

Anomalous Electrochemical Phenomena during Corrosion of Aluminium in NaOH Solutions at Low Cathodic and Anodic Polarization

S. A. AWAD and S. S. MAHMOUD

Department of Chemistry, University College for Girls, Ain Shams University, Heliopolis, Cairo, Egypt

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The rates of corrosion of aluminium in aqueous 0.03 to 0.4 M-NaOH solutions were measured at 20 °C, under imposed cathodic as well as anodic current densities up to 160 $\mu\text{A cm}^{-2}$. The rates were determined from the loss in mass of aluminium, as well as by measuring the volume of evolving hydrogen. The results were in contradiction with the fundamentals of electrode kinetics. Thus, within certain current density range, the cathodic reaction (*viz.* hydrogen evolution) is retarded by cathodic currents, and activated by anodic currents. On the other hand, the anodic reaction is accelerated with cathodic currents, and inhibited with anodic ones although the surface is active. To avoid breakdown of electrode kinetics, it is suggested that the entities initiating the cathodic and anodic reactions originate simultaneously from the surface metal atoms. A surface equilibrium is always established between the charged entities and the neutral metal atoms. Pronounced changes in the surface pattern at low polarization lead to anomalous electrochemical phenomena.

In the course of investigation of the anodic and corrosion behaviour of aluminium, it was observed that the corrosion current determined from polarization curves, corresponds to a much smaller corrosion rate, than that at which the metal corrodes under currentless conditions [1]. Such a phenomenon contradicts the requirements of the electrochemical theory of corrosion. A similarly surprising phenomenon is the observation made by *Tomashov* and *Modestova* [2] that the rate of self-dissolution of aluminium in NaCl solutions (determined by measuring the volume of evolving hydrogen gas) increases with the density of the applied anodic current.

The above observations might reveal that the mechanism of corrosion is not so simple as postulated by the electrochemical theory of corrosion. However, the above phenomena were observed under anodic treatment; and hence, before any trial to explain them, the behaviour under cathodic treatment has to be investigated. This paper describes the corrosion behaviour of aluminium in NaOH solutions (in which the metal surface is oxide-free [3]), under imposed cathodic and anodic currents.

EXPERIMENTAL

The rate of corrosion was determined gasometrically, as well as by the mass loss technique. Experiments were performed on pieces of aluminium of the size 5 cm \times 5 cm and 0.8 mm thick, cut from anal. grade aluminium sheet. The test pieces were

first degreased with acetone, washed with conductivity water, dried in alcohol and ether and then weighed.

The experiments were carried out in a Pyrex glass cell, composed of two compartments: a relatively wide one for the aluminium test piece, and the other one for the platinum counter electrode. The two compartments are connected with a tube, in which a sintered glass disc is sealed; this retards the diffusion of the products at the counter electrode towards the aluminium piece. The cover of the wide compartment is in the form of a tight ground glass joint. Near the rim of the wide compartment, a side tube is sealed, through which the hydrogen gas is collected and determined gasometrically. For the measurement of potential of aluminium during the passage of current, a tube is sealed near the bottom of the wide compartment, the tip of which is drawn into a capillary (Luggin capillary) that touches the surface of aluminium piece. This tube leads *via* a salt bridge to a saturated calomel electrode.

After filling the cell with the alkali solution, the aluminium piece was suspended in its compartment. The appropriate current was switched on and the test piece was left there for one hour. After that period the volume of hydrogen gas was determined. The cover of the wide compartment was then removed and the piece withdrawn, rinsed with conductivity water and finally dried and weighed.

The solutions were prepared using conductivity water and anal. grade NaOH. The volume of hydrogen was corrected to a pressure of 10⁵ Pa, taking the vapour pressure of water into account.

The runs were carried out under galvanostatic conditions. Highly stabilized currents were supplied by means of a GELMAN D.C. power supply. The current was measured with a multirange micro-milliammeter, and the potential with a Cambridge valve pH-meter-millivoltmeter, readable to 1 mV.

