

Ionic Conduction Studies of Anodic Oxide Films on Aluminium in Aqueous Electrolytes

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Abstract

Conduction studies during growth of aluminium oxide films in various aqueous electrolytes of different concentrations and compositions have been made. The data has been obtained at different current densities, field strength, temperature, composition, concentration and resistivity of the electrolytes. These studies have been made by eliminating the difference of film growth caused by different surface conditions. The rate of increase of field strength with logarithm of ionic current density is found to be independent of temperature. It is observed that entrance barrier energy is greater than the corresponding diffusion barrier energy which suggests that the rate- controlling step during anodic oxidation of aluminium is the ionic movement across the film and not at the metal / oxide interface. Dewald's³ theory of double barrier was found to explain the temperature independence of Tafel slopes. It is observed that during growth of aluminium oxide films single barrier theory of Cabrera & Mott⁴ is not applicable. It is found that Dewald's³ theory which takes into account space charge effect is better than other theories during anodic oxidation of aluminium. The data have been obtained during growth of aluminium oxide films in different electrolytes of various concentrations and compositions. Formation of anodic oxide films on aluminium has been done at different temperatures, current densities and at varying field strength.

I. Introduction

In an attempt to understand the mechanism at high field ionic conduction on metals like tantalum, niobium and aluminium one of the key characteristics which must be considered is that the ionic current produced by a given electrostatic field in the oxide depends upon history of the film. Ionic conduction process is affected by the method, a film is made. The latent ionic conductivity changes with in seconds and continues to change for hours at room temperature at zero field after halting film growth. On reapplying a constant field a steady state is eventually obtained after an initial transient and the ionic current density is then constant for a given field 'E' which is independent of thickness. The ionic charge transport depends upon electric field strength across the oxide film. The views suggested by different workers regarding ionic conduction either within the film and/or at the interface as rate controlling step are at variance. Present investigation has been made to know the exact mechanism during growth of anodic aluminium oxide films in various electrolytes at different current densities at varying temperatures. Theories of ionic conduction during anodic oxidation of aluminium has been discussed.

II. Material and Methods

Specimens of aluminium ($2 \times 10^{-4} \text{m}^2$) with a short tags were cut from 99.9% pure aluminium sheets and the edges of the specimens were abraded with fine emery paper to make them smooth. The specimens surfaces were cleaned by dipping them in 10% NaOH solution for 2-3 sec and washing them with distilled water. The chemical polishing of these specimens was done by dipping them in a freshly prepared etching mixture of concentrated O-phosphoric acid, sulphuric acid and nitric acid in the ratio of 70:25:5 at 350-360K for 2-4sec. The specimens were washed with distilled water and dried in a current of hot air and finally etched just before anodization. The tags of the specimens were covered with a thick anodic film in an electrolyte in which further anodization on square portion of the specimen was to be carried out. The specimens thus prepared were placed in a glass cell and was connected to a platinum electrode which served as cathode during formation of oxide film. Anodic polarization of aluminium specimens was carried out at constant current and the supply of current was cut-off by an electronic control after the desired film formation voltage was reached. Before anodization, the tags of aluminium specimens were covered with thick anodic film in their own electrolyte solutions so that oxidation takes place only on square portion of the specimens. The time for

the passage of current for formation of film through successive intervals of voltage was recorded by an electronic timer. The experiments for studying conduction mechanism process were performed in solutions of potassium nitrite, sodium nitrite and potassium iodide. The solutions were made with conductivity water and their electrolytic resistivities were measured using a digital conductivity bridge. The thickness of the film formed was determined using Faraday law. The density of aluminium oxide film was taken as 3.565g/cm^3 as reported by Tazima⁵ for calculating thickness of oxide film formed on aluminium.

