Ionic Conduction at High Field in Anodic Oxide Films on Tantalum Metal in Aqueous Electrolyte at Various Temperatures

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ABSTRACT

The study of anodization process on Tantalum metal was carried out in Malic acid electrolyte at different temperatures range and various current densities. This anodization process of metal electrode makes sure the adequate fabrication of oxide film. Anodization of Ta metal provides a satisfactory fabrication of oxide film and the kinetic data is altogether reliable for any current density set. We study the ionic conduction mechanism of anodic oxide film in Malic acid electrolyte at high field strength. Different variables of Dewald's theory have been measured as a component of current density & temperature.

Keywords: Anodization, Oxide film, Current, Voltage

I. INTRODUCTION

In the last few decades, researchers depicted the growth kinetics of anodic oxide film on Niobium and Tantalum metals by applying Guntherschulze – Betz [1] and Cabrera Mott [2] approaches in Malic acid electrolyte at various temperatures and current densities. Cabrera – Mott's single barrier theory could not explain the data successfully. As per this theory tafel slope should be dependent on temperature but during anodic oxide film growth on metals, the rate of increase of forming field with logarithm of ionic current density (tafel slope) is autonomous of temperature in aqueous electrolytic solution. Dignam model [3] has not been also successful because its temperature independent Morse function parameter hypothesis in light of the fact that Morse function parameter μ*, w* and i_o were found to be temperature dependent in our prior studies.

An appreciable contribution (11% to 20%) of the quadratic term is observed for the range of current densities studied. Our results demonstrate that net activation energy W (E) should not be influenced by temperature and current density. The observed inappropriateness of these theories might be due to the neglect of the presence of space charge in anodic film or the pre history of the specimens may be influencing the results. In this section, we study the elimination caused by the pre history of the film and then look at the results examined by the space charge. The growth kinetics of anodization was investigated with modification in experimental procedure which could keep away numerous an intrinsic errors which might have arised in the experiments. Dewald [4, 5] assimilated the two probabilities of rate limitation, which incorporate effects of space charge within the anodic film, first at anodic film interface adjacent to the parent metal and next, rate limitation within the bulk anodic film in to the formation. The Dewald's double barrier hypothesis allow for the effect of space charge. This hypothesis is an extension of Cabrera – Mott's single barrier theory and considers the effect of space charge in the oxide films which develops when the time required for an excess interstitial ion to move from one side of the film to the next is not all that much smaller than the time needed by the ion to

go over the interface. Dewald proposed his theory to clarify the temperature independent Tafel slope which had been found by Vermilyea [6]. A few analysts [7-9] have depicted their results in agreement with Dewald's dual barrier control model. For the growth of anodic oxide film, Dewald theory may be the correct model for the detection of space charge experimentally. In the study of barrier type films, Vermilyea [10] has demonstrated that due to low level of space charge probably i.e. enough to produce a 1% difference in the mean electric field strength across the film, the absolute indication of such space charge may be difficult to obtain. Young [11], on the other hand, has reported some evidence on the basis of capacitance changes in Ta_2O_5 films formed anodically. Depending upon the idea of thermally activated hopping of ionic point defects in accordance with Boltzmann statistics, Diggle and Vijh derived a fundamental transport equation for the space charge gradient model and concluded that under steady current conditions, the total amount of space charge inside of a film increases with thickness, with a tendency to level off towards some constant value with increasing thickness at lower current densities. At a given current density, the region of large space charge becomes relatively more confined to the interfaces as the film thickness increases. The whole amount of space charge held by the anodic oxide film increases with the increased current level in accordance to the order of current density profiles for a given thickness. Young's conclusion on Nb and Ta metals showed a temperature autonomous Tafel slope and consequently single barrier hypothesis of Cabrera and Mott totally disagreed. Diggle and Vijh [12] concluded that although the Dewald hypothesis seemed to imply that Tafel slope changed with thickness because of space charge in an extremely distinct manner. According to them, space charge caused the rate limiting step to alter from an interface barrier to conduction within the anodic film. Hence, Tafel slope go through a corresponding transition with diverse hopping separations accepted for each of these breaking points. These examinations show to observe the investigation of space charge effect through the ionic conduction mechanism of anodic oxide films and to discover the exact nature of Tafel slope variation. In our present perception, by applying the technique of Bray, Jacob and Young [13], we study the ionic conduction mechanism of anodic oxide film in Malic acid electrolyte at high field strength. Different variables of Dewald's theory have been measured as a component of current density & temperature.

