# THE INFLUENCE OF ELECTROLYTE ADDITIVES ON THE ANODIC DISSOLUTION OF ALUMINUM IN ALKALINE SOLUTIONS

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## Summary

The anodic dissolution of aluminum in alkaline solutions is accelerated by the addition of small quantities of gallium or indium ions to the electrolyte. This process increases the possibilities for using commercially available aluminum and its alloys in high-rate batteries.


## Zusammenfassung

Die anodische Auflösung des Aluminiums in alkalischen Lösungen wird durch den Zusatz geringer Mengen von Gallium- oder Indiumionen zum Elektrolyten beschleunigt. Dieses Verfahren erweitert die Möglichkeiten, handelsübliche Aluminiumwerkstoffe in Hochleistungsbatterien einzusetzen.


## Introduction

On the basis of theoretical considerations aluminum is a promising material for the negative electrode of galvanic high-energy systems. Its low equivalent weight combined with its highly negative standard potential result in energy densities, when combined with a suitable counterelectrode, which are only surpassed by lithium systems. Its comparatively low price, due to the fact that it is the most common metal found in the earth's crust, and its good handling characteristics are further arguments for its consideration.

The choice of a suitable electrolyte, however, presents difficulties: aluminum being a very base metal has a standard electrode potential far more negative than the potential at which hydrogen can be evolved from water at a metal electrode. Thus, in aqueous solutions a corrosion reaction takes place at the aluminum electrode and hydrogen is evolved. The self-corrosion of the metal is to a great extent avoided in a neutral medium through the formation of a protective oxide film, but at the same time its discharge characteristics are compromised.

This protective film does not develop in alkaline solutions as the amphoteric aluminum hydroxide dissolves and aluminates are formed; the result is the continuous evolution of hydrogen. The anodic part of the current generating reaction

$$Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^- \tag{1}$$

is concurrent with the corrosion reaction

$$Al + 3H_2O \rightarrow Al(QH)_3 + \tfrac{3}{2}H_2^\uparrow \tag{2a}$$

$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-. \tag{2b}$$

The aluminate ion when present in sufficiently high concentration associates into high molecular weight jelly-like oxo compounds. At high current densities concentration polarization takes place at the electrode surface, so that for alkaline aluminum cells electrolyte circulation is required.

The two problems mentioned above have so far prevented the utilization of aluminum in alkaline batteries, although there has been no lack of effort to reduce the magnitude of the corrosion reaction [1 - 3], for example, by means of inhibitors.

In the last few years, it has been suggested that the principle of primary reserve batteries be applied to aluminum electrodes with an alkaline electrolyte [4]. During storage the self-discharge reactions are prevented by separation of the electrodes and electrolyte. When current is to be drawn from the battery the space between the electrodes is filled with electrolyte. For obvious reasons, this design is mainly intended for short duration discharge; the expensive construction principle of reserve batteries can only be justified by high energy density and especially by high power density.

It is a known fact, that at high current densities the most negative potentials can be achieved through the utilization of approximately 7N KOH solution. The dissolution of the protective film on the electrode surface takes place mainly in this concentration range; however, it can be increased considerably at higher temperatures [4, 5]. For example, at a given potential one observes approximately five times greater aluminum dissolution current density at 70 °C than at room temperature. Further temperature increase is not desirable for battery technical reasons and to increase the power density further, variations in the composition of the anode have been evaluated.

A higher degree of purity of the basic aluminum causes a shift of the zero current potential towards more negative values, because the electrode contains fewer components with a low hydrogen overvoltage; typical of these are iron and copper. These substances also contaminate the electrolyte.

The earliest results concerning the electrochemical influence of the alloying constituents of aluminum in sea-water were reported by Reding and Newport in 1966 [6]; they showed how certain alloying elements resulted in electrodes with more negative potentials than the pure metal. This work was continued and applied to aluminum–air cells with neutral electrolytes by Despić et al. [7 - 10]. They found, that predominantly gallium, indium and thallium and combinations of these are advantageous alloying components.

