OPEN ACCESS

Corrosion Testing of Anodized Aerospace Alloys: Comparison Between Immersion and Salt Spray Testing using Electrochemical Impedance Spectroscopy

To cite this article: B. J. Usman et al 2020 J. Electrochem. Soc. 167 041505

View the article online for updates and enhancements.
Corrosion Testing of Anodized Aerospace Alloys: Comparison Between Immersion and Salt Spray Testing using Electrochemical Impedance Spectroscopy

B. J. Usman,1,*,z F. Scenini,1,2 and M. Curioni1,**

1Corrosion and Protection Centre, Department of Materials, University of Manchester, M13 9PL Manchester, United Kingdom
2Materials Performance Centre, Department of Materials, University of Manchester, M13 9PL Manchester, United Kingdom

The corrosion performance provided by two anodizing treatments aiming at obtaining films with comparable thickness but different pore morphology was evaluated by immersion, salt spray, and a hybrid tests. The hybrid test was performed in cycles by alternating between immersion and salt spray tests. The corrosion progression was evaluated at selected times by electrochemical impedance spectroscopy (EIS). The EIS indicated that, during immersion test, the self-sealing of the pores due to the precipitation of aluminium hydroxide was favored, and it provided a substantial contribution to the improved corrosion resistance. Vice versa, during salt spray testing, the continuous flow of electrolyte promoted aluminium oxide film dissolution. The EIS study was complemented by the surface appearance and composition of specimens before and after exposure using Field Emission-Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray (EDX) analysis. Overall, the relative performance of the anodic oxides was shown to be dependent on the exposure conditions. In fact, an anodic film with finer pores behaved better during immersion tests, whereas films with coarser pores provided better corrosion protection during salt spray testing.

Outstanding mechanical properties of 2xxx aluminium alloys enable their application in the aerospace industry. However, galvanic coupling of copper-containing particles with aluminium matrix usually results in reduced corrosion performance.1 Anodizing in acidic electrolytes is one of the most widely employed surface treatment for improving corrosion resistance. In the aerospace industry, chromic acid anodizing (CAA) was the most popular method for producing anodic films with excellent corrosion protection.2 However, due to the environmental and toxicological problems, the use of hexavalent chromium at industrial level is restricted by the EU directive of the Registration, Evaluation, Authorization and restriction of Chemicals (REACH) in 2017.3,4 The quest for green and effective replacements to the CAA led to a continuous evolution of new chromate-free alternatives.

There are significant research efforts on new chromate-free anodic oxide coatings from varying approaches ranging from a tuning of anodizing parameters such as voltage5,6 or changing the chemistry of anodizing baths using acids such as sulphuric,7 phosphoric,8 oxalic,9 tartaric,10 etc. The use of mixed acids electrolytes such as tartaric-sulphuric,10,11 sulphuric-boric,12 sulphuric-boric-phosphoric13 or modifying the bath with corrosion inhibitors14,15 are other recent approaches.

Corrosion testing is an important aspect for the qualification and certification of materials for aerospace vehicles and the design of actual structures and components. Corrosion of anodic oxide films under immersion1,2,6,12,16,17 and salt spray tests13,17,18 has been extensively studied. However, the two environments are unlikely to provide the same relative performance ranking since they differ in many important factors that affect the corrosion rate and mechanism.

The first important difference between SST and immersion lies in the thickness of the electrolyte that contacts the metal surface, a thin film in the first case, and a bulk electrolyte in the second. Previous works on stagnant electrolytes have indicated that the thickness of the electrolyte can affect the corrosion rate19,20 and that electrolyte with thickness below 50 μm generally causes lower corrosion rates than thicker or bulk electrolytes. Electrolyte thicknesses above 200 μm induce corrosion that is similar to that induced by bulk electrolytes.19 Nevertheless, these observations on stagnant electrolytes cannot be directly transferred to the salt spray electrolyte film because the continuous spraying renews the electrolyte.

The presence of a thin film electrolyte that is continuously refreshed by electrolyte droplets in contact with air before being deposited is clearly better oxygenated compared to a bulk electrolyte in proximity of the surface of an immersed metal at the steady-state, where a stable diffusion regime has been established. As a result, the cathodic reaction of oxygen reduction, and hence corrosion, should proceed faster in the case of refreshed thin-film electrolyte compared to the case of a bulk electrolyte. However, the ohmic resistance associated with the flow of ionic current in a thin electrolyte is much higher than that for a bulk electrolyte. As a result, for a bulk electrolyte, the geometrical distance between an active anodic site and an active cathodic site has little effect on corrosion propagation; if an electrochemical reaction is supported in any location of the metal, the current is made available to sustain a corresponding anodic (or cathodic) reaction anywhere else on the metal surface. Thus, from this viewpoint, the immersion test should result in faster corrosion than salt spray test. Finally, the effects associated with local pH variations, dissolution and re-precipitation should be considered. Thin electrolyte film is associated with lower volume and saturation can be attained quickly. Therefore, in the presence of a thin electrolyte, local pH variations, the formation of partially protective films by precipitation of corrosion products or, when applicable, of corrosion inhibitors should be favored compared to bulk electrolyte conditions. However, the salt spray case is complicated by the fact that the electrolyte is thin, but at the same time is continuously refreshed. The refreshing of the thin electrolyte might rebalance local pH and reduce the tendency of corrosion products or corrosion inhibitors species to precipitate. Overall, it is impossible to qualitatively predict the net result of these contrasting effects.