II. METHODS AND MATERIAL

Tantalum samples of 2 cm² expose area with a short tag were cut by a dye from metal sheet (99.8% pure). The edges and surface of samples were rubbed with 600; 1000; 1500; 2000 grit fine grade emery paper to make the surface smooth. The specimens were plunged in 100g/L KOH solution at temperature 80°C for 3 minute with constant stirring to remove the greasy particles and then washed with doubled distilled water. Chemical polishing of the sample was done by dipping in freshly prepared etching mixture of 98% H_2SO_4; 70% HNO_3; 48% HF (5:2:2 v/v) for 3 - 5 seconds in a Teflon beaker and then immediate washing with distilled water. Finally any remaining polluting influence left adhering to the surface was evacuated by putting the specimen in boiled water for 10 minute. Finally the sample was dried in a stream of hot air. The whole process was repeated again just before the utilization of the sample. The experimental set up for the anodization of Ta metal in 0.1M Malic acid electrolyte was also the same. In order to exclude the surface roughness and unlike chemical polishing, the specimen was anodically oxidized at constant current density (i_1) and film up to 30V was formed. Because of constant current anodization, the surface appearance of film improved. After that, specimen was anodized with current density i_2 ($i_2 = 10i_1$) and oxide film formed continuously up to 50V. At that point, current density was again changed to i_1 and film up to 160V was formed. Again current density adjusted to i_2 and anodization was proceeding up to 170V. The advantage of taking $i_1 = 10i_2$ was that the tafel slope is given by the equation

$$\tau = \frac{E1 - E2}{2.303}$$

Here

E_1, E_2 = Value of field strength

i_1 = Lower current density

i_2 = Higher current density

Hertzberg et al[14] reported the density of Ta_2O_5 film i.e. 4.36 kgmdm³. Electronic clock was used to record the time for the passage of current for film formation by means of progressive interims of voltage. The anodic polarization procedure is schematically outlined in fig. 3.1-3.3 for a particular current density set (1.0-10.0mA/cm²) for Ta metal at distinctive temperatures (20°C; 30°C; 40°C). Indistinguishable results were got at various sets of current densities employed (0.25 – 2.5; 0.5 – 5.0; 1.0 – 10.0; 1.5 – 15.0 mA/cm²) for the growth of anodic oxide film on Ta metal at different temperatures of Malic acid electrolyte. This anodization process of metal (Ta) electrode makes sure the adequate fabrication of oxide film. The data of the value of field strength at specific current density set and at a particular temperature were tabulated by the repetition of these observations up to five times. Anodization of Ta metal provides a satisfactory fabrication of oxide film and the kinetic data is altogether reliable for any current density set.

III. RESULTS AND DISCUSSION

Anodization data of Ta metals in 1M Malic acid electrolyte at various current densities and at different temperatures has been given in Table I. Figures 1-3 represent the plot between voltage versus time of anodization for Ta metals at different temperatures.

TABLE I

DATA FOR ANODIC POLARIZATION AT DIFFERENT CURRENT DENSITY SETS AND AT DIFFERENT TEMPERATURES IN 0.1M MALIC ACID ELECTROLYTE ON TANTALUM METAL

Voltage of Formation (Volts)	Time for Anodization (Seconds)	Voltage of Formation (Volts)	Time for Anodization (Seconds)	Voltage of Formation (Volts)	Time for Anodization (Seconds)
Current Density Set : 0.25-2.5mA/ cm²					
293.15K		**303.15K**		**313.15K**	
20	17	20	29	20	32
30	31	30	45	30	47
30	95	30	298	30	341
35	203	35	447	35	523
40	293	40	670	40	679
45	377	45	746	45	815
50	458	50	866	50	940
50	461	50	868	50	942
60	467	60	874	60	947
70	479	70	884	70	960
80	491	80	898	80	975
90	503	90	912	90	989
100	515	100	926	100	1003
110	527	110	940	110	1017
120	538	120	954	120	1031
130	550	130	967	130	1045
140	562	140	981	140	1059
150	574	150	995	150	1072
160	586	160	1008	160	1085
150	640	150	1198	150	1246
155	718	155	1232	155	1344
160	796	160	1328	160	1440
165	872	165	1510	165	1537
170	948	170	1630	170	1647

