

Complex behaviour of aluminium dissolution in alkaline aqueous 2-propanol solution

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Abstract

The corrosion behaviour of pure aluminium in oxygenated 1 M potassium hydroxide using aqueous 2-propanol over a wide range of concentrations (0 to 56 vol.%) is examined by potentiodynamic Tafel polarization measurements at 25 °C. Analysis of the corrosion potential (E_{corr}), corrosion current (i_{corr}), polarization resistance (R_p), and cathodic (i_{cath}) and anodic (i_{anod}) exchange currents reveals that 2-propanol at low concentration acts as a corrosion accelerator for aluminium. At high concentrations, however, corrosion is abated markedly, and at a concentration of 56 vol.% the corrosion rate almost vanishes. The results are explained in terms of weakening of the barrier-type, inner oxide film on aluminium at a low 2-propanol concentration and a blocking effect at a high concentration through interaction via the oxygen centre of the 2-propanol molecule.

Keywords: Aluminium; Propanol; Potassium hydroxide

1. Introduction

Earlier research [1,2] on the development of electrolytes and cathodes for aluminium batteries is extended to examine the corrosion behaviour of aluminium in alkaline aqueous 2-propanol media. The motivation for this work originates from the fact that isopropanol, or 2-propanol (2-PrOH), is often used as a solvent in protective aluminium paints [3], and that isopropoxide (2-PrO⁻) has been found to act as the anode depolarizer for aluminium batteries [1].

The accelerating and inhibiting effects of different additives in alkaline aluminium battery electrolyte has been examined by Zaromb and co-workers [4,5] and summarized in a subsequent paper [6]. Krishnan and Subramanyan [7] studied the effect of calcium-combined organic acids on the corrosion behaviour of aluminium in alkaline solutions. Investigations on aluminium corrosion in non-aqueous solvent have been reported [8] and a few promising battery systems have been patented [9–11].

Several workers have examined [12–17] the corrosion behaviour of aluminium in weakly-to-strongly alkaline media in order to understand the probable mechanistic path for aluminium dissolution. Recently, Hirai et al. [18] reviewed the effect of organic polymer inhibitors on aluminium corrosion and studied the behaviour of alkyl ammonium chlorides and

ammonium cation polymers as corrosion inhibitors. Another recent study, based on weight-loss measurement and anodic polarization of aluminium in alkaline citrate cum stannate solution, has been reported by Kapali et al. [19]. In spite of several attractive features of alkaline aluminium batteries and the work performed in this field, the problem of anode corrosion in alkaline battery fluid during rest conditions has still to be resolved.

The prime requirement for the battery fluid of aluminium batteries is that it will lower aluminium corrosion through cathodic inhibition. An attempt in this direction is made in the research described here.

2. Experimental

2.1. Electrodes

The working electrode was a 99.9% pure aluminium rod supplied by Johnson and Matthey. It was washed with dry distilled acetone and then polished. The rod was fixed in a bracket holder to provide a working electrode of area 1 cm². A graphite counter electrode was used. The reference electrode was a freshly prepared saturated calomel electrode (SCE). All potentials are reported with respect to the SCE.

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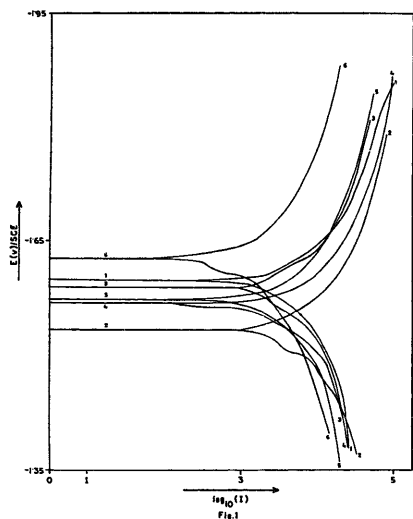


Fig. 1. Tafel polarization curves for pure aluminium in 1 M KOH with and without 2-propanol at $25 \pm 0.5^\circ\text{C}$: (1) without 2-propanol; (2) with 2 vol.% 2-propanol; (3) with 5 vol.% 2-propanol; (4) with 10 vol.% 2-propanol; (5) with 30 vol.% 2-propanol, and (6) with 50 vol.% 2-propanol.