It is accepted that the corrosion of porous anodic oxide films initiates at defective sites on the film/alloy interface resulted from partially anodized intermetallic particles during exposure of anodized surfaces. Thereafter, corrosion propagates in the alloy substate beneath the anodic film, which ultimately results in damage to the bulk anodic film.16,18 At the same time, precipitation of
aluminum hydroxide, Al(OH)₃ due to self-sealing of the porous oxide may take place depending on the nature of the environment. The formation of the precipitation products is known to decrease capacitance as well as enhance the corrosion resistance of the porous layer. However, the difference in the rate of the formation of precipitation product under the influence of thin and highly oxygenated electrolytes during the salt spray compared to the bulk electrolyte carrying less oxygen during immersion test have not yet been considered. Similarly, the possibility of the hindrance of the precipitation products formation or washing away of the pre-existing oxide and precipitated hydration products if at all it is formed, due to the continuously refreshed electrolytes during the salt spray tests is often ignored.

Until now, little attention has been devoted to the understanding of the difference in corrosion of anodic films under immersion and salt spray. Therefore, this work aims at enhancing the fundamental understanding of the implications of the selection of corrosion testing methodologies. This was achieved by investigating the corrosion behaviour of bare and anodized AA2024-T3 during exposure to immersion and salt spray testing, whilst maintaining constant all the other parameters, such as temperature, electrolyte concentration and exposure time.

Porous anodic oxides are particularly convenient substrates for this study, due to the immediate relevance to the aerospace sector, and the fact that film parameters such as thickness and pore diameter can be easily controlled by controlling the anodizing charge and anodizing voltage respectively. Anodic films formed in tartaric-sulphuric acid (TSA) electrolyte have been widely studied, and it has been established that thicker films are generally beneficial for corrosion protection. However, in practice, film thickness has to be limited to a few microns because of the decay in fatigue life. Higher anodizing potential generates coarser morphology while lower anodizing potential produces finer ones but the overall thickness of oxide is dependent on the charge passed. When tested by immersion, finer pores produced at lower voltages provide better corrosion resistance compared to coarser pores produced at higher voltage despite the faster partial-sealing during the former. In this work, the selection of bare and anodized alloy as testing substrates has been made because the study of the bare alloy enables understanding of the phenomena related only to the metal attack and the possible precipitation of corrosion products. On the other hand, the study of the behaviour of porous anodic oxides with different morphologies enables understanding of the phenomena related to the partial sealing or film degradation as a function of exposure conditions.

For decades, EIS was proved to be a powerful tool for the study of mechanism and kinetics of corrosion processes. In particular, EIS was extensively used for the study of corrosion behaviour of porous anodic films due to its ability to resolve the porous and barrier layer properties as a function of frequency. For this reason, EIS was used to follow the corrosion processes under different exposure types while optical images were taken after each test for visual

![Figure 1](image1.png)  
Figure 1. (a) Time evolution of the current density and (b) time evolution of the charge density for anodizing of AA 2024 in TSA solution at 7 and 14 V.

![Figure 2](image2.png)  
Figure 2. FE-SEM images showing surface morphologies of anodized specimens at (a) 14 V and (b) 7 V.
observation. The magnitude of the partial hydration of the porous layer evidenced by EIS spectra at medium-high frequency was complemented by high-resolution SEM images. Furthermore, the elemental composition of the substrates before and after corrosion was investigated using Energy Dispersive X-ray (EDX) analysis. Finally, an important correlation was found between the electrochemical and surface characterization studies.

Experimental

Materials.—Specimens of size 4 × 6 cm² were cut from 1.6 mm thick AA 2024-T3 wrought alloy sheets using a guillotine. Thereafter, the specimens were degreased in acetone, etched in 100 g l⁻¹ of sodium hydroxide at 60 °C for 30 s, desmutted in 30% vol. nitric acid at room temperature for 30 s, and finally rinsed with deionized water. Each specimen was masked with stopping-off lacquer 45 leaving exposed an area of 9.45 cm².

Anodizing.—Two anodizing cycles were employed to produce the anodic oxides on the alloy. The first cycle was performed at a cell potential of 14 V for 1500 s in TSA composed of 0.46 M sulfuric and 0.533 M tartaric acid, at 37 °C. These parameters resulted in an anodizing charge of 10.5 C cm⁻² and an oxide layer thickness of approximately 3 μm. The second anodizing cycle was performed maintaining all other conditions constant (including the final anodizing charge), except that the anodizing potential that was 7 V. The time required to achieve the same anodizing charge of 10.5 C cm⁻² at 7 V was 3200–3300 s. This procedure aims to obtain two anodic oxides with approximately the same thickness, due to the similar anodizing charge, but different pore morphology, due to the different anodizing voltage. In particular, the film obtained at 14 V had a coarser morphology compared to the films anodized at 7 V. After anodizing, the specimens were rinsed with deionized water and dried in a stream of cool air.

