \quad \text{(Equation 6)}$$

Figure 3 Schematic illustration of the formation of the superhydrophobic surface prepared by SA passivation on NaOH etched aluminum alloy substrate.
It should be mentioned that, the appearance of –OH bonding on the NaOH etched aluminum alloy substrate is responsible for the formation of a superhydrophobic aluminum alloy substrate. However, the as-received aluminum alloy substrate without –OH bonding was unable to be passivated by SA solution, where it shows a maximum CA of 110 ± 1°.

Furthermore, the peaks at 414, 536 and 607 cm\(^{-1}\) in zone (iv) may have appeared due to the Al-O bonding. The peaks at 1582 cm\(^{-1}\) in zone (iii) as well as 750 cm\(^{-1}\) in zone (iv) have also been assigned to the bending absorption mode of –OH, and the intensity of the peaks was also found to increase with the SA passivation time. The increasing intensity of the –OH peak as well as –CH\(_2\) bonding with increasing passivation time indicate that greater AlSA formation took place, or, in other words, more amounts of SA molecules were adsorbed on the NaOH etched aluminum alloy substrates during the passivation process. Furthermore, in zone (iii), the infrared absorption peaks at 1586 and 1466 cm\(^{-1}\) were arising from –COOAl bonding; these peaks are more distinct on the IR spectrum of the samples passivated for 24 min (Figure 2(a5)). This is also in line with the analysis from SEM images (Figure 1(c-e)), where an increasing SA passivation time led to a thicker deposition of flake-like micro-nanostructures.

Compared with the –COOZn bonding at 1550 cm\(^{-1}\) presented in our recent publication on the superhydrophobic aluminum alloy substrate by SA-functionalized ZnO nanoparticles [32], the –COOAl bonding has shifted towards higher a wavenumber of 1586 cm\(^{-1}\) due to the lower atomic number of Al compared to that of Zn.

In addition, the two main sharp absorption peaks in zone (ii), which appeared at 2917 and 2851 cm\(^{-1}\)
are ascribed to the asymmetric, symmetric C-H stretching modes, respectively, of –CH\textsubscript{2} groups on the AISA molecules. Additionally, a very small peak at 2956 cm\textsuperscript{-1} was present in the spectrum due to the asymmetric in-plane C-H stretching mode of the –CH\textsubscript{3} group on the AISA molecules. The presences of absorption bands from –OH, –COO\textsubscript{Al}, -CH\textsubscript{2} as well as –CH\textsubscript{3} confirmed the engrafting process of SA on NaOH etched aluminum alloy substrates, as modeled in Figure 3. The model illustrates how hydrophilic components, such as –COO and –OH, bonding with the aluminum alloy substrates kept the hydrophobic components, such as –CH\textsubscript{2} and –CH\textsubscript{3}, away from the surface, which effectively reduced the surface energy; hence, they are responsible for the superhydrophobic properties. In our previous study, -CH\textsubscript{2}, -CH\textsubscript{3} and –COO absorption peaks were also observed in the spectrum of superhydrophobic copper surfaces fabricated by one-step electrochemical modification [30]. It should be mentioned that unlike copper stearate (CuSA), which does not have any –OH bonds [13], AISA has two –OH bonds [34].

Because the intensity of the IR absorption peak of a molecule is proportional to its quantity, the peak area of –CH\textsubscript{2} peak was monitored with the SA passivation time. It was observed that the intensity of the –CH\textsubscript{2} peak of the passivated SA molecules increased with increasing SA passivation time, as shown in Figure 2(a2-a5). Figure 2(b) depicts the variation of the peak areas of the –CH\textsubscript{2} and –CH\textsubscript{3} peaks as a function of the SA passivation time. Initially, a fast and almost linear increase in the peak area was observed. The peak area was calculated to be 216 for the sample with 5 s-SA passivation; the peak area increased to 388 for the sample with 1 min-passivation; the peak area further increased to 886 for the sample with 24 min-SA passivation. Further increase of the peak area to 1115 was also observed for the sample with 60 min-passivation. These observations are
consistent with the morphological analysis by SEM, where an increase in the SA passivation time led to an increase in the density and thickness of AlSA flake-like micro-nanostructures. Both XRD and XPS have been carried out to complement the observation of FTIR and validate the model on the formation of aluminum stearate. Figure 4 shows the low angle XRD between 2-12° and high angle XRD between 12-70° for both NaOH etched aluminum alloy substrate and SA passivated NaOH etched aluminum alloy substrates.

