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ORIGINAL PAPER

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Corrosion mechanism of pure aluminium in aqueous alkaline solution

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Abstract The corrosion of pure aluminium in alkaline solution has been explored using an open circuit potential transient, potentiodynamic polarization experiment and a.c. impedance spectroscopy. The steady-state value of the open circuit potential ($E_{\mathrm{ocp}}^{\mathrm{ss}}$) of pure aluminium in alkaline solution was observed to decrease with increasing rotation rate of the specimen, which is ascribed to the enhanced anodic reaction. The extent of anodic polarization for the aluminium dissolution reaction on pure aluminium at $E_{\mathrm{ocp}}^{\mathrm{ss}}$ was found to be greater than that of cathodic polarization for the water reduction reaction. This indicates that the rate of corrosion of pure aluminium is mainly determined by the anodic reaction in alkaline solution. Based upon the experimental results, a corrosion mechanism for pure aluminium has been proposed in the presence of the native surface oxide film in alkaline solution, involving consecutive oxide film formation and dissolution, and simultaneous water reduction.

Key words Alkaline solution · Aluminium · Open-circuit potential transitent · Oxide film · Water reduction

Introduction

Aluminium/air batteries are being currently developed as power sources for electric vehicle propulsion [1–9]. The performance of an aluminium/air battery is determined by the electrochemical and corrosion properties of the aluminium anode to a significant extent. Pure aluminium is too reactive to be used directly in concentrated alkaline solutions. This high reactivity results in an unacceptably high corrosion rate of the aluminium anode, which is responsible for the main loss of the aluminium fuel. So, it is important to discuss the corrosion mechanism of the aluminium anode in alkaline solution for the development of aluminium/air batteries.

The dissolution of the surface oxide film on aluminium owing to chemical attack by hydroxide ions OH^- will depend on the concentrations of OH^- and aluminate ions $Al(OH)_4^-$ at the film/solution interface. So, transport of OH^- and $Al(OH)_4^-$ ions through the solution to and away from the metal/solution interface, respectively, is expected to influence the anodic dissolution process of aluminium metal. However, several authors [7, 10] reported that the effect of transport of OH^- and $Al(OH)_4^-$ ions on the anodic current density of pure aluminium is not significant in alkaline solutions higher than 1 M KOH. Considering that the diffusion of OH^- ions through the solution to the film/solution interface may be influenced by the concentration of OH^- ions in the bulk solution, it is necessary to take a relatively weak alkaline solution for studying the effect of OH^- and $Al(OH)_4^-$ transport.

The anodic dissolution mechanism of aluminium in alkaline solutions has been investigated by several researchers [7, 11]. Macdonald et al. [11] proposed a model for anodic aluminium dissolution involving the stepwise addition of hydroxide ions to surface aluminium atoms. Chu and Savinell [7] suggested a similar anodic dissolution mechanism in which two fast steps of aluminium ionization and hydroxide formation reactions are combined with the last slow film dissolution reaction by OH^- attack. In their studies [7, 11], aluminium hydroxide formation was assumed to be possible when surface aluminium atoms are exposed directly to the solution. However, since the native oxide film could be inherently present on the surface of aluminium metal in alkaline solutions [10, 12, 13], the anodic aluminium dissolution mechanism should encompass the presence of surface oxide film on aluminium in alkaline solution.

The present work was undertaken to investigate the corrosion mechanism of pure aluminium in aqueous alkaline solutions. For this purpose, the electrochemical

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properties of a pure aluminium rotating disc electrode were measured on the disc specimen as a function of rotation rate and NaOH concentration in aqueous solutions by using an open circuit potential transient, potentiodynamic polarization experiment and a.c. impedance spectroscopy. The experimental results obtained are discussed in terms of transport of OH^- and $Al(OH)_4^-$ ions through the solution, the rate-determining step of the corrosion reaction, and the coupling between the partial anodic reaction and the partial cathodic reaction on the native surface oxide film on pure aluminium.

