Relevant aspects in the stability performance of different anodic alumina (AAO) films in aqueous sulfate solutions

Fakiha El-Taib Heakal a,⁎, Omnia S. Shehata b, Ahmed M. Awad c

a* Chemistry Department, Faculty of Science, Cairo University, Giza 12613, Egypt
b Physical Chemistry Department, National Research Centre, Dokki, Giza 12622, Egypt
c Chemical Engineering & Pilot Plant Department, National Research Centre, Dokki, Giza 12622, Egypt

ARTICLE INFO

Received 13 December 2016
Received in revised form 15 March 2017
Accepted 17 March 2017
Available online 21 March 2017

Keywords:
AAO
Colored film
Anodization
AFM
FE-SEM
EIS
Stability

ABSTRACT

Nanoporous anodic aluminium oxide (AAO) is a well-known template in different fields of nanotechnology, due to its potential applications in a widespread industrial sector. Therefore, electrochemical performance of different fabricated AAO films was thoroughly investigated in both molar sulfuric acid and aqueous sulfate solutions relative to the behavior of their bare aluminium substrate. The prepared samples included one-step anodized film (1st), first anodized electrolytic polished film (EP), self-organized two-step anodized film (2nd) and electrodeposited copper atoms in the pores of the 2nd anodized film (colored). Surface characterization and electrochemical results revealed that properties and stability of the four fabricated samples are strictly influenced by the method adopted in their preparation. In both tested media, electrolytic polished sample (EP) offered the highest stability and corrosion protection for its Al substrate. Generally, the performance decreased in the following order: EP > 1st > 2nd > colored > bare Al. Interestingly, for each tested sample our data revealed a better behavior in H₂SO₄ than in Na₂SO₄ solution, since alumina film is more predisposed to dissolution in solution with higher pH values.

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1. Introduction

Anodizing is considered to be the most widespread method for surface treatment of metals and alloys with excellent mechanical properties and broad market prospective. For aluminium metal, its spontaneously formed native film is typically of ca. 2–4 nm thickness, which tends to develop as the anodic potential is increased. The application of a high potential often improves hardness and corrosion resistance by thickening the passive film, where at room temperature the thickness increases by about 1.2 nm V⁻¹ [1]. Formation of anodic alumina (Al₂O₃) films is generally the most commonly effective way to protect the surfaces of aluminium alloys in different fields of industry and as decoration coatings to improve their mechanical properties [2–4]. In the meantime, the porous anodic aluminium oxide (AAO) is considered to be a very suitable material in nanoscience and nanotechnology due to the fact that its nanoporous morphology and arrangement can be controlled by changing the process parameters [5,6].

Recently, much attention has been paid to the tunable synthesis of nanoporous AAO in order to obtain templates for nanofabrication with desired geometrical features in the production of nanowires, nanotubes or nanodots from different materials [7–9]. It allows also enhancing the electric, magnetic, catalytic, optical and sensing properties of the deposited materials for the small size (4–200 nm) and high-aspect ratio of the produced nanostructures [10]. Additionally, AAO itself possesses many interesting properties like surface chemistry or luminescence due to electrolyte anion incorporation in its walls [11] and the presence of F-centers in the formed oxide [12]. Furthermore, AAO membrane has been used extensively in recent years for filtration and biofunctionalization [13,14], as well as for ammonia and humidity sensing at room temperature [15]. Using the two-step anodization process, self-ordered nanoporous structures of aluminium oxide membranes can be obtained with variable distance between pores and high pore density on surface compared to membranes obtained by other methods [16]. Normally, two types of anodized alumina layers can be obtained including the thin barrier adherent compact and thick porous oxide ones [17,18]. The laboratory-made AAO membranes are usually fabricated by self-organized two-step anodizing in sulfuric [19], nitric [20], oxalic [21], phosphoric acid [22], as well as in mixed phosphoric and acetic acid solutions [23].