Figure 4 X-ray diffraction (XRD) patterns of (1) chemical etched aluminum alloy substrate and (2) stearic acid (SA) passivation on NaOH etched aluminum alloy substrate in the 2θ range of (a) 12-70° and (b) 2-12°, (Aluminum stearate is abbreviated as AISA).

The X-ray diffraction (XRD) patterns of (1) chemical etched aluminum alloy substrate and (2) stearic acid (SA) passivation on NaOH etched aluminum alloy substrate are presented in Figure 4. As evident from the patterns at higher 2θ range of 12-70° in Figure 4(a), the characteristic peaks of Al (111), Al (200) and Al (220) at 38.47°, 44.72° and 65.1°, respectively, due to the aluminum alloy substrate [JCPDS # 01-085-1327]. Others small peaks are due to the intermetallic phases or the
alloying elements. Figure 4 (b) shows the low angle XRD pattern between $2^\circ$ to $12^\circ$. Figure 4(b2) shows two distinct diffraction peaks at $2.26^\circ$ and $6.68^\circ$ as compared to Figure 4(b1). These two peaks are due to the formation of aluminum stearate (AlSA). It is also complementary with the FTIR spectra of the SA-passivated NaOH etched aluminum alloy substrate, where the formation of aluminum stearate (AlSA) is discussed.

Figure 5 XPS spectra of the SA passivated NaOH etched aluminum alloy substrates (a) survey, (b) C 1s, (c) O 1s, (d) Al 2p
Figure 5(a) shows the survey spectrum of the SA passivated NaOH etched aluminum alloy substrate. Two strong peaks of C 1s and O 1s are accompanied with a small peak of Al 2p. The Figure 5(b) shows the high resolution peak of C 1s that composed of a strong peak at 285 eV corresponds to C-C or C-H bonds and a tiny peak at 288.6 eV due to the –COO peak due to the formation of aluminum stearate. The ratio of the peaks area of –COO and C-C is found to be the 0.06 which is the fingerprint on the engrafting of stearic acid on a metal surface. Similar observations are reported on interaction of stearic acid with zinc [35, 36]. Figure 5(c) shows the O 1s peak that composed to two peaks having binding energy 530.2 eV and 531.9 eV corresponds to the bonding of Al-O and Al-OH, respectively [36]. Figure 5(d) shows the Al 2p that has two distinct peaks at 74.4 eV and 77.5 eV due to the bonding of Al-O and Al-OH, respectively [37]. The high resolution XPS peaks analysis on the C 1s, O 1s and Al 2p confirm the presence of –COO, C-H (or C-C) as well as Al-O and Al-OH as found by FTIR in Figure 2 and proposed in the model in Figure (3).

Figure 6(a-c) depict the variation of surface rms roughness, CA and CAH as a function of SA passivation time on the NaOH etched aluminum alloy substrates. The substrate has a surface rms roughness of 1.38 ± 0.17 µm and a CA of 34 ± 4°. The surface rms roughness and CA of the 5 s-SA passivated NaOH etched aluminum alloy substrate increased to 2.23 ± 0.18 µm and 145 ± 2°, respectively, due to the formation of flake-like micro-nanostructures of AlSA. The transition from a hydrophilic surface, i.e., the NaOH etched aluminum alloy substrate, to superhydrophobic surfaces
occurred at the 1 min-SA passivation time mark, with a surface rms roughness of $2.29 \pm 0.2 \mu m$, a CA of $154 \pm 2^\circ$ and a CAH of $1.88 \pm 0.4^\circ$. The appearance of surface superhydrophobicity was due to the formation of low surface energy AlSA, evident from the FTIR spectra, XRD patterns and XPS spectrum in Figure 2(a), Figure 4 and 5, respectively, as well as the presence of a micro-nanorough flake-like morphology, evident from the SEM images in Figure 1(d). The surface rms roughness remained constant from 1 min- to 24 min-SA passivation time but there was a slight tendency towards reduced roughness for SA passivation longer than 24 min. This reduction might be an indicator of the compactness of the passivated AlSA formation on the NaOH etched aluminum alloy substrates. On the other hand, the CA and CAH of the surfaces prepared by SA passivation were observed to remain constant with SA passivation times between 1 min to 60 min. The CA variation with SA passivation time has been reported in the literature [17, 38]. Ruan et al. prepared a superhydrophobic aluminum alloy substrate via chemical etching with HCl/HF solution followed by passivation with a different fatty acid. An optimum modified time of 1.5 h on the etched aluminum alloy substrate (with a CA of 167.6°) was observed by using lauric acid as the modifier, and the CA reduced to 155.2° for 2 h passivation [17]. The authors mentioned that the appearance of the optimum CA might have resulted from the change of surface morphology and microstructure due to different etching and modification parameters. However, the change of the surface morphology or the chemical composition with passivation time in their study was not investigated as performed here using SEM and FTIR, XRD as well as XPS. In the study by Kim et al., a superhydrophobic substrate with a CA of $153^\circ$ was produced by using a reactive ion etching process combined with hydrophobic coatings with PTFE [38]. The variation of the morphology
with PTFE passivation time was found to contribute to the variation of the CA. However, the chemical composition, one of the most important factors in superhydrophobicity, was not analyzed in their study. In the literature, NaOH as an etchant has been utilized to prepare superhydrophobic aluminum alloy substrates utilizing both one- and two-step processes [6, 21, 39].