Salt spray test.—The salt spray chamber was operated according to the ASTM B117 standard. The sodium chloride concentration of 5.0 wt% was used to create fog droplets near-neutral pH with the temperature of the cabinet chamber maintained at 35 °C. The anodized specimens were divided into 3 groups. The first group was continuously exposed to the spray, as per the “traditional” ASTM B117 practice and are referred to as “salt spray” hereon. The second group was placed in the same salt spray chamber in an open cylindrical container containing the same solution that was used to operate the salt spray chamber, such as the specimen was completely immersed in the solution and the solution was partially refreshed by the spray; these samples are referred to as “immersion.” The third group of specimens was alternatively exposed to 50% of “traditional” salt spray (same condition as the first group), and 50% of immersion (same condition as the second group). The test initially started with salt spray and ended with immersion and in each case, the exposure period was 24 to 48 h. These samples are referred to as “hybrid.”

EIS.—Electrochemical impedance spectroscopy measurements were used to monitor the progress of corrosion on each specimen. For this purpose, each of the specimens from each of the groups was briefly extracted from the salt spray chamber, immersed in a beaker containing the same solution used in the salt spray chamber, and connected to a Solatron Modulab Potentiostat. The AC amplitude of the EIS perturbating signal was 5 mV (rms) and the frequency range inspected was 100 kHz to 0.01 Hz. A three-electrode cell was used, with a silver-silver chloride reference electrode and a platinum counter electrode. EIS was performed once a stable free corrosion potential was attained. Generally, a stable corrosion potential was observed shortly after immersion in the EIS test solution, since all the specimens were continuously exposed to the same solution prior to EIS measurement. The corrosion potential was generally between −0.6 to −0.7 V vs Ag/AgCl depending on the exposure time and the nature of the specimen.

Surface characterization.—For visual observation, canon scanner LiDE 220 was used to image the surface morphology of specimens after electrochemical test before they are taken back to the exposure chamber. Zeiss Ultra 55 SEM was used for observation of the specimens’ surface morphology at high magnification using an accelerating voltage of 1.5 kV. A Quanta 250 was used for the EDX analysis using an accelerating voltage of 20 kV.

Figure 3. EDX mappings of the test substrates (a) before anodizing and after anodizing at (b) 14 V and (c) 7 V.
accelerating voltage used with the Zeiss Ultra 55 SEM was selected to minimize the interaction volume between incident electron beam and specimen, thereby producing images representative of the specimen surface. Prior to the final surface characterization, corrosion products were removed in 30% vol. nitric acid for 20 min. All specimens were exposed to the same treatment regardless of exposure condition.

Results

Characterization of the test substrates.—Figure 1 presents the time evolution of the (a) current density and (b) charge density for the two anodizing conditions at 14 V and 7 V in the TSA electrolyte. For each case, two representative responses are reported to show the good reproducibility of the anodizing behavior. According to Fig. 1b, the charge density at the end of both 7 V and 14 V cycles was closely similar and so the thickness of the resulting porous anodic oxide is also expected to be similar. However, due to the difference in anodizing voltage, the films’ appearance and particularly pore sizes were different for the two anodizing cycles. Figure 2 shows the top surface of the anodic oxides, where it is possible to observe that a higher anodizing voltage resulted in a coarser morphology while lower anodizing voltage was characterized by finer morphology. Micrographs of cross sections of anodic oxides obtained in closely similar conditions, showing clearly the dependence of pore size on applied voltage can be found in previous works.5,31

Figure 3 shows the EDX mapping of the substrates under investigation. The bright color shows a higher amount of the element mapped. For the bare alloy, in Fig. 3a, aluminum dominates composition on the surface and dark regions in the Al maps associated to the large second phase particles. At the dark regions
on aluminum maps, a high amount of the second phase elements, copper and magnesium was observed on their maps. For the anodized specimens, the surfaces had a uniform distribution of aluminum and oxygen. Unlike for the bare alloy, a higher amount of oxygen and a lower amount of aluminum were observed due to the formation of aluminum oxide ($\text{Al}_2\text{O}_3$) film. Another observation was that, for the anodized specimens, the second phase particles present on the bare alloy disappeared due to their dissolution during the anodizing process. The nominal elemental compositions of the test substrates obtained from EDX analysis before exposure to the corrosive environments were listed in Table I.