On the other hand, it is worth noting that Masuda and Fukuda [24] are the first who succeeded to obtain a highly ordered metal nanohole array (Pt and Au) fabricated by two-step replication of the honeycomb structure of porous anodic alumina (PAAn). Since then, much efforts have been directed to electrolytically colored PAA films on aluminium by AC polarization in salts of various metals such as Ni [25,26], Sn...
This electrochemical coloring method has attracted much attention owing to its low cost, operation simplicity and the produced extra quality deep black coloration could be suitable as efficient solar energy panels [29]. In a previous work by Heakal et al. [30] the effect of various detachment techniques on surface stability of non-colored and colored two-step nanoporous AAO films was scrutinized in acid chloride medium. In the present work preparation and characterization of different AAO films were attempted and thoroughly investigated for their electrochemical performance in aggressive sulfuric acid and sulfate solutions to highlight the relevant aspects in their behavior with respect to their base aluminium substrate. Various successive steps were adopted to fabricate the different AAO films as in the following sequence: (i) one anodized step (1st); (ii) electrolytic polished step (EP); (iii) second anodized step (2nd); and (iv) electrophoretic copper atoms into the pores of the honeycomb structure (colored). Several physical techniques such as atomic force microscopy (AFM), scanning electron microscopy (SEM), and micro-hardness determination were employed to characterize all tested samples. Moreover, their electrochemical behaviors were investigated using potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) measurements and the results were confirmed by FE-SEM images.

2. Experimental

2.1. Sample preparation

The aluminium samples used as substrate material in this study were coupons of 10 cm x 3 cm x 0.2 cm. The samples were cut from aluminium sheet (50005 alloy type) with chemical composition (wt%): Si 0.3; Mg 0.8; Fe 0.7; Cu 0.2; Mn 0.2; Zn 0.25; Cr 0.1; other minor elements 0.15; and balance Al. Each coupon was first abraded consecutively with finer grade SiC papers down to 600 grade, degreased with acetone, etched in 12 wt% NaOH for 10 min to eliminate any remaining surface oxide. After rinsing thoroughly with deionized water, it was further desmutting into 20 wt% HNO3 solution for 30 s only followed by rinsing with deionized water. Finally, the sample was cleaned by ultrasonication in acetone for 15 min and dried in air flow for being used as a bare Al substrate. Freshly prepared 17 wt% sulfuric acid solution with deionized water was used as an electrolyte for the first and second anodizing processes. A cooling system was designed to control the electrolyte temperature at 17 °C prior to starting anodization.

The first anodized sample (designated as 1st), was prepared by applying 15 V electric potential from an electric DC power source (GW lab GPR-3030) during anodizing the clean aluminium substrate against a large lead cathode for 15 min in 17 wt% sulfuric acid solution. This anodization period was found to give the best result as compared to other longer time periods of 30 or 45 min as described elsewhere [30]. The sample was then removed from the bath, rinsed with an adequate amount of deionized water and used in the subsequent various measurements.

To prepare the electrolytic polished sample (designated as EP), a 1st sample was subjected to an electrolytic polishing step in 55 wt% H3PO4 solution for a very short time (30 s) at constant anodic potential with low current density of ~15 mA cm−2. This step was carried out to just polish the non-organised outermost porous part of the first prepared AAO film on Al substrate leaving its innermost barrier layer intact. The two-step anodized film was synthesized by anodizing an EP sample for 30 min duration to re-build up a new well organized porous structure, where this sample was referred to as 2nd in the present work. Finally, the colored sample was prepared by depositing metallic copper in the pores of the 2nd film. This was carried out by fixing a 2nd anodized sample as working electrode in the electrolytic coloring cell containing 4.0 wt% CuSO4 solution at pH 2 and a graphite counter electrode, then applying a constant AC potential of 15 V rms at 50 Hz for 10 min. The duty cycle applied was dedicated for reduction of dissolved Cu2+ ion and its deposition as Cu atom into the porous layer leading to development of a homogeneous black colored film. More details are given in our previous work [29,30].

2.2. Surface examination

Surface topography of each sample was performed to evaluate its roughness using atomic force microscope (AFM), Shimadzu SPM-9600 Non-Contact Mode (Japan). Also, surface morphologies and microstructures of the prepared films before and after immersion in the electrolyte were characterized from the images of field emission scanning electron microscope (FE-SEM), Quanta FEG250 (Japan). Moreover, hardness of the tested samples was measured using Vicker micro-hardness tester (HMV, Shimadzu, Japan) load 100 g in a time period of 15 s.

