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The application of electrochemical impedance techniques to aluminium corrosion in acidic chloride solution

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Electrochemical impedance techniques are applied to the study of aluminium corrosion in hydrochloric acid solution in the passive region. Impedance spectra are obtained in stationary solution and in solution moving due to electrode rotation. The form of the spectra shows the importance of multistep dissolution, ionic migration through the oxide layer, relaxation effects and the influence of chloride ion.

1. Introduction

Impedance spectroscopy has found wide application in the study of corrosion phenomena [1]. A number of impedance studies of pure and anodized aluminium [2–7], and of aluminium alloys [8–11] have been described. In recent years much new data have been obtained on the electrochemical behaviour of aluminium in many different aqueous media using a variety of other techniques, particularly regarding the role played by the oxide layer [12–16] and pitting corrosion due to the presence of chloride ions [12, 16–22].

It has been proposed that corrosion of aluminium can occur through the oxide film by ionic migration followed by some dissolution process at the oxide/electrolyte interface [15]. An alternative mechanism, developed to account for results obtained in strongly alkaline solution, was the stepwise addition of hydroxyl groups to surface aluminium atoms, with the eventual formation of $Al(OH)_4^-$ [7]. With regard to pitting there is evidence of the formation of a salt film within the pits through which corrosion occurs [19]. Even in highly acidic solutions such as hydrochloric acid, the oxide film has to be taken into account [17].

In this paper impedance techniques are applied to the study of aluminium corrosion in acidic chloride solution in the 'passive' zone immediately positive of the open circuit potential (OCP), and the implications of their shape in terms of possible corrosion mechanisms is discussed.

2. Experimental details

A rotating disc electrode of area $0.20\,cm^2$, fabricated from pure aluminium (5 N) (Johnson Matthey Ltd.), in a Teflon sheath was fitted into an Oxford Electrodes rotating assembly. Its surface was prepared by mechanical polishing with alumina down to $1\,\mu m$ particle size, cleaned and left in 0.1 M HCl until a stable open circuit potential was obtained. A platinum foil auxiliary electrode and SCE reference electrode were employed.

Impedance spectra were recorded using a Solartron 1250 Frequency Response Analyser with 1286 Electrochemical Interface controlled by a HP9816S microcomputer. The frequency range was 0.01–10 kHz, with a 5 mV r.m.s. perturbation, small enough to ensure linearity; the auto integration facility with max. 1% standard deviation was used. Frequencies lower than 0.01 Hz were not employed as the data acquisition time of the FRA was long compared to the time evolution of the interfacial region and significant dispersion in the impedance values was encountered.

3. Results and discussion

3.1. *General remarks*

Figure 1 shows the extent of the region under study from the OCP to -0.70 V with respect to SCE. The electrode was pretreated electrochemically by a potential cycle from the OCP to 0.0 V and back at $10\,mV\,s^{-1}$. Stable OCP values were -0.95 and -0.87 V for stationary and moving solution ($W = 4$ Hz), respectively; these values were the same in deaerated and non-deaerated solution. The OCP moves positive with rotation of the electrode, but above a rotation speed of approximately 1 Hz, its value is almost independent of the rate of solution movement. Since the OCP values are the same in aerated and de-aerated solution it is concluded that the cathodic current is due to hydrogen ion reduction, as expected at this pH.

The voltammetric curve positive of the OCP can be divided into three regions: the first linear 'passive' region from the OCP to -0.73 V; the second with larger corrosion current up to -0.2 V, and a third positive of -0.2 V where much higher currents are recorded. The potential of the rather abrupt transition to a non-passive region is the same for stationary and

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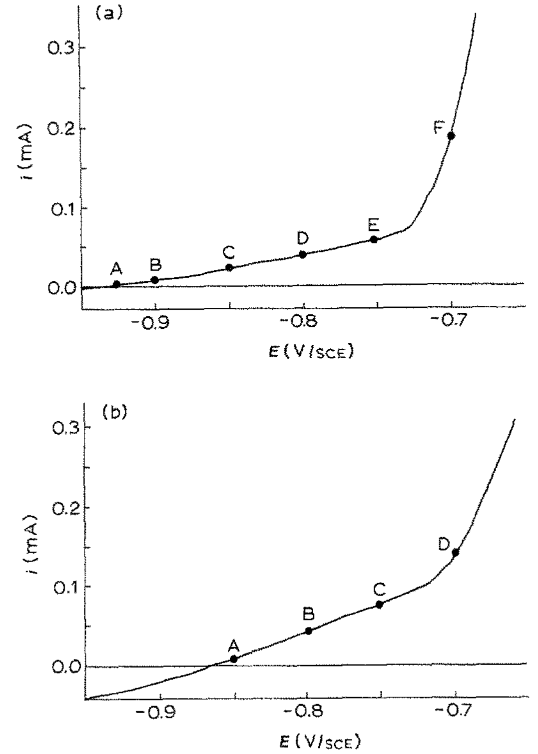

Fig. 1. Portions of voltammetric curves of (a) stationary and (b) rotating (at 4 Hz) aluminium disc electrode in 0.1 M HCl recorded at 10 mV s^{-1}. Letters denote potentials at which impedance spectra are shown in Figs 2 and 3.