We have recently reported the formation of superhydrophobic aluminum alloys substrates,
fabricated by electrodeposition of copper on aluminum alloy substrates followed by electrochemical modification using SA organic molecules, which provided similar CA [15]. Furthermore, Sarkar et al. (including one of the current authors) also studied superhydrophobic properties of ultrathin rf-sputtered Teflon films coated HCl etched aluminum alloy substrates [14]; the authors reported the effect of the etching time on the aluminum alloy substrates. A maximum CA of 164 ± 3° was observed on the ultrathin rf-sputtered Teflon coated aluminum substrates that were HCl etched for 2.5 min. Another study in our group fabricated superhydrophobic aluminum alloy substrates by monodispersive silica nanoparticles spin coating [40].

3.2 Corrosion resistance properties of superhydrophobic aluminum alloy substrates

Figure 7(a) shows the potentiodynamic polarization curves of the as-received aluminum alloy substrate, NaOH etched aluminum alloy substrate, and 5 s-, 1 min-, and 24 min-SA passivated NaOH etched aluminum alloy substrates. $I_{\text{corr}}$ was calculated from the extrapolation of the cathodic curves [41]. $R_p$ was calculated by the Stern-Geary equation, given by

$$R_p = \frac{\beta_a \beta_c}{2.31 I_{\text{corr}}(\beta_a + \beta_c)}$$

(Equation 7)

where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel slopes, respectively.
Figure 7(a) Potentiodynamic polarization curves of as-received aluminum alloy substrate, NaOH etched aluminum alloy substrate, and 5 s-, 1 min-, and 24 min-SA passivated etched aluminum alloy substrates. Variation of (b) $I_{corr}$ and (c) $R_p$ as a function of the SA passivation time on NaOH etched aluminum alloy substrates.

The $I_{corr}$ and $R_p$ of as-received aluminum alloy substrate were found to be $2.89 \pm 0.8 \mu A/cm^2$ and $3.79 k\Omega\cdot cm^2$, respectively. The NaOH etched aluminum alloy substrate exhibited a larger $I_{corr}$ of $16.29 \pm 2.8 \mu A/cm^2$ as well as a smaller $R_p$ of only $2.24 k\Omega\cdot cm^2$. This could be explained by the increase of surface area as well as the loss of the protective oxide layer during the chemical etching.
process. This is consistent with the existing literatures, where it has been shown that the increase of surface roughness leads to similar trends in I\textsubscript{corr} and R\textsubscript{p} [42-44]. For example, in the study by Walter \textit{et al.} [43], different surface roughness of AZ91 magnesium alloy, were obtained by polishing with different grits of silicon carbide (SiC) and 3 \(\mu\)m diamond paste, measured using atomic force microscopy (AFM). Consequently, it was observed that the I\textsubscript{corr} of the AZ91 alloy in potentiodynamic polarization tests increased from 2.19 \(\mu\)A/cm\(^{2}\) to 6.92 \(\mu\)A/cm\(^{2}\) with an increase in the surface roughness from 0.08 \(\mu\)m to 0.43 \(\mu\)m.

Table 1 CA and CAH values and their respective I\textsubscript{corr} and R\textsubscript{p} values calculated by the Stern-Geary equation, as extracted from Figures 6 and 7 for SA passivation on NaOH etched aluminum alloy substrates for a range of passivation times.