III. Results and Discussion

In case of cation mobile system, the ionic conduction taking place, can be either at high field or at low field. In case of high field conduction, it is assumed that the electric field strength is high enough to prevent movement of cations against the field direction whereas in low field conduction it cannot be assumed that movement of cations against the field direction is negligible. The rate of anodic growth of aluminium oxide films is different in all the electrolytes studied. The variation in voltage of formation with time during which charge was passed at different current densities in 0.1M solution of sodium nitrite at 298K is plotted in Fig.1. Similar plots were obtained for solutions of potassium nitrite and potassium iodide. The plots are linear upto voltage of formation of 180V and become concave towards the time axis at higher formation voltage. The linear behaviour of these plots (upto film formation of 180V) showed the constancy of field strength & independence of film thickness. However, at higher film formation voltages i.e more than 180V, the dependence of field strength on film thickness is observed. The plot of formation voltage against time during oxidation of aluminium in various concentrations of sodium nitrite is shown in Fig.2. Similar plots are obtained for other electrolytes. These plots are linear up to certain formation voltage that indicates that field strength is independent of thickness of film upto certain voltage of formation thereafter field strength is dependent on thickness of the film. Plot of field strength against reciprocal of temperature at different current densities are found to be linear and the slopes calculated from this plot shows its non-dependence on current density. The plot between field strength versus logarithm of current density at different temperatures are also linear and slopes calculated from this plot show that it is independent of temperature which rules out the applicability of single barrier theory of Cabrera-Mott⁴ suggesting that Tafel slope is proportional to absolute temperature. Under high field conditions, Guntherschulze and Betz⁹ established that average

field strength E and ionic current density ' i ' under steady state conditions are related by an equation

$$i = A \exp BE \dots (1)$$

where A and B are constants involving parameters of transport. For simple electrochemical reactions, charge transport is controlled by the step which has highest potential energy with respect to the rate determining step. Constants A and B have been determined in presence of different electrolytes by least squares method at different temperatures. The values of constant ' B ' are 5.61×10^{-8} , 5.05×10^{-6} and $5.92 \times 10^{-6} \text{ Vm}^{-1}$ in aqueous solutions of potassium nitrite, sodium nitrite and potassium iodide, respectively. The values of constant B are almost of same magnitude in various electrolytes which shows that Tafel slope is independent of temperature. It is found that values of constant ' A ' increase with increase in temperature. The values of constant ' A ' calculated using Guntherschulze-Betz equation for sodium nitrite are 2.128×10^{-8} , 3.247×10^{-8} & $3.797 \times 10^{-8} \text{ Am}^{-2}$ at 308, 323 and 338K, respectively. Similarly, values of constant ' A ' at 298K are found to be 2.78×10^{-8} and 3.89×10^{-8} for potassium nitrite and potassium iodide respectively which shows its dependence on nature of the electrolyte (Table 1-3). Since the plots between E and $1/T$ for different current densities in various electrolytes are linear and parallel, therefore, the Tafel slope is independent of current density. The Tafel slope is also observed to be independent of temperature in all the electrolytes. Such an observation rules out the applicability of single barrier theory of Cabrera-Mott⁴ to such films because according to this theory, the Tafel slope should be proportional to absolute temperature. The double barrier theory of Dewald³ which is an extension of the oxidation theory of Cabrera-Mott⁴ considers the effect of space charge in the oxide film which develops if the time required for an excess interstitial ion to move from one side of the film to the other is not very much smaller than the time required for the ion to cross the interface. The fundamental basis of his treatment of the case was that the metal ions are the only source of net space charge. In Cabrera-Mott⁴ theory, the space charge was considered to be negligible which led electric field strength to be a function of thickness of oxide further, according to this theory the Tafel slope should be proportional to absolute temperature whereas Dewald³ proposed his theory to account for the almost temperature independent Tafel slope. It appears that increase in temperature causes increase in activation distance from the mean position and hence increases charge-distance activation product. Though there is an appreciable contribution of the quadratic term yet the parameters, the zero-field activation dipole, the Morse-function parameter and current density are found to be temperature dependent which were assumed to be temperature independent by

Dignam⁶. Therefore, Dignam's⁶ theory of ionic conduction does not explain data on aluminium oxide films satisfactorily. This may be probably due to the neglect of space charge in the film. It has been found that the rate of increase of field strength with logarithm of ionic current density is independent of temperature during growth of oxide film on aluminium in various electrolytes which suggests that single barrier theory of Cabrera and Mott⁴ is not applicable. The double barrier theory of Dewald³ has been found to explain the temperature-independence of Tafel slopes. It is found that the zero field activation energy & net activation energy is almost constant at different temperatures which substantiates with double barrier theory of Dewald³ of temperature independence of Tafel slopes. During anodic oxidation of aluminium it is found that rate of increase of forming field with logarithm of ionic current density is independent of temperature in different electrolytes which suggests that Cabrera-Mott⁴ theory of single barrier is not applicable as space charge effect caused by accumulation of charged ions in the oxide film was not taken into account during oxidation of aluminium.

