Gravimetric Measurement of Oxygen Evolution during Anodizing of Aluminum Alloys

J. M. Torrescano-Alvarez, M. Curioni,* and P. Skeldon*

Corrosion and Protection Group, School of Materials, The University of Manchester, Manchester M13 9PL, United Kingdom

A gravimetric method based on changes in buoyancy force of a submerged gas-collecting container has been optimized to measure the evolution of oxygen during anodizing of an aluminum alloy. Previously, the gravimetric method has been used to measure hydrogen evolution from magnesium and aluminum during corrosion processes, either at the free corrosion potential or under relatively low polarization. However, during anodizing, the comparatively higher values of current applied and the heating effects associated with power dissipation might introduce artefacts in the gas measurement. Optimization of the experimental setup enabled reduction or elimination of such artefacts, so that a reliable measurement could be obtained. The results show that typically about 15 to 20% of the current applied to an AA 2024-T3 aluminum alloy during anodizing in sulfuric acid under the present conditions was used in generating oxygen.

Anodic treatments are commonly used to produce protective oxide films and coatings on metals such as aluminum, magnesium, titanium and their alloys. During such processes, in addition to the electrochemical oxidation of the substrate that produces the desired protective layer, oxygen may be generated electrochemically as a side reaction. For aluminum, oxygen generation during anodizing can be significantly increased by the addition of certain alloying elements or by the presence of impurities in the substrate, such as, for example, copper and iron. The oxygen may be formed at locations of intermetallic particles, where the high concentration of alloying elements locally modifies the composition, morphology and electronic properties of the oxide. Oxygen can also form above the matrix regions, when elements such as iron or copper in solid solution are oxidized and their ions incorporated into the oxide. The resultant modifications of the oxide properties enable the reaction

$$2O^{2-} \rightarrow O_2 + 4e^-$$

to proceed within the oxide resulting in the development of nanobubbles of oxygen gas within the anodic film.

Owing to the plasticity of the amorphous alumina during the growth of the film, and the high pressure of the contained oxygen gas, the bubbles are able to grow within the film until the film eventually ruptures and the gas is released to the electrolyte. The liberation of oxygen has been proposed to account for changes in the morphology of the porous oxide structure. In particular, the process is believed to be responsible for the degeneration of the well-ordered porous morphology, typically observed on high purity aluminum, into a globular or sponge-like morphology typically observed on copper containing alloys, such as those of the 2xxx series and 7xxx series. The morphology of the porous films on these alloys is of great technological interest, since anodizing is one of the most commonly applied corrosion-protection measures, and anticorrosion performance and oxide morphology are closely related. As a consequence, the understanding of the interaction between the anodizing conditions, the evolution of oxygen and the resulting film morphology deserves detailed attention.

The oxygen released during plasma electrolytic oxidation has been measured by volumetric gas collection. The evolution of oxygen in this anodic treatment is likely to be excessive as a result of peroxide decomposition due to the interaction with both hydroxyl ions and radicals at the discharge–electrolyte interface as a result of the decomposition of water. The resolution of the volumetric gas-collection method is limited by the fact that at least a fraction of a millilitre of gas must be generated before a reliable estimation of the gas volume can be made. Therefore, it is generally inadequate for performing real-time experiments, where the evolution of oxygen gas is monitored continuously together with the anodizing current or voltage.

A potentially much more sensitive method of gas detection has been demonstrated recently based on the change in the buoyancy of a submerged gas collection vessel. The technique has been applied to the measurements of hydrogen evolution during corrosion of magnesium and aluminum, either at the free corrosion potential or under polarization. However, the application of this method to the measurement of oxygen evolved during anodizing requires particular attention, since the currents during anodizing are often higher than the corrosion currents of magnesium and aluminum, and significant power dissipation occurs at the specimen surface due to Joule heating and aluminum oxidation.

In the present study, the gravimetric method is optimized to measure oxygen evolved during anodizing and is applied to measure oxygen liberation during formation of porous anodic films on high purity aluminum and AA 2024-T3 alloy.