Current Density Set : 0.5-5.0mA/ cm²					
293.15K		**303.15K**		**313.15K**	
20	12	20	14	20	16
30	17	30	21	30	23
30	25	30	67	30	125
35	65	35	147	35	214
40	106	40	217	40	289
45	145	45	279	45	351
50	185	50	338	50	408
50	186	50	339	50	409
60	189	60	342	60	412
70	194	70	349	70	420
80	200	80	356	80	427
90	206	90	362	90	434
100	212	100	369	100	441
110	217	110	376	110	448
120	224	120	383	120	455
130	229	130	389	130	462
140	234	140	395	140	469
150	240	150	402	150	478
160	245	160	408	160	485
150	269	150	469	150	558
155	309	155	509	155	610
160	328	160	551	160	660
165	363	165	593	165	712
170	398	170	635	170	732

Current Density Set : 1.0-10.0mA/ cm²					
293.15K		**303.15K**		**313.15K**	
20	5	20	7	20	9
30	8	30	10	30	13

30	10	30	15	30	45
35	12	35	39	35	96
40	31	40	62	40	147
45	50	45	84	45	191
50	68	50	105	50	230
50	69	50	106	50	232
60	70	60	108	60	235
70	73	70	111	70	238
80	76	80	114	80	242
90	79	90	117	90	246
100	81	100	120	100	251
110	83	110	123	110	255
120	85	120	126	120	259
130	87	130	129	130	263
140	91	140	132	140	267
150	93	150	135	150	271
160	95	160	138	160	275
150	101	150	147	150	321
155	109	155	163	155	342
160	117	160	181	160	367
165	121	165	198	165	393
170	131	170	216	170	417

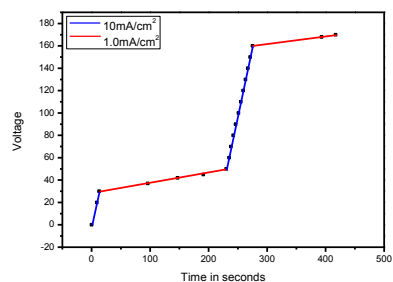|					
165	171	165	189	165	190
170	185	170	202	170	203

Figure 1: Plot of Voltage vs. Time of Anodization for Ta Metal at 20°C temperature
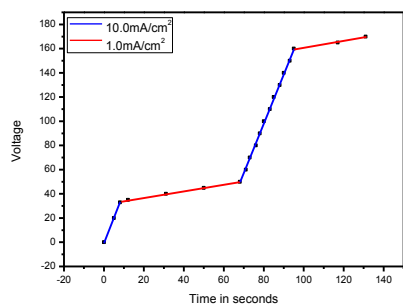

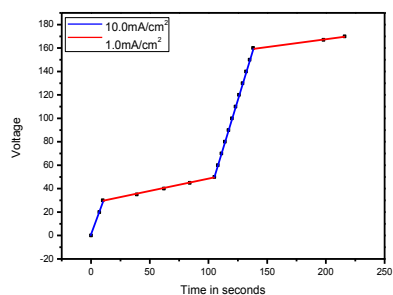Figure 2: Plot of Voltage vs. Time of Anodization for Ta Metal at 30°C temperature

Figure 3: Plot of Voltage vs. Time of Anodization for Ta Metal at 40°C temperature

Current Density Set : 1.5-15.0mA/ cm^2					
293.15K		303.15K		313.15K	
20	4	20	4	20	5
30	6	30	7	30	7
30	13	30	16	30	25
35	35	35	35	35	49
40	55	40	59	40	72
45	74	45	79	45	92
50	92	50	97	50	110
50	93	50	98	50	111
60	94	60	99	60	112
70	96	70	101	70	115
80	98	80	104	80	117
90	101	90	106	90	119
100	103	100	109	100	121
110	105	110	111	110	123
120	108	120	114	120	125
130	110	130	116	130	127
140	111	140	118	140	129
150	112	150	121	150	131
160	114	160	123	160	134
150	148	150	155	150	138
155	162	155	163	155	145
160	176	160	176	160	157

The values of field strength at particular current density and temperature were calculated by Faraday's law method and the values are presented in table II. The field strength increases with increase in current density but decreases with rise in temperature. The plots of field strength (E) versus reciprocal of temperature (1/T) for all current density sets are presented in figure 4. The plots of E vs. 1/T irrespective of current density employed are linear and parallel indicated that the difference of field at all temperatures for a given current density set is

constant and hence, the Tafel slope is independent of temperature. The values of Tafel slope at all current density sets and temperatures were calculated using field values and are given in table V. The Tafel slope increases with current density.