<table>
<thead>
<tr>
<th>Sample condition/SA passivation time</th>
<th>Contact angle CA (°)</th>
<th>Contact angle hysteresis CAH (°)</th>
<th>Corrosion current density I\textsubscript{corr} ((\mu)A/cm(^{2}))</th>
<th>Polarization resistance R\textsubscript{p} (kΩ·cm(^{2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received Al</td>
<td>87 ± 3</td>
<td>-</td>
<td>2.89 ± 0.8</td>
<td>3.79 ± 1.8</td>
</tr>
<tr>
<td>Etched Al</td>
<td>34 ± 4</td>
<td>-</td>
<td>16.29 ± 2.8</td>
<td>2.24 ± 0.98</td>
</tr>
<tr>
<td>5 s</td>
<td>145 ± 2</td>
<td>-</td>
<td>8.16 ± 2.3</td>
<td>2.50 ± 1.4</td>
</tr>
<tr>
<td>1 min</td>
<td>154 ± 2</td>
<td>1.88 ± 0.4</td>
<td>1.76 ± 0.64</td>
<td>14.53 ± 2.72</td>
</tr>
<tr>
<td>8 min</td>
<td>155 ± 1</td>
<td>2.03 ± 0.3</td>
<td>1.30 ± 0.53</td>
<td>21.83 ± 5.16</td>
</tr>
<tr>
<td>Time (min)</td>
<td>$I_{corr}$ (µA/cm²)</td>
<td>$R_p$ (kΩ·cm²)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------</td>
<td>---------------------</td>
<td>----------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>156 ± 1</td>
<td>2.09 ± 0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>156 ± 1</td>
<td>2.21 ± 0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>156 ± 1</td>
<td>1.96 ± 1.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In our case, the hydrophobic aluminum alloy substrate, prepared by 5 s-SA passivation on a NaOH etched aluminum alloy substrate, exhibited a lower value of $I_{corr}$ of 8.16 ± 2.3 µA/cm² and a higher $R_p$ of 2.5 kΩ·cm² compared with the aluminum alloy substrate treated with only NaOH etching, implying that the hydrophobic substrate inhibits corrosion of the substrate. However, these results are still inferior to that of the as-received aluminum alloy substrate, indicating that the hydrophobic surface having a water CA of 145 ± 2° is not resistant enough to prevent chemical attack from a corrosive environment.

However, both the anodic and cathodic current densities of superhydrophobic substrates, prepared with SA passivation longer than 1 min on NaOH etched alloy substrates, were significantly reduced, as observed in Figure 7(a). This reduction is due to a restricted supply of oxygen, as well as due to water-limiting oxygen and water reduction [45]. It is generally believed that the air trapped on the superhydrophobic surfaces behave as a dielectric for a parallel plate capacitor, which inhibits the electron transfer between the aluminum alloy substrate and the electrolyte and hence protects the substrate. The reduction in anodic current density of the superhydrophobic aluminum alloy substrates indicated that the anodic dissolution process was inhibited or postponed compared with the as-received aluminum alloy substrate [46]. Table 1 and Figure 7(b-c) show the variation of $I_{corr}$ and $R_p$ of the prepared samples. It should be mentioned that the 1 min-passivated NaOH etched aluminum alloy substrate, exhibiting a CA of 154 ± 2°, had a
much lower $I_{\text{corr}}$ of $1.76 \pm 0.64 \, \mu A/cm^2$ and a higher $R_p$ of $14.53 \, k\Omega \cdot cm^2$ compared with the as-received aluminum alloy substrate. With increasing SA passivation time up to 8 min and 16 min, $I_{\text{corr}}$ values of the superhydrophobic aluminum alloy substrates reduced to $1.3 \pm 0.53 \, \mu A/cm^2$ and $0.31 \pm 0.12 \, \mu A/cm^2$, and $R_p$ values increased to 21.83 $k\Omega \cdot cm^2$ and 101.59 $k\Omega \cdot cm^2$, respectively. The $I_{\text{corr}}$ further decreased notably to $0.035 \pm 0.003 \, \mu A/cm^2$ and $R_p$ increased to 283.28 $k\Omega \cdot cm^2$ for 24 min-SA passivation on NaOH etched aluminum alloy substrate. The $R_p$ was found to increase as high as 521.59 $k\Omega \cdot cm^2$ after 60 min-SA passivation. It can be concluded that the $I_{\text{corr}}$ value for the superhydrophobic aluminum alloy substrates were much lower than that of the as-received sample, and $I_{\text{corr}}$ was found to decrease gradually with the increase of SA passivation time; on the other hand, the $R_p$ values increased with the extended SA passivation time. Both the reduced $I_{\text{corr}}$ and the enhanced $R_p$ indicate that preparation by chemical etching followed by SA passivation process is effective for improving the corrosion resistance properties. It has been further shown that the corrosion inhibition of superhydrophobic surfaces by longer SA passivation times is superior to that of shorter passivation times.