**Experimental**

**Specimen preparation.** Sheets of 99.94% aluminum (10 ppm Mg, 20 ppm Fe, 50 ppm Cu, 480 ppm Si), with a thickness of 0.3 mm, and AA 2024-T3 alloy (0.06 wt% Si, 0.07 wt% Fe, 4.19 wt% Cu, 0.42 wt% Mn, 1.36 wt% Mg, 0.002 wt% Cr, 0.03 wt% Zn, 0.01 wt% Ti, bal. Al), with a thickness of 1 mm, were cut to provide specimens of aluminum and AA 2024-T3 alloy.

The alloy specimens were electroplated for 180 s at 20 V in an 80 vol% C$_2$H$_5$OH (Fisher Scientific, 99.99% pure) and 20 vol% HClO$_4$ (Sigma Aldrich, 60 vol%) solution at 5°C. The alloy specimens were etched for 60 s in a 10 vol% NaOH (Fisher Scientific, 98.3%) solution at 60°C, then desmutted for 30 s in a 30 vol% HNO$_3$ (Fisher Scientific, 70 vol%) solution at room temperature. Following these treatments, the specimens were rinsed in deionized water and dried in a cool air stream. Each specimen was then coated with a mixture of bees wax (Acros Organics, bleached) and colophony (Aldrich chemistry, natural resin) leaving a working area of 1 or 10 cm$^2$. The specimens with an exposed area of 1 cm$^2$ were used for anodizing at 50 mA cm$^{-2}$, whereas the specimens with an exposed area of 10 cm$^2$ were used to anodize at 5 mA cm$^{-2}$. As a result, the total current applied during tests conducted at different anodizing current densities was maintained constant.

**Anodizing conditions and oxygen measurements.** Oxygen evolution measurements were carried out during galvanostatic anodizing of aluminum and AA2024-T3 alloy specimens in a 10 vol% H$_2$SO$_4$
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Figure 1. Experimental set-up for in situ gravimetric measurements of oxygen evolution.

(Fisher Scientific, 96 vol%) electrolyte at either −1 or 24 ±1°C. The experimental set-up is illustrated in Figure 1 and described in detail elsewhere.17 The anodizing process was carried out in a jacketed beaker connected to a Julabo FL601 recirculating cooler to control the electrolyte temperature. The counter electrode was a platinum wire (1 cm long, 0.01 cm diameter) placed relatively close to the electrolyte surface. The small size of the counter electrode and its placement nearby the surface ensured that the contact time between hydrogen bubbles generated at the cathode and the anodizing solution was minimized, thereby minimizing the loss of oxygen dissolved in the electrolyte into hydrogen bubbles evolving at the cathode. The increased cathodic overpotential associated with the use of a small cathode does not represent an issue in experiments conducted at constant applied current. The specimen was mechanically connected to the oxygen-collecting cylinder. The electrolyte was not stirred in order to avoid interference from turbulence with the oxygen measurements. A thermometer was attached to the cylinder to monitor the temperature of the electrolyte close to the specimen. The temperature was maintained within ±0.5°C of the selected value during anodizing. In addition, in the proximity of the specimen, a small platinum wire with dimensions similar to the cathode, with the surface exposed to the anodizing electrolyte, was also attached to the collecting cylinder (Fig. 1). Either the specimen or the platinum wire could be connected to the power supply by an insulated copper wire. Thus, two independent working electrodes were available under the collecting cylinder, the aluminum specimen and the platinum electrode. The accuracy of the gravimetric method for the quantification of oxygen evolution was evaluated by using the platinum electrode, since faradaic reactions due to oxidation of the electrode are avoided21 and all the applied current is used to produce oxygen gas. Furthermore, the current values obtained from the platinum electrode were used as a reference to assure the accuracy of each experiment.

The test arrangement was held by a support inside a scale (Ohaus Galaxy 160D, resolution 0.1 mg) and balanced, with the weight change due to the generation of the buoyancy force obtained from the collected oxygen recorded. The air trapped in the oxygen-collecting cylinder after immersion was partially or completely removed by a curved plastic tube attached to a syringe. Anodizing was performed at a constant current provided by a DC power supply (Metronix 6911). Since 1 mole of an ideal gas occupies 22.33 and 24.38 l at −1 and 24°C respectively and the density of the electrolyte is 1.08 kg l−1, a hydrostatic force of 24.11 and 26.33 kg per mol of oxygen is generated at each electrolyte temperature. The weight change-time data were differentiated to yield the current using the conversion factor of 266.76 and 244.31 A kg−1 min−1 at −1 and 24°C respectively.

