



Short communication

Further studies of the anodic dissolution in sodium chloride electrolyte of aluminium alloys containing tin and gallium

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ABSTRACT

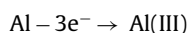
As part of a programme to develop a high power density, Al/air battery with a NaCl brine electrolyte, the high rate dissolution of an aluminium alloy containing tin and gallium was investigated in a small volume cell. The objective was to define the factors that limit aluminium dissolution in condition that mimic a high power density battery. In a cell with a large ratio of aluminium alloy to electrolyte, over a range of current densities the extent of dissolution was limited to $\sim 1000 \text{ C cm}^{-2}$ of anode surface by a thick layer of loosely bound, crystalline deposit on the Al alloy anode formed by precipitation from solution. This leads to a large increase in impedance and acts as a barrier to transport of ions.

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1. Introduction

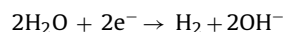
Earlier papers have reported that aluminium alloys containing both tin and gallium could be dissolved anodically at high current densities, $>250 \text{ mA cm}^{-2}$ in sodium chloride solution [1–4]. These studies generally employed rather small electrodes in substantial volumes of electrolyte, e.g. electrode strips $5 \text{ mm} \times 1 \text{ mm}$ in 25 cm^3 of electrolyte. In these conditions, all of the Al alloy strip could be dissolved. In an Al/air battery designed to have a high energy and/or power density, the volume of electrolyte is, however, a major factor determining the weight of the battery (aluminium has a low density and a low equivalent weight, while the air cathode has negligible weight). Hence, in this paper, we report studies of the anodic dissolution of the aluminium alloys in a small parallel plate cell designed to have a much increased ratio of aluminium metal to electrolyte. The object was to understand the factors that limit the extent of dissolution in the conditions to be found in a high power density Al/air battery.

Unlike the aluminium electrode in alkaline solutions where the product of anodic dissolution is largely the soluble anion, $\text{Al}(\text{OH})_4^-$, in neutral, sodium chloride the product chemistry is complex. While the reaction is certainly



the speciation of the Al(III) is unclear and may depend on kinetics as well as thermodynamics. In addition, it is likely to change with either the Al(III) concentration and/or pH, i.e. the extent of battery discharge. Possible Al(III) species include Al^{3+} , an aluminium hydroxide, alumina in various states of hydration and/or chloro-complexes.

For convenience, the cathode was carbon steel and the cathode reaction was therefore the evolution of hydrogen



It should be noted that in common with the oxygen reduction reaction in neutral solution, it involves the formation of one hydroxide ion/electron and therefore should have the same influence on the pH of the electrolyte. The dissolution of the aluminium alloy at high rates in the cell with a H_2 evolving cathode required the application of a voltage between the two electrodes; much of this cell voltage results from the IR drop through the interelectrode gap.

2. Experimental

All the experiments employed the aluminium alloy, I0, prepared by Innoval Ltd. and with the added elements 0.4 wt% Mg, 0.07 wt% Sn and 0.05 wt% Ga; the structural characterisation of this alloy has been reported [1]. The electrolyte was usually 2 M NaCl, prepared using deionised water from a Whatman Analyst purification system and Analytical Grade sodium chloride from Fisher Scientific. Except where otherwise stated, the experiments were carried out at room temperature, $293 \pm 2 \text{ K}$.

