

Kinetics of Growth of Anodic Oxide Film on Tantalum in Aqueous Citric Acid

R K NIGAM*, K C KALRA & PARVEEN KATYAL

Department of Chemistry, Maharshi Dayanand University, Rohtak 124001

Received 1 October 1986; revised 19 January 1987; Accepted 4 March 1987

Steady state kinetic data for the growth of oxide film on tantalum in aqueous citric acid have been obtained by eliminating the difference of film growth caused by different surface conditions. The rate of increase of field with logarithm of ionic current density (Tafel slope) is independent of temperature. Various parameters of anodic oxidation have been evaluated using Dewald's theory. The entrance barrier energy is greater than the corresponding diffusion barrier energy and this suggests that the rate-controlling step in the kinetics of growth of anodic film is the ionic movement across the film and not at the metal/oxide interface. The value of net activation energy calculated using Dewald's theory agrees well with the value calculated using Dignam's equation. The data suggest that Dewald's theory which takes into account the space charge effect is better than other theories on film growth kinetics.

The study of kinetics of growth of anodic oxide films has received considerable attention¹⁻¹⁰, because of the importance of such films in capacitor technology. In a recent paper from our laboratory¹⁰, it has been shown that the rate of increase of forming field with logarithm of ionic current density (Tafel slope) was independent of temperature in the anodic growth of oxide film of tantalum in aqueous electrolytes. Hence single barrier theory of Cabrera and Mott¹ was not applicable. Dignam's⁶ model (quadratic variation of field with ionic current density) was capable of explaining temperature-independent Tafel slopes since an appreciable¹⁰ contribution (24-37%) of the quadratic term was observed for the range of current density studied. The net activation energy, $W(E)$ and the zero field activation energy (ϕ) were found to be temperature-independent. However, this approach did not take into account the space charge caused by the accumulation of charged ions in the oxide film. The double barrier theory of Dewald⁴ could also explain the temperature-independence of Tafel slopes. Therefore, in the title investigation the differences caused by different surface conditions were eliminated by using an improved method of surface preparation. Applicability of Dewald's theory⁴ has been critically examined.

Materials and Methods

Tantalum specimens (99.99% purity) 2×10^{-4} m² in area were prepared in the manner described earlier¹⁰. The specimen was anodized first at current density (i_1) and a film was formed (upto a formation voltage of 30 V). This film improved the surface condition of the specimen because the

current efficiency was constant. The current density was changed to i_2 ($i_1 = 10i_2$) and anodization was continued to a voltage slightly higher than 30 V. After this the current density was adjusted to i_1 and film upto 150V was formed. Again the current density was changed i_2 and anodization was continued for some more time (2 min). The advantage of taking $i_1 = 10i_2$ was that the Tafel slope was given by Eq. (1)

$$\tau = \frac{E_1 - E_2}{2.303} \quad \dots (1)$$

where E_1 is the field at a higher current density (i_1) and E_2 is the field at a lower current density (i_2). The values of E_1 and E_2 were calculated for the same formation voltage. If the applied voltage ΔV produced a thickness Δx of the anodic oxide film then Δx could be easily determined from the charge passed for the formation of film at constant current density. The density of the Ta₂O₅ film was taken as 7.93 kg dm⁻³ as reported by Young⁹. Citric acid used was of AR (BDH) grade.

Results and Discussion

A plot between voltage of formation versus time of anodization for the current density pair 50,5 Am⁻² at 298 K is given in Fig. 1. Similar plots were obtained at other current density pairs (30,3; 70,7; 90,9; 110,11; and 130,13 Am⁻²) and also at other temperatures (275, 288, 308, 323 and 338 K). Each set of observation was repeated five times and the values of field strength at a particular current density set and at a particular temperature were calculated and the values are