Dewald's theory makes allowance for the existence of space charge within the film and hence, the field (E) which is the function of thickness (x) in the oxide is given by

$$E(x) = E_0 + \frac{1}{\beta}\ln(1 + \beta\gamma n_0 x) \qquad (1)$$

Where

$$\beta = \frac{aq}{kT}$$

And

$$\gamma = 4\pi q/\epsilon \qquad (2)$$

Here 'a' is a bulk half jump distance , 'q' is the charge on mobile ion, 'k' is the Boltzmann constant, 'T' is the absolute temperature, ϵ is the dielectric constant of oxide and n_0 is the number of ions cm^{-3} at x = 0. The field due to surface charge (E$_0$) could be given by

$$E_0 = \frac{kT}{bq}\ln\left(\frac{i_0}{N_s\vartheta_s q}\right) + \frac{\varphi}{bq} \qquad (3)$$

n_0 has been evaluated by substituting E$_0$ from Eq. (3) in the expression for current in the film at x = 0, that is,

$$i_0 = 2a\vartheta q n_0 \exp[-(U - aE_0 q)/kT] \qquad (4)$$

In steady state

$$i_0 = i(X) = i \; and$$

From Eq. (3) and Eq. (4)

$$n_0 = \frac{(N_s\vartheta_s q)^{a/b}}{2aq\vartheta}i^{1-a/b}\exp\left(-\frac{w}{kT}\right) \qquad (5)$$

Where w = af/b-U and i is the current density in unit of Am^{-2} and not in cm^{-2} as in Dewald's paper. The experimental field could be given by

$$E = -\frac{\Delta V}{\Delta X} = \frac{1}{\Delta X}\int_x^{x'}E(X)dX \qquad (6)$$

Hence, substituting from Eq. (1) the theoretical expression for experimental field and the derived Tafel slopes were:

$$E = E_0 + \frac{1}{\beta}\left[\left(1 + \frac{1}{\beta n_0\gamma\Delta X}\right)\ln(1 + \beta\gamma n_0\Delta X) - 1\right] \quad (7)$$

And

$$\tau = \frac{\partial E}{\partial \ln i} = \frac{kT}{aq}\left[1 + \frac{\left(\frac{a}{b} - 1\right)\ln(1 + \beta\gamma n_0\Delta X)}{\beta\gamma n_0\Delta X}\right] \qquad (8)$$

Or

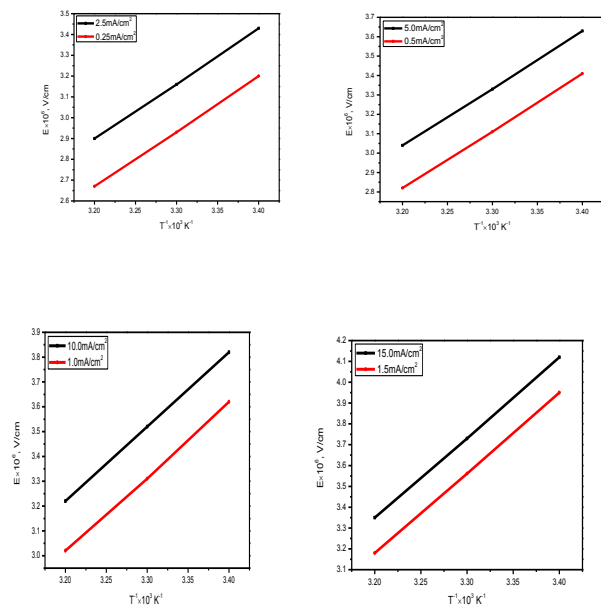$$\tau = \frac{kT}{aq}\left[1 + \frac{\left(\frac{a}{b} - 1\right)\ln(1 + \delta)}{\delta}\right] \qquad (9)$$

Figure 4: Plot of E vs. T^{-1} for Tantalum metal

$$\delta = \beta\gamma n_0\Delta X$$
$$= \frac{2\pi q}{\vartheta\epsilon kT}(N_s\,\vartheta_s q)^{\frac{a}{b}}i^{1-\frac{a}{b}}\exp\left(-\frac{W}{kT}\right)\Delta X \quad (10)$$