The results are remarkably reproducible; the potentials are reproducible to ± 5 mV, the loss in mass of aluminium to ± 0.1 mg and the volume of hydrogen to ± 0.03 cm³. The results were duplicated and the mean was computed.

All tests were carried out at 20 °C. The potentials are recorded on the normal hydrogen scale.

RESULTS

The volume of hydrogen, evolved during the corrosion of aluminium in pure 0.03–0.4 M-NaOH, was measured at 20 °C and the pressure of 10^5 Pa, as a function of imposed cathodic and anodic current densities up to $160 \mu\text{A cm}^{-2}$. The values of rate of hydrogen evolution are given in Figs. 1 and 2. The potentials of aluminium were measured at the different current densities. Fig. 3 shows the results obtained under anodic polarization. It is obvious that the potential increases only by few millivolts within the whole current density range studied. Under cathodic polarization the potential decreases by few millivolts. From the change in potential, and the transfer coefficient α for hydrogen evolution at alu-

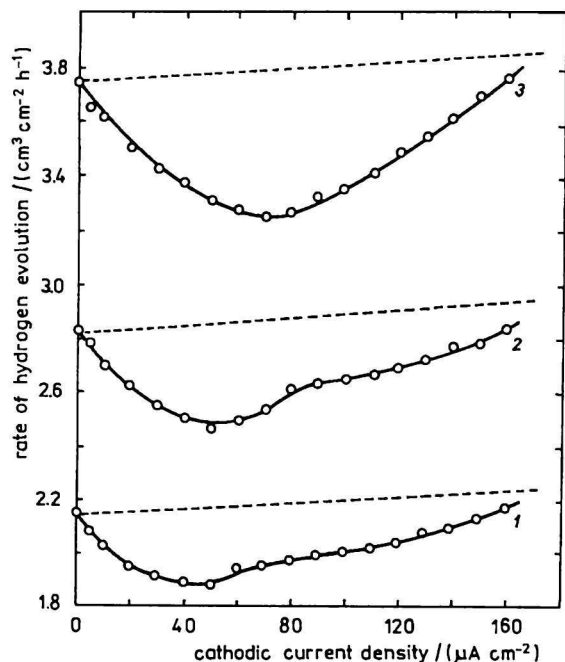


Fig. 1. Effect of cathodic current density on the rate of hydrogen evolution at aluminium in NaOH solutions with concentrations $c/(\text{mol dm}^{-3})$: 1. 0.1; 2. 0.2; 3. 0.3. ----- the total theoretical rates in given solutions.

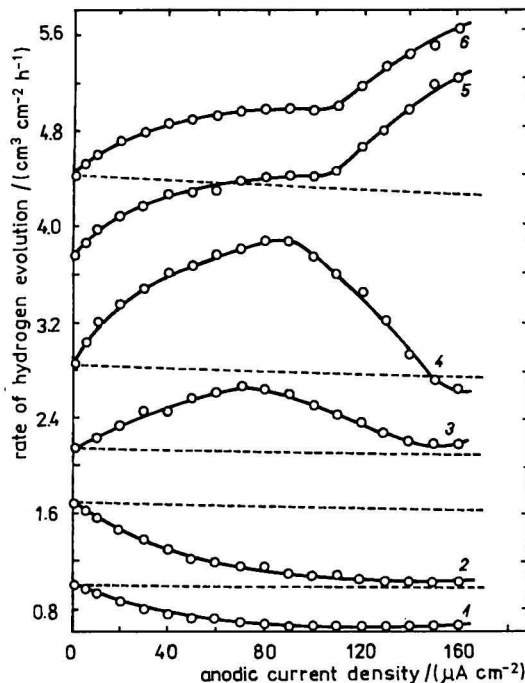


Fig. 2. Effect of anodic current density on the rate of hydrogen evolution at aluminium in NaOH solutions with concentrations $c/(\text{mol dm}^{-3})$: 1. 0.03; 2. 0.05; 3. 0.1; 4. 0.2; 5. 0.3; 6. 0.4. ----- the theoretical rates in given solutions.

minium (which amounts to 0.52 [4]), the expected volumes of hydrogen at different current densities were calculated. These are represented by dashed lines in Figs. 1 and 2.