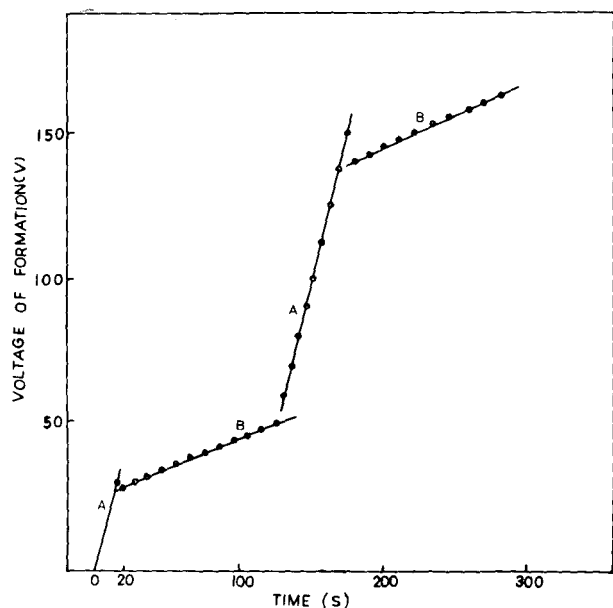


Fig. 1 - Plot of voltage of formation versus time of anodization at 298 K. [A- 50 Am⁻²; B- 5 Am⁻²].

Table 1 - Calculated Values of Field Strength E₁ (E₂ Values in Parentheses) for Various Current Density Pairs

Temp. (K)	(30, 3) E ₁	(50, 5) E ₁	(70, 7) E ₁	(90, 9) E ₁	(110, 11) E ₁	(130, 13) E ₁
275	7.519 (7.039)	7.596 (7.111)	7.867 (7.294)	8.043 (7.541)	8.293 (7.694)	8.885 (8.243)
288	7.211 (6.751)	7.366 (6.823)	7.526 (7.051)	7.778 (7.217)	7.874 (7.305)	8.372 (7.768)
298	7.025 (6.508)	7.132 (6.607)	7.374 (6.836)	7.536 (6.992)	7.630 (7.079)	8.004 (7.426)
308	6.829 (6.326)	6.892 (6.384)	7.092 (6.575)	7.289 (6.763)	7.361 (6.830)	7.699 (7.143)
323	6.561 (6.078)	6.604 (6.117)	6.870 (6.369)	6.973 (6.398)	7.035 (6.528)	7.245 (7.229)
338	6.287 (5.824)	6.339 (5.872)	6.599 (6.118)	6.710 (6.155)	6.743 (6.187)	6.839 (6.275)

E₁ and E₂ values in Vm⁻¹ × 10⁻⁸

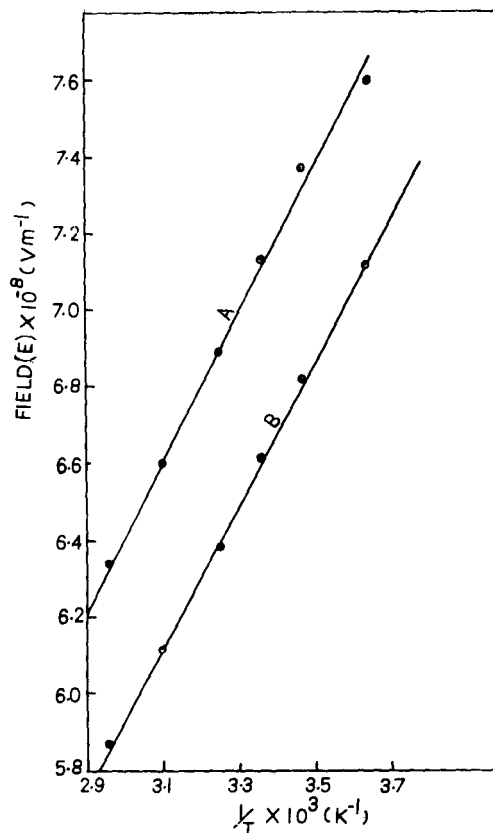


Fig. 2 - Plot of E versus 1/T. [A- 50 Am⁻²; B- 5 Am⁻²].

presented in Table 1. The reproducibility in the field values was $\pm 0.005 \times 10^8 \text{ Vm}^{-1}$. The field strength increases with current density but decreases with temperature for all the current density pairs studied.