Results

Optimization of experimental setup.—Oxygen measurements on platinum.—Figures 2a and 2b present the results of oxygen measurements using the platinum electrode. An anodic current was passed...
through the platinum electrode for 300 s, then the current was interrupted for 300 s, and subsequently a higher value of current was applied for 300 s at a selected current, then the current was interrupted and so on. The first applied current was 5 mA, followed by 10, 20, 30, 40, 50, 60 and 70 mA. The resultant changes in weight due to the buoyancy force are shown in Fig. 2a. The current associated with oxygen evolution and measured by the gravimetric method was very close to the applied current, with a difference not exceeding 3% (Fig. 2b). Notably, no peaks immediately after current onset, or minima immediately after current interruption, were observed. Figure 2c presents the corresponding voltage-time response measured during the test. The cell potential increased with increasing the value of the applied current, from about 3 V at 5 mA to about 5 V at 50 mA. Unreported tests, performed under similar conditions, revealed that the good agreement between the electrical current applied and the oxygen measurement was maintained regardless of the amount of air present in the collecting cylinder before the current onset.

Artefacts during anodizing aluminum alloys.—The results obtained during initial oxygen measurement performed while anodizing AA 2024-T3 specimens are presented in Figures 3a–3d. The experiments comprised application of 50 mA anodic current for 600 s to the alloy specimen (labelled as AA 2024-T3 in the figures), 600 s current interruption, application of 50 mA anodic current to the platinum electrode nearby the aluminum specimen for 600 s (labelled as Pt in the figures), current interruption for 600 s. By comparison of all the graphs in Figure 3, it is evident that artefacts are generated during some of the experiments. In particular, a peak followed by a long decay is observed sometimes at the beginning of the anodizing step. When such a peak is observed, a minimum is also observed immediately after the current is interrupted. The minimum values of current appear to be well below 0 mA and a slow increase towards 0 mA is observed during the 600 s without current. Importantly, in all cases, the peak and minimum were not observed during and after the application of the same anodic current to the control platinum electrode. Whereas the peak observed at the onset of anodizing could in principle be associated with enhanced initial oxygen evolution, the negative peak after the current interruption is necessarily an experimental artefact, not connected to the anodizing behavior. A large number of similar experiments, including ones in which the electrolyte was saturated with oxygen before anodizing, disclosed that the presence or absence of such a peak and minimum is independent of the level of oxygen saturation of the test solution, but correlates with the amount of residual air present in the oxygen collection cylinder before the anodizing step, i.e. the more the residual air, the more pronounced the peak. If the air is completely removed from the collecting cylinder before commencing the experiments, no initial peak and no negative minimum are observed, as exemplified in Figure 3d. Furthermore, the
graphs in Figure 4 show that the artefacts observed during oxygen measurements did not affect the voltage-time response.

**Oxygen measurements during anodizing.—Aluminum.**—Figure 5 shows the typical behavior of the current associated with oxygen evolution obtained during anodizing of aluminum at 50 mA cm\(^{-2}\) at \(-1\) °C (Fig. 5a) and 24 ± 1 °C (Fig. 5b) for 600 s, followed by a current interruption for 600 s and then by 600 s of galvanostatic polarization of the control platinum electrode at 50 mA. The respective voltage-time curves are presented in Figures 5c and 5d. Following the initial thickening of the barrier layer and the formation of embryo pores, the growth of the porous film at \(-1\) °C occurred under a voltage that rose slightly, from 24.0 V at the start of major pore growth to 24.7 V at the termination of anodizing (Fig. 5c). In contrast, at 24 °C, the major pores formed under a constant voltage of 17.5 V (Fig. 5d). The measurements on pure aluminum were made since it is expected that evolution of oxygen on this material is negligible.\(^{22,23}\) In repeated tests, the average oxygen current for the aluminum was within 3.5 mA of zero. Since the current applied to the 1 cm\(^2\) working area was 50 mA, the maximum current due to oxygen was at worst 7% of the applied current. Under the present test conditions, small amounts of oxygen may be evolved from the specimens due to the presence of 50 ppm copper in the aluminum. Some oxygen may also be generated at the edges between the exposed aluminum and the beeswax mask.