**EIS results.**—Figure 4 shows representative EIS spectra as a function of time for the bare alloy surface (not anodized) under immersion, salt spray and hybrid conditions. In all three conditions, the impedance responses were closely similar. In particular, a large time constant was evident at a medium-low frequency and the low-frequency value of the impedance modulus ($|Z|$) was between 10 and 20 k$\Omega$ for the entire duration of the exposures. Up to 192 h,

| Table I. Elemental composition of the test substrates. |
|---------------------------------|-----|-----|-----|-----|-----|-----|
| Composition (wt%) | Al  | O   | Cu  | Mg  | Mn  | S   |
| Bare AA 2024-T3      | 93.0| 1.0 | 4.7 | 0.8 | 0.5 | —   |
| 14 V anodized AA 2024-T3 | 49.5| 45.7| 0.4 | 0.4 | 0.1 | 3.8 |
| 7 V anodized AA 2024-T3   | 50.6| 45.7| 0.5 | 0.3 | 0.1 | 2.7 |
exposure time had little or no effect on the EIS response, indicating that corrosion was onset at the early stages and progressed steadily, without the formation of protective corrosion products. After 504 h, the specimens under salt spray showed a slight decline in the low-frequency value of \(|Z|\) compared to the immersed and hybrid specimens. Generally, at low frequency, the phase shift was greater than zero and the impedance modulus did not show a flat plateau, indicating that a diffusion-controlled reaction, such as oxygen reduction, contributed to the EIS response. This feature was observed for all the EIS spectra. At very high frequency (above 50 kHz), a slight increase in impedance modulus was observed. This is likely to be an experimental artefact due to the parasitic capacitance of the cell and of the measurement cables, and it is not discussed further.

The time evolution of the EIS responses for the specimens anodized at 14 V and 7 V exposed to immersion, salt spray and hybrid conditions are presented in Figs. 5 and 6 respectively. Regardless of the exposure conditions, more complex spectra than for the bare alloy specimens were observed. In particular, two time constants were evident, one at medium-low frequency and one at medium-high frequency. The former is associated to the charge transfer processes related to the barrier layer of the pores and, at longer immersion times to the corrosion of the substrate; conversely, the latter is associated to the response of the porous anodic oxide covering the surface. Under all the exposure conditions, the low-frequency impedance modulus decreased with time which suggests a decrease in the corrosion resistance. However, the medium-high frequency behavior differentiated the specimens based on the exposure type. For the immersed samples, there was a decline of the phase angle spectrum and a corresponding increase in impedance modulus at medium-high frequencies, as evidenced by the shift of

![Figure 6. Series of Bode plot EIS spectra for 7 V-anodized AA2024-T3 specimens at (a) and (b) 24 h (c) and (d) 192 h and 504 h (e) and (f). IMM = immersion, HYB = Hybrid, SSP = Salt spray.](image_url)

Journal of The Electrochemical Society, 2020 167 041505
...the spectra to right. Both scenarios suggest a progressive decrease in the overall capacitance and increase in the porous layer resistance. Contrary, the phase angle peak slightly increased for both the salt spray and hybrid specimens especially between 192 and 504 h. In the same vein, there is a decrease in impedance modulus at medium-high frequencies as seen by the shift of the spectra to the left, both of which indicate an increase in the overall capacitance and decrease in the porous layer resistance. When anodized samples are immersed in test solution, the electrolyte may be absorbed by the pores in the anodic film and the anhydrous alumina reacts with the absorbed water, which leads to the formation of voluminous hydrated alumina due to self-sealing. It is known from the previous works that the self-sealing effect results in the decrease in capacitance and increase in the porous layer resistance.\textsuperscript{21,22} Therefore, the decrease in the capacitance for samples under immersion test and contrasting increase in the capacitance for samples under salt spray and hybrid test may suggest precipitation of self-sealing products in the pores during immersion and dissolution of oxides during salt spray respectively. The stagnant bulk electrolyte might favor the formation of the precipitation products due to the partial hydration of porous oxide whereas the refreshing thin electrolyte hinders or washes away the partial hydration products. This observation was confirmed by FE-SEM and EDX characterization of the corroded surfaces that will be presented later.

Figure 7 presents the comparison between the bare alloy, 7 V and 14 V anodized AA2024-T3 specimens after different exposure modes for 504 h. NA = Non-anodized.
Under immersion (Figs. 7a and 7b), the low-frequency impedance modulus was similar for both anodizing cycles, and about one order of magnitude higher than the bare alloy. At higher frequencies, the spectrum for the specimen anodized at 7 V showed significantly higher impedance modulus than the specimen anodized at 14 V, suggesting a greater extent of pore self-sealing. During hybrid exposure (Figs. 7c and 7d) and salt spray (Figs. 7e and 7f) conditions, the behavior of the 7 V and of the 14 V anodized specimens was broadly similar, with the impedance modulus of the 7 V specimen being marginally lower in both cases.

Corroded surfaces.— Morphological characterization.—Figures 8a and 8b presents the images of the bare alloy, 7 V anodized and 14 V anodized after corrosion for 504 h in the three exposure conditions before and after removal of corrosion products respectively. The images of the specimens taken as a function of time are provided in the supplementary figures for the bare (Fig. S1 is available online at stacks.iop.org/JES/167/041505/mmedia), anodized at 14 V (Fig. S2) and anodized at 7 V (Fig. S3) samples. Regardless of the nature of the specimens’ surface, all the specimens were exposed to the same treatment for the removal of the corrosion products. The most important difference observed was the presence of electrolyte pathways/trenches on the test substrates under salt spray and hybrid tests which was absent for the immersed specimens. For the bare alloy, all the specimens showed significant corrosion, with general darkening of the surface and formation of pits, from the very early stages of the tests. The morphology of the alloy that was exposed to immersion showed finer corrosion features compared to the alloy exposed to salt spray and hybrid testing. For both 14 V and 7 V anodized specimens, corrosion products appeared around 192 h for hybrid and salt spray exposure and then continuously worsened with time as shown in Figs. S2 and S3 respectively. The appearance of the corrosion products at this time may suggest reaction of the corrosive environment with aluminum which became exposed due to the washing away of the film by the refreshing electrolytes as it lands on the surface. This can be corroborated by trenches of the electrolytes on the surface of the panels. For the specimens exposed to immersion, corrosion in form of small pits initiated around 360 h for the specimens anodized at 14 V and was absent until 504 h for the specimens anodized at 7 V. For the same anodizing conditions and time, corrosion was generally more severe during salt spray or hybrid exposure than during immersion. The observation of the untreated specimen, that the corrosion attack was finer and more homogeneous during immersion that during salt spray, was also qualitatively confirmed for the anodized specimens.

