

## Ionic Conduction in Anodic Oxide Films on Tantalum in Aqueous Electrolytes

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Steady state kinetic data for anodic growth of films on tantalum in aqueous solutions of oxalic, tartaric and citric acids at different temperatures have been obtained. The constant ( $A$ ) of Guntherschulze and Betz equation is temperature-dependent while  $B$  is temperature independent. The constant ( $A$ ) also depends on the nature of the electrolyte. Tafel slope is independent of temperature in the temperature range of 275-338 K. Such an observation rules out the applicability of single-barrier theory of Cabrera-Mott for anodic growth of film. Dignam's quadratic variation of field with ionic current density has been examined and  $\phi$ , the zero-field activation energy;  $C$ , the dimensionless constant;  $\mu^*$ , the zero-field activation dipole;  $W(E)$ , the net activation energy;  $\omega^*$ , the Morse-function parameter; and current density ( $i_0$ ) have been evaluated. It has been found that  $\mu^*$ ,  $\omega^*$  and  $i_0$  are temperature-dependent whereas  $\phi$ ,  $W(E)$  and  $C$  are temperature-independent. All these parameters depend on the nature of the electrolyte. The quantities  $C$  and  $W(E)$  do not depend on current density;  $\phi$  changes slightly; and  $\mu^*$ ,  $\omega^*$  and  $i_0$  change appreciably with the change in current density.

In most of the mechanisms on the growth of anodic oxide films, ionic conduction either within the film and/or at the interface is assumed to be the rate-controlling step<sup>1-13</sup>. In view of this disagreement, there is need for further investigation in this area. In the present investigation, steady state kinetic data for anodic growth of films on tantalum in aqueous electrolytes at a wide range of temperatures and varying current densities have been obtained. The behaviour of Tafel slope and critical assessment of ionic conduction theories with special reference to Dignam's approach<sup>9</sup> has been made.

### Materials and Methods

Tantalum specimens (2 cm<sup>2</sup> in area) with a short tag were cut from a sheet of tantalum (99.9% purity). The edges of the specimens were abraded with fine emery paper to make them smooth. The specimens were dipped in KOH melt to clean the surfaces and finally washed with distilled water. The chemical polishing of the specimens was done by dipping them in a freshly prepared mixture of 98% H<sub>2</sub>SO<sub>4</sub> + 70% HNO<sub>3</sub> + 48% HF (5:2:2, v/v) for 3-5 sec, washed with distilled water and then placed in boiling water for 10 min to remove any remaining impurities. The tags of the specimens were covered with a thick anodic film formed in 0.1 M citric acid at room temperature. The specimens thus prepared were placed in glass cells and were surrounded by platinum gauzes which served as cathodes.

Anodic polarization of tantalum was carried out at constant current, using a constant current generator (General Electronics, India) designed specially for this purpose. The supply of current was cut-off by an

electronic control after the desired voltage of film formation was reached. The time for the passage of current for forming film through successive intervals of voltage was recorded by an electronic timer ( $\pm 0.01$ s). The electrolytes used were oxalic, tartaric and citric acids (all AR, BDH). The thickness of the film was determined using Faraday's law. The density was taken as 7.93 g/cm<sup>3</sup> as reported by Young<sup>14</sup>. The thickness was also measured using an ellipsometer (GAERTNER, USA).

### Results and Discussion

The variation in formation voltage with time during which charge was passed at different current densities (0.5, 1.0, 5.0 and 10.0 mA/cm<sup>2</sup>) in 0.1 M aqueous solutions of citric acid at 298K are plotted in Fig. 1. Similar plots were obtained at other temperatures and also using 0.1 M oxalic and tartaric acids. The plots were found to be linear upto a film formation voltage of 200V and became concave towards the time axis at higher formation voltages. The linearity of the plots upto film formation voltage of 200V showed that the field strength was independent of film thickness. However, at higher formation voltages (> 200V), the dependence of field strength on film thickness was observed. The plots of field strength ( $E$ ) against  $1/T$  at different current densities are plotted in Fig. 2 and those of field strength against  $\log(\text{current density})$  at different temperatures are plotted in Fig. 3. The slope  $\partial E/\partial(1/T)$  was independent of current density, indicating non-applicability of the theory of ionic conduction, after making an allowance for space charge<sup>3</sup> for these films. The slope  $\partial E/\partial \ln i$  (Fig. 3) was independent of temperature, thereby ruling out the applicability