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Table.1

Temperature (K)	Constant A (Am⁻² x 10⁸)	Constant B (mV⁻¹ x 10⁸)
Electrolytes-Potassium nitrite		
278	0.58	4.49
288	0.96	4.61
298	2.78	4.57
308	4.32	4.54
323	6.07	4.63
338	10.19	4.59

Table.2

Temperature (K)	Constant A (Am⁻² x 10⁸)	Constant B (mV⁻¹ x 10⁸)
Electrolyte-Sodium nitrite		
278	0.39	3.59
288	0.71	3.62
298	1.32	3.56
308	2.13	3.51
323	3.25	3.60
338	3.80	3.53

Table.3

Temperature (K)	Constant A (Am⁻² x 10⁸)	Constant B (mV⁻¹ x 10⁸)
Electrolyte-Potassium Iodide		
278	0.69	5.62
288	1.25	5.58
298	3.89	5.64
308	5.67	5.61
323	7.31	5.55
338	9.62	5.59

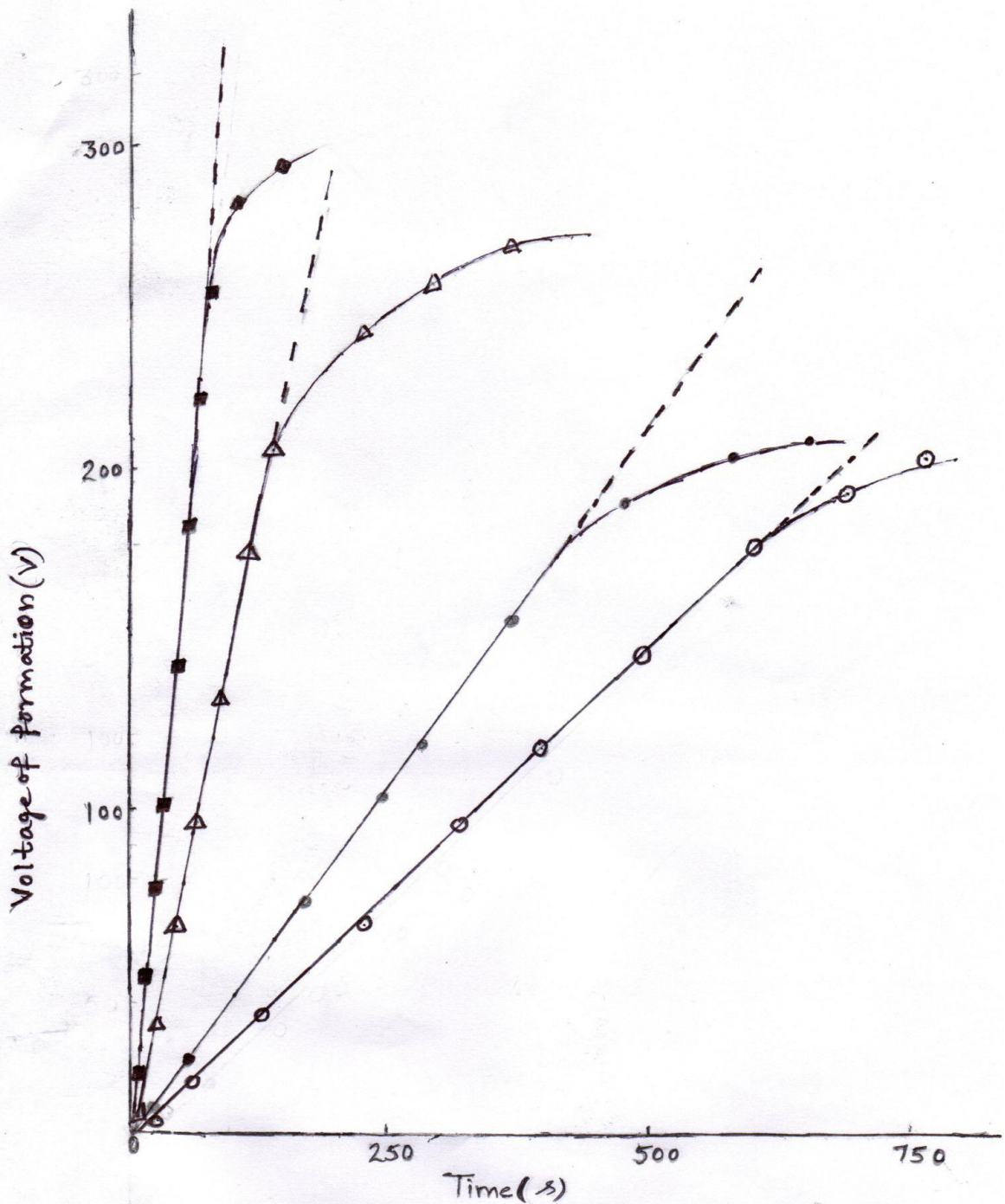


Fig.1. Variation of voltage of formation with time at different current densities. \circ , 5.0 Am^{-2} ; \bullet , 10.0 Am^{-2} ; Δ , 50.0 Am^{-2} ; \blacksquare , 100.0 Am^{-2}