Experimental

In this work, the experiments were done with a 99.99% purity aluminium rotating disc specimen of 2.8 mm diameter. The disc specimen was ground successively with silicon carbide papers to 2000 grit and then rinsed with distilled water, followed by drying in a stream of air. The rotation rate of the disc specimen was controlled by rotating disc electrode apparatus (EG&G model 636). The electrolytes used were 0.01 M, 0.1 M and 1 M NaOH aqueous solutions. A platinum wire and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

Just after immersing the pure aluminum rotating disc specimen for 2 s in the solution, the resulting open circuit potential was measured versus time at various rotation rates of 0 rpm to 100 rpm with an EG&G model 273 Galvanostat/Potentiostat. The potentiodynamic polarization experiments were conducted using a EG&G model 273 Galvanostat/Potentiostat with a scan rate of 0.5 mV s^{-1} on the disc specimen under two different conditions: one was selected to vary the rotation rates from 20 rpm to 100 rpm in 0.01 M NaOH solution; the other was to use various NaOH concentrations (0.01 M, 0.1 M and 1 M) in the solution at 0 rpm. The steady-state value of anodic current density i_{ss} was measured on the disc specimen under an applied anodic potential of 1 V_{SCE} as a function of the rotation rate of in 0.01 M, 0.1 M and 1 M NaOH solutions.

A.c. impedance measurement was performed at various rotation rates of the disc specimen with a Zahner IM5D impedance analyzer by superimposing an a.c. signal of 5 mV amplitude on open circuit potential over 1–10^5 Hz in 0.01 M, 0.1 M and 1 M NaOH solutions. In order to determine the film capacitance, the impedance data obtained were analyzed on the basis of the equivalent electric circuit used in previous work [14] by using the complex nonlinear least-squares (CNLS) fitting method written first by Macdonald [15] and later modified in our laboratory [16].

Results

Figure 1 presents open circuit potential transients obtained from a pure aluminium rotating disc specimen at various rotation rates in 0.01 M NaOH solution. The open circuit potential increased with time and then reached a steady-state value E^{ss}_{ocp}, as designated by the arrow. The value of E^{ss}_{ocp} was found to be about −1.38 V_{SCE} at 0 rpm and to be lowered with the increasing rotation rate of the disc specimen. The increase in open circuit potential with time is known to arise from the growth of a surface oxide film [13, 17, 18].

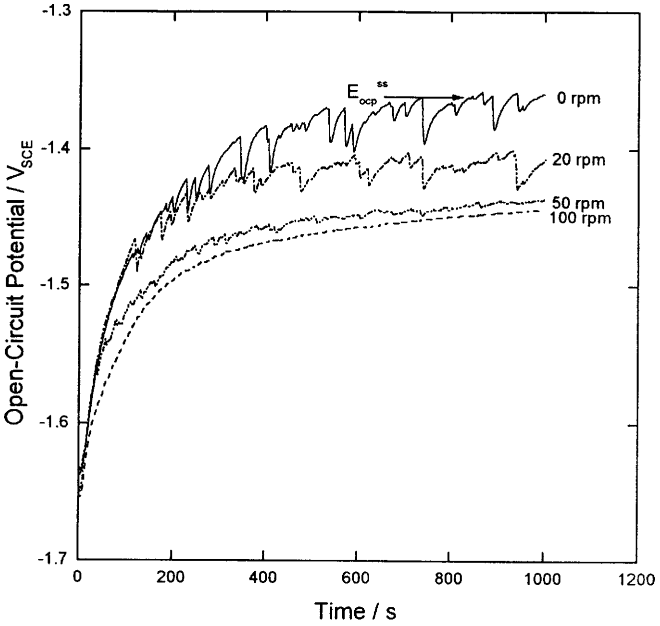

Fig. 1 Open circuit potential transients obtained from a pure aluminium rotating disc specimen at various rotation rates of 0–100 rpm in 0.01 M NaOH solution