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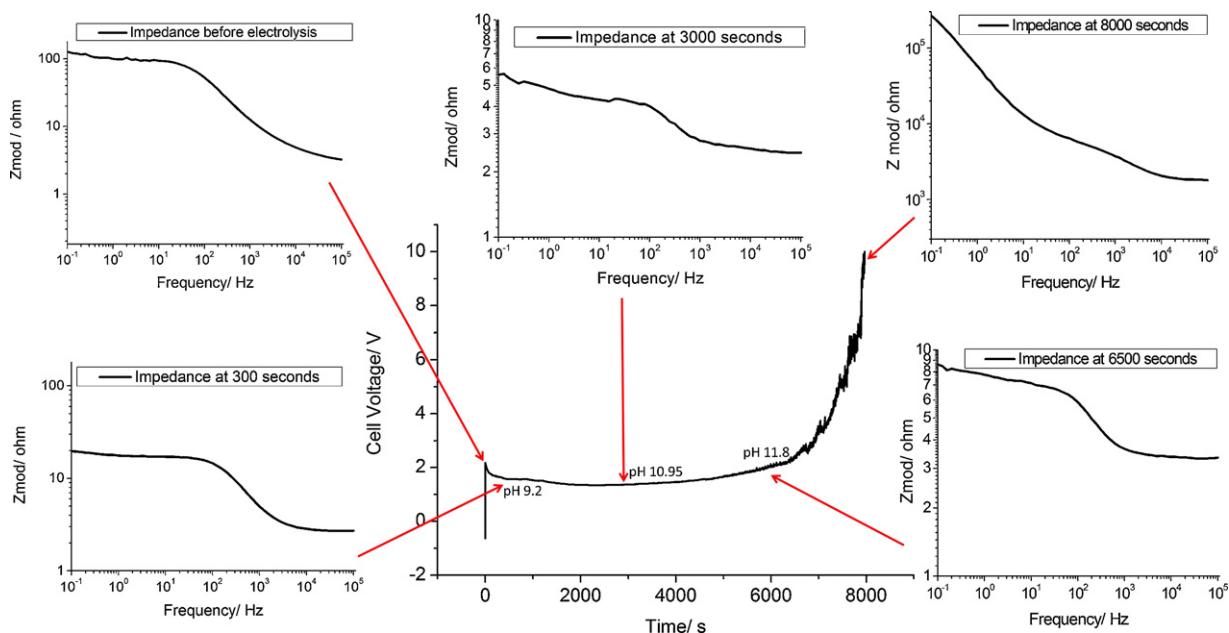


Fig. 1. Plot of cell voltage vs. time for a cell with an aluminium alloy anode. Electrolyte 2 M NaCl. Current density 170 mA cm^{-2} . Also shown are the pH and the impedance of the Al alloy on open circuit as a function of frequency at intervals during the electrolysis.

The anodic dissolutions were carried out in a Perspex 'box' cell with dimension $3 \text{ cm} \times 1 \text{ cm} \times 5 \text{ cm}$ high. The aluminium alloy and mild steel electrodes were plates, $3 \text{ cm} \times 1 \text{ cm}$, clipped to opposite sides of the box so that the interelectrode gap was $\sim 2.4 \text{ cm}$. The cell was filled with electrolyte to a height of 2.5 cm when the electrolyte volume was 6 cm^3 . In fact, the cell was designed to have $\sim 1 \text{ g}$ of aluminium. The complete dissolution of the aluminium would require the passage of $\sim 10^4 \text{ C}$ if the current efficiency was 100% (i.e. no aluminium corrosion competes with the anodic dissolution). In addition, it would lead to a solution of Al(III) with a concentration of $\sim 6 \text{ M}$ (if the Al(III) was fully soluble) or the formation of $\sim 2 \text{ g}$ of solid Al_2O_3 or $\sim 3 \text{ g}$ of solid $\text{Al}(\text{OH})_3$ (if complete precipitation occurred). For AC impedance experiments, a SCE reference electrode was placed into the interelectrode gap as close as possible to the anode surface.