Values of δ cannot be calculated empirically, instead of we found that values of parameters, 'a', 'b' and 'W' which allowed Eq. (9) to represent the experimental values of Tafel slope. The ten- fold increase in i at constant temperature change the field which can be represented by Eq. (11):

$$\Delta E = \Delta E_0 + \frac{1}{\beta}[F(\delta)_{i=i_0} - F(\delta)_{i=i_2} \qquad (11)$$

Where

$$F(\delta) = \left(1 + \frac{1}{\delta}\right)\ln(1 + \delta) \qquad (12)$$

δ/θ is the value of space charge at higher current density (i$_1$). Now, if δ denoted the value of $\beta n_0\Delta X$ at i$_2$ then,

$$\delta_{i=i_1} = \delta \times 10^{1-a/b} = \frac{a}{b} \qquad (13)$$

Therefore

$$\Delta E_0 - \Delta E = \frac{1}{\beta}\left[F(\delta) - F\left(\delta/\theta\right)\right] \qquad (14)$$

Here ΔE is the change in the field brought about by increase in current density ten times and is given by Eq. (14); ΔE_0 is the change in the field due to surface charge and its value is $2.303kT/bq$, $F(\delta)$ is the function dependent on the space charge δ. Hence, Eq. (14) can be written in the form

$$2.303\,a/b - \beta\Delta E = F(\delta) - F\left(\frac{\delta}{\theta}\right) \qquad (15)$$

Using Eq. (9) and Eq. (15), the parameter 'a' and 'b' were determined as under:

i. The values of 'a' and 'b' were assumed and hence the value of θ was evaluated.

ii. $F(\delta) - F\left(\delta/\theta\right)$ [R.H.S. of Eq. (15)] was represented graphically as function of δ.

iii. The values of $2.303\,a/b - \beta\Delta E$ [L.H.S. of eq. (15)] at different temperature were evaluated. Values of ΔE were taken from plots of E versus 1/T.

iv. From (i) and (iii) by interpolation the values of $\delta(T)$ were determined.

v. Using the values of δ, 'a' and 'a/b' the theoretical value of Tafel slope (τ) was calculated. Such calculations was repeated until values of 'a' and 'b' were found such that an agreement with experimental values of Tafel slope was obtained. There were two widely different values of a/b ratio which allowed a quantitative fit to all the data available. Ratio a/b along with absolute values of 'a' and 'b' are presented in table III. Only for these values of a/b, it was possible to achieve a temperature independent Tafel slope. The value of 'a' and 'b' increase with increase of current density and there is a slight increase of a/b ratio whether it is 1.295 or 1.316 is difficult to decide. Dewald used the value of a/b ratio, which gave minimum value of 'a' and 'b'. Using the same criterion we have chosen a/b $\approx$1.295 for further calculation of various parameters.

The values of δ for a particular set of current density decrease with increase of temperature in table IV. The effect of space charge is more clearly observed at a temperature when δ is greater than unity. This effect becomes pre dominant as the temperature is lowered. The space charge factor δ depends mainly on exp. (-W/kT) (from Eq. 10). Knowing δ and E, the surface charge field E_0 has been evaluated using Eq.7. The values of E_0/T were computed and plotted against 1/T (Fig. 5). According to Eq. 3 such plots should be linear with a slope Φ/bq. From the slopes, the value of Φ were obtained and are given in table V. Using the relation $U=a\Phi/b-w$, the value of U were calculated and reported in table V. Both the entrance barrier energy (Φ) and diffusion barrier energy (U) seem to increase with current density and magnitude of U is greater than Φ at all the current density sets. This suggests that rate determining step would be the ionic movement at the metal/oxide interface and not across the film. However, at high field the correct activation energies would be (Φ-Ebq) and (Φ-Eaq) instead of Φ and U. Therefore, using average values of field for each current density set taking charge on each Ta atom in Ta_2O_5 film as $5e^-$ and using values of 'Φ', 'U', 'b' and 'a' from T from table V, the value of (Φ-Ebq) and (U-Eaq) were computed are recorded in table V. The value of (Φ-Ebq) is lesser than (U-Eaq) at each current density set and this again suggests that the rate determining step would be the ionic movement at the metal/oxide interface. Though there is a substantial contribution of space charge (δ>1) at low temperature yet the rate controlling step is at the metal/oxide interface. This is a misleading conclusion. It seems that our choice of a/b = 1.295 is not correct and next we used a/b = 1.316 and calculated the values of various parameters at different current densities and temperatures adopting the same procedure as given above the values are recorded in table V. The values of Φ were obtained from the plots of E_0/T versus 1/T (Fig.4) at each current density set.