2.3. Electrochemical measurements

Electrochemical tests were performed for each sample at room temperature (25 °C) in a conventional three-electrode cell with Ag/AgCl reference electrode and platinum sheet as the counter electrode. The working electrodes were the non-anodized bare Al substrate or one of the prepared anodized samples (1st, EP, 2nd and the colored one) all with a geometrical surface area of 1 cm2. Aqueous solution of 1 M H2SO4 or 1 M Na2SO4 was used as the electrolyte; and each one was prepared from chemically pure reagent and deionized water. The workstation used for the electrochemical measurements was Metrohm Autolab B.V. (version PGSTAT302N, Switzerland) operated with the Nova 1.10 software. Before starting the AC or DC experiments, the working electrode was left immersed in the test solution for 5 min in order to reach a stable potential value. Thereafter, the AC impedance responses were recorded at the open circuit potential (OCP) with a sinusoidal excitation signal of 10 mV peak-to-peak in the frequency range 106 to 10−1 Hz. Potentiodynamic polarization curve was always scanned after the EIS measurement with a rate of 1 mV s−1 in the positive-going direction of potential starting from −0.8 V to −0.2 V (vs. Ag/AgCl).

3. Results and discussion

3.1. Physical characterization

Fig. 1 shows the four fabricated coated samples together with the used Al sheet. Compared to the silvery metallic appearance of bare Al, a light grey transparent film is evident for the 1st sample, becoming much lighter for the EP sample, dark grey for the 2nd one and turning to deep black for the colored film. Atomic force microscopy (AFM) is an effective tool to distinguish the topography of microstructure. Such a technique can assess the roughness (Ra) which expresses the variability in terms of disparity of bulges and depressions throughout a metal surface. Fig. 2 shows AFM 3-dimensional images for the surfaces of bare Al and the four fabricated coatings. For bare Al surface (Fig. 2a) an average Ra value was estimated to be 967 nm, and slightly decreased to 960 nm for the 1st AAO film (Fig. 2b). After a 30-second electrolytic polishing step that served only to remove the non-ordered porous layer of the 1st AAO film leaving its innermost barrier layer intact, the roughness value was reduced significantly to 941 nm (Fig. 2c). However, in regard to the 2nd sample shown in Fig. 2d the roughness Ra value increased to 991 nm due to the formation of a huge number of nanoporous AAO film, and decreased again after coloring this film (Fig. 2e). Additionally, the recorded maximum vertical distance between the top and bottom sites was reduced in the order 2nd > EP > colored > 1st > bare Al, implying that the native film formed naturally in air on abraded aluminium surface is thinner than any film formed by anodization.

SEM images were exploited to further characterizing the microstructures of the different fabricated films relevant to the plain granular surface of the bare Al substrate shown in Fig. 3a. The EP sample (Fig. 3c)
3.2. Electrochemical behavior

3.2.1. Polarization measurements

Polarization behavior of the fabricated coated samples together with bare Al surface was followed by scanning the potential in the positive going direction from $-0.8$ V to $-0.2$ V (vs. Ag/AgCl) after the sample had OCP for 5 min in 1 M H$_2$SO$_4$ or 1 M Na$_2$SO$_4$ solution. Fig. 5 shows that cathodic polarization curves of all anodized samples are generally much higher in H$_2$SO$_4$ than in Na$_2$SO$_4$ solution. This experimental fact indicates that hydrogen evolution reaction (HER) on AAO surface is much enhanced by lowering the solution pH. On the other hand, the whole Tafel plot for any sample is shifted positively in H$_2$SO$_4$ than in Na$_2$SO$_4$ solution, suggesting higher stability of the coated samples in sulfuric acid than in sulfate solution. This behavior implies that H$_2$SO$_4$ solution is less aggressive for the coated anodic alumina films than Na$_2$SO$_4$ solution. Moreover, uncoated Al substrate in the two media always exhibits the highest cathodic and anodic polarization current values than those for the AAO coated samples. Accordingly, it is expected that bare Al is more vulnerable to corrosion attack in both tested media due to the lower protection capability of its native oxide film compared to the fabricated anodic oxide layers. All these coatings evidence good sealing properties which preclude Al substrate from corrosion attack. Recent study on the corrosion protection of Al in aqueous 0.5 M NaCl solution has been performed by ultra-thin atomic layer...
deposited alumina coatings grown to 10, 20 and 50 nm in thickness at 250 °C. The results revealed that spurious interfacial Al2O3 growth at the substrate/coating interface promotes sealing for thinner film (10 nm), but excellent coating performance was provided with 20 and 50 nm coatings which decreased significantly the corrosion current and increased also the pitting potential [31].