The electrolyses were controlled with an EG & G model 273 Potentiostat run by Powersuite software. The AC impedance spectra were obtained with a Gamry Instruments Model 600 potentiostat and analysed using Gamry Framework software. The spectra were recorded at the open circuit potential over the frequency range of 10^{-2} – 10^4 Hz using an AC voltage perturbation with an amplitude of $\pm 10 \text{ mV}$.

pH was measured with a Hanna Instruments model 210 micro-processor pH meter. The cell was placed in a Cole-Parmer 8891 ultrasonic bath with 60 Hz frequency for some experiments. Scanning electron microscopy images were recorded using a Jeol JSM 5910 fitted with an Oxford Inca 300 EDX. The samples for surface SEM were only washed well with water and dried. For cross-sections, the samples were cut and mounted in epoxy resin (Struers Epofix Resin) so that the cross-section was exposed. The exposed surface was then (i) polished successively with 600, 1200 and 4000 grade emery paper, each for 1 min until examination of the surface by optical microscopy showed only fine scratches in the same direction (ii) polished with $6 \mu\text{m}$ diamond paste on a OP-mol cloth for 3 min (iii) repeatedly polished with $1 \mu\text{m}$ diamond paste on a DP-mol cloth for 3 min until scratches could not be seen with the optical microscope. Between each stage, the surface was rinsed with distilled water before being dried.

3. Results

Fig. 1 reports a plot of cell voltage vs. time during an electrolysis with a constant current density of 170 mA cm^{-2} for a cell with the Innoval Al alloy, I0, as the anode, a mild steel cathode and a SCE reference electrode in the 2 M NaCl. During the electrolysis, the cell voltage and the pH of the solution was monitored while the cell was observed by eye. In addition, at intervals the electrolysis was stopped and the impedance of the anode was determined at the open circuit voltage of the Al alloy electrode; the impedance diagrams and pH are also shown in **Fig. 1**. Initially, the cell voltage was $\sim 2 \text{ V}$ with rapid evolution of H_2 from the cathode and a very slow stream of gas from the Al alloy anode (H_2 gas reflecting slow, competing chemical corrosion of the alloy). Over the first $\sim 2000 \text{ s}$ ($\sim 350 \text{ C cm}^{-2}$), the solution in the cell remained clear suggesting that Al(III) has some solubility in 2 M NaCl (or that the solution

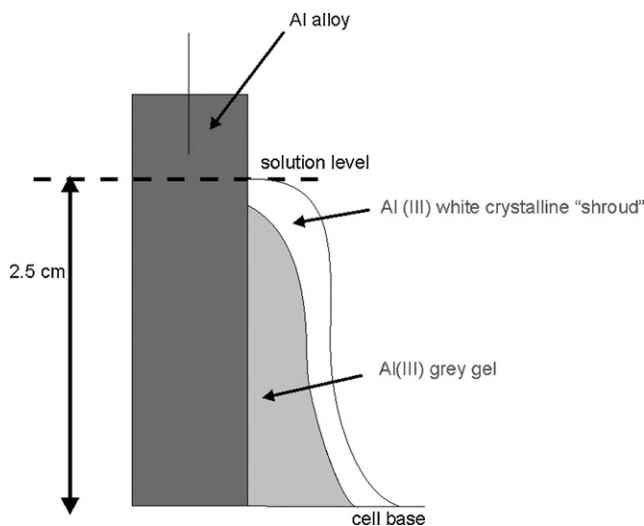


Fig. 2. Schematic of the aluminium alloy anode after the anodic dissolution of the alloy I0 in 2 M NaCl and the cell voltage has risen to 10 V.