2.2. Electrolytes

2-propanol (BDH, AR) was distilled before use and considerable amounts of the head and the tail fractions were discarded. A solution of 1 M KOH (BDH, AR) and different compositions (2 to 56 vol.%) of mixed solvents containing 1 M KOH were prepared by adding appropriate amounts of 2-propanol and double-distilled water.

2.3. Cell

A three-electrode, conventional cell of 125 ml volume was used. The cell comprised an aluminium (A1) working elec-

trode of 1 cm^2 area, a graphite counter electrode, and an agar-agar KCl salt bridge to an external SCE.

2.4. Equipment

All experiments were conducted at $25 \pm 0.5^\circ\text{C}$ and used a computer-controlled potentiostat/galvanostat (Vibrant, Model VSMCS 30, Lab-India) with an interface and other accessories. The current-potential data were acquired by data-acquisition software and fed to the computer for processing and analysis. Tafel and current-potential plots were produced on a printer.

Prior to each experiment, the working electrode A1 was kept at open-circuit conditions in the electrolyte for 15 min to attain equilibrium. After 15 min, the Tafel lines were recorded at a potential scan rate of 0.5 mV s^{-1} .

The oxygen solubilities in 1 M KOH and 1 M KOH with 2-propanol were determined by the well-known Winkler iodometric method [20]. All corrosion measurements were performed in oxygenated solution that was exposed to air.

3. Results and discussion

The Tafel polarization curves for aluminium in 1 M KOH dissolved in aqueous and mixed aqueous (2 to 56 vol.% of 2-PrOH) medium are shown in Fig. 1. These polarization curves are almost similar in nature, but close scrutiny shows that the equilibrium potential (E_{eq}) in aquo-organic media differs from that in aqueous media. From the direction of the shift in E_{eq} , it appears that while the corrosion rate is enhanced in the presence of a small 2-PrOH concentration, the rate is substantially reduced in 2-PrOH rich media.

Corrosion parameters, such as corrosion potential (E_{corr}), corrosion current (i_{corr}), anodic Tafel slope (b_a), cathodic Tafel slope (b_c) and polarization resistance (R_p), are presented in Table 1. It may be noted that, similar to the E_{eq} , the corrosion potential (E_{corr}) in 1 M KOH containing a low concentration of 2-PrOH is shifted to more positive values and, thereby, indicates anodic polarization. On the other hand, for 30 vol.% 2-PrOH onwards, the E_{corr} shifted to more negative values, and this indicates cathodic polarization. At a high 2-PrOH concentration, significant changes in the anodic

Table 1
Corrosion parameters of aluminium in 1 M KOH with and without 2-propanol at $25 \pm 0.5^\circ\text{C}$

Electrolyte (vol.%)	Corrosion potential, E_{corr} (V vs. SCE)	Corrosion current, i_{corr} (mA cm^{-2})	Tafel slope, V decade^{-1}		Polarization resistance, R_p ($\Omega\text{ cm}^2$)
			anodic (b_a)	cathodic (b_c)	
1 M KOH	-1.57	11.18	0.374	0.260	5.98
1 M KOH + 2% 2-PrOH	-1.51	15.93	0.317	0.308	2.29
1 M KOH + 5% 2-PrOH	-1.53	14.67	0.411	0.367	4.61
1 M KOH + 10% 2-PrOH	-1.56	11.65	0.384	0.268	5.90
1 M KOH + 30% 2-PrOH	-1.57	7.98	0.399	0.278	8.93
1 M KOH + 50% 2-PrOH	-1.62	2.89	0.299	0.271	21.40
1 M KOH + 56% 2-PrOH	-1.61	1.23	0.262	0.268	46.91

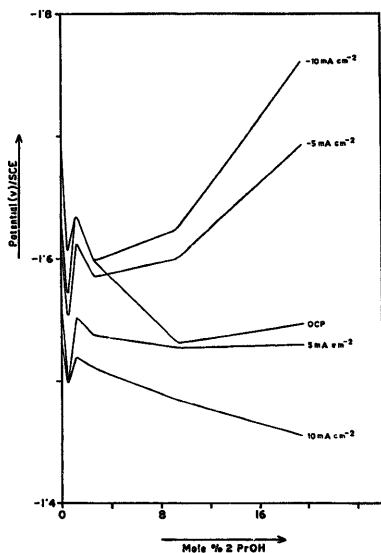


Fig. 2. Aluminium potential vs. 2-propanol concentration at open-circuit potential and 10 and 5 mA cm⁻² current densities.