It is observed from table V, the magnitude of Φ is smaller than U at all current density sets, thus indicating that the rate determining step for ionic movement would be within the film and not at the metal/oxide interface. The values of (Φ-Ebq) and (U-Eaq) are not much different from each other

suggesting that both the metal/oxide interface barrier are important, for the conduction of ions. With the increase of current density, the value of (Φ-Ebq) becomes slightly less than (U-Eaq), thus showing that the rate controlling step also shifting from metal/oxide interface to diffusion barrier within the film. W is net activation energy, therefore, it should not be affected by temperature and current density.

The value of W using Dewald theory at current density set $10mAcm^{-2}$ 0.8007 eV for Ta metal (table V). The value of W(E) at current density $10mAcm^{-2}$ reported, using Dignam was 0.557 eV for Ta metal.. Thus value of net activation energy calculated using Dewald theory agrees well with the value calculated using Dignam equation. Since Dewald theory takes into account space charge contributions in addition to surface charge contribution, it can be concluded that Dewald theory explain our data more satisfactorily and hence it is found suitable.
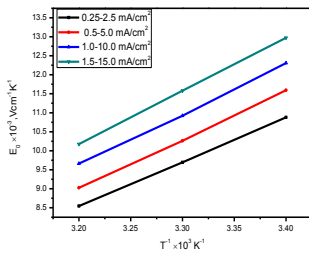

Figure 5: Plot of E_0T^{-1} vs. T^{-1} (Ta metal)

TABLE II
FIELD STRENGTH E_1 & E_2 (V_{CM-1}) AT HIGHER AND LOWER CURRENT DENSITIES AT VARIOUS TEMPERATURE OF ANODIZATION FOR TANTALUM METAL

Current Density Set (mA/cm²)	Field (V/cm)	Field Strength (E×10⁻⁶) at different temperatures		
		293.15K	303.15K	313.15K
0.25-2.5 mA/cm²	E_1	3.43	3.16	2.90
	E_2	3.20	2.92	2.67
0.5-5.0 mA/cm²	E_1	3.63	3.33	3.04
	E_2	3.41	3.11	2.82
1.0-10.0 mA/cm²	E_1	3.82	3.52	3.22
	E_2	3.62	3.31	3.02
1.5-15.0 mA/cm²	E_1	4.12	3.80	3.35
	E_1	3.63	3.33	3.04

TABLE III
BOTH SETS OF VARIOUS VALUES OF PARAMETER 'a' AND 'b' AND 'a/b' SATISFYING EQ.(9) FOR Ta METAL

Current Density	aA°	aB°	a/b	aA°	aB°	a/b
0.25-2.5	6.20	4.71	1.316	4.72	5.85	0.806
0.5-5.0	7.08	5.29	1.338	5.25	6.48	0.810
1.0-10.0	7.75	5.81	1.333	5.84	7.27	0.901
1.5-15.0	8.82	6.65	1.326	6.20	8.09	0.766

TABLE IV
VALUE OF SPACE CHARGE TERM δ OF DEWALD'S THEORY FOR DIFFERENT CURRENT DENSITY SETS AT VARIOUS TEMPERATURES FOR TANTALUM METAL

Current Density Set (mA/cm²)	Temperature K		
	298.15K	308.15K	318.15K
	When a/b> 1		
0.25-2.5	0.18	0.42	0.92
0.5-5.0	0.15	0.37	0.82
1.0-10.0	0.13	0.33	0.74
1.5-15.0	0.11	0.29	0.66
	When a/b< 1		
0.25-2.5	9.8	3.92	1.6
0.5-5.0	15.2	5.32	1.9
1.0-10.0	20.2	6.74	2.3
1.5-15.0	26.0	7.32	2.7

TABLE V
VALUE OF VARIOUS PARAMETERS FOR TANTALUM METAL FROM DEWALD'S THEORY AT DIFFERENT CURRENT DENSITY SETS FOR TANTALUM METAL