In 1977 similar observations were reported by Moden and Perkons for alkaline electrolytes [11]: aluminum with less than 0.1% gallium and approximately 1% magnesium shows the desired electrochemical properties, *i.e.*, high current densities at very negative potentials. According to the authors the magnesium only serves to improve the mechanical characteristics of the material. As the latter alloys are not yet commercially available, the question arose whether an increase of the power density with unalloyed electrodes in alkaline solutions could be achieved in other ways.

## Experimental results and discussion

The objective of the research program was to discover the influence on the anodic dissolution which various metal ions have, when added to the electrolyte. For this purpose the most favourable conditions described in the literature were chosen as the baseline for this test program: all experiments were carried out with a commercially available grade of aluminum of nominal 99.9% purity, which was alloyed with 0.5% magnesium. The electrolyte was unstirred 7N KOH solution at a temperature of $60 \pm 1$ °C. The working electrode area was 1 cm$^2$ and the potentials, given by a Wenking Potentiostat 70 HP 10, were potentiodynamically changed by a Voltage Scan Generator, Wenking VSG 72, and automatically recorded. Under the described conditions only the anodic part of the current density–potential curves was plotted with a scan rate of 10 mV/s. Of the large amount of information contained therein, primarily the zero current potential and the slope of the curve were chosen as evaluation criteria.

Some additives showed no measurable electrochemical influence; examples are zinc and tin ions. A shift of the zero current potential towards more negative values was found to a minor extent with lead and boron ions and, to a larger extent, with antimony, arsenic and thallium ions. The shift of the rest potential with antimony ions amounted to approximately 100 mV, and with arsenic or thallium ions approximately 200 mV shift was observed. With the antimony, arsenic and thallium ions the curve was shifted in the negative direction, but the slope did not change and there was no significant improvement in the potential of the cell under load.

Both effects, *i.e.*, the shift of the current density–potential curve in the negative direction and the improvement of polarization characteristics, are simultaneously achieved by mercury and indium ions and even more clearly by gallium ions [12]. The reproducibility of the tests with mercury was inconsistent; this was probably due to the fact that, during the discharge, amalgams could develop on parts of the aluminum electrode.

Indium and gallium ions, by contrast, show a reproducible, considerable influence on the current–potential curve. In Fig. 1 the impact of these two additives are shown and, for comparison purposes, a curve is given for electrolyte without any additives. It becomes clear that 1 g Ga/l electrolyte results in a shift of the zero current potential by approximately 250 mV and im-
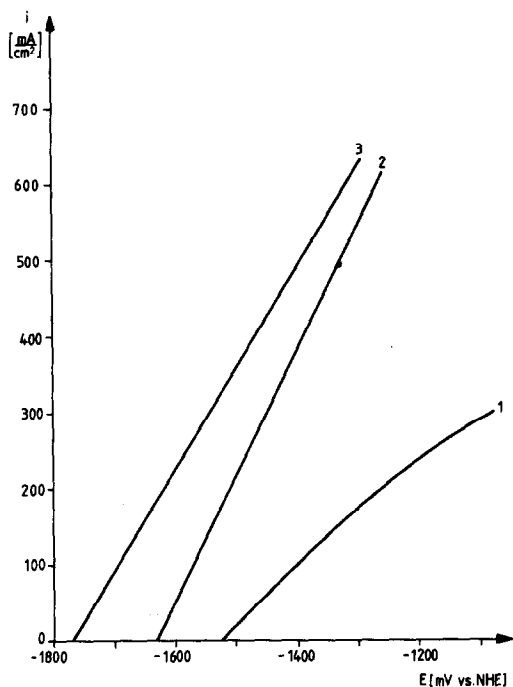
Fig. 1. Anodic polarization curves for aluminum electrodes in different electrolytes: (1) 7N KOH, (2) 7N KOH + 1 g $In^{3+}$/l, (3) 7N KOH + 1 g $Ga^{3+}$/l. Electrode: Al 99.9 alloyed with Mg 0.5%. Temperature: 60 °C. Scan rate: 10 mV/s.

proved polarization characteristics. The same quantity of indium ions results in a shift of the OCV by approximately 100 mV and an even better polarization characteristic. These results are not affected by the scan rate in the tested range of 1 - 1 000 mV/s. It was found that the above mentioned effects depend only on the presence of the respective metal ions at a certain concentration in the electrolyte, and not on the manner in which they appear in the solution, *i.e.*, whether they resulted from the dissociation of chemical compounds or from the anodic dissolution of the elements.