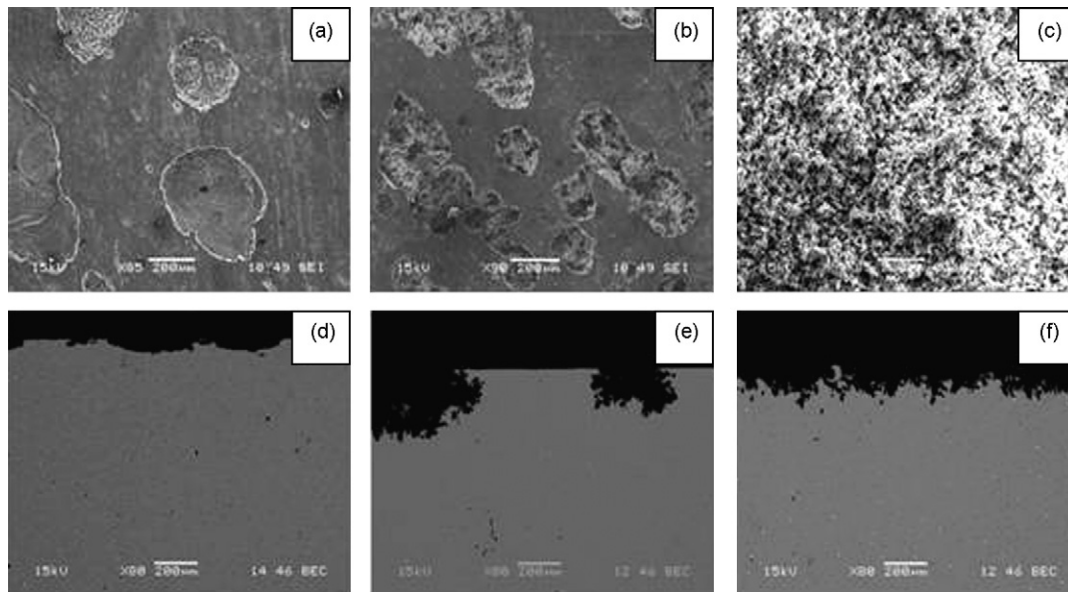


Fig. 3. SEM images of the surfaces and cross sectional SEM images at (a and d) 300 s, (b and e) 3000 s and (c and f) 6500 s of anodic dissolution of the aluminium alloy, I0, in 2 M NaCl with a current density of 170 mA cm^{-2} . The Al alloy anodes were removed from the cell, rinsed well with water, then dried and prepared for SEM. (a)–(c) SEM of the surfaces and (d)–(f) SEM of the cross-section.

can be supersaturated) while the cell voltage and the interfacial impedance both decreased as the number of pits and their dimensions increased [1]. Beyond 2000 s, the whole solution became cloudy as a white solid (presumably $\text{Al}(\text{OH})_3$ or Al_2O_3) began to precipitate throughout the solution. The pH had increased only slightly from the initial pH of 7. At longer times, the cell voltage began to increase slowly but beyond 6000 s ($\sim 1000 \text{ C cm}^{-2}$), the increase in cell voltage becomes steep, reaching a value $>10 \text{ V}$ after 8000 s. At this time, the interfacial impedance had also risen by a factor of 1000. At this stage, the solution is much cloudier and the Al alloy surface has become covered by a 'shroud' of tightly packed, white crystalline material, maybe 2 mm thick. When this shroud was carefully removed, it could be seen that there was a further layer of grey gel between the shroud and the metal, see the sketch of Fig. 2. The pH of the bulk electrolyte had risen to 11.8 and a test with litmus paper showed that the gel was acid. Hence, one explanation of the grey gel, is that it is the $\text{Al}(\text{III})$ product from the anode in an acidic environment; this would be likely if the shroud acted as a barrier preventing the hydroxide formed at the cathode from interacting with the $\text{Al}(\text{III})$ formed at the anode. These experimental observations were reproducible and contrasted totally with experiments with a small Al anode ($\sim 0.1 \text{ g}$) in a large volume of electrolyte ($\sim 100 \text{ cm}^3$) when all the alloy dissolves and a cloudy solution results.