The active corrosion parameters were estimated and compiled in Table 1. The results emphasize that these parameters are strictly influenced not only by the type of the fabricated anodic alumina film, but also depend on the test medium in which it is exposed. The corrosion current density \(j_{corr}\) that’s proportional to the corrosion rate, is given by the intersection of the cathodic and anodic Tafel lines extrapolation [30]. However, in order to avoid the presence of some degree of nonlinearity in the Tafel slope regions of the obtained polarization curves, the cathodic and anodic Tafel segments calculated by linear regression of the points after ± 50 mV from the steady OCP assumed by each sample were extrapolated and the point of intersection with the potential of zero current (i.e. \(E_{corr}\)) determined \(j_{corr}\) value [32]. Fig. 5 and Table 1 clearly demonstrate that \(E_{corr}\) tends towards more negative potential values in the following sequence: EP < 1st < 2nd < colored < bare Al. Besides, for any given sample \(E_{corr}\) is decreased, i.e. being more negative, in sulfate than in acid solution due the increase in its pH simply from the Nernst equation. Values of \(j_{corr}\) in Table 1 confirm well the above trend where in both sulfate electrolytes \(j_{corr}\) becomes higher following the same \(E_{corr}\) ranking. Meanwhile, \(j_{corr}\) value for the same sample is higher in Na2SO4 than in H2SO4 (cf. Fig. 6). The increase in the corrosion susceptibility is likely attributed to difference in the chemical nature of the formed corrosion films when the acidity or pH of the corrosive environment is changed.

According to the reported literature, the film formed initially on Al after immersion for a short period of time in sulfate solution was closer to the oxyhydroxide (AlOOH) phase [33]. In neutral pH sulfate solution, this film grows thicker during either cathodic or anodic polarization. Nevertheless, in acidic pH sulfate solution this film dissolves to a very thin oxyhydroxide that is replaced by alumina (Al2O3) film during anodic polarization, which has a superior protection than the former film. Moreover, it had been proven that addition of OH\(^-\) ions to NaCl solution raised the anodic dissolution rate of Al and as well the cathodic reduction rate, implying uniform thinning of Al oxide film due to the chemical dissolution by the OH\(^-\) attack [34]. In our work, the presence of an oxyhydroxide during cathodic polarization in both solutions is believed to be due to local alkalinization of solution near the working electrode surface. This is because in aerated acidic solution, the cathodic reaction can be the proton reduction (Eq.1), while in aerated neutral solution the cathodic reaction would be mostly water reduction (Eq. 2), which is expected to be dominant at such low potential than oxygen reduction [31]:

\[
2H^+ + 1/2O_2 + 2e^- \rightarrow H_2O \quad (1)
\]

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)
\]

However, the Pourbaix diagram for the Al-water system illustrates that in non-complexing solutions of pH roughly between 4 and 9, Al2O3 passive film remains stable [35]. According to Eqs. (1) & (2) the cathodic reaction in Na2SO4 solution leads to a local increase of pH in the interface region more than that in H2SO4 solution. This can spawn conditions favorable for formation of soluble aluminate ions (AlO2\(^-\)) in sulfate solution and pointing out to the critical role of pH effect on the dissolution process. Thereby, the corrosion rate will be higher in sulfate than in sulfuric acid medium, which marks a comparative decrease in the protection capability of the surface oxide film on Al sample. Interestingly, this can be likely attributed to a diminution in the stability performance of a given alumina film in Na2SO4 relative to its behavior in H2SO4 since alumina film is more predisposed to dissolution in solution with higher pH values as it will be further confirmed from the following AC results.