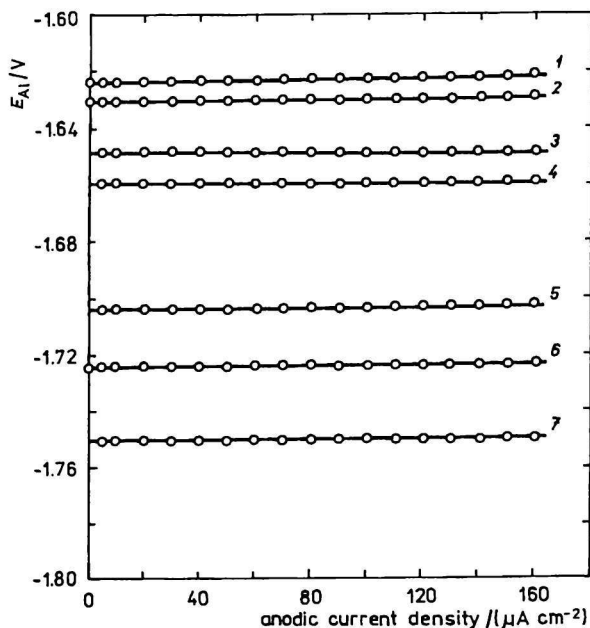


Fig. 3. Effect of anodic current density on the potential of aluminium in NaOH solutions with concentrations $c/(\text{mol dm}^{-3})$: 1. 0.03; 2. 0.05; 3. 0.1; 4. 0.2; 5. 0.3; 6. 0.4; 7. 0.5.

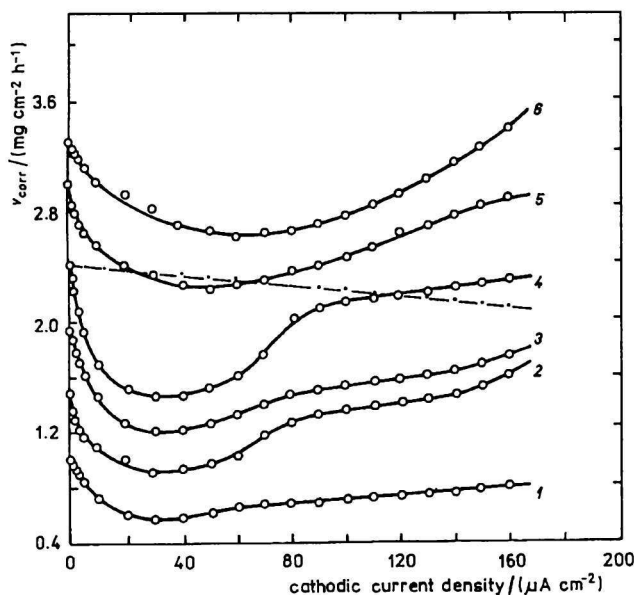


Fig. 4. Effect of cathodic current density on the rate of corrosion of aluminium in NaOH solutions with concentrations $c/(\text{mol dm}^{-3})$: 1. 0.05; 2. 0.10; 3. 0.15; 4. 0.20; 5. 0.25; 6. 0.30. --- the theoretical v_{corr} in 0.20 M solution.

The rates of corrosion v_{corr} were also determined by the mass loss technique at different cathodic and anodic current densities. The results are shown in Figs. 4 and 5. Again, the theoretical values were calculated from the change in potential and the transfer coefficient for anodic dissolution of the metal (which amounts to 3 [4]). The theoretical values are