Table 1 reports the charge passed and observations from a series of six experiments to further understand the observed behaviour. It is clear that the shroud of compact white crystals has a dominant role in the termination of the dissolution reaction. When the shroud is removed from the electrode without other damage to the surface, the Al alloy can continue to dissolve, see experiments 2 and 3. Experiment 2 shows that the increase in electrolyte pH to 11.8 and the presence of solids dispersed in the solution or at the base of the cell had little effect on the charge density that could be passed. Indeed, experiment 3 shows that the alloy anode can be reused despite its surface being pitted from corrosion without decreasing the charge density that can be passed. In contrast if the shroud is maintained in place but the electrolyte is changed, experiment 4, only a much smaller charge density can be passed. It was also found that a modest rise in temperature, experiment 5, led to no increase in the capability of the cell to pass charge. On the other hand, carrying

out the anodic dissolution in an ultrasonic bath, experiment 6, led to a $\sim 50\%$ increase in charge passed before the increase in cell voltage; this results from some mechanical breakdown of the shroud. In a further series of experiments, it was found that the charge den-

Table 1

The anodic dissolution of the Al alloy, I0, in the small volume cell filled with 2 M NaCl. Current density 170 mA cm^{-2} . Room temperature except where otherwise stated.

Experiment	Charge before steep rise in cell voltage ^a (C cm^{-2})	Comments	
1	Fresh Al alloy anode Fresh electrolyte New Al alloy anode	1090 935	A 'shroud' formed on alloy anode. The increase in electrolyte pH and the presence of dispersed solid in the cell, has little influence on anode performance.
2	Shroud remove with first anode Electrolyte reused		
3	Al alloy anode reused but shroud removed external to cell Fresh electrolyte	1070	Once freed of shroud, the Al alloy anode can continue to be dissolved anodically.
4	Al alloy anode reused but without the shroud being removed Fresh electrolyte Fresh Al alloy anode	120 1090	The shroud limits anodic dissolution. Increase in temperature does not lead to increased charge density.
5	Fresh electrolyte Temperature: 311 K Fresh Al alloy anode	1585	More material in base of cell as shroud broken up to some extent.
6	Fresh electrolyte In ultrasonic bath		

^a Charge density until the cell voltage increases to 3 V.

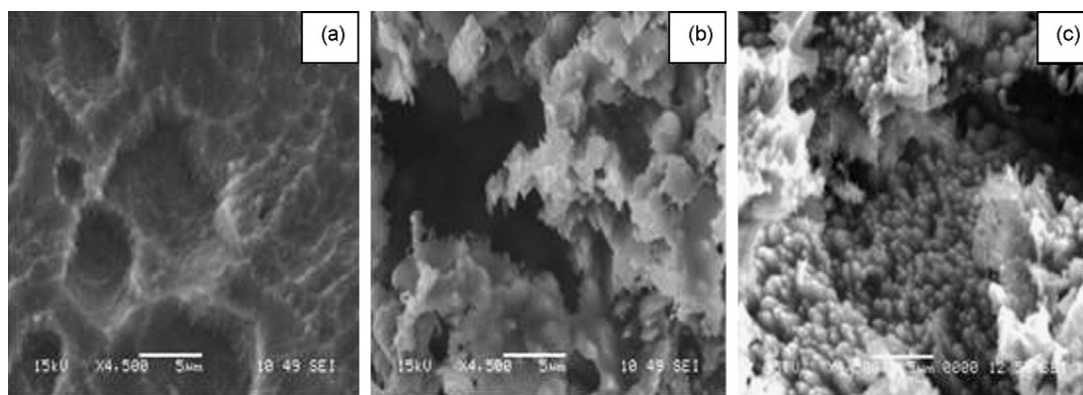


Fig. 4. High resolution SEM images of the inside surfaces of the pits as a function of charge passed. The images are taken after (a) 300 s, (b) 3000 s and (c) 6500 s of anodic dissolution aluminium alloy, I0, in 2 M NaCl with a current density of 170 mA cm^{-2} . The Al alloy anodes were removed from the cell, rinsed well with water, then dried.

sity passed before a steep increase in cell voltage was independent of current density over the range investigated, $50\text{--}200 \text{ mA cm}^{-2}$.