![Fig. 3. SEM micrographs of the tested samples (a) bare Al, (b) 1st, (c) EP, (d) 2nd and (e) colored.](image)

![Fig. 4. Micro-hardness of bare Al and Al samples coated with different porous AAO films fabricated by various treatments.](image)
3.2.2. EIS measurements

Electrochemical impedance spectroscopy (EIS) has become a more mature technique that can effectively express the electrochemical behavior of nano-coatings and can be convenient to compare their stabilities in solutions [30,36]. The spectra of each sample were recorded at OCP as a function of frequency \( f \) over the range \( 10^5 – 10^{-1} \) Hz after 5 min immersion in naturally aerated quiescent solution. Figs. 7 and 8 display Bode (a) and Nyquist (b) plots for bare and coated Al samples in 1 M H\(_2\)SO\(_4\) and 1 M Na\(_2\)SO\(_4\) solutions, respectively. Generally, the coated samples considerably demonstrate higher magnitude of absolute impedance \( |Z| \) (Figs. 7a and 8a) and wider frequency range of capacitive response (Figs. 7b and 8b) in comparison with the bare Al. This behavior is likely attributed to the strong protective nature of AAO film irrespective of its fabrication history. The Bode plots displayed in Fig. 7a for the three coated samples: EP, 1st and 2nd in H\(_2\)SO\(_4\) solution show that although electrochemical impedance is measured down to a LF value of 0.1 Hz, no resistive region (horizontal line with a phase angle ~0°) can be discerned like in case of colored and bare Al samples, or like the behavior experienced by the Bode plots of all tested samples in Na\(_2\)SO\(_4\) solution (Fig. 8a). Those plots seem to exhibit two merging phase maxima in the MF region. Additionally, the phase crest (\( \Theta_{\text{max}} \)) increased and became broaden concomitantly with the increased absolute impedance \( |Z| \) at the LF range following the order: EP > 1st > 2nd > colored > bare Al (very low). On the opposite side, all spectra on the Nyquist format are in good consistency with the above trend, as the plots can be divided into two distinct groups based on their patterns. The first group includes EP, 1st and 2nd coated samples in H\(_2\)SO\(_4\) solution (Fig. 7b) with Nyquist plots having no ideal semicircle capacitive loop. Instead, the plots are arcs of semicircles with their centers depressed below the x-axis [30,37,38]. Both the subtended angle of the arc and its length increase gradually as follows: EP > 1st > 2nd, reflecting a similar decreasing tendency for interaction between sample surface and acidic sulfate medium at the film/electrolyte interface. The second group describes the behavior of colored and bare Al samples in H\(_2\)SO\(_4\).

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_{\text{corr}} ) (V) ((\text{Ag/AgCl}))</th>
<th>( j_{\text{corr}} ) (( \mu )A cm(^{-2}))</th>
<th>( b_c ) (mV/dec)</th>
<th>( b_a ) (mV/dec)</th>
<th>( R_{\text{pol}} ) (k( \Omega ) cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 1 M H(_2)SO(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare Al</td>
<td>−0.502</td>
<td>35.6</td>
<td>−65</td>
<td>69</td>
<td>0.41</td>
</tr>
<tr>
<td>1st</td>
<td>−0.429</td>
<td>7.7</td>
<td>−58</td>
<td>85</td>
<td>1.94</td>
</tr>
<tr>
<td>EP</td>
<td>−0.424</td>
<td>1.8</td>
<td>−54</td>
<td>62</td>
<td>6.96</td>
</tr>
<tr>
<td>2nd</td>
<td>−0.467</td>
<td>10.4</td>
<td>−85</td>
<td>72</td>
<td>1.63</td>
</tr>
<tr>
<td>Colored</td>
<td>−0.481</td>
<td>13.4</td>
<td>−102</td>
<td>90</td>
<td>1.54</td>
</tr>
<tr>
<td>(b) 1 M Na(_2)SO(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare Al</td>
<td>−0.643</td>
<td>75.0</td>
<td>−90</td>
<td>66</td>
<td>0.22</td>
</tr>
<tr>
<td>1st</td>
<td>−0.518</td>
<td>8.7</td>
<td>−86</td>
<td>67</td>
<td>1.88</td>
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<tr>
<td>EP</td>
<td>−0.448</td>
<td>2.7</td>
<td>−79</td>
<td>61</td>
<td>5.24</td>
</tr>
<tr>
<td>2nd</td>
<td>−0.548</td>
<td>14.7</td>
<td>−92</td>
<td>102</td>
<td>1.45</td>
</tr>
<tr>
<td>Colored</td>
<td>−0.592</td>
<td>19.5</td>
<td>−124</td>
<td>104</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Fig. 5. Cathodic and anodic polarization curves for the tested samples recorded after 5 min immersion in (a) 1 M H\(_2\)SO\(_4\) and (b) 1 M Na\(_2\)SO\(_4\) at scan rate of 1 mV s\(^{-1}\).