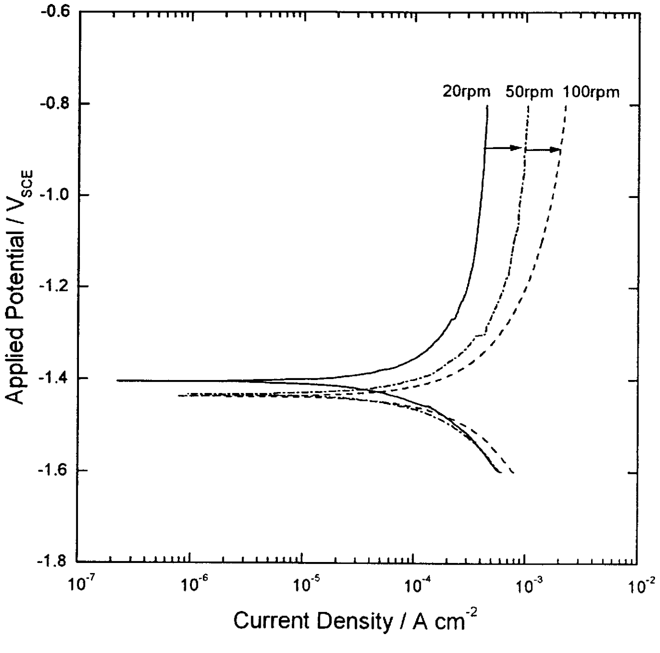

Fig. 2 Potentiodynamic polarization curves obtained from a pure aluminium rotating disc specimen at various rotation rates of 20–100 rpm with a scan rate of 0.5 mV s^{-1} in 0.01 M NaOH solution. The potential was swept in the positive direction from a cathodic potential of −1.6 V_{SCE} to an anodic potential of −0.8 V_{SCE}

Figure 2 shows potentiodynamic polarization curves obtained from a pure aluminium rotating disc specimen with a scan rate of 0.5 mV s^{-1} in the anodic direction at various rotation rates in 0.01 M NaOH solution. It is noted that the anodic current density became much higher in value with the increase in rotation rate, but the cathodic current density appeared just slightly to climb with the rotation rate. By considering the fact that the increase in the anodic reaction rate on open circuit generates excess electrons with negative charges on the surface of pure aluminium, it is reasonable to infer that the enhanced anodic reaction with rotation rate is responsible for the decrease in E^{ss}_{ocp} with rotation rate in Fig. 1.

Figure 3 gives plots of steady-state anodic current density i_{ss} against the rotation rate of a pure aluminium rotating disc specimen in 0.01 M, 0.1 M and 1 M NaOH solutions. The slope of the logarithmic plot of i_{ss} vs. rotation rate was found to be lower than 0.5 and it decreased with increasing NaOH concentration. A slope lower than 0.5 suggests that the anodic current density is not determined by the thickness of the diffusion layer. The increase of i_{ss} with rotation rate is attributed to the oxide film becoming thinner with the rotation rate [19]. From the lowered slope of the logarithmic plot of i_{ss} vs. rotation rate with NaOH concentration, it is very likely that other researchers [7, 10] failed to realize such a slightly positive effect of the rotation rate on the anodic current density in a comparatively concentrated alkaline solution.

Figure 4 demonstrates the change in the capacitance of the surface oxide film obtained from a pure aluminium rotating disc specimen at open circuit with NaOH concentration. The film capacitance increased with increasing NaOH concentration. The film capacitance is generally given by

$$C = \varepsilon_{ox}\varepsilon_{o}/d \qquad (1)$$

where ε_{ox} is the relative permittivity of the surface oxide film, ε_{o} is the permittivity of the vacuum, and d represents the thickness of the surface oxide film. Assuming that ε_{ox} is not changeable with NaOH concentration, it can be said that the film thickness is reduced with increasing NaOH concentration. This is likely because ε_{ox} shows very limited values between 7 and 9 in various aqueous solutions [20].

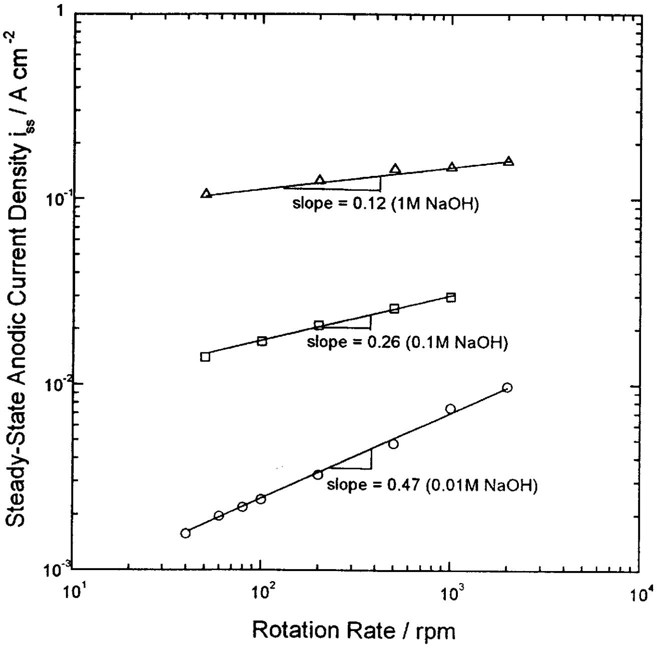

Fig. 3 Plot of steady-state anodic current density against rotation rate of a pure aluminium rotating disc specimen on a logarithmic scale at an applied potential of 1 V_{SCE} in 0.01 M (○), 0.1 M (□) and 1 M (△) NaOH solutions