It was observed that the corrosion potential ($E_{\text{corr}}$) increased as a function of the SA passivation time, from -0.627 V for 5 s-SA passivation to -0.578 V for 60 min-passivation on NaOH etched aluminum alloy substrates. This also suggests increasing corrosion resistance of the samples with extended passivation time. The more positive $E_{\text{corr}}$ indicated that the surface could better prevent corrosion owing to the increasing density of AlISA molecules formed on the etched aluminum alloy substrates. Brassard et al. [31] has discussed the variation of $E_{\text{corr}}$ on different Zn coated steel substrates followed by passivation with RTV-silicone and showed that superhydrophobic surfaces
had higher $E_{\text{corr}}$ compared to as-received aluminum alloy substrates. In our case, however, the $E_{\text{corr}}$
increased with an increasing number density of AISA molecules, that is, the $E_{\text{corr}}$ still increased even
when the CA remained constant on the superhydrophobic substrates prepared by different SA
passivation times on the NaOH etched aluminum alloy substrates.

In the present study, another method was applied for calculating $R_p$, namely from the slope of
the linear potential-current (E-I) curves by varying the potential ±10 mV around the corrosion
potential ($E_{\text{corr}}$) and using Ohm’s law (as shown in Figure 8(a))

$$R_p = \frac{\Delta E}{\Delta I}$$  \hspace{1cm} (Equation 8)

where E and I are the potential and current, respectively.

The $R_p$ calculated by Ohm’s law ($R_{p1}$) values versus the $R_p$ calculated by Stern-Geary equation
($R_{p2}$) values are plotted in Figure 8(b). As can be observed, there is excellent agreement between
the $R_p$ values calculated by the two methods. Furthermore, to evaluate the difference between $R_{p1}$
and $R_{p2}$, the relative error between them can be expressed as follows:

$$\text{Relative error} = \left| \frac{R_{p2} - R_{p1}}{R_{p2}} \right| \times 100\%$$  \hspace{1cm} (Equation 9)

According to the calculation, the relative error associated with corresponding $R_{p1}$ and $R_{p2}$
values is in the range of 10-20%, which indicates a good agreement between the $R_p$ calculated by
both Ohm’s law and the Stern-Geary equation. The presence of small differences between the $R_p$
values may be due to the differences in the Tafel slopes ($\beta_a$ and $\beta_c$) and the slope of $\frac{\Delta E}{\Delta I}$ chosen in
the analysis of the polarization curves. In this article (as well as in Table 1), the presented $R_p$ was
calculated using Stern-Geary equation (Equation 7).

The corrosion inhibition mechanism of superhydrophobic substrates by NaOH etching and SA
passivation is similar to that in our previous study on the corrosion properties of superhydrophobic copper surfaces [30]. In that study, the superhydrophobic copper surfaces, fabricated by one-step electrochemical modification in an ethanolic SA solution, demonstrated improved corrosion resistance properties with increasing electrochemical modification time. In the present study, the corrosion properties of the etched and passivated substrates are significantly improved compared to the as-received substrate. The presence of the superhydrophobic AISA flake-like morphology on the aluminum alloy substrate acted as a physical barrier to retard electrolyte penetration, as demonstrated by the gradual reduction of $I_{\text{corr}}$ as well as enhanced $R_p$ for longer SA passivation times. The corrosion test performed by Saleema et al. on a superhydrophobic aluminum alloy substrate prepared by a one-step process using a mixture of NaOH and FAS-17 solution did not provide any polarization data [6]; however, the superhydrophobic substrates formed corrosion pits after the polarization experiment. In the published literature, polarization curves have been widely used to analyze the corrosion resistance of superhydrophobic substrates; however, the $R_p$ of superhydrophobic substrates compared with those of the as-received substrates were not presented in these studies [3, 47-49]. On the other hand, superhydrophobic coatings have been fabricated using myristic acid with cerium chloride solution on copper substrates [50]. In this study, polarization curves were presented to quantify the corrosion properties of Ce deposited superhydrophobic coatings, which had better corrosion resistance than the bare copper substrate. As the authors did not present the $R_p$ of their coatings, we have used their values for $\beta_r$, $\beta_c$ and $I_{\text{corr}}$ to calculate the $R_p$ of superhydrophobic Ce coatings in NaCl solution (3.5 wt.%) using the Stern-Geary equation (Equation 7): the calculated value of $R_p$ was found to be 7.81 kΩ·cm$^2$. This calculated $R_p$
value of for the Ce coated superhydrophobic copper substrate is much less than those for our fabricated superhydrophobic substrates. Evidently, the $R_p$ value of our superhydrophobic substrate prepared by 60 min-SA passivation after NaOH etching is 66 times more than that of the superhydrophobic copper substrate with Ce coating.