Fig. 6. Comparison of the corrosion current density \( j_{\text{corr}} \) (\( \mu \)A cm\(^{-2}\)) for the tested samples in 1 M H\(_2\)SO\(_4\) and 1 M Na\(_2\)SO\(_4\).
solution (Fig. 7b) as well as all tested samples in Na₂SO₄ solution (Fig. 8b) with Nyquist plots exhibiting semicircle capacitive loops. The loop diameter increases continuously in accordance to the increase in the |Z| value (Fig. 8a) with bare Al substrate having the lowest diameter length among all the tested samples. This marks a comparative decrease in the corrosion resistance of bare Al sample due to a poor protective nature of its native surface film, whereas the fabricated AAO coatings on the other samples can offer superior protection performance against corrosion. Based on the present impedance spectra stability and protection performance of the tested AAO samples can be ranked in the order: EP > 1st > 2nd > colored > bare Al, in good agreement with the aforementioned polarization results.

3.2.3. Equivalent circuit parameters
EIS data is commonly analyzed by fitting it into an appropriate equivalent circuit (EC) model in order to obtain a quantitative assessment for the various impedance parameters. Actually, self-organized porous type AAO films are produced when Al is electrochemically oxidized in electrolytes in which the oxide film is slightly soluble. These films are generally known to be duplex in nature, consisting from thin inner barrier layer covered with an outer relatively thick porous layer [30,39]. Besides, the impedance analysis of porous oxide films onto Al usually shows an inductive loop at LF associated with dissolution of the oxide layer [40,41]. However, appearance of all these phenomena may not be sometimes possible [31,34,41]. Based on the above considerations, the impedance data were simulated to a suitable EC model (Fig. 9) representing a coated metal/electrolyte solution interface [36,41,42] using the Nova 1.10 software. This model was found to give

![Fig. 7](image1.png)  
**Fig. 7.** a. Bode Plots for AAO coated samples and bare Al in 1 M H₂SO₄ solution. b. Nyquist plots for AAO coated samples in 1 M H₂SO₄ solution (inset: bare Al).

![Fig. 8](image2.png)  
**Fig. 8.** a. Bode Plots for AAO coated samples and bare Al in 1 M Na₂SO₄ solution. b. Nyquist plots for AAO coated samples in 1 M Na₂SO₄ solution (inset: bare Al).

![Fig. 9](image3.png)  
**Fig. 9.** The equivalent circuit (EC) used to fit and analyze the experimental EIS results.
the best reasonable fitting to the experimental results with an average maximum error of 1.8%. The circuit model includes two parallel time constants connected serially to the solution resistance ($R_s$). The first time constant is the parallel combination ($R_{bc}C_p$) assigned to the behavior of the outer porous part of the AAO film at HF range, while the second time constant is the parallel combination ($R_{pb}C_p$) describing the LF behavior of the inner barrier part at the base of the porous layer that covers the whole Al substrate. Thus, the estimated values of the electrical circuit parameters obtained in the two sulfate solutions are compiled in Table 2. Inspection of the data in Table 2 and Fig. 10 can reveal several interesting points.

(a) The resistance of the barrier layer ($R_b$) is generally with a much higher value than that for the outer porous layer ($R_p$), indicating that the inner layer of the AAO film is more corrosion resistant than its outermost porous part. Thereby, the inner layer resistance dominates the rate of charge transfer reaction as well as the film stability in the prevailing environment.

(b) In the two tested media, $R_b$ and $R_p$ values are both highest for EP coating and lowest for bare Al. The decreasing trend in their values and also be in the value of the total film resistance ($R_t = R_b + R_p$) that follows the order: EP > 1st > 2nd > colored > bare Al, in good agreement with the results of the polarization resistance ($R_{pol}$) (Table 1).