**AA 2024-T3 alloy.**—Figures 6a and 6b show the oxygen current obtained during anodizing the AA 2024-T3 alloy for 600 s at 5 and 50 mA cm\(^{-2}\) at 24 °C. It should be noted that for the former condition, the specimen area was increased to 10 cm\(^2\) so that the total anodizing current applied in the two tests was the same. This is needed since the reliability of the measurement is validated against the total oxygen current measured from the platinum electrode after the anodizing step is terminated. The voltage-time responses during anodizing of the alloy and polarization of the platinum are shown in Figures 6c and 6d. Apart from a peak that lasted for a short time after the onset of anodizing at 5 mA cm\(^{-2}\), the oxygen currents were similar, about 7 mA, at both 5 and 50 mA cm\(^{-2}\). For the low-current density condition (5 mA cm\(^{-2}\)), the initial peak observed at the lower current density coincided with an initial low voltage plateau, which is well known to be associated with oxidation of copper-rich intermetallic particles.\(^{24,25}\) The data indicate that approximately 14% of the applied current was consumed by oxygen evolution. The voltage-time curves revealed steady voltages, of 8 and 24 V at 5 and 50 mA cm\(^{-2}\) respectively, during the growth of the porous films. Thus, neither current density nor the voltage had a significant influence on the total amount of oxygen evolved during anodizing of the alloy.

Figure 7 presents the oxygen current measured during anodizing for 3600 s at 50 mA cm\(^{-2}\) and temperatures of \(-1\) and 24 °C. The results at \(-1\) °C revealed a small peak at the start of anodizing, up to about 8 mA, followed by a trough, with the lowest value of about 6 mA (Fig. 7a). The current was then approximately constant at about 7 mA up to 400 s of anodizing, during which time the voltage increased from about 29 to 32 V. The current subsequently increased to about 10 mA at about 925 s and then remained at a relatively steady value in the range of 10 to 12 mA until the termination of anodizing at 3600 s, representing 20 to 24% of the applied current. This period of comparatively minor variations in current coincided with an increase in the anodizing voltage from about 44 to 55 V (Fig. 7b). Such a large voltage rise did not occur during anodizing of relatively pure aluminum (Fig. 5c), indicating it is a feature associated with the influence of the composition of the alloy on the film properties and the evolution of oxygen. The current associated with oxygen evolution at 24 °C varied by only a small amount during the whole time of anodizing, remaining within the range of 8 to 10 mA, corresponding to 16 to 20% of the applied current (Fig. 7c). The anodizing voltage in the period of porous film growth also changed by only a small amount, increasing from 24 to 26 V (Fig. 7d). At both temperatures, the current was about 10 mA at later times, indicating that about 20% of the applied current was consumed by oxygen evolution.

**Discussion**

The gravimetric method for measurement of oxygen during anodizing is closely similar to that used to measure hydrogen during corrosion. However, the measurement requires more attention since artefacts can be easily generated. Typically, such artefacts appear as spurious peaks and minima in the oxygen current curves, and cannot be directly related to phenomena occurring at the electrode surface. In particular, the negative minima observed after current interruption cannot be associated to a process occurring on the electrode, since the oxygen bubbles generated during anodizing rapidly detach from the electrode and float towards the collecting cylinder, where they produce the buoyancy force. Consequently, a negative minimum after the interruption of the anodizing current cannot be due to a process occurring on the electrode, because the oxygen producing the buoyancy force is already in the collecting cylinder, which is physically separated from the electrode. The use of an in-situ calibration method, such as the platinum control electrode used here, demonstrates that such peaks and minima are not related to systematic errors in the measurement, since the artefacts are always absent for identical measurement on platinum.

In principle, the negative peaks in the oxygen current could be associated with the dissolution into the test electrolyte of the oxygen gas accumulated in the cylinder. This arises from the fact that the total
Figure 5. Calculated current for oxygen evolution during anodizing of aluminum for 600 s at 50 mA cm\(^{-2}\) in 10 vol% H\(_2\)SO\(_4\) at (a) \(-1^\circ\)C and (b) 24°C. (c, d) Respective voltage-time responses.