Current Density Set (mA/cm²)	ᵮ	W	Φ	U	Φ-U	Φ-Ebq	U-Eaq
	When a/b >1						
0.25-2.5 mA/cm²	9.86	0.6278	2.364	2.132	0.223	1.379	1.3512
0.5-5.0 mA/cm²	13.34	0.7966	3.487	3.213	0.258	2.338	2.3014
1.0-10.0 mA/cm²	12.47	0.8007	4.045	3.694	0.332	2.693	2.6202
1.5-15.0mA/cm²	11.16	0.8771	4.133	3.778	0.334	2.532	2.4774
	When a/b >1						

0.25-2.5 mA/cm^2	9.86	0.6278	2.364	2.132	0.223	1.379	1.3512
0.5-5.0 mA/cm^2	13.34	0.7966	3.487	3.213	0.258	2.338	2.3014
1.0-10.0 mA/cm^2	12.47	0.8007	4.045	3.694	0.332	2.693	2.6202
1.5-15.0mA/cm^2	11.16	0.8771	4.133	3.778	0.334	2.532	2.4774

IV. CONCLUSION

The space charge effect of the Dewald's double barrier control theory has been examined and by using this theory various parameters of anodic oxidation have been evaluated. The entrance barrier energy has been found greater than the corresponding diffusion barrier energy when ratio of the half jump distances of the diffusion barriers to that of entrance barrier (a/b) is less than unity. This suggests that the rate controlling step is at metal/metal oxide interface. But the entrance barrier energy is of the same order that of diffusion barrier energy when the jump distances ratio is more than one. Therefore, the rate controlling step in the kinetics of growth of anodic oxide film is not only at metal/ metal oxide interface but also across the film. The contribution of space charge has been obtained during the growth of anodic oxide film on Ta metal and it is found increases with increase of temperature. Therefore, our data could be explained satisfactorily by Dewald's theory if a/b is greater than one.

V. REFERENCES

[1] N. Verma, J. Jindal, K. C. Singh. 2017. Journal of Indian Chemical Society (2017), ISSN NO: 0019-4522

[2] N. Cabrera and N. F. Mott. 1948. Reports on Progress in Physics. (1948), ISSN NO:0034-4885 DOI: 10.1088/0034-4885/12/1/308

[3] M. J. Dignam. 1979. Journal of Electrochemical Society. (1979), ISSN NO: 1945-7111DOI: 10.1149/1.2128923

[4] J. F. Dewald. 1955. Journal of Electrochemical Society. (1955), ISSN NO: 1945-7111DOI: 10.1149/1.2429983

[5] J. F. Dewald. 1957. Journal of Physics and Chemistry of Solids. (1957), ISSN NO: 0022-3697 DOI: 10.1016/0022-3697(57)90006-9

[6] D. A. Vermilyea. 1953. Acta Metallurgica. (1953), ISSN NO: 0001-6160 DOI: doi.org/10.1016/0001-6160(53)90101-1

[7] N. Verma, B. Mari, K.C. Singh, M. Mollar, J. Jindal. 2016. Acta Physica Polonica A. (2016), ISSN NO: 0587-4246 DOI: 10.12693/APhysPolA.129.297

[8] R. K. Nigam, K. C. Singh and S. Maken. 1988. Thin Solid Films. (1988), ISSN NO: 0040-6090DOI: 10.1016/0040-6090(88)90027-2

[9] S. Hornkjol and T. Hurlen. 1990. Electrochimica Acta. (1990), ISSN NO: 0013-4686DOI: 10.1016/0013-4686(90)87097-L

[10] D. A. Vermilyea. 1957. J. Electrochemical Society. (1957), ISSN NO: 1945-7111DOI: 10.1149/1.2428521

[11] L. Young. 1956. Transactions of the Faradey Society. (1956), ISSN NO: 0014-7672DOI: 10.1039/TF9565200502

[12] J. W. Diggle and A. K. Vijh, "Oxide and oxide films", 3rd ed., Marcel Dekkar, New York.

[13] A. R. Bray, P.W.M. Jacobs and L. Young. 1958. Proceedings of the Physical Society. (1958), ISSN NO: 0370-1328DOI: 10.1088/0370-1328/71/3/314

[14] F. Holtzberg, A. Reisman, M. Berry and M. Berkenblit. 1957. Journal of American Chemical Society. (1957), 79, ISSN NO: 0002-7863DOI: 10.1021/ja01566a004