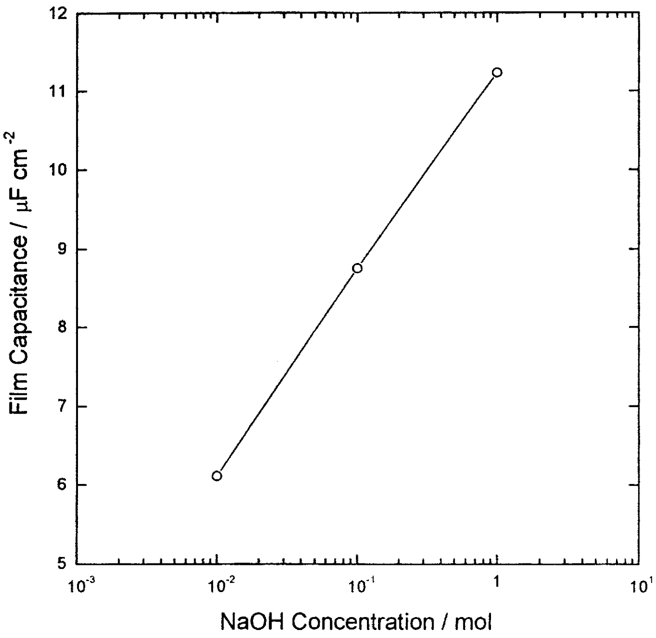

Fig. 4 Plot of the capacitance of the surface oxide film formed on a pure aluminium rotating disc specimen on a semi-logarithmic scale at 0 rpm on open circuit against the NaOH concentration of the solution

Figure 5 exhibits potentiodynamic cathodic polarization curves obtained from a pure aluminium rotating disc specimen at 0 rpm in 0.01 M, 0.1 M and 1 M NaOH solutions. Cathodic current density did not show the limiting value which is indicative of oxygen reduction reaction, but showed much higher than several mA cm^{-2} even under a small cathodic polarization of 50 mV. The relatively higher cathodic current density suggests that the whole reduction rate is mainly determined by water reduction. This is borne out by the facts that cathodic polarization of the water reduction reaction on pure aluminium is considerably enlarged at an open circuit in alkaline solution and water is sufficiently supplied for the reduction reaction at the film/solution interface.

Discussion

Corrosion mechanism

Corrosion of metals is known to proceed by the action of local cells, which are established by metals,

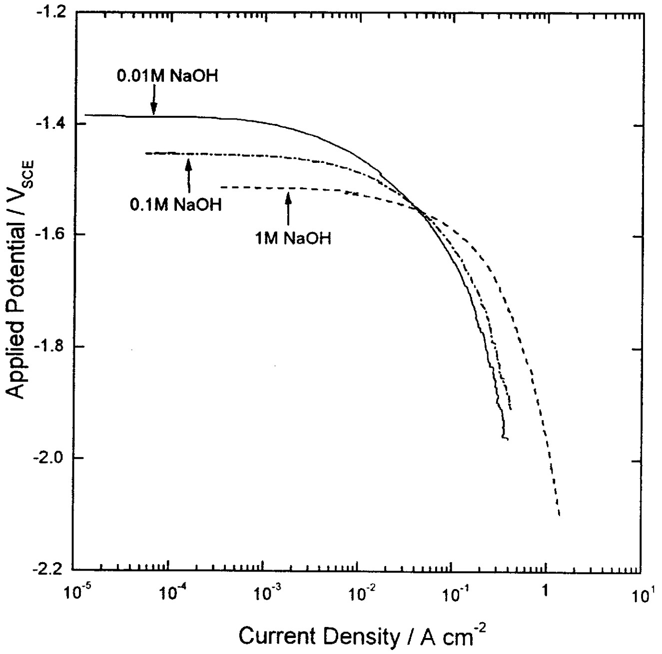

Fig. 5 Potentiodynamic polarization curves obtained from a pure aluminium rotating disc specimen at 0 rpm with a scan rate of 0.5 mV s^{-1} in 0.01 M NaOH (—), 0.1 M NaOH (– · –) and 1 M NaOH (– – –) solutions. The potential was scanned in the negative direction