Figure 8(a) Potential-current (E-I) curves from varying the potential ±10 mV around the corrosion potential (Ecorr) for calculating $R_p$ by Ohm’s law; (b) Correlation between $R_p$ calculated by (i) Ohm’s law ($R_{p1}$) and (ii) the Stern-Geary equation ($R_{p2}$). $R^2$ quantifies a measure of the goodness-of-fit of the linear regression.

Figure 9 shows the morphological and chemical composition changes of the hydrophobic substrates prepared by 5 s-SA passivation and of superhydrophobic substrate that was prepared by 24 min-SA passivation after corrosion tests. Compared with the image of the hydrophobic substrate before corrosion testing, (Figure 9(a)), the SEM image of hydrophobic aluminum alloy substrate after corrosion testing clearly indicates the formation of corrosion pits as marked by arrows in Figure 9(c); additionally, the CA was found to decrease from 145 ± 2° to 124 ± 6° after the corrosion test.
The intensities of the –CH$_2$, -CH$_3$ and -COO peaks in the FTIR spectrum of the hydrophobic substrate after corrosion were found to clearly decrease, as shown in the inset of Figure 9(e). However, the surface morphology of superhydrophobic substrate remained the same before and after the corrosion test, as shown in Figure 9(b, d)). Furthermore, no discernible variation in the intensities of the –CH$_2$, -CH$_3$ and -COO peaks in the FTIR spectrum of the superhydrophobic substrate were found before and after the corrosion test, as shown in Figure 9(f)). The inset images of water drops also indicate the wetting properties remained the same. These results are consistent with those from the polarization curves, which indicated that the superhydrophobic aluminum alloy substrates had superior corrosion resistance as compared with both the as-received and hydrophobic aluminum alloy substrates. As mentioned before, in the study by Saleema et al. on the corrosion resistance property of superhydrophobic aluminum substrates prepared by chemical etching [6], a poor corrosion resistance was observed in the superhydrophobic substrates, where a number of pits formed after corrosion testing. Several other studies have also reported on the corrosion resistance properties of superhydrophobic substrates [51-53]; however, until the current study, other works have not reported on the variations in morphological, compositional and wetting properties of superhydrophobic substrates.
Figure 9 SEM images of the surfaces of the (a) 5 s- and (b) 24 min-passivated NaOH etched aluminum alloy substrates before corrosion, and (c-d) the surfaces after
corrosion testing, respectively. The inset images show the water drops on the corresponding surfaces. Figure 9(e-f) shows FTIR spectra of the 5 s- and 24 min-passivated NaOH etched aluminum alloy substrates before (I) and after (II) corrosion, respectively.