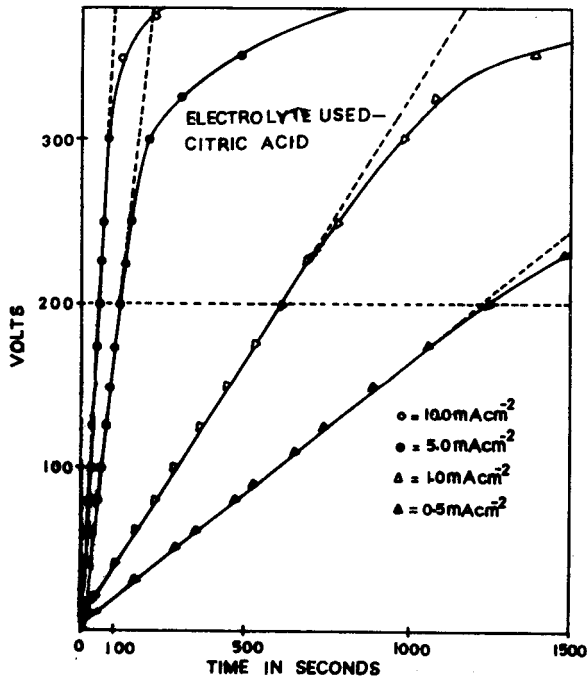


Fig. 1—Variation of voltage of formation with time at 298K at different current densities. [(O) 10.0 mA/cm<sup>2</sup>; (●) 5.0; (Δ) 1.0; and (▲) 0.5]

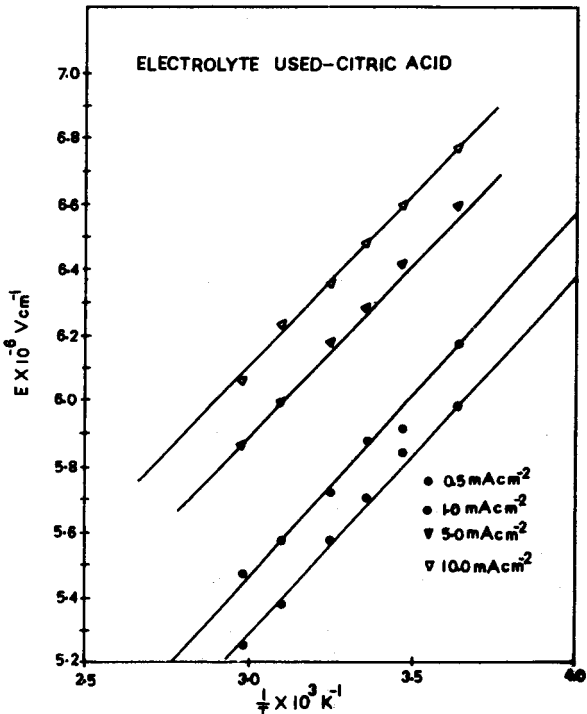


Fig. 2—Plot of  $E$  versus  $1/T$  [(▽) 10.0 mA/cm<sup>2</sup>; (▼) 5.0; (○) 1.0 and (●) 0.5]

of single barrier theory of Cabrera-Mott to such films because according to this theory, the Tafel slope should be proportional to absolute temperature.

Guntherschulze-Betz<sup>7</sup> constants  $A$  and  $B$  of the relation (1)

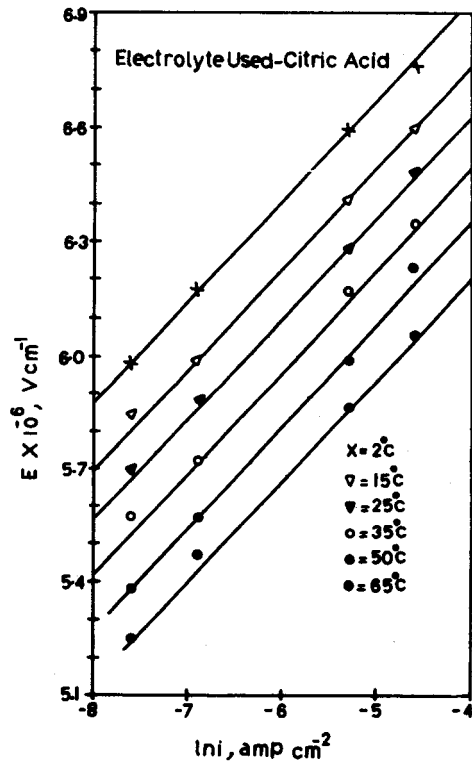


Fig. 3—Field variation with  $\ln$  (ionic current density) at different temperatures [(x) 2°C; (▽) 15°C; (▼) 25°C; (○) 35°C; (◊) 50°C; and (●) 65°C]