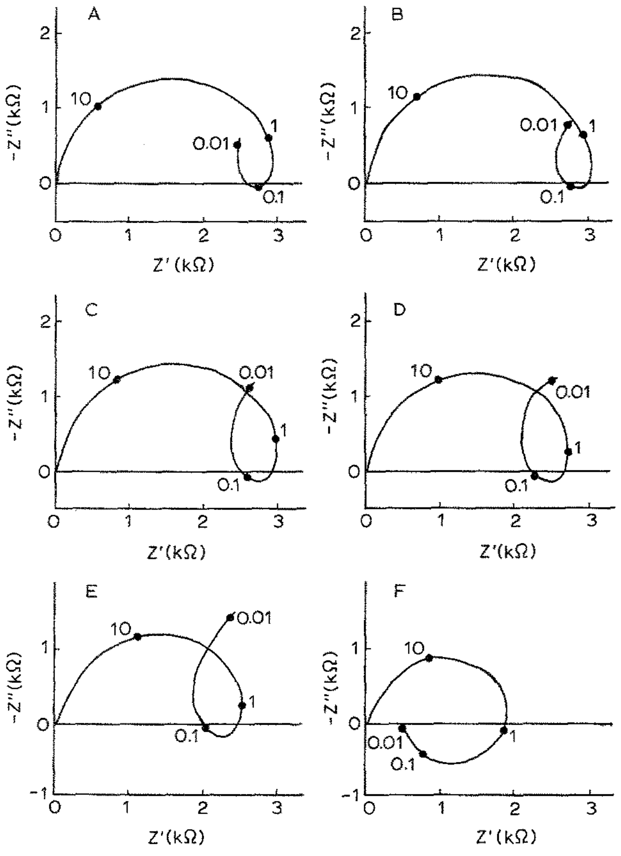

Fig. 2. Impedance spectra recorded at points A to F on the curve in Fig. 1a. Frequencies shown in Hz.

rotating electrodes at -0.73 V as Fig. 1 shows. This potential is associated with the commencement of pitting and perhaps with a salt formation potential [23]. The slope of the linear 'passive' region of the current-voltage curve, with which we are concerned here, corresponds at 10 mV s^{-1} to 3.3 kΩ.

The shape of the spectra, as shown in Figs 2 and 3, is similar to those obtained for iron in acidic media [24] and to some extent to aluminium in alkaline solution [6, 7]; the form is the same for stationary or moving solution. The larger currents than those observed for iron or nickel demonstrate the more open structure of the oxide film. Three loops are distinguishable: a high frequency capacitative loop, a medium frequency inductive loop and a low frequency capacitative loop. Frequencies associated with the maxima of the first two loops were determined from plots such as Fig. 4 and are given in Tables 1 and 2. No other features are found from Fig. 4 type plots.

Each frequency region is now considered in turn.

3.2. *'High' frequency*

At high frequencies a charge transfer process is taking place. In stationary solution this is fairly independent of the applied potential in the region chosen, with a charge transfer resistance of approximately 3 kΩ, Table 1, the value increasing slightly on rotating the electrode. The semicircle is depressed below the real axis as is typical for many corrosion processes. Assuming, for physical visualization, a simple parallel *RC* circuit a capacity value of the order of 30–60 μF cm^{-2} is calculated. Figure 5 shows that this decreases with increasing potential at a stationary electrode but is virtually constant at 4 Hz rotation speed. Positive of the passive region, where the low frequency loop disappears, the *C* values are significantly different.