An attempt has been made to evaluate the corrosion resistance of superhydrophobic surfaces using electrochemical impedance spectroscopy (EIS) as a complementary tool to polarization resistance. EIS was performed after immersing the samples in a salt solution for approximately 10 hr. The EIS data have been analyzed in light of the analysis presented on the superhydrophobic surfaces prepared on aluminum alloy substrates by Liu et al. [29] and Liang et al. [27]. Figure 10 shows the Nyquist and Bode plots as well as the equivalent electrical circuits for the EIS data from the as-received aluminum alloy substrate and the superhydrophobic aluminum alloy substrate prepared by 24 min-SA passivation. The graphs were plotted from the fitted data based on the equivalent electrical circuit (see the supporting information for both original and fitted EIS plots). Specifically, Figure 10(a) shows the Nyquist plots, which present the real component of impedance ($Z_{\text{real}}$ or $Z'$) versus the imaginary component ($Z_{\text{imaginary}}$ or $Z''$) on a linear scale. Additionally, Figure 10 shows the Bode plots, (b) modulus of impedance ($|Z|$) vs. frequency and (c) phase angle vs. frequency. The diameter of the semicircle in the Nyquist plot signifies the charge transfer resistance ($R_{\text{ct}}$) of the double layer formed at the interface between the sample surface and the corrosive medium. The semicircle diameter of the Nyquist plot of the as-received aluminum alloy substrate was found to be 1.46 k$\Omega$·cm$^2$ and is presented as an inset in Figure 10(a). On the other hand, two semicircles were observed on the Nyquist plot of the superhydrophobic aluminum alloy substrate, as shown in Figure
Among them, the smaller semicircle with a diameter of 29 kΩ·cm² at higher frequency (close to the coordinate origin) represents the resistance of the superhydrophobic thin films ($R_{SH}$), and the second large semicircle with a diameter of 95 kΩ·cm² represents charge transfer resistance ($R_{ctSH}$) of the double layer at the interface between the superhydrophobic surface and the salt solution. The large value of impedance of the superhydrophobic film compared to the as-received aluminum alloy surfaces shows that the superhydrophobic surfaces are more resistant against corrosion.

Figure 10(a) Nyquist plots, (b) Bode modulus diagrams and (c) Bode phase angle diagrams of as-received aluminum alloy substrate and superhydrophobic aluminum
alloy substrate. (d) Electrical equivalent circuits for EIS of (d1) as-received aluminum alloy substrate and (d2) superhydrophobic aluminum alloy substrate. The insets image in (a) shows the enlargement of the high frequency region of the plots.

The top of Figure 10(b) shows the Bode plot of the superhydrophobic substrate, and bottom portion shows the Bode plot of the as-received aluminum alloy substrate. As observed in the bottom part of Figure 10(b), the as-received aluminum alloy substrate had a $|Z|$ value of only 11.6 $\Omega \cdot \text{cm}^2$ at the high frequency of $10^4$ Hz, in good agreement with the results presented by Liu et al. [29] and Liang et al. [27]. However, the superhydrophobic substrate exhibited a $|Z|$ value of 1.74 k$\Omega \cdot \text{cm}^2$, which is nearly 150 times larger than that of the as-received aluminum alloy substrate at the same frequency. Similarly, at the low frequency of 0.01 Hz, the $|Z|$ value of the as-received aluminum alloy substrate was found to be 1.06 k$\Omega \cdot \text{cm}^2$. In contrast, it was as high as 73.4 k$\Omega \cdot \text{cm}^2$ on the superhydrophobic aluminum alloy substrate. In general, AC impedance at high frequencies is the response of coatings with the solution and, at low frequency, reflects $R_{ct}$ and the double-layer capacitance [54]. It is well known that the larger value of $|Z|$ in the low frequency region signifies a better barrier in the thin film [52]. Therefore, according to the analysis of the Bode plots, the superhydrophobic substrate was found to have better corrosion resistance as compared with the as-received aluminum alloy substrate. It agrees well with the results from the polarization experiments, where $R_p$ of the superhydrophobic surface was larger than that of the as-received aluminum alloy substrate, as shown in Table 1. This is comparable to the study by Liu et al. [29], where it was concluded, based on results from Bode plots, that the corrosion resistance of the graphene coated aluminum alloy was an order of magnitude higher than that of the uncoated aluminum alloy substrate. In the present
study, compared with the as-received substrate, the corrosion resistance of the superhydrophobic aluminum alloy substrate was close to two orders of magnitude higher at low frequencies. This indicates that our superhydrophobic aluminum alloy substrate has better corrosion resistance than the graphene coated substrate [29]. This difference may be due to differences in the physical properties of graphene, in the case of Liu et al., and aluminum stearate, in the current case.