The surfaces of the aluminium alloy anode after washing thoroughly with water were investigated by scanning electron microscopy. Fig. 3 shows both SEM images of the surface and also cross sectional SEM images at three times (300 s, 3000 s and 6500 s) during anodic dissolutions of the Innoval alloy, I0, carried out in 2 M NaCl at a current density of 170 mA cm^{-2} . When the electrolysis was terminated early in the anodic dissolution, there are a number of isolated pits with different dimensions randomly distributed across the surface. By 300 s, there is evidence that the larger of these 'pits' is more correctly viewed as a collection of overlapping smaller pits and the average depth of the pits is $60 \mu\text{m}$. When the dissolution was continued to 3000 s, the pits have increased slightly in number and, to some extent, also expanded over the surface. The largest change is, however, that the damage to the surface now extends to a much greater depth, typically $200\text{--}300 \mu\text{m}$. By 6500 s, the whole of the original surface of the alloy has been oxidised away as the pits have expanded and spread so that they cover the whole surface.

Higher resolution SEM images were also recorded. Using the BEC detector is/was then frequently possible to identify one or more tin inclusions within a pit. Using the SEI detector, it was possible to see some interesting changes to the morphology of the deposits within the pit. Fig. 4 illustrates the SEI images obtained after the electrolyses were terminated at three different times. After 300 s, Fig. 4a the interior of the pit appeared largely free of product deposit and the surface is characterised by a series of rounded hollows. By 3000 s, Fig. 4b, it becomes impossible to see the alloy surface itself and the interior is largely filled with a crystalline deposit. With further dissolution, Fig. 4c, there continues to be angular crystalline deposit but a new structure consisting of small rounded centres also becomes evident. This change in the surface layer presumably results from the formation of the shroud. The decrease in local pH could be leading to a film with a different composition and/or structure although it should be stressed that, on removal of the shroud, further anodic dissolution occurs without any additional limitation, see Table 1.

4. Discussion

Earlier papers [1,2] have reported studies of the mechanism for the high rate dissolution of Al alloys containing Sn and Ga in

2 M NaCl. It has been shown that anodic dissolution is possible at very high rates, $>200 \text{ mA cm}^{-2}$, close to the open circuit potential (-1.50 V vs. SCE) and that dissolution occurs preferentially around the tin inclusions leading to rounded pits. Moreover, in cells with a low ratio of the weight of Al alloy to weight (volume) of the electrolyte, the whole sample of alloy could be dissolved. Here, the interest was to determine the extent of dissolution when the ratio of the weight of Al alloy/electrolyte was increased markedly as would have to be the case in a high power density battery.

With the cell used containing $\sim 1 \text{ g}$ of the Innoval Al alloy, I0, and 5 cm^3 of electrolyte (and a Al alloy/electrolyte area interface of 2.5 cm^2), the extent of anodic dissolution was limited to 1000 C cm^{-2} of Al alloy surface. The limitation on the extent of constant current dissolution did not arise from changes to the electrolyte composition or to the formation of a protective surface anodic film. Rather the cell voltage rose rapidly because of the formation of a thick layer of loosely bound, crystalline deposit—if this layer was removed, anodic dissolution recommenced with the initial cell voltage. This 'shroud' is fragile and easily removed and its formation is probably dependent on the existence of physical support beneath it. Hence, the extent of aluminium dissolution is also a function of the cell design. For example, leaving a volume below the electrodes into which the Al(III) product may fall might inhibit or prevent the formation of the shroud but this would have the effect of increasing the weight of electrolyte in the battery and thereby diminishing the power density.

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References

- [1] M. Nestoridi, D. Pletcher, R.J.K. Wood, S. Wang, R.L. Jones, K.R. Stokes, I. Wilcock, *J. Power Sources* 178 (2008) 445.
- [2] P.R. Birkin, M. Nestoridi, D. Pletcher, Submitted for publication.
- [3] C.D.S. Tuck, J.A. Hunter, G.M. Scamans, *J. Electrochem. Soc.* 134 (1987) 2970.
- [4] C.D.S. Tuck, *Faraday Discuss.* 94 (1992) 171.