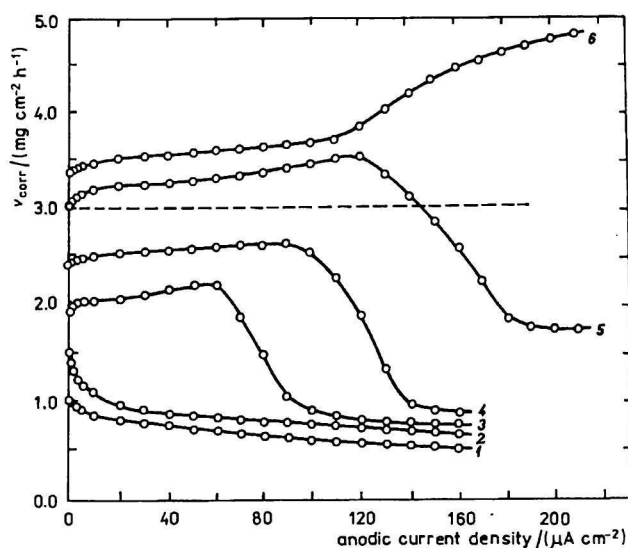


Fig. 5. Effect of anodic current density on the rate of corrosion of aluminium in NaOH solutions with concentrations $c/(\text{mol dm}^{-3})$: 1. 0.05; 2. 0.10; 3. 0.15; 4. 0.20; 5. 0.25; 6. 0.30. ----- the theoretical v_{corr} in 0.25 M solution.

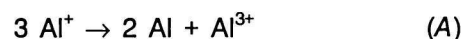
represented by dashed lines for some solutions in Figs. 4 and 5.

DISCUSSION

Cathodic Inhibition of Metal Dissolution

As a matter of fact, when a cathodic current is applied to a corroding metal, the cathodic half-reaction is promoted, whereas the anodic half-reaction is decelerated. The mass loss technique gives the rate of the anodic half-reaction, still going on under the applied cathodic current. The results shown in Fig. 4 obviate that the anodic reaction does not follow the theoretical path, but the corrosion rate shows sharp decrease with the applied current density. This indicates that the anodic reaction is subjected to some sort of cathodic inhibition.

Before we discuss this phenomenon, it is worthy to mention that the electrochemical dissolution of aluminium starts with the formation of a monovalent species, Al^+ . This species undergoes self-oxidation to the trivalent state Al^{3+} according to the scheme [4]



The trivalent ions go into solution as aluminate. Reaction (A) is the rate-determining step [4]; this means that the surface contains always an amount of Al^+ ions.

Now, the assumption is made that corrosion of Al is anodically controlled, *i.e.*, corrosion is governed by reaction (A). When a cathodic current is applied, some of the Al^+ ions are neutralized, and the concentration of Al^+ , therefore, decreases. This leads to the reduction of the rate of reaction (A), and consequently v_{corr} is diminished as the cathodic current density is increased.

Retardation of Hydrogen Evolution with the Cathodic Current

The results given in Fig. 1 show that the rate of hydrogen evolution does not increase as expected from the theoretical relation, but decreases markedly with the increase of the cathodic current density. This is in fact the core of the problem: why the metal becomes less able to deliver electrons, when it is supplied with a current of electrons.

Because of this explicit contradiction with the fundamentals of electrode kinetics, we found ourselves obliged to conclude that at least during self-dissolution the free electrons do not cross the interface, but electrons are delivered from a certain chemical species, that is considered as electron carrier. Besides, owing to the strict correlation be-

tween the anodic and cathodic reactions (such that if the former is inhibited, the latter is retarded), we concluded that the entities initiating both reactions originate simultaneously in the same chemical process according to the equation



The positive ions undergo self-oxidation (reaction (A)) and go into solution as aluminate. The negative ions exchange the electrons with the acceptor in solution as follows



The steady state concentrations of the different entities (Al^+ , Al^- , and Al atoms) always satisfy a characteristic constant for the surface equilibrium (B). It follows that this disproportionation reaction proceeds from the left to the right to compensate for the ions escaping from the surface. As previously assumed, corrosion is anodically controlled, *i.e.*, governed by reaction (A). Hence, on applying a cathodic current, the steady state concentration of Al^+ is decreased and the rate of reaction (A) is diminished. In other words, the rate of escape of Al^+ from the surface is reduced, and consequently the disproportionation reaction proceeds at a smaller rate. Since this reaction produces equal number of Al^+ and Al^- , the rate of hydrogen evolution decreases with the cathodic current density.