The next objective was to optimize quantitatively the addition of metal ions to the electrolyte. The potentials *vs.* NHE of an aluminum electrode (Al 99.9 alloyed with 0.5% Mg) at 600 mA/cm² under constant conditions (7N KOH, 60 °C) were determined as a function of the gallium concentration in the electrolyte, and are shown in Fig. 2.

In the range observed the potential is improved with increasing gallium content. At concentrations lower than 0.1 g Ga/l the curve falls rapidly. On the other hand, it should be mentioned that with increasing gallium concentration the rate of hydrogen evolution clearly increases. It has been shown that an optimum compromise between depolarizing the anodic dissolution reaction and reducing the corrosion reaction is attained at approximately 0.2 g Ga/l electrolyte under the given conditions.
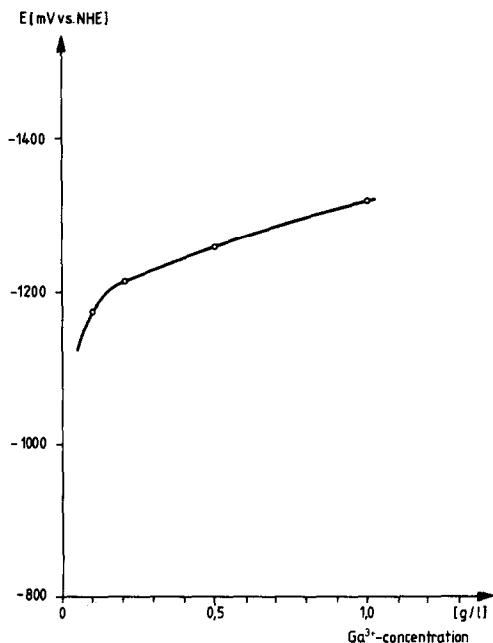
Fig. 2. Potential of Al 99.9 alloyed with Mg 0.5% electrode under load 600 mA/cm$^2$. Temperature: 60 °C. Electrolyte: 7N KOH + Ga$^{3+}$ addition.

In order to shed light on how the gallium ions affect the dissolution process of aluminum, scanning electron microscope photographs were taken of the electrode surfaces. Figure 3 shows an aluminum electrode partially discharged under the above mentioned conditions in an electrolyte containing no additives, at a magnification of × 750.

The × 3 000 magnification in Fig. 4 clearly shows the surface erosion characteristic with hot KOH solution; it appears as flat troughs.

Figure 5, also at × 3 000, shows a partially discharged aluminum electrode in an electrolyte containing 0.2 g/l gallium. As well as the deep furrow in the middle of the picture many small cracks in the metal are noticeable. This cracking becomes even more evident if an electrode at OCV is exposed to the electrolyte containing gallium. Figure 6 at a magnification of × 150, and Fig. 7 at a magnification of × 750, would indicate that the influence of the gallium ions is such that they collect at the grain boundaries and there, by opening up the grain boundary areas, increase the effective electrode surface. This enlargement, in combination with increased electrolyte agitation as a result of the greater rate of hydrogen evolution, allows higher current densities at the same potential.