Recently, Liang et al. fabricated silica-based superhydrophobic coatings on aluminum alloy substrates and performed EIS analysis [27]. In their work, the $|Z|$ at 10 kHz of the superhydrophobic aluminum alloy substrate with a silica-based film, immersed for 30 minute in a salt solution, was reported to be $100 \ \Omega \cdot \text{cm}^2$; the $|Z|$ of the same sample was reported to be $2.5 \ \Omega \cdot \text{cm}^2$ after increasing the immersion time to 24 hr. This reported $|Z|$ value is even lower than those of their as-received aluminum alloy substrates. While comparing the impedance at 0.01 Hz, the $|Z|$ value of the 30 min-immersed silica-based film coated superhydrophobic samples was reported to be $560 \ \text{k}\Omega \cdot \text{cm}^2$, which further reduced to $16 \ \text{k}\Omega \cdot \text{cm}^2$ after 8 hr of immersion. This value is very similar to that from our observations.

The Bode phase plot of the superhydrophobic substrate exhibits the two time constants, as shown in Figure 10(c). At the frequency of 25 Hz, the phase angle of the as-received aluminum alloy substrate arrived at the maximum value of $78^\circ$. However, the phase angle of the superhydrophobic surface exhibited the minimum value of $18.4^\circ$ at a similar frequency. It is comparable with the study of Liu et al., where two time constants were observed on the superhydrophobic aluminum alloy substrate fabricated by graphene spin coating [29]. The authors observed that the maximum phase angle value for the AA2024 aluminum alloy substrate was $75^\circ$ and the lowest phase angle
value of for the sample with the superhydrophobic graphene coating was 40° at the same frequency. It is well known that phase angle (\(\phi\)) is defined by the expression in Equation 10.

\[
\phi = \arctan\left(\frac{Z_{\text{imaginary}}}{Z_{\text{real}}}\right) \quad \text{(Equation 10)}
\]

Thus, a smaller phase angle indicates a larger value of \(Z_{\text{real}}\) (or \(Z'\)), which corresponds to a large diameter in the Nyquist plot. In the current results from the Bode plots, the obtained phase angle of 18.4° for the superhydrophobic substrate is much smaller than that of 40° as reported by Liu et al., suggesting our superhydrophobic surface has better corrosion resistance than samples from the latter.

Figure 10(d1) shows the equivalent electrical circuit of the as-received aluminum alloy surface in reaction with the salt solution, as modeled by EIS. In this circuit, \(R_s\) is the resistance of the solution; \(R_c\) and CPE are the charge transfer resistance and the constant phase element associated with the double layer formed at the interface between the aluminum surface and salt solution, respectively.

In the case of superhydrophobic coatings on the aluminum surface, an extra resistance \(R_{\text{SH}}\) and constant phase element \(CPE_{\text{SH}}\) have been included in the circuit due to the dielectric nature of the superhydrophobic coating. As the interaction of the salt with the superhydrophobic surface will be different compared to that with untreated aluminum, the charge transfer resistance and constant phase element associated with the double layer at the interface have been presented by \(R_{\text{cSH}}\) and \(CPE_{\text{cSH}}\). The assumption of this model is well supported by the observation of two time constants in the Bode plot.
Finally, the mechanical properties of the superhydrophobic substrate are very important for its uses against surface erosion, friction and corrosion [30]. The adhesion strength of all surfaces prepared by SA passivation after NaOH etching was found to be 5B, tested according to the ASTM D3359 standard.

4. Conclusions

Chemical etching of aluminum alloy substrates by NaOH followed by stearic acid (SA) passivation was used to prepare superhydrophobic aluminum alloy surfaces, and their corrosion resistance properties were investigated. The SA passivation process produces flake-like aluminum stearate micro-nanostructures on NaOH etched aluminum alloy substrates. The number density of these flake-like structures is observed to increase with the extension of SA passivation time. Investigations into the wetting properties of these surfaces demonstrated water contact angles of more than 150° after 1 min of SA passivation, which remained constant to 60 min of passivation time. However, the polarization resistance determined from polarization curves increases gradually from 3.79 to 521.59 kΩ·cm² for the as-received aluminum alloy substrates and the superhydrophobic surface prepared SA passivation for 60 min, respectively. Electrochemical impedance spectroscopy (EIS) shows that the moduli of impedance |Z| at lower frequencies for the as-received aluminum substrate and superhydrophobic aluminum substrate are 1.06 kΩ·cm² and 73.4 kΩ·cm², respectively. The higher values of the polarization resistance and modulus of impedance of the superhydrophobic aluminum surfaces with respect to the as-receive aluminum
alloy surface demonstrate that the superhydrophobic surfaces prepared by chemical etching
followed by SA passivation have superior corrosion resistance properties.

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References

(Primary Sources
Secondary Sources)

Uncategorized References