Tafel slopes are noted. With increasing 2-PrOH concentration, the values of the cathodic and anodic Tafel slopes are close together and thus suggests that the process becomes mixed-controlled. The corrosion current (i_{corr}) values in alkaline 2-PrOH (with small 2-PrOH concentrations) are increased. By contrast, the corrosion current is reduced considerably in 2-PrOH rich media.

The concentration dependence of the potential at various current densities is shown in Fig. 2. Cathodic potential values are indicated by negative current densities. The cathodic, anodic and open-circuit potential (OCP) curves are shifted to the positive (anodic) side at a low concentration of

2-PrOH, but at a high concentration, the cathodic potential curves are shifted to the more negative (cathodic) side. Thus, it is clear that, at a low concentration, 2-PrOH affects the anodic process while, at a high concentration, it affects the cathodic process.

The polarization resistance (R_p) value also corroborates the above conclusions. The corrodability of aluminium increases at low 2-PrOH concentrations and, thus, lowers the R_p . Therefore, it is an interesting feature that 2-PrOH has both accelerating and abating effects on aluminium corrosion, as determined by its concentration.

To understand the mechanism by which 2-PrOH affects the aluminium corrosion reaction, the partial cathodic (i_{cath}) and anodic (i_{anod}) exchange currents for oxygen and water reduction and aluminium dissolution have been evaluated by extrapolating the straight-line portion of the Tafel plot back to zero overpotential. The results are given in Table 2. These exchange-current values, along with the corrosion current (i_{corr}) have been plotted against the mol% of 2-PrOH, and are shown in Fig. 3. It clearly indicates that at 2 vol.% (0.5 mol%) 2-PrOH, the corrosion current increases and its cathodic and anodic part both increases. With increasing 2-PrOH concentration, however, the rate decreases and the cathodic and anodic exchange currents both decrease with converging nature. At about 56 vol.% (23.5 mol%) 2-PrOH, the exchange currents meet at almost zero current and i_{corr} is negligibly small at this concentration. Thus, there is a media (1 M KOH in 56 vol.% 2-PrOH) where aluminium does not undergo any dissolution, even in the presence of alkali.

From the above results, it seems that aluminium corrosion in alkaline solution, even in the presence of a small concentration of 2-PrOH, is anodically controlled ($b_a > b_c$). The anodic reactions may be represented by an electron-transfer reaction, followed by ion migration and depolarization. The process can be summarized according to the following scheme:

(i) *electron transfer reaction:*



These are fast steps.

Table 2

Cathodic (hydrogen evolution) and anodic (anode dissolution) exchange-current densities for aluminium in 1 M KOH with different mol% of 2-PrOH at $25 \pm 0.5^\circ\text{C}$

Proportion of 2-PrOH (mol%)	Anodic exchange-current density, i_{anod} (mA cm ⁻²)	Cathodic exchange-current density, i_{cath} (mA cm ⁻²)
Blank	9.07	12.42
0.50	14.62	18.40
1.25	12.72	16.24
2.61	10.21	12.38
9.38	7.17	8.50
19.45	2.54	3.04
23.50	1.19	1.26

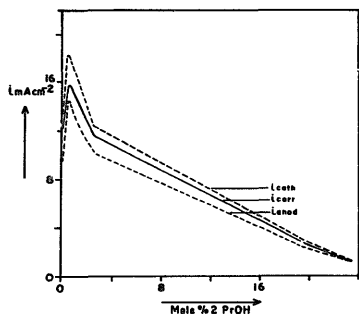
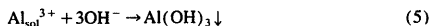


Fig. 3. Dependence of corrosion current (i_{corr}), cathodic exchange current (i_{cath}) and anodic exchange current (i_{anod}) of aluminium on 2-propanol concentration.