The plot of field strength(E) versus reciprocal of temperature (1/T) for one current density pair (50, 5 Am⁻²) is plotted in Fig. 2. Similar plots were obtained for other current density pairs. The plots of E versus 1/T irrespective of current density employed are linear and parallel indicating that the difference of field at all temperatures for a given current density pair is constant and

hence the Tafel slope is independent of temperature. The values of Tafel slope at a particular temperature and at a particular current density pair were calculated using the field values obtained in all the repeat experiments. The maximum deviation in Tafel slope was $\pm 0.01 \times 10^7 \text{ Vm}^{-1}$. The Tafel slope at a particular current density set was highly reproducible over a wide range of temperature e.g. for current density pair 50, 5 Am⁻² at 275, 288, 298, 308, 323 and 338 K, the values of Tafel slopes were 2.05, 2.04, 2.05, 2.06, 2.05 and $2.05 \times 10^7 \text{ Vm}^{-1}$ respectively. The Tafel slopes at other current density pairs were also calculated in the same manner. The mean values of Tafel slopes at various current density sets are reported in Table 2.

Since the Tafel slope was independent of temperature, applicability of Dewald's theory⁴ was attempted. Using Dewald's theory⁴, the expression for the change in the field (ΔE) brought about by increase in the current density ten times is given by Eq. (2)

$$\Delta E = \Delta E_0 - 1/\beta \left[F(\delta) - F\left(\frac{\delta}{\theta}\right) \right] \dots (2)$$

Table 2 – Various Parameters for Aqueous Electrolyte Film from Dewald's Theory at Different Current Density Sets

Current density set (Am ⁻²)	Tafel slope $\tau \times 10^{-7}$ (Vm ⁻¹)	Entrance half jump distance b (nm)	Bulk half jump distance a (nm)	Entrance barrier energy $\phi \times 10^{19}$ (J)	Diffusion barrier energy $U \times 10^{19}$ (J)	Net activation energy $W \times 10^{19}$ (J)	$(\phi - Ebq) \times 10^{19}$ (J)	(U-Eaq) $\times 10^{19}$ (J)
30,3	1.99	0.2219	0.3684	2.325	3.370	0.489	1.141	1.403
50,5	2.05	0.2145	0.3684	2.362	3.580	0.477	1.205	1.592
70,7	2.09	0.2102	0.3684	2.385	3.714	0.466	1.213	1.660
90,9	2.18	0.1993	0.3684	2.394	3.975	0.452	1.259	1.876
110,11	2.21	0.1967	0.3684	2.447	4.138	0.444	1.310	2.009
130,13	2.29	0.1884	0.3684	2.493	4.440	0.436	1.354	2.211

where ΔE_0 is the change in the field due to surface charge; $F(\delta)$ is a function dependent upon the space charge δ and is equal to $(1 + 1/\delta) \ln(1 + \delta)$; δ/θ is the value of space charge at higher current density (i_1) and is equal to $\delta/10^{(ab-1)}$ where a and b are bulk and entrance half-jump distances; and β is aq/kT where q is the charge on the film, k is the Boltzmann constant and T is the temperature. Substituting $\Delta E_0 = 2.303 kT/bq$ in Eq. (2) we get

$$2.303 a/b - \beta \Delta E = F(\delta) - F(\delta/\theta) \quad \dots (3)$$

The Tafel slope (τ) using Dewald's theory⁴ is given by Eq. (4)

$$\tau = \frac{kT}{aq} \left\{ 1 + \left(\frac{a}{b} - 1 \right) \ln \frac{(1 + \delta)}{\delta} \right\} \quad \dots (4)$$

Using Eqs (3) and (4), the parameters a and b were determined as under:

(i) Values of a and a/b were assumed and hence the value of $\theta(10^{(ab-1)})$ was evaluated.