comprising a partial anodic reaction and a partial cathodic reaction occurring simultaneously on the metal surface [21]. So, in order to follow the mechanism underlying the corrosion of metals, it is necessary to explore what partial anodic reactions and partial cathodic reactions involve and to determine which of them prevails in the gross corrosion reaction to a greater extent. In addition, the presence of the native surface oxide film (Fig. 1) should be considered in studying the corrosion mechanism of pure aluminium in alkaline solution. The anodic aluminium dissolution reaction in the presence of the native surface oxide film can be classified into a direct metal dissolution reaction by the movement of aluminium ions through the film and an indirect metal dissolution reaction by consecutive oxide film formation and dissolution. In previous work [14, 19] it was shown that the direct metal dissolution, which involves direct ejection of aluminium ions from the film into the solution, can never occur in alkaline solution because aluminium ions are not stable thermodynamically in alkaline solution. Hence, for study of the corrosion mechanism of pure aluminium in alkaline solution, it is enough to consider indirect metal dissolution by consecutive film formation and dissolution as a partial anodic reaction.

It is generally accepted [19, 20, 22] that the film formation proceeds electrochemically by the incorporation of hydroxide ions into the film and migration through the film towards the aluminium/film interface in the presence of a thick oxide film on the surface of aluminium as:

$$\mathrm{Al} + 3\mathrm{OH}^- = \mathrm{Al(OH)_3} + 3\mathrm{e}^- \qquad (2)$$

The aluminium hydroxide film formed electrochemically will be dissolved chemically by OH^- attack at the film/solution interface:

$$\mathrm{Al(OH)_3} + \mathrm{OH}^- = \mathrm{Al(OH)_4^-} \qquad (3)$$

where $\mathrm{Al(OH)_4^-}$ represents the aluminate ions. Increasing the rotation rate of the specimen results in a fast supply of OH^- ions to the film/solution interface and rapid removal of $\mathrm{Al(OH)_4^-}$ ions away from the film/solution interface. So, the raised anodic current density with the rotation rate of the disc specimen in Figs. 2 and 3 is attributable to the enhanced chemical film dissolution rate due to enriched OH^- ions and depleted $\mathrm{Al(OH)_4^-}$ ions at the film/solution interface with the rotation rate. A partial anodic dissolution reaction of pure aluminium in alkaline solution can be obtained by combining electrochemical film formation (Eq. 2) and chemical film dissolution (Eq. 3), which can be written as:

$$\mathrm{Al} + 4\mathrm{OH}^- = \mathrm{Al(OH)_4^-} + 3\mathrm{e}^- \qquad (4)$$

The electrons produced by the partial anodic reaction (Eq. 4) will be consumed immediately by such partial cathodic reactions as the oxygen reduction reaction:

$$\frac{3}{4}\mathrm{O_2} + \frac{3}{2}\mathrm{H_2O} + 3\mathrm{e}^- = 3\mathrm{OH}^- \qquad (5)$$

and/or the water reduction reaction:

$$3\mathrm{H_2O} + 3\mathrm{e}^- = \frac{3}{2}\mathrm{H_2} + 3\mathrm{OH}^- \qquad (6)$$

The short-circuited corrosion reaction of pure aluminium in alkaline solution can be obtained by combining Eqs. 4 and 5:

$$\mathrm{Al} + \mathrm{OH}^- + \frac{3}{4}\mathrm{O_2} + \frac{3}{2}\mathrm{H_2O} = \mathrm{Al(OH)_4^-} \qquad (7)$$

and/or by combining Eqs. 4 and 6:

$$\mathrm{Al} + 3\mathrm{H_2O} + \mathrm{OH}^- = \frac{3}{2}\mathrm{H_2} + \mathrm{Al(OH)_4^-} \qquad (8)$$

As a consequence of the overall corrosion reaction (Eq. 7), only aluminium metal dissolution can occur. On the other hand, hydrogen evolution takes place simultaneously with the dissolution of aluminium metal as a result of the overall corrosion reaction (Eq. 8). The observation of gas bubbles on the corroding aluminium surface shows that the corrosion of pure aluminium in alkaline solution proceeds mainly by water reduction according to Eq. 8. This is strongly substantiated by the experimental findings of a relatively higher cathodic current density with no limiting current density value (Fig. 5). Therefore, it is concluded that the overall corrosion reaction of pure aluminium in alkaline solution can be divided into two substeps of a partial anodic reaction comprising the electrochemical formation and chemical dissolution reactions of the film, and a partial cathodic reaction of water reduction reaction.