Figure 6. (a,b) Calculated current for oxygen evolution during anodizing of AA 2024-T3 alloy in 10 vol% H\(_2\)SO\(_4\) for 600 s at 5 and 50 mA cm\(^{-2}\) respectively, at 24°C. (c,d) Respective voltage-time responses.
An important difference between the anodizing step (producing artefacts if residual air is present) and the control step on platinum (not producing artefacts, regardless of the residual air) is that the applied voltage is substantially different. In particular, during platinum polarization, the voltage does not exceed 5 V, whereas during anodizing it can reach more than 30 V. As a consequence, the heat generated on the electrode surface and transmitted to the surrounding solution is substantially higher during anodizing than during polarization of platinum. For example, when anodizing at 50 mA at a voltage of 25 V, 1.25 W are continuously dissipated due to Joule heating, which is the main heat source. This is equivalent to approximately 18 cal/min, an amount of energy sufficient to raise by a fraction of a degree the temperature in the oxygen-collecting cylinder. Thus, if some heat is produced in the proximity of the electrode and transmitted to the evolving bubbles and to the collected gas (assuming that the heat capacity of the gas is negligible compared to that of the liquid) a significant variation in the buoyancy force can be generated due to the expansion of the gas in the collecting cylinder. For example, a temperature rise of 1 °C in a gas volume initially at 24 °C would result in a volume increase of $33.65 \times 10^{-3} \mu L$ (equivalent to an increase in the buoyancy force of $36.35 \times 10^{-3} \text{mg}$) or $67.31 \mu L$ (equivalent to a buoyancy force of 72.69 mg) if 0.01 or 20 ml of gas is present in the collecting cylinder, respectively.

Considering that the weight variation associated with the current applied is of the order of $68.45 \times 10^{-3} \text{mg s mA}^{-1}$, it is clear that...
the greater the amount of the gas in the collecting cylinder (regardless of the composition) the higher the current peaks when the current is switched on (heating transient) and the lower the negative minima when the current is switched off (cooling transient). In addition, this interpretation is in agreement with the observations on platinum, where the effect is absent because the heating effect is negligible, due to the much lower potential and the absence of metal oxidation and film formation reactions. For the reasons described above, in order to obtain reliable oxygen measurement during anodizing, it is not necessary to control the oxygen concentration in the electrolyte, but it is imperative that all the residual air is removed from the gas-collecting cylinder.

Considering now the anodizing results, the effect of the anodizing condition on the oxygen evolution behavior can be evaluated by comparing the results of Figures 6 and 7. It appears that, at room temperature, the amount of oxygen evolved does not depend on the applied current (Fig. 6). For the same value of current, slightly different behaviors in oxygen evolution are observed at low and room temperature (Fig. 7). In particular, the oxygen current appears to progressively increase with time in low temperature conditions, mirroring to some extent the qualitative behavior of the voltage-time response. Correspondingly, at room temperature, the current associated with oxygen evolution is steady, similarly to the voltage-time response.

It is clear that the amount of oxygen evolved is related, as already well known, to the composition of the anodized substrate: aluminum produces little or no oxygen during anodizing, whereas an aluminum copper alloy produces a significant amount of oxygen. The precise amount of oxygen evolved from an anodized alloy will depend on the types and concentrations of alloying elements present, the thermomechanical processing conditions and the conditions of film growth.

Conclusions

1. The gravimetric method can be used to quantify oxygen evolution during anodizing of aluminum and aluminum alloys, providing a measure of both the total quantity of oxygen evolved and the dependence of the evolution rate on the anodizing time, provided that adequate care is given to remove all residual air from the collecting cylinder.
2. The approach showed that during anodizing of AA 2024-T3 alloy at 50 mA cm\(^{-2}\) in 10 vol% H\(_2\)SO\(_4\) at 24 °C, oxygen is evolved at relatively steady rate. Under this anodizing condition, the voltage varies by only a small amount during film growth.
3. In contrast, during anodizing at 50 mA cm\(^{-2}\) and −1°C, the voltage rises significantly during film growth. However, the rise in voltage has a comparatively minor influence on the rate of oxygen evolution.
4. The evolution of oxygen usually consumes about 15 to 20% of the applied current density during galvanostatic anodizing of the alloy under the chosen anodizing conditions.

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