Anodic Activation of Hydrogen Evolution

In agreement with the observation of *Tomashov* and *Modestova* [2], application of an anodic current activates evolution of hydrogen; thus, in solutions of concentration above 0.05 mol dm^{-3} the volume of hydrogen increases with the anodic current density (*cf.* Fig. 2). This drastic problem becomes, in the light of the above views, easily understood. Thus, when an anodic current is imposed, the steady state concentration of Al^+ is increased, and the rate of removal of these ions according to reaction (A) is promoted. Hence, equal number of Al^- ions deliver electrons to solution, and the volume of hydrogen is increased with the increase of the anodic current density. At a given current density, the anodic current ceases to activate hydrogen evolution, and the volume of hydrogen decreases with further increase of anodic polarization. This is discussed in the next part.

Anodic Retardation of Metal Dissolution

Measurements of v_{corr} by the mass loss technique gave quite similar results (*cf.* Fig. 5). It is a well-

known fact that anodic polarization promotes the anodic half-reaction. Hence, the decrease of v_{corr} with anodic current (after attaining a maximum value) seems peculiar, unless it is taken to indicate the onset of passivity. Passivation occurs as a result of depletion of OH^- ions, which dissolve away the metal hydroxide as aluminate. This likelihood was tested by calculating the transition time τ which is the time interval required for the concentration near the metal surface to drop to zero. The transition time is calculated from the relation [5]

$$\tau^{1/2} = \frac{F}{2j} c \sqrt{\pi D} \quad (1)$$

where c is bulk concentration of OH^- , D its diffusion coefficient, and j is the applied current density. If D is taken as $5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, as calculated from the Nernst–Einstein equation [6], the highest current density applied (*viz.* $160 \mu\text{A cm}^{-2}$) requires the transition time to be 3.2×10^{11} , 5.8×10^{11} , and $9 \times 10^{11} \text{ s}$ in 0.15, 0.2, and 0.25 M solutions, respectively. These very large values of τ show beyond doubt that the period of experiment (3600 s) does not lead to any significant change in OH^- concentration near the metal surface, and the metal is not therefore subject to passivation.

The decrease of the anodic reaction rate (mass loss) with anodic polarization, although the metal is still active, contradicts once more the principles of electrode kinetics. The only possible explanation lies again in the common origin of the anodic and cathodic reactions, according to eqn (B). Under anodic polarization some Al^- ions are oxidized to Al atoms; this decreases the steady state concentration of Al^- ions. Thus, above a given current density, corrosion becomes cathodically controlled (and the volume of hydrogen decreases with the anodic current density, *cf.* Fig. 2). Under these conditions the surface releases a number of Al^+ ions (as aluminate), which is just equal to the number of electrons delivered in the cathodic reaction. That is why v_{corr} decreases with the anodic current, although the metal is active (*cf.* Fig. 5).

Effect of Concentration on Corrosion Behaviour

It is noteworthy that the shape of the curves changes with the alkali concentration. Thus, in concentrated solutions v_{corr} in Fig. 5 as well as the volume of hydrogen in Fig. 2 showed continuous increase with the anodic current density, and no maxima were observed. On the other hand, in dilute solutions v_{corr} and the volume of hydrogen did not show any rise, but decreased directly with the very beginning of anodic polarization. These results reveal that the surface pattern depends on the so-

lution concentration. The effect of concentration arises from the fact that the potential of the metal decreases as the concentration is increased (*cf.* Fig. 3). This leads to the neutralization of some Al^+ ions, and the Al^- concentration is correspondingly increased. It is then possible that in concentrated solutions the initial concentration of Al^- is considerably large, so that it is not effectively diminished with the applied currents. Hence, corrosion continues to be anodically controlled within the whole current density range studied. On the other hand, in dilute solutions Al^- concentration is markedly small, and corrosion is cathodically controlled.

One may ask about the condition under which these anomalous phenomena disappear, and the electrode obeys the requirements of electrode kinetics. The answer is that this happens when the

surface reaches a stationary pattern that no longer changes with further polarization.

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