(c) The oxide film thickness ($d_f$) is a direct function of its reciprocal capacitance according to the simple relation: $d_f = ε_oε_r A/C_f$, where $ε_o$ is the permittivity of the space ($ε_o = 8.85 \times 10^{-14} \text{ F/cm}$), $ε_r$ is the relative dielectric constant of the oxide film (for Al$_2$O$_3$, $ε_r = 9.8$ [43]) and $A$ is the sample area (cm$^2$). In H$_2$SO$_4$ solution, the thickness of barrier layer for bare Al sample is the lowest ($d_{fb} = 0.74$ nm). This thickness increases to 3.25 nm for the 1st AAO film, and becomes thicker (4.49 nm) for the EP sample which has also the highest $R_b$ value compared with the other fabricated AAO coatings.

(d) The data in Fig. 10a evidence a decrease in $d_f$ value for AAO film on the 2nd sample (2.01 nm). A plausible explanation is that during the second anodizing step, self-organized nanoporous layer stems on the expense of the based barrier layer that remains after the electropolishing step. The second AAO coating is thus characterized by a thinner inner barrier layer covered with a much thicker outer porous layer. This fact can be further supported from its AFM image (Fig. 2d), revealing that the average roughness ($R_a = 991$) and the maximum vertical height ($527.40$ nm) for the 2nd sample are both significantly larger when compared to their values for the other samples.

(e) In addition, after coloring the second AAO films by electrodepositing copper atoms inside its nanopores, the relative thickness of its barrier inner layer re-increases ($d_{fb} = 3.24$ nm). Thickening of the barrier layer, which constitutes the base of the pores may occur during the positive cycle of the applied AC voltage used in the coloring step for this sample [30].

(f) On the other hand, similar trends are also obtained for the behavior of these films in 1 M Na$_2$SO$_4$ solution. The main difference is that the impedance parameters are all inferior to their values in acid sulfate solution. This agrees with the above polarization data (Table 1 and Fig. 6) showing unhabitually that all of our tested samples exhibit better corrosion resistance in H$_2$SO$_4$ than in Na$_2$SO$_4$ solution.

3.3. Surface examination

Three chosen coated samples (EP, 1st and 2nd) were immersed for 90 min in both 1 M H$_2$SO$_4$ and 1 M Na$_2$SO$_4$ solutions to scrutinize their surface morphologies. The six FE-SEM images shown in Fig. 11a–f reveal clear differences between the surface morphology of each sample in each medium. As it can be seen, samples exposed to H$_2$SO$_4$ solution (Fig. 11a, b & c) have quite variant morphologies than those exposed to Na$_2$SO$_4$ solution (Fig. 11d, e & f). Inspection of the microstructures for specimen surfaces indicates strong damage in sulfate solution than in acid, but to a varying degree depending on the type of AAO coating. The most detrimental effect is shown for the 2nd sample (Fig. 11f) where after 90 min exposure in Na$_2$SO$_4$ solution its AAO surface film reveals formation of a microstructure having many interconnected micro-cavities. Improving this feature to a little extent occurs in the image for the 1st sample (Figs. 11e), and to much more extent for the EP sample (Fig. 11d). On the other hand, after 90 min exposure in H$_2$SO$_4$ solution the micrograph of this latter sample (Fig. 11a) reveals