Rate-determining step

It is generally known for polarization to occur in some degree at both anodes and cathodes on the surface of corroding metals [21]. In order to calculate the extent of polarization occurring at the anode and cathode, it is necessary to know the equilibrium potentials of the partial anodic and cathodic reactions. The equilibrium potential of the aluminium dissolution reaction in alkaline solution is given by [23]:

$$E_0 = -1.262 - 0.0788\ \mathrm{pH} + 0.0197\ \log[\mathrm{Al(OH)_4^-}](\mathrm{V_{SHE}}) \qquad (9)$$

where $[\mathrm{Al(OH)_4^-}]$ represents the concentration of aluminate ions in the solution. When $[\mathrm{Al(OH)_4^-}]$ is lower than unity, which is the case in this work, the equilibrium potential for the aluminium dissolution reaction is found to be less than the potential of $-1.262 - 0.0788$ pH, depending upon pH value of the solution. The equilibrium potential for the water reduction reaction, which is the main cathodic partial reaction in alkaline solutions (Fig. 5), is given by [23]:

$$E_0 = -0.059\ \mathrm{pH}(\mathrm{V_{SHE}}) \qquad (10)$$

The extent of anodic and cathodic polarizations on the surface of the specimen on opencircuit was determined as the difference between the equilibrium potential and the steady-state open circuit potential. The calculated anodic and cathodic polarizations are listed in Table 1. It is apparent that anodic polarization is much larger than cathodic polarization in alkaline solutions, which is ascribed to the presence of the native surface oxide film. Therefore, we can say that anodic control prevails in the corrosion of pure aluminium in alkaline solution. This is in accordance with the result suggested from the analyses of polarization curves by Paramasivam et al. [24].

Conclusions

1. The steady-state value of the open circuit potential (E^{ss}_{ocp}) of pure aluminium in alkaline solution was observed to decrease with increasing rotation rate of the specimen. The anodic current density became much higher with rotation rate in alkaline solution, but the cathodic current density showed just a slight increase with rotation rate on potentiodynamic polarization curves. This means that the decrease in open circuit potential with rotation rate is associated with the enhanced anodic reaction.

2. The extent of anodic polarization of the aluminium dissolution reaction at E^{ss}_{ocp} was calculated to be larger than that of cathodic polarization of the water reduction reaction in 0.01 M, 0.1 M and 1 M NaOH solutions. This reveals that corrosion of pure aluminium is under anodic control in alkaline solutions.

3. A reaction scheme for pure aluminium corrosion in alkaline solution is proposed in the presence of the native surface oxide film as follows. The anodic partial reaction on the surface of pure aluminium in alkaline solution consists of consecutive reactions of electrochemical film formation at the aluminium/film interface, owing to the movement of $\mathrm{OH^-}$ through the film towards aluminium, and chemical film dissolution due to $\mathrm{OH^-}$ attack at the film/solution interface. The water reduction reaction is responsible for the main cathodic partial reaction on pure aluminium and it is coupled with the anodic partial reaction comprising the film formation and dissolution, thereby establishing a short-circuited corrosion cell on pure aluminium in alkaline solution.

Table 1 The steady-state value of the open circuit potential (E^{ss}_{ocp}) of pure aluminium measured at 0 rpm, and the extent of anodic polarization of the aluminium dissolution reaction and cathodic polarization of water reduction at E^{ss}_{ocp} in 0.01 M, 0.1 M and 1 M NaOH solutions

	E^{ss}_{ocp}	Anodic polarization	Cathodic polarization
0.01 M NaOH	$-1383\ \mathrm{mV_{SCE}}$	>1065 mV	434 mV
0.1 M NaOH	$-1452\ \mathrm{mV_{SCE}}$	>1067 mV	450 mV
1 M NaOH	$-1514\ \mathrm{mV_{SCE}}$	>1076 mV	459 mV

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