This loop has been ascribed to high field ionic migration in the oxide layer or multistep dissolution. In the former case migration of Al^{3+} and O^{2-} will be involved, and possibly of Al^{+} generated at the metal/oxide interface to the oxide/electrolyte interface [15]. The multistep dissolution mechanism for aluminium

Table 1. Parameters from the high frequency loop: diameter of loop, R_{ct}; frequency of imaginary axis maximum, f_{max}; capacity, C

Polarization (V/SCE)	R_{ct} (kΩ)	f_{max} (H_3)	C (μF cm^{-2})
Stationary electrode			
−0.93	3.0	4.5	60
−0.90	3.0	4.6	58
−0.85	3.0	5.8	47
−0.80	3.0	6.7	40
−0.75	2.8	8.0	37
−0.70	2.2	8.0	46
Rotating elecltrode (4 Hz)			
−0.85	3.8	6.3	34
−0.80	3.6	6.3	36
−0.75	3.0	8.0	34
−0.70	2.2	13.0	29

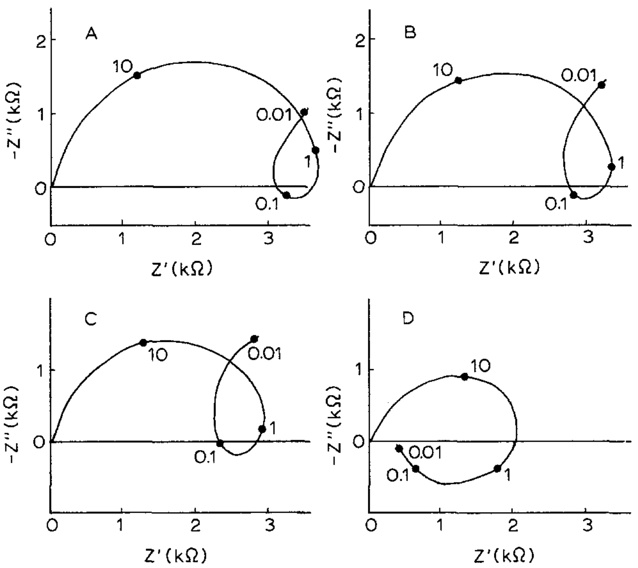

Fig. 3. Impedance spectra recorded at points A to D on the curve in Fig. 1b. Frequencies shown in Hz.

in alkaline solution (4 M KOH) accounts for the impedance spectra by considering that surface aluminium atoms are oxidised in a stepwise fashion until the soluble aluminate complex is formed; this means that the oxide film thickness is essentially zero, which is reasonable at such a high pH [7]. In the study described here an oxide film does exist, so that ionic migration does need to be taken into account.

The variation in C may well be to do with the role played by chloride. It has been postulated that the high field would enable chloride to be sucked into the oxide layer [12]. However, a very recent radiotracer study suggested that chloride is chemically bonded to the oxide surface [22], subsequently being removed in the form of aluminium chloro and oxychloro complexes. In moving, with respect to stationary, solution the soluble products are more easily removed and increased mass transport furnishes larger quantities of chloride ion to the electrode surface: the variation in calculated capacity values could therefore differ.

Table 2. Parameters from the medium frequency loop: frequency of imaginary axis maximum, $f^*_{\max}$; positive and negative real axis intercepts, R_+ and R_-; relaxation time τ calculated from Equation 1

Polarization (*V/SCE*)	$f^*_{\max}$ (*Hz*)	R_+ (*k*Ω)	R_- (*k*Ω)	τ (*s*)
Stationary electrode				
−0.93	0.10	2.9	2.65	1.74
−0.90	0.13	3.0	2.7	1.36
−0.85	0.16	3.0	2.5	1.19
−0.80	0.20	2.75	2.25	0.98
−0.75	0.22	2.5	1.95	0.93
−0.70	0.20	1.9	0.5	3.00
Rotating electrode (4 *Hz*)				
−0.85	0.16	3.6	3.1	1.16
−0.80	0.20	3.3	2.7	0.97
−0.75	0.30	2.9	2.3	0.67
−0.70	0.25	2.0	0.3	3.61

3.3. *'Medium' frequency*

In passive films an inductive loop can occur corresponding to the surface or bulk relaxation of species in the film [2, 24]. If it is a true passive film then we can associate the frequency at the minimum in the loop, ω^*, with a relaxation time, τ, [25], although this should be corrected for the width of the inductive loop. An expression for this correction is given in [25] for a relaxation process at the film/solution interphase and can be written as:

$$\tau = \left(\frac{1}{\omega^*}\right)\left(\frac{R_+}{R_-}\right) \qquad (1)$$

Here R_+ is the more positive and R_- the more negative value of R where the loop intersects the real axis. For depressed semicircles and other complications the full validity of Equation 1 is not clear, but can give an idea of what is occurring at the interface. Table 2 and Fig. 6 show results obtained from the data of Figs 2 and 3. It can be seen that there is a decrease in τ values for stationary and for moving solution with increasing