(ii) $F(\delta) - F(\delta/\theta)$ (the right hand side of Eq. 3) was represented graphically as a function of δ .

(iii) The value of $2.303 a/b - \beta \Delta E$ (the left hand side of Eq. 3) at different temperatures was evaluated.

(iv) From (ii) and (iii) by interpolation the value of δ was determined.

(v) Using the values of δ , a and a/b , the theoretical value of Tafel slope (τ) was calculated.

Such a calculation was repeated until values of a and b were found such that an agreement with experimental values of Tafel slopes were obtained. For our present data the value of a as 0.3684 nm fitted successfully for every set of current density. The value of a and b at different current density pairs are reported in Table 2. The value of b decreases with current density. The values of δ at

 Table 3 – Values of Space Charge Term δ of Dewald's Theory for Different Current Density Sets at Various Temperatures

Temp. (K)	δ at current density sets (Am ⁻²)					
	(30, 3)	(50, 5)	(70, 7)	(90, 9)	(110, 11)	(130, 13)
275	0.159	0.129	0.099	0.073	0.048	0.029
288	0.752	0.705	0.664	0.632	0.600	0.582
298	1.332	1.263	1.197	1.163	1.124	1.105
308	2.046	1.940	1.863	1.797	1.748	1.725
323	3.447	3.242	3.111	2.980	2.907	2.865
338	5.404	5.009	4.778	4.515	4.402	4.311

different temperatures and for different pairs of current density show that δ increases with temperature (Table 3). The effect of space charge is more clearly observed at a temperature when the value of δ is greater than unity. This effect becomes predominant as the temperature is further raised. The ratio of bulk and entrance jump distances for our data varies between 1.66 and 1.95. No such variations could be observed by Dewald⁴, probably due to non-availability of data for a wide range of current density and temperature.

According to Dewald's theory (Eq VIII, Appendix), the space charge factor (δ) depends mainly on $\exp(-W/kT)$, the value of W can be evaluated from the plot of $\log \delta$ versus $1/T$. Such a plot is shown in Fig. 3 for only one pair of current density set (50, 5 Am⁻²). The plots are linear for all the current density pairs. The values of W calculated at each current density pair are given in Table 2. The value of W has positive sign all along and its magnitude decreases with current density and varies between 0.489 and 0.436×10^{-19} J for the range of current density. Knowing δ and E , the surface charge field (E_0) has been evaluated using Eq. (VI) (Appendix). The values of E_0/T were computed and are plotted against $1/T$ in Fig. 4. For each current density

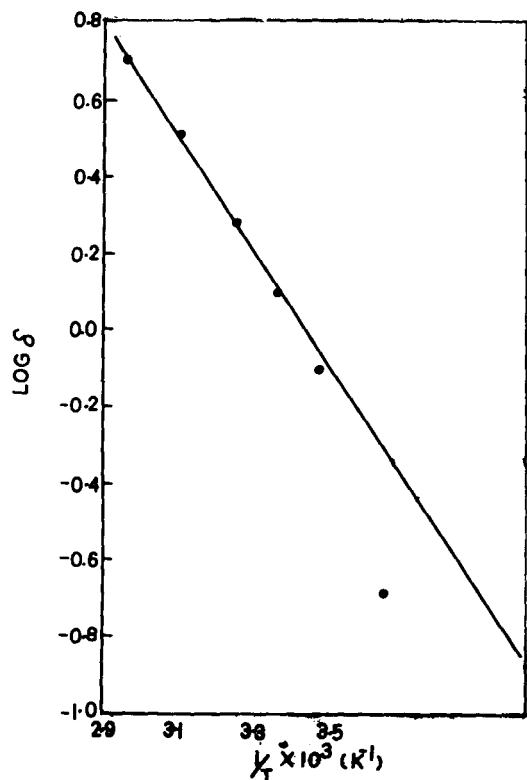


Fig. 3 - Plot of $\log \delta$ versus $1/T$.

pair such plots are linear. According to Eq (II) (Appendix) such plots should be linear with a slope ϕ/bq . From the slopes, the values of ϕ (entrance barrier energy) were obtained and are given in Table 2. Using the relation $U = a/b\phi - W$ the values of U have also been calculated and are reported in Table 2.