Furthermore, images obtained by FE-SEM are presented in Fig. 9. For the bare alloy, the corrosion sites appear smaller and more homogeneously distributed for the alloy that was immersed into the electrolyte compared to the alloy that was exposed to salt spray (Figs. 9a–9c)), and this is in agreement with the optical images. On the other hand, the specimens under salt spray displayed larger corrosion sites and coarser surfaces. Interestingly, both the features typical of immersion (i.e. small corrosion sites) and of salt spray (coarser corrosion sites with trenches) were observed on the alloy that underwent hybrid exposure.

For the anodized surface, as seen in Fig. 9d–9i for the 14 V and 7 V respectively, the difference between immersion and salt spray was more evident. Immersed specimens had smooth and uniform film surfaces with cracks typically observed when anodic oxide is hydrated while salt spray and hybrid specimens had a coarse appearance with an evident deterioration of the film due to the dissolution induced by the refreshing of the corrosive electrolyte. To gain an insight into the condition of the pores after the exposures, high magnification images were taken from areas that were less corroded by FE-SEM and displayed in Fig. 10.
differences were observed between the immersed specimens which had partially sealed pores Fig. 10a, 10d and hybrid and salt spray tests where the pores appeared relatively opened (Fig.10b, 10e and 10c, 10f).

Overall, for both the 7 V and the 14 V cycles, exposure to continuous immersion appeared to induce less damage compared to salt spray and alternated immersion. A Qualitative observation indicated that the anodic oxide obtained at 7 V performed better than those obtained at 14 V during continuous immersion. However, an equivalent or marginally worse performance was observed for the 7 V anodic film than that anodized at 14 V during salt spray and alternated immersion condition as observed in Fig. 9. Thus, is in agreement with the EIS result presented in Fig. 7, appearance of the specimens as well as nature of the pores after corrosion clearly indicated that specimens were differentiated by exposure type.

EDX analysis.—EIS and morphological studies indicated significant differences between immersion and the other exposure types for the corrosion of anodized surfaces. For this reason, EDX analyses were conducted on the corroded and as-anodized specimens to enable understanding of the changes in elemental composition.

Figs. 11 and 12 show the EDX mapping profiles of the corroded specimens under different exposure conditions for the 14 V and 7 V anodizing respectively. Regardless of the anodizing cycle, the immersed specimens were characterized by a uniform presence of Al and O throughout the surfaces. In contrast, the samples under immersion and salt spray and hybrid salt spray presented irregular pattern of distribution of Al and O. Two types of regions were identified; “corroded areas” where there was presence of high Al and lack of O due to the removal of Al₂O₃ by the action of moving electrolytes and “film remnant zones” where the film was less affected. The corroded areas had a high proportion of Al and less O due to the removal of Al₂O₃ film and subsequent exposure of Al substrate. Conversely, the zones where films still remained has a relatively high amount of Al and O which are the major constituents of the film.

Figures 13b and 13c shows the nominal composition of the elements present on the corroded surfaces of 14 V and 7 V anodized specimens respectively. A Comparison of the composition of the substrates before and after corrosion leads to a better understanding of the changes during exposure types. For both the anodizing cycles, the amount of aluminum decreased and oxygen increased on the

Figure 9. FE-SEM images of the (a)–(c) bare alloy (d)–(f) 14 V-anodized and (g)–(i) 7 V anodized specimens after corrosion under different exposure conditions; (a), (d), (g) immersion, (b), (e), (h) Hybrid and (c), (f), (i) salt spray tests.
anodized surfaces after the immersion test compared to the initial composition. This is due to the formation of partial hydration product, Al(OH)$_3$ which has less aluminum and more oxygen content than the pre-existing Al$_2$O$_3$ on the substrate. The oxygen content in Al(OH)$_3$ is 1.4 times more than that of Al$_2$O$_3$ whereas, the latter has 1.5 times more aluminum content than that of the Al(OH)$_3$. Thus, the formation of the aluminum hydroxide during immersion leads to the reduction of Al and to an increase in the amount of O compared to the initial anodized material. Contrary, the other exposures had higher Al and lesser O compared the anodized specimens before corrosion and this effect was more evident on the salt spray test. Moreover, there was the presence of a high amount of the major alloying element, Cu after the hybrid and salt spray tests. In fact, the significant amount of Al and Cu content suggests the washing away of the alumina films and subsequent exposure of the alloy substrate during the salt spray and hybrid tests.