(ii) ion migration and depolarization:



These are all slow steps. Here, the subscript 'm' denotes the metal surface, 'ox' denotes the oxide film, and 'sol' refers to the solution side.

The oxide film consists of two regions [16], namely, an inner barrier and an outer non-barrier. At low concentrations, 2-PrOH weakens the inner barrier oxide film so as to increase the ion migration from the metal surface to the solution through the outer non-barrier part and, hence, increase the anodic current and reduce the resistance polarization. At high concentrations of 2-PrOH, however, a blocking layer of 2-PrOH is considered to form over the metal surface through interaction of the oxygen centre of 2-PrOH. This layer reduces significantly the Al^{3+} ion transport to the solution.

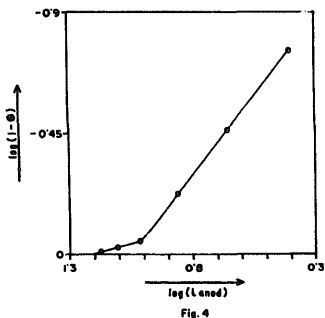


Fig. 4. $\log(1-\theta)$ vs. $\log i_{\text{anod}}$ plot for pure aluminium in 1 M KOH with 2-propanol at $25 \pm 0.5^\circ\text{C}$.

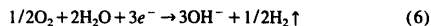
Table 3
Dissolved oxygen in 1 M KOH with and without 2-PrOH at $25 \pm 0.5^\circ\text{C}$

Electrolyte (vol.%)	Oxygen concentration ($\times 10^7$ mol cm^{-3})
1 M KOH	14.3
1 M KOH + 10% 2-PrOH	12.8
1 M KOH + 30% 2-PrOH	11.8
1 M KOH + 50% 2-PrOH	10.0

In fact, at about 23.5 mol% of 2-PrOH, the process of ion migration is totally stopped. The entire surface is covered with a non-penetrating layer of 2-PrOH, where both the cathodic and the anodic currents are negligibly small. Thus, it can be assumed that the fractional coverage (θ) of aluminium surface is $\theta = 1$ at 23.5 mol% (0.235 mole fraction) of 2-PrOH concentration and $\theta = 0$ in the absence of 2-PrOH i.e., in 1 M KOH solution.

The fractional coverage (θ) of the aluminium surface in different mole fractions of 2-PrOH can be estimated by assuming linear Langmuir adsorption. Since the Al^{3+} concentration at the solution phase just outside the oxide layer is related to the bare aluminium surface ($1-\theta$), a plot of $\log(1-\theta) - \log i_{\text{anod}}$ (Fig. 4) clearly indicates two linear plots with different slopes. In the high coverage (2-PrOH rich) region, the slope is greater than in the low coverage region. This indicates a different order of interaction of 2-PrOH at low and high coverage. At low coverage, 2-PrOH may penetrate into the oxide layer, depolarize the aluminium surface and, thus, increase the bare surface concentration.

It may be noted that, with increasing concentration of 2-PrOH, the exchange current for the cathodic reaction is also sharply reduced. The cathodic reaction may be summarized as:



With increasing 2-PrOH concentration, the concentration of water and oxygen (Table 3) are considerably reduced.

Thus, from the present analysis, it seems that the protective action of 2-PrOH, even in the presence of alkali, is probably due to its formation of a non-penetrating 2-PrOH layer over the metal surface. Again, at low concentration, it enhances aluminium corrosion by accelerating ion migration and depolarization through weakening of the oxide film.

4. Conclusions

The disadvantage of alkaline aluminium/air batteries is that the anode (pure aluminium) has to be removed from the battery fluid during rest conditions. In this condition, oxide and carbonate layers can form over the anode surface. Hence, alkali solution containing 23.5 mol% of 2-PrOH may be used as a 'dipping fluid' during battery rest conditions.

Furthermore, these studies suggest that the use of a small concentration of 2-PrOH in alkaline aluminium/air batteries may be useful for increasing the anode efficiency.

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