Both the entrance barrier energy (ϕ) and diffusion barrier energy (U) seem to increase with current density and magnitude of ϕ is smaller than that of U at all the current density sets (Table 2). This suggests that the rate-determining step would be the ionic movement across the film and not at the metal/oxide interface. However, at high field the correct activation energies would be $(\phi - Ebq)$ and $(U - Eaq)$ instead of ϕ and U . Therefore using average value of field for each current density set, taking charge on each tantalum atom in Ta_2O_5 film as $5e$ and using the values of ϕ , U , b , a from Table 2, the values of $\phi - Ebq$ and $U - Eaq$ were computed and are recorded in Table 2. The value of $\phi - Ebq$ is smaller than $U - Eaq$ at each current density set and this confirms our contention that the rate-determining step would be the ionic movement across the film. The value of W using Dewald's theory⁴ at current density set 50, 5 Am^{-2} is $0.477 \times 10^{-19} \text{ J}$. (Table 2). The value of $W(E)$ at current density 50

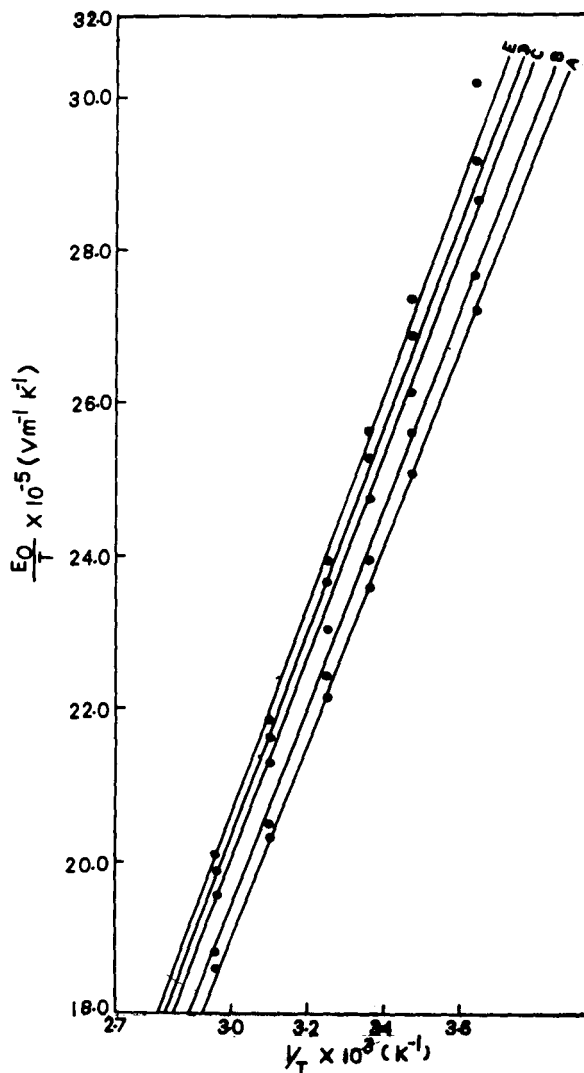


Fig. 4 - Plot of E_0/T versus $1/T$. [A - $30, 3 \text{ Am}^{-2}$; B - $50, 5 \text{ Am}^{-2}$; C - $70, 7 \text{ Am}^{-2}$; D - $90, 9 \text{ Am}^{-2}$; E - $110, 11 \text{ Am}^{-2}$].

Am^{-2} , reported earlier¹⁰, using Dignam's equation was $0.482 \times 10^{-19} \text{ J}$. Thus the value of net activation energy calculated using Dewald's theory agrees well with the value calculated using Dignam's equation. Since Dewald's theory takes into account space charge contribution in addition to the surface charge contribution, it can be concluded that Dewald's theory explains our data more satisfactorily.