At a magnification of × 750, Fig. 8 shows the surface of an aluminum electrode, which was first exposed for approx. 30 s to an electrolyte containing gallium at OCV and was then partially discharged at 600 mA/cm$^2$. Characteristic of the explanation given is the simultaneous occurrence of the deep cracks at the grain boundaries and the flat erosion of the grains.
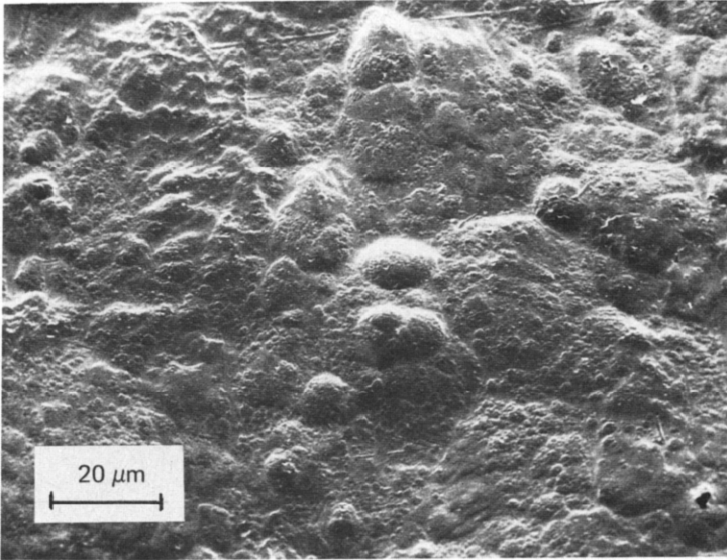
Fig. 3. SEM of the surface of an aluminum electrode, partially discharged in 7N KOH (no additives) at 60 °C.
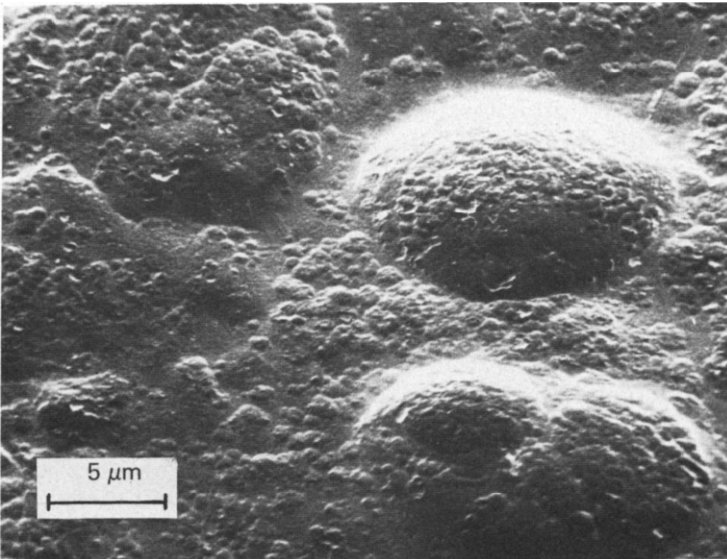


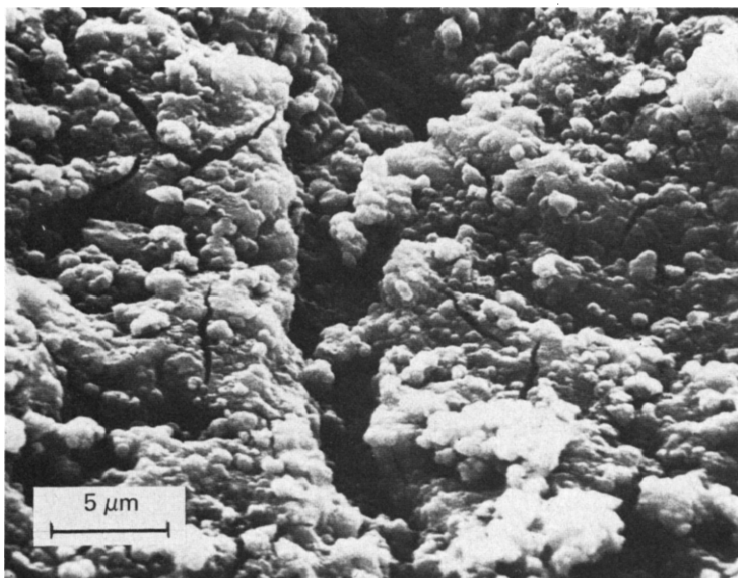Fig. 4. SEM as Fig. 3, but at higher magnification.