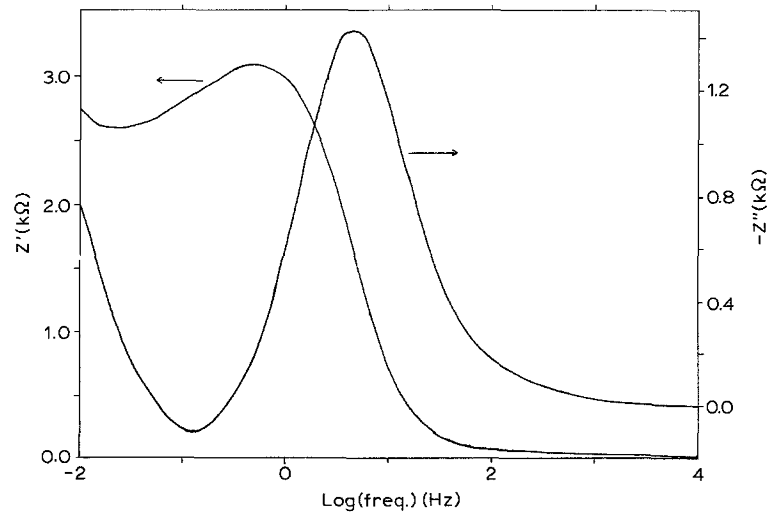

Fig. 4. Plot of real and imaginary components of impedance against log (frequency). Data from Fig. 2B.

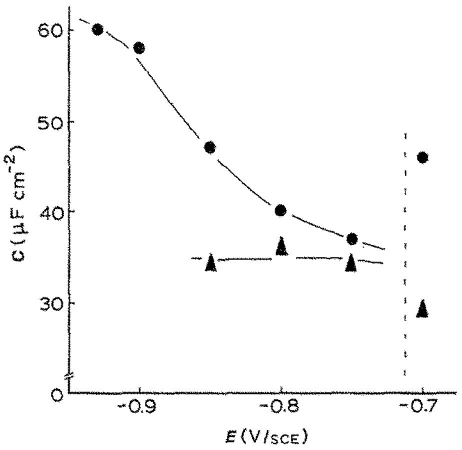

Fig. 5. Variation of capacity, C, with potential in high frequency loop: (●) stationary and (▲) rotating electrode. (– – –) signifies transition to non-passive region.

potential in the passive zone. Positive of this zone the values increase markedly. The existence of the relaxation time explains the overshoots found in the transient response of aluminium in chloride solutions [16].

3.4. *'Low' frequency*

The low frequency capacitative loop can be associated with the existence of a passive current. If aluminium were truly passive, then this loop would be of infinite radius with an infinite polarization resistance and giving essentially a straight vertical line in the complex plane. Small-amplitude cyclic voltammetry and the non-zero slope of the i–E curves show that this is indeed not a valid assumption [26]. However, qualitatively it is understandable, since immediately positive of the passive region the low frequency loop disappears, Fig. 2F and Fig. 3D. In short, the non-barrier aspects of the 'passive' film are shown.

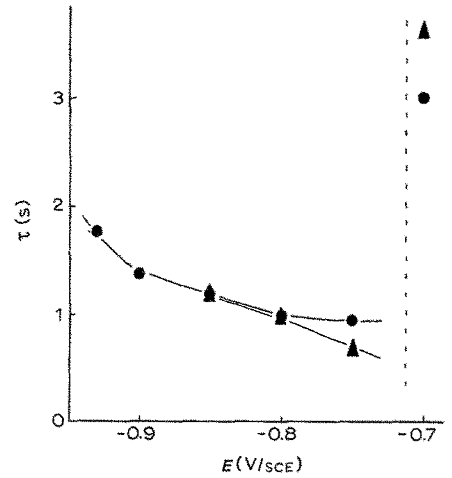

Fig. 6. Variation with potential of relaxation time, τ, associated with the inductive loop for (●) stationary and (▲) rotating electrode. (– – –) signifies transition to non-passive region.

4. Conclusions

Electrochemical impedance spectroscopy has been used in the study of aluminium corrosion in acidic chloride media in the passive region positive of the OCP at stationary and rotating aluminium electrodes. The spectra exhibit high frequency and low frequency capacitative loops, with an inductive loop at intermediate frequencies. The low frequency loop disappears positive of the passive region. The form of the spectra is explained by a multistep dissolution mechanism, including high field ionic migration through the aluminium oxide layer, and oxide film relaxation effects.

Acknowledgement

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