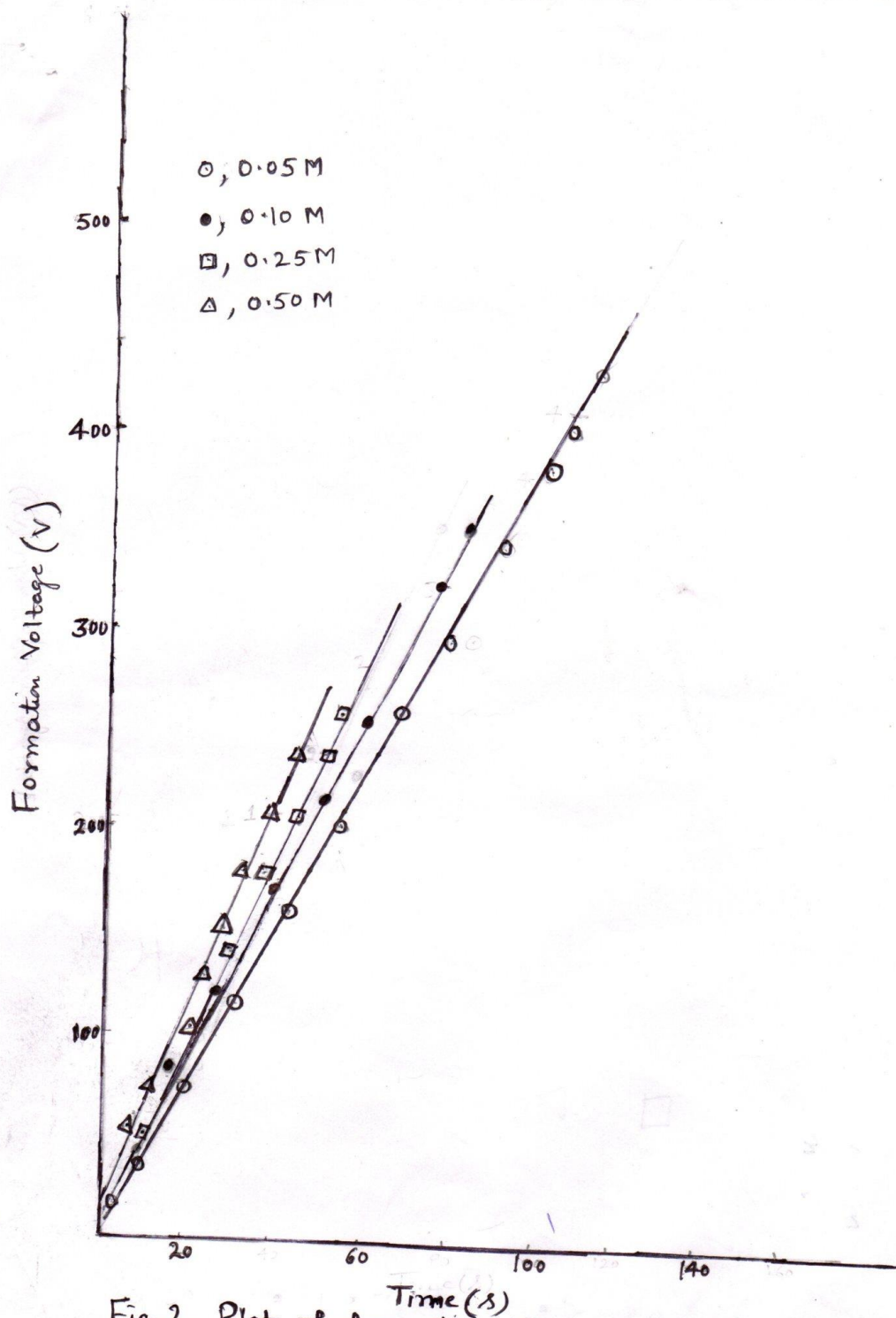


Fig.2. Plot of formation voltage versus time at different concentrations in sodium nitrite solution.

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