Thus, in agreement with EIS and morphological studies, EDX analysis confirmed the possibility of partial hydration during the immersion test and dissolution of the oxide film during hybrid and salt spray tests. For this reason, immersed specimens were protected by the hydration products while hybrid and salt spray specimens were highly corroded by the continuously refreshed electrolytes striking the surface.

**Discussion**

The present work aimed to compare the degradation behavior under three exposure conditions that were identical for chemistry and temperature but differed for the way the test environment interacts with the surface. For salt spray, the sodium chloride solution formed a thin layer of electrolyte above the specimen surface, which continuously flowed. During immersion, a large
volume of quiescent electrolyte is continuously in contact with the corroding surfaces. It is expected, therefore, that significant differences in the interaction between electrolyte and corroding surface will develop during the corrosion process, depending on the exposure conditions.

**Bare alloy.**—Before exposure to the aggressive environments, the bare alloy was covered by an air-formed oxide film and it could be considered free of corrosion products. Some intermetallic particles might be exposed to the surface and might constitute preferential sites for corrosion initiation. Regardless of the exposure conditions, after sometime, localized corrosion initiates on the alloy surface, with some regions where the anodic reaction localizes, acidification takes place, and metal is lost into the environment; other regions where the cathodic reaction and associated alkalization localize, trenching of the alloy matrix nearby cathodically active intermetallic can occur. Conversely, at some locations, somewhere in between the highly acidic corrosion front and the alkaline sites supporting the cathodic reaction, the pH has intermediate values which creates conditions that are favorable for the precipitation of corrosion products. In general, the precipitation of corrosion products could be beneficial if it can provide some level of protection to the substrate; however, it is also possible that corrosion product does not affect the overall corrosion rate, if loosely adherent or very porous.

The findings presented in this work are useful to understand the differences of behavior of the alloy in the two exposure conditions, i.e., salt spray and immersion. According to Fig. 4, EIS responses measured at various stages of immersion and of salt spray revealed that up to 192 h, the corrosion resistances were very similar. However, longer testing times suggests that salt spray marginally induced more corrosion. Likewise, a surface study of the corroded bare alloy, clearly revealed that the morphology of the corrosion attack is different during immersion and salt spray, with finer and more homogeneously distributed corrosion sites observed after immersion than after salt spray. Three main factors might be responsible for the changes in the corrosion resistance and the morphologies between immersion and salt spray on the bare alloy. Firstly, the oxygenated fog interacting with the surface of the specimens caused more cathodic oxygen reduction reaction. Secondly, the dissolution action of the salt spray electrolytes striking the surface of the samples may also have contributed to the degradation of the surface thereby decreasing corrosion resistance. Interestingly, Fig. 9 shows the coarse corroded areas on the surface of the salt spray samples which are absent on the immersed surfaces. Another possibility of the difference in corrosion performance is the geometrical effects associated with the formation and precipitation of corrosion products during salt spray exposure. As corrosion is initiated, some of the metal is consumed and some corrosion products precipitate away from the active anodic or cathodic sites. As precipitation proceeds, the corrosion products alter the flow of the thin electrolyte, and stabilize the localization phenomena, producing regions where the oxygen-carrying electrolyte is continuously refreshed and regions where the flow of new electrolyte is minimal. Thus the characteristic dimensions of the corrosion sites during salt spray exposure is larger than that observed during immersion. It is useful to note that, during hybrid testing, both

![Figure 11](image-url). EDX mappings of the 14 V anodized specimens after (a) immersion (b) hybrid and (c) salt spray for 504 h.
types of corrosion sites (large and small) as observed in Fig. 9. Therefore, it is reasonable to assume that the large corrosion sites propagate during salt spray exposure, whilst the small corrosion sites form and propagate during immersion testing.

In summary, for the bare alloy, it appears that the difference in corrosion resistance and the morphology are associated to the ease of oxygen access, dissolution of the surface film by salt spray droplets and the fact that the geometrical effects due to the precipitation of corrosion products play a significant role during salt spray, but have little influence during immersion.

**Anodized alloy.**—Compared to the bare alloy, the effect of the exposure condition is more complex for the anodized specimens. This is immediately evident from the fact that, unlike for the bare alloy, the EIS spectra measured at various stages of exposure, are significantly different depending on the exposure conditions (Figs. 5 and 6).

At the beginning of the test, a certain number of defective sites in the anodic film are unavoidably present on the surface, due to the complex alloy microstructure. For example, whenever anodizing is interrupted, some of the intermetallics exposed to the surface will only be partially oxidized and might provide locations for corrosion initiation. Further, even when oxidized completely, the remnants of second phase particles introduce defects in the anodic oxide, such as voids or cracks, which can form preferential sites for corrosion initiation.16,18 These defective sites, and the associated corrosion processes, determine the low-frequency response of the anodized alloy during EIS measurement.21,22

At the same time, the vast majority of the surface was covered by a homogeneous anodic oxide, with relatively uniform pore morphology. As suggested earlier, this oxide can undergo self-sealing during exposure to a bulk and stagnant environment and the pores can be progressively closed by an aluminum hydroxide layer. The part of the surface covered by the homogeneous oxide determines the high-frequency response during EIS spectra, and the process of self-sealing can be followed by considering the time evolution of the corresponding time constant.