Appendix

According to Dewald's theory the field E is a function of thickness of the oxide and is given by Eq (I)

$$E(x) = E_0 + 1/\beta \ln(1 + \beta\gamma n_0 x) \quad \dots (I)$$

where $\beta = aq/kT$, $\gamma = 4\pi q/\epsilon$ (ϵ is the dielectric

constant of the oxide) and n_0 gives the number of mobile ions per dm^3 at $x=0$. E_0 , the field due to surface charge, is given by Eq.(II)

$$E_0 = \frac{kT}{bq} \ln \left(\frac{i}{N_s v_s q} \right) + \frac{\phi}{bq} \quad \dots \text{(II)}$$

where N_s is the concentration of ions on the surface; v_s is the vibrational frequency normal to the barrier; q is the charge on the film; and ϕ is the entrance barrier energy. n_0 is evaluated by substituting E_0 (Eq.I) in the expression for the current in the film at $x=0$ and

$$i_0 = 2avq n_0 \exp\{- (U - aE_0q) / kT\} \quad \dots \text{(III)}$$

In the steady state $i_0 = i(x) = i$, and from Eqs (II) and (III)

$$n_0 = \frac{(N_s v_s q)^{ab}}{2avq} i^{(1-ab)} \exp \left(- \frac{W}{kT} \right) \quad \dots \text{(IV)}$$

Here $a\phi/b - U$ of Dewald's theory has been put equal to W and i is the current density in A/m^2 instead of ions/ cm^2/s . The experimental field is given by Eq. (V).

$$E = - \frac{\Delta v}{\Delta x} = \frac{1}{\Delta x} \int_x^x E(x) dx \quad \dots \text{(V)}$$

Substituting Eq. (I) in Eq. (V) the theoretical expressions for the experimental field and the derived Tafel slopes are given by Eqs (VI)-(VIII)

$$E = E_0 + \frac{1}{\beta} \left\{ \left(1 + \frac{1}{\beta \gamma n_0 \Delta x} \right) \ln \left(1 + \beta \gamma n_0 \Delta x \right) - 1 \right\} \quad \dots \text{(VI)}$$

$$\text{and } \tau = \left(\frac{\partial E}{\partial \ln i} \right)_T = \frac{kT}{aq} \left\{ 1 + (a/b - 1) \frac{\ln(1 + \beta \gamma n_0 \Delta x)}{\beta \gamma n_0 \Delta x} \right\} \quad \dots \text{(VII)}$$

$$\text{or } \tau = \frac{kT}{aq} \left\{ 1 + (a/b - 1) \frac{\ln(1 + \delta)}{\delta} \right\}$$

where

$$\delta = \beta \gamma n_0 \Delta x = \frac{2\pi q}{v \epsilon kT} (N_s v_s q)^{ab} i^{(1-ab)} \exp \left(- \frac{W}{kT} \right) \Delta x \quad \dots \text{(VIII)}$$

Acknowledgement

One of the authors (PK) thanks the CSIR, New Delhi, for the award of a junior research fellowship.

References

- 1 Cabrera N & Mott N F, *Rep Prog Phys*, **12** (1948-49) 163.
- 2 Guntherschulze A & Betz H, *Z Phys*, **92** (1934) 367.
- 3 Vermilyea D A, *Acta Metall*, **1** (1953) 282.
- 4 Dewald J F, *J electrochem Soc*, **102** (1955) 1.
- 5 Dignam M J, *Can J Chem*, **42** (1964) 1155.
- 6 Nigam R K & Arora I K, *Electrochim Acta*, **17** (1972) 2133.
- 7 Nigam R K & Chaudhary R S, *Indian J Chem*, **8** (1970) 343.
- 8 Young L, *J electrochem Soc*, **110** (1963) 589.
- 9 Young L, *Proc Roy Soc, A* **244** (1958) 41.
- 10 Nigam R K, Kalra K C & Katyal P, *Indian J Chem*, **25 A** (1986) 1080.