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Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_b$ (kΩ cm$^2$)</th>
<th>$C_b$ (μF cm$^{-2}$)</th>
<th>$R_p$ (kΩ cm$^2$)</th>
<th>$C_p$ (μF cm$^{-2}$)</th>
<th>$R_{bc}$ (kΩ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 1 M H$_2$SO$_4$</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare Al</td>
<td>1.09</td>
<td>11.68</td>
<td>0.075</td>
<td>3.36</td>
<td>1.58</td>
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<tr>
<td>1st</td>
<td>26.3</td>
<td>2.67</td>
<td>13.2</td>
<td>1.94</td>
<td>2.89</td>
</tr>
<tr>
<td>EP</td>
<td>101</td>
<td>1.93</td>
<td>33.5</td>
<td>1.62</td>
<td>1.67</td>
</tr>
<tr>
<td>2nd</td>
<td>12.0</td>
<td>4.32</td>
<td>6.52</td>
<td>1.18</td>
<td>1.16</td>
</tr>
<tr>
<td>Colored</td>
<td>8.69</td>
<td>2.68</td>
<td>0.482</td>
<td>1.27</td>
<td>4.75</td>
</tr>
<tr>
<td>(b) 1 M Na$_2$SO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bare Al</td>
<td>0.26</td>
<td>15.82</td>
<td>0.012</td>
<td>10.56</td>
<td>0.93</td>
</tr>
<tr>
<td>1st</td>
<td>5.40</td>
<td>2.58</td>
<td>0.013</td>
<td>3.00</td>
<td>1.03</td>
</tr>
<tr>
<td>EP</td>
<td>13.80</td>
<td>2.54</td>
<td>0.770</td>
<td>3.24</td>
<td>2.26</td>
</tr>
<tr>
<td>2nd</td>
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<td>4.62</td>
<td>0.027</td>
<td>0.76</td>
<td>1.79</td>
</tr>
<tr>
<td>Colored</td>
<td>1.98</td>
<td>6.46</td>
<td>0.027</td>
<td>4.18</td>
<td>6.85</td>
</tr>
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</table>
almost no visible attack, but for the 1st sample (Fig. 11b) a very few pits can be seen in the image, and their number increased further in the image of the 2nd sample (Fig. 11c). The surface analysis results suggest a relatively higher stability for the fabricated AAO films in sulfuric acid than in sulfate solution. However, in each medium EP film has always better sealing and protection performance. Our conclusion validates properly the polarization and electrochemical impedance results.

4. Conclusions

Surface analysis and physical methods were used to characterize four different prepared AAO films relevant to their bare Al substrate. The fabricated samples include one-step anodized film (1st), first anodized electrolytic polished film (EP), self-organized two-step anodized film (2nd) and electrodeposited copper atoms in the pores of the 2nd anodized film (colored). Electrochemical polarization and impedance techniques were then employed to investigate their stability performance in both molar sulfuric acid and sulfate solutions compared to the behavior of bare Al. Generally, the results reveal that protection capability and surface stability of the four fabricated samples are strictly influenced by the method adopted in their preparation. Interestingly, the positive shift in $E_{\text{corr}}$ and the decrease in $j_{\text{corr}}$ for any sample in $\text{H}_2\text{SO}_4$ than in $\text{Na}_2\text{SO}_4$ solution implies that sulfuric acid is less aggressive than sulfate solution. This is likely attributed to local alkalization in the interface region, which will form soluble aluminate anions ($\text{AlO}_2^-$) in the sulfate solution. In either solution the corrosion resistance of the fabricated AAO films decreases in the following order: EP > 1st > 2nd > colored > bare Al. EIS data were successfully analyzed using two parallel time constants EC to describe the behavior of the inner barrier and outer porous layers comprising the AAO film. The resistance of the barrier layer ($R_b$) has always higher value than that for the porous layer ($R_p$), thereby dominating the rate of charge transfer reaction and the film stability in the prevailing environment. The increasing trend for the sealing performance and protection capability of the various fabricated films follows the same above ranking. Surface examination using FE-SEM images support well the electrochemical results and validate the above trend.

References

The image contains a page with several references cited in the text, each formatted in a typical academic citation style. The references cover a range of topics including electrolytic coloring of anodized aluminum, technique for self-assembly of tin nanoparticles, characterization of black Ni and Sn, self-ordering of cell configuration, and many others. The references are from various journals and conference proceedings, indicating a comprehensive coverage of research in the field of anodic aluminum oxide (AAO) and its applications.

The references are cited in a standard academic format, which is typical for scientific articles. Each reference includes the authors' names, the title of the paper, the name of the journal or conference, and the publication year. The references are numbered sequentially, with each reference corresponding to a point in the text where it is cited.

The page contains a variety of mathematical symbols and equations, which are common in scientific literature. These symbols and equations are used to represent chemical reactions, mathematical relationships, and physical properties. The presence of these symbols and equations indicates that the page is part of a scientific or technical article, likely discussing the properties and applications of anodic aluminum oxide (AAO) and related materials.

In summary, the page is a typical scientific reference page, filled with citations that provide further reading and background information on the topics discussed in the text. The references are well-organized and formatted according to standard academic citation styles, making it easy for readers to locate and access additional information on the topics covered in the text.