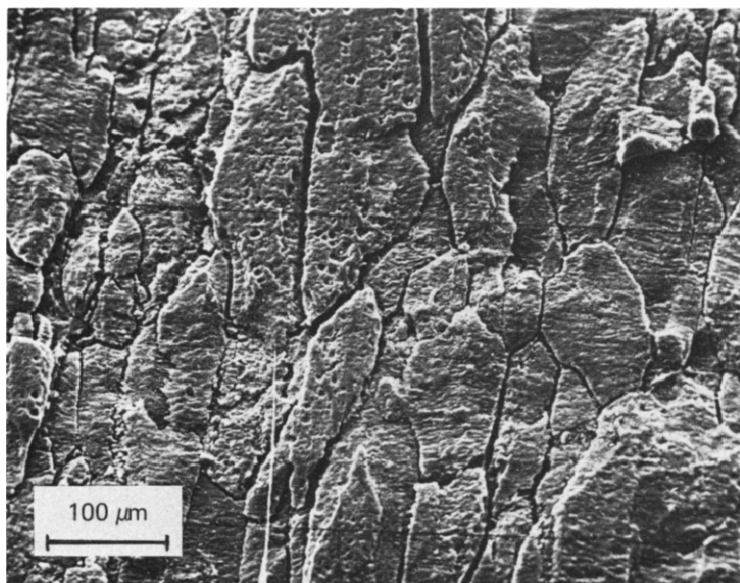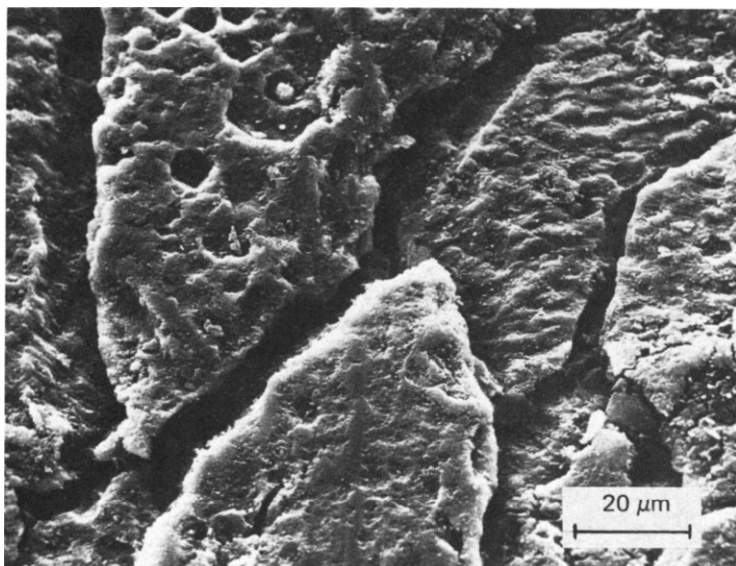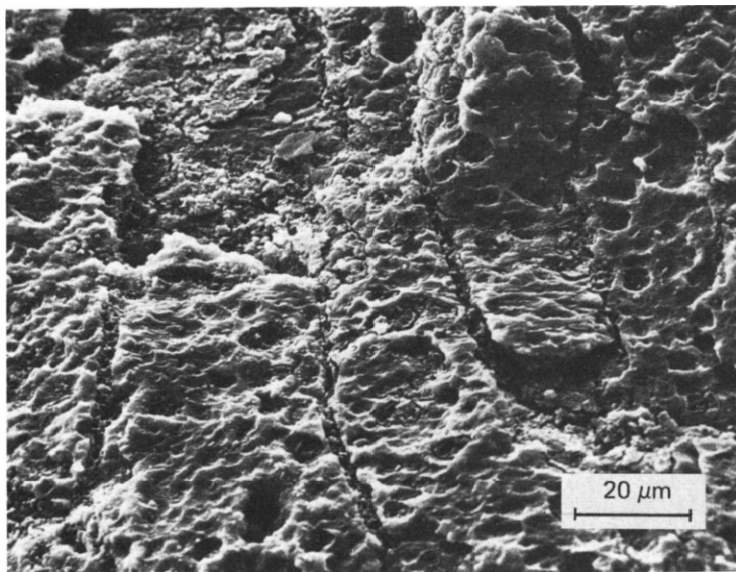Fig. 5. SEM of the surface of an aluminum electrode partially discharged in 7N KOH + 0.2 g/l $Ga^{3+}$ at 60 °C.



Fig. 6. SEM of the surface of an aluminum electrode exposed for approx. 30 s to 7N KOH + 0.2 g/l $Ga^{3+}$ (no external discharge).

Fig. 7. SEM as Fig. 6, but at higher magnification.



Fig. 8. SEM as Fig. 7, but, in addition, partially discharged.

## Acknowledgements

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