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

have been determined in the presence of three electrolytes by the method of least squares at different temperatures. By and large the values of constant ( $B$ ) are largely of the same magnitude in different electrolytes ( $3.35 \times 10^{-6}$ ,  $3.44 \times 10^{-6}$  and  $3.75 \times 10^{-6}$  cm V<sup>-1</sup> in the presence of oxalic, tartaric and citric acids respectively). The near constant values of  $B$  explain the temperature-independence of Tafel slope. However, the values of constant ( $A$ ) increase with increase in temperature in each of the aqueous electrolyte studied, e.g.  $A = 0.992 \times 10^{-12}$ ,  $0.672 \times 10^{-12}$ ,  $4.169 \times 10^{-12}$  and  $28.118 \times 10^{-12}$  amp cm<sup>-2</sup> at 275, 288, 308 and 338K respectively in oxalic acid. The temperature dependence of  $A$  may be due to increase in the number of active sites. The values of  $A$  also depend upon the nature of the electrolyte used, e.g. the values of  $A$  at 298K in the presence of oxalic and citric acids are  $2.61 \times 10^{-12}$  and  $0.126 \times 10^{-12}$  amp cm<sup>-2</sup> respectively. The higher value of  $A$  in the presence of oxalic acid may be due to more number of ions available since the first dissociation constant of oxalic acid ( $6.3 \times 10^{-2}$ ) is greater than that of citric acid ( $8.7 \times 10^{-4}$ ).

Dignam<sup>9</sup> justified quadratic variation of field with ionic current density to explain the field and temperature dependence of Tafel slopes. According to him at

high field the relation between ionic current density and field strength is given by the relation (2).

$$i = i_0 \exp - \left[ \phi - \mu^* E \left( 1 - \frac{\mu^* E}{C\phi} \right) \right] / kT \quad \dots (2)$$

In Eq. (2)  $\phi$  is zero-field activation energy,  $C$  is a dimensionless constant and  $\mu^*$  is the zero-field activation dipole. If the plot of  $E$  versus  $1/T$  is linear and  $S = \partial E / \partial (1/T)$  and also  $\partial S / \partial \ln i = 0$  (i.e. the Tafel slope is independent of temperature) the parameters  $\mu^*$ ,  $C$  and  $\phi$  can be computed from Eq. (2). In Fig. 3, the linear curves are parallel, i.e.  $\partial S / \partial \ln i = 0$ . Values of  $C$ ,  $\mu^*$  and  $\phi$  were calculated as functions of temperature at varying current densities in the presence of all the three electrolytes and the data are recorded in Table 1. The values of  $\mu^*$  increase with temperature at each of the current density studied. At a particular temperature the value of  $\mu^*$  depends on current density and also on the nature of the electrolyte used. The constant  $C$  and  $\phi$  are observed to be temperature-independent but depend on the nature of the electrolyte. The constant  $C$  does not depend on current density whereas  $\phi$

varies slightly with increase in current density. The dependence of  $\mu^*$  on temperature as well as the variation of  $\mu^*$  and  $\phi$  with nature of electrolyte and current density were not observed by Dignam<sup>9</sup> due to non-availability of steady data for a wide range of temperature, current density and the nature of electrolyte. The Dignam equation of ionic conduction can also be written as<sup>9</sup>

$$i = i_0 \exp \left\{ - \left[ \phi - \omega^* E \left( 1 - \ln \frac{\omega^* E}{2\phi} - \frac{\omega^* E}{2\phi} \right) \right] / kT \right\} \quad \dots (3)$$

where  $\omega^*$  is the Morse-function parameter (and has the same dimensions as  $\mu^*$ ) and is given by Eq. (4)

$$\omega^* = \left\{ \left[ 1 + \frac{2}{C} \left( \frac{\mu^* E}{\phi} \right)^2 \right]^{1/2} - 1 \right\} \frac{\phi}{E} \quad \dots (4)$$

The values of  $\omega^*$  were calculated employing the values of  $\mu^*$ ,  $E$ ,  $C$  and  $\phi$  and were found to depend (like  $\mu^*$ ) on temperature, nature of the electrolyte and current density. Such data for the oxalic acid are given in Table