In addition, it is expected that a certain level of interaction might take place between the corrosion at defective sites and the self-sealing process. If the defective sites are sufficiently small, then the precipitation of aluminum hydroxide generated by the dissolution of the adjacent anodic oxide might be beneficial, and prevent or hinder corrosion propagation. Vice versa, if the defective sites are large, or after corrosion has produced sufficiently large regions not covered by the anodic oxide, the precipitation of hydration products from the porous skeleton is unlikely to significantly prevent corrosion propagation.

The results presented here indicate that the three testing methods induce differences in corrosion behavior and are responsible for the different relative performance of the two anodic oxides despite their similar thickness. In particular, the oxide with finer pores (7 V) behaves better during immersion compared to the oxide with coarser pores (14 V). In fact, during immersion the conditions are favorable to self-sealing while during salt spray and hybrid testing, the mechanical action of the salt fog landing on the specimen’s surface led to the removal of the film oxide and subsequently, the underlying metal substrate is exposed to corrosion. Thus, the film with finer pores behaved better,
since finer pores are easy to be filled by precipitation product. Vice versa, under salt spray and hybrid conditions the performance of the two anodic oxides is inverted because finer pores prepared at 7 V are easier to be removed/washed away by continuous electrolyte droplets striking the surface than coarser films prepared at 14 V. This was clearly seen in the optical microscope of specimens after corrosion products removal in Fig. 8b and confirmed by EDX in Figs. 11b, 11c and 12b, 12c for the 14 and 7 V respectively.

Overall, there is a good qualitative correlation between EIS and varying morphologies of films corroded under different exposure conditions. From EIS studies, immersed specimens were characterized by a gradual increase in the medium-high frequency impedance and decrease in capacitance due to continuous self-sealing of the pores. In agreement, optical images (Fig. 8) showed smooth surfaces without corrosion products. Similar to this, SEM images in Fig. 9d, 9g presented smooth surfaces with cracks believed to be due to precipitation of hydration products.18 Most importantly, high magnification SEM in Fig. 10a, 10d showed the surface with relatively sealed pores. On the other hand, for hybrid and salt spray exposures, EIS indicated a decline in the medium-high frequency impedance and increase in capacitance due to dissolution of the film which subsequently led to the exposure of the bare alloy. This was evidenced by the highly corroded surfaces of the specimens with huge corrosion products as a result of reaction of the bare alloy with the corrosive environment. This was further supported by the SEM images in Fig. 9e, 9f and 9h, 9i with heavily roughened and corroded surfaces. The high magnification SEM images, unlike for the immersed specimens showed relatively opened pores for specimens under salt spray and hybrid exposure. Above all, EDX analysis confirmed the EIS and SEM studies through maps which showed elemental distribution and composition of the corroded specimens.

Finally, the findings highlight how the selection of test conditions can affect the relative ranking in performance of similar protective treatments, but at the same time the consideration of the difference in results can provide insight into the corrosion protection mechanism.

Conclusions

The results of this work indicate that the exposure condition has little effect on the EIS response of the bare alloy, suggesting that neither exposure to salt spray or immersion results in the formation of partially protective corrosion products. On the bare alloy, immersion produces a more homogeneous and finer corrosion attack compared to the salt spray, most likely due to the limited influence of the geometry of the corrosion products on the underlying corrosion in immersion conditions, where the electrolyte is quiescent. Vice versa, during salt spray, the formation of corrosion products that protrude from the surface and affect the flow of the thin electrolyte layer results in a coarser and less homogeneous corrosion attack. For the purpose of evaluating the corrosion performance of anodic oxides, immersion was generally less aggressive than salt spray. This is likely to be due to the fact that the flowing electrolyte during salt spray prevent effective precipitation of aluminium hydroxide and consequent beneficial self-sealing of the pores. Comparing two closely similar anodic oxides, differing only for pore diameter, the film obtained at 7 V (smaller pores) performed better than that obtained at 14 V (larger pores) if tested by immersion. Opposite behavior was observed when the two anodic oxides were tested by salt spray. Regardless of the test conditions, there is generally a good qualitative correlation between the EIS response and the surface appearance of the treated specimens.

Acknowledgments

Bashir J. Usman acknowledges the receipt of PhD scholarship from Petroleum Technology Development Fund (PTDF), Nigeria. The authors also acknowledge the support of The Engineering and Physical Sciences Research Council (LightForm—EP/R001715/1 Programme grant).