Table 1—Values of  $E$ , and Experimental and Calculated Values of  $\mu^*$ ,  $C$ ,  $\phi$ ,  $\omega^*$ ,  $W(E)$  and  $i_0$  Using Dignam Equation (Electrolyte-oxalic acid)

Temp (K)	$E \times 10^{-6}$ V cm <sup>-1</sup>	$\mu^*$ e <sup>0</sup> A	$C$	$\phi$ (eV)	$\omega^*$ e <sup>0</sup> A	$W(E)$ eV	$\log i_0$
Current density = 0.5 mA/cm <sup>2</sup>							
275	6.27	15.02	3.17	1.20	3.43	0.491	5.71
288	6.01	15.76	3.17	1.21	3.57	0.497	5.40
298	5.77	16.25	3.17	1.21	3.65	0.502	5.19
308	5.56	16.76	3.17	1.20	3.78	0.497	4.83
323	5.27	17.53	3.17	1.20	3.92	0.500	4.51
338	5.02	18.31	3.17	1.20	4.08	0.503	4.20
Current density = 1.0 mA/cm <sup>2</sup>							
275	6.47	15.21	3.19	1.24	3.47	0.501	6.18
288	6.24	16.01	3.19	1.25	3.67	0.501	5.78
298	5.98	16.49	3.19	1.24	3.77	0.500	5.46
308	5.76	17.01	3.19	1.24	3.87	0.503	5.23
323	5.52	17.88	3.19	1.24	4.09	0.500	4.80
338	5.26	18.69	3.19	1.24	4.26	0.501	4.48
Current density = 5.0 mA/cm <sup>2</sup>							
275	6.93	15.79	3.24	1.31	3.71	0.498	6.83
288	6.70	16.65	3.24	1.32	3.95	0.495	6.37
298	6.46	17.20	3.24	1.32	4.06	0.498	6.12
308	6.25	17.78	3.24	1.32	4.20	0.497	5.84
323	5.94	18.61	3.24	1.32	4.38	0.500	5.51
338	5.71	19.54	3.24	1.32	4.63	0.495	5.09
Current density = 10.0 mA/cm <sup>2</sup>							
275	7.16	16.02	3.26	1.35	3.79	0.502	7.20
288	6.90	16.85	3.26	1.36	4.01	0.502	6.79
298	6.68	17.45	3.26	1.36	4.16	0.501	6.48
308	6.45	18.02	3.26	1.36	4.29	0.502	6.23
323	6.19	18.96	3.26	1.37	4.52	0.505	5.88
338	5.94	19.89	3.26	1.37	4.77	0.501	5.48

1 as representative of other two electrolytes, viz. tartaric and citric acids (similar trend in the values of these parameters was also found in the case of tartaric and citric acids). The values of net activation energy  $W(E)$  were computed using relation (5)

$$W(E) = \phi - \mu^* E \left( 1 - \frac{\mu^* E}{C\phi} \right) \quad \dots (5)$$

and the data are reported in Table 1. The values of  $W(E)$  vary with the nature of the electrolyte but are independent of current density. The data also show that  $W(E)$  is not dependent on temperature when oxalic acid is used as an electrolyte. However, small variations are observed when tartaric and citric acids are used. In Eq. (2), the quantity  $\mu^* E/C\phi$  measures the extent of contribution of the quadratic term. The contributions of the quadratic term over the entire range of data were observed to be within 24-27%, 27-31% and 34-37% for oxalic, tartaric and citric acids respectively.

From Eqs (2) and (5), we get

$$i_0 = i \exp W(E)/kT \quad \dots (6)$$

The values of  $i_0$  were calculated using Eq. (6) and the results recorded in Table 1 indicate  $i_0$  to be temperature-dependent and not independent as assumed by Dignam<sup>9</sup>. The values of  $i_0$  were also found to change with change in current density or nature of the electrolyte.

It appears that increase in temperature causes increase in activation distance from the mean position

and hence increases charge-activation distance product ( $\mu^*$ ). This also explains the increase of  $\omega^*$  with temperature.  $\phi$  and  $W(E)$  are activation energies and therefore should not be normally affected by temperature. The increase in the values of  $\mu^*$  and  $\omega^*$  with current density may be due to increased charge. The number of mobile ions (and also the magnitude of charge) will vary in different aqueous media and will thereby vary the magnitude of  $\mu^*$ ,  $\omega^*$  and  $i_0$ . The constant  $C$  has no dimensions and hence is not affected both by temperature and current density.

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