ORCID

B. J. Usman © https://orcid.org/0000-0002-5566-2373

References

1. V. R. Capelossi, M. Poelman, I. Recloux, R. P. B. Hernandez, H. G. de Melo, and M. G. Olivier, *Electrochim. Acta*, 124, 69 (2014).
2. G. Boisier, N. Pébère, C. Druge, M. Villatte, and S. Suel, *J. Electrochem. Soc.*, 155, C521 (2008).
3. F. Zhang, P. Ju, M. Pan, D. Zhang, Y. Huang, G. Li, and X. Li, *Corros. Sci.*, **144**, 74 (2018).
4. B. Priet, G. Odemer, C. Blanc, K. Giffard, and L. Arurault, *Surf. Coatings Technol.*, **307**, 206 (2016).
5. M. Curioni, P. Skeldon, J. Ferguson, and G. E. Thompson, *J. Appl. Electrochem.*, **41**, 773 (2011).
6. A. Carangelo, M. Curioni, A. Acquesta, T. Monetta, and F. Bellucci, *J. Electrochem. Soc.*, **163**, C907 (2016).
7. Z. Ding, B. A. Smith, R. R. Hebert, W. Zhang, and M. R. Jaworowski, *Surf. Coatings Technol.*, **350**, 31 (2018).
8. S. Ono and N. Masuko, *Surf. Coatings Technol.*, **169–170**, 139 (2003).
9. V. López, E. Otero, A. Bautista, and J. A. González, *Surf. Coatings Technol.*, **124**, 76 (2000).
10. M. Curioni, P. Skeldon, E. Koroleva, G. E. Thompson, and J. Ferguson, *J. Electrochem. Soc.*, **156**, C147 (2009).
11. M. Curioni, A. A. Zuleta, E. Correa, X. Pan, A. Baron-Wiechec, P. Skeldon, J. G. Castaño, F. Echeverría, and G. E. Thompson, *Trans. IMF*, **90**, 290 (2012).
12. L. Zhang, G. E. Thompson, M. Curioni, and P. Skeldon, *J. Electrochem. Soc.*, **160**, C179 (2013).
13. M. Saeedikhani, M. Javidi, and A. Yazdani, *Trans. Nonferrous Met. Soc. China (English Ed.*), **23**, 2551 (2013).
14. M. Saeedikhani, M. Javidi, and S. Vafakhah, *Trans. Nonferrous Met. Soc. China*, **27**, 711 (2017).
15. V. Moutarlier, M. P. Gigandet, B. Normand, and J. Pagetti, *Corros. Sci.*, **47**, 937 (2005).
16. Y. Ma, H. Wu, X. Zhou, K. Li, Y. Liao, Z. Liang, and L. Liu, *Corros. Sci.*, **158**, 108110 (2019).
17. R. Wang, L. Wang, C. He, M. Lu, and L. Sun, *Surf. Coatings Technol.*, **360**, 369 (2019).
18. Y. Ma, X. Zhou, Y. Liao, X. Chen, C. Zhang, H. Wu, Z. Wang, and W. Huang, *J. Electrochem. Soc.*, **163**, C369 (2016).
19. Y. L. Cheng, Z. Zhang, F. H. Cao, J. F. Li, J. Q. Zhang, J. M. Wang, and C. N. Cao, *Corros. Sci.*, **46**, 1649 (2004).
20. H. R. Zhou, X. G. Li, J. Ma, C. F. Dong, and Y. Z. Huang, *Mater. Sci. Eng. B*, **162**, 1 (2009).
21. X. Zhao, Y. Zuo, J. Zhao, J. Xiong, and Y. Tang, *Surf. Coatings Technol.*, **200**, 6846 (2006).
22. J. Suay, E. Giménez, T. Rodriguez, K. Habbib, and J. Saura, *Corros. Sci.*, **45**, 611 (2003).
23. M. Curioni, P. Skeldon, G. E. Thompson, and J. Ferguson, *Adv. Mater. Res.*, **38**, 48 (2008).
24. A. Carangelo, M. Curioni, A. Acquesta, T. Monetta, and F. Bellucci, *J. Electrochem. Soc.*, **163**, C619 (2016).
25. P. Skeldon, G. E. Thompson, S. J. García-Vergara, L. Iglesias-Rubianes, and C. E. Blanco-Pinzon, *Electrochem. Solid-State Lett.*, **9**, B47 (2006).
26. S. J. García-Vergara, P. Skeldon, G. E. Thompson, and H. Habazaki, *Electrochim. Acta*, **52**, 681 (2006).
27. D. Elabar, A. Némcová, T. Hashimoto, P. Skeldon, and G. E. Thompson, *Corros. Sci.*, **100**, 377 (2015).
28. Y. Huang, H. Shih, H. Huang, J. Daugherty, S. Wu, S. Ramanathan, C. Chang, and F. Mansfeld, *Corros. Sci.*, **50**, 3569 (2008).
29. V. López, J. A. González, E. Otero, E. Escudero, and M. Morcillo, *Surf. Coatings Technol.*, **153**, 235 (2002).
30. C. A. Matzdorf, W. C. Nickerson, B. C. Rincon Troconis, G. S. Frankel, L. Li, and R. G. Buchheit, *Corrosion*, **69**, 1240 (2013).
31. M. Curioni, M. S. D. Miera, P. Skeldon, G. E. Thompson, and J. Ferguson, *J. Electrochem. Soc.*, **155**, C387 (2008).
32. C. Su, W. Wu, Z. Li, and Y. Guo, *Corros. Sci.*, **99**, 42 (2015).