

Conduction Studies and Current Efficiency Measurements of Anodic Oxide Thin Films on Tantalum.

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Abstract-

Conduction studies and current efficiency measurements of tantalum oxide thin films in various aqueous electrolytes of different concentrations and compositions of have been made. Conduction data during anodic oxidation of tantalum 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 tantalum is the ionic movement across the film and not at the metal / oxide interface. The current efficiencies of such films are unity upto an electrolyte concentration of 0.1M. It is found that at higher electrolyte concentration the experimental mass-gain of tantalum specimen during anodization is greater than that expected for the formation of tantalum oxide on tantalum which indicates that mass gain is due to incorporation of anions into the bulk of oxide film which substantiates with the result that the breakdown voltage is affected only by incorporation of anions into the oxide film.

Keywords – Tantalum, Conduction, Anodic Oxide , Thin Films

I. Introduction

During growth of anodic tantalum oxide films 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 tantalum oxide films in various electrolytes at different current densities at varying temperatures. Theories of ionic conduction during anodic oxidation of tantalum has been discussed. 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 tantalum in various electrolytes which suggests that single barrier theory of Cabrera and Mott⁴ is not applicable. The double barrier theory of Dewald⁵ has been found to explain the temperature-independence of Tafel slopes. During growth of oxide films, the difference caused by different surface conditions has been eliminated. current efficiencies of tantalum oxide thin films in presence of different electrolytes have been evaluated.

II. Materials and Methods

Specimens of tantalum (2×10^{-4} in area) with a short tag were cut from tantalum sheet (purity 99.9%). The edges of the specimens were abraded with fine emery paper to make them smooth. The surfaces of the specimens were cleaned by dipping them in molten KOH and chemical polishing of these specimens was carried out in a mixture of 98% sulphuric acid, 70% nitric acid and 48% hydrofluoric acid in the ratio of 5:2:2 for 3-5 sec. After chemical polishing, these specimens were placed in boiling water for about 10 min. to remove any remaining impurities from the surface of the specimens. The specimens were anodized at constant current density using an electronically operated constant current power supply. The supply of current was cut-off after the desired voltage of film formation is reached. The time for the passage of current for formation of film through successive intervals of voltage was recorded by an electronic timer. The thickness of the film was determined using Faraday law. The density of tantalum oxide film was taken as 7930 Kg m^{-3} as reported by Young⁶.

III. Results and Discussion

The linear plots between voltage of formation and time upto 200V shows that field strength is independent of film thickness. However, at higher voltages of formation, dependence of field strength on film thickness is observed. The plot of field strength against reciprocal of temperature at different current densities is shown in Fig.1. The values of 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 is shown in Fig.2. The slopes of this plot show that it is independent of temperature which rules out the applicability of single barrier theory of Cabrera-Mott⁴. which suggests that Tafel slope is proportional to absolute temperature. Guntherschulze-Betz⁷ constants A & B (Eqn.1)

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

have been determined in presence of different electrolytes by least squares method at different temperatures.

The values of 'B' are 4.61×10^{-8} , 4.42×10^{-8} and $4.71 \times 10^{-8} \text{ Vm}^{-1}$ in aqueous solutions of ammonium sulphate, cadmium chloride and ammonium nitrate, 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 ammonium sulphate are 1.097×10^{-12} , 3.139×10^{-12} , 6.769×10^{-12} at 298, 313 and 328K, respectively. Similarly, values of constant 'A' at 298K are found to be 3.87×10^{-12} and 2.18×10^{-12} for cadmium chloride and ammonium nitrate, respectively which shows its dependence on nature of the electrolyte. It is observed quadratic variation of field with ionic current density to explain the field and temperature dependence of Tafel slopes (Table 1.)

The data for the experimental mass-gain as a result of anodic oxidation and the calculated mass-gain due to oxidation (when current efficiency is unity) for the growth anodic oxide in different concentrations of various electrolytes are reported in Table 2. At each electrolyte concentration current efficiency is found to be same irrespective of the charge passed. The experimental and calculated mass-gain are close to each other upto an electrolyte concentration of 0.1M when current efficiency is close to unity which implies that the entire current passed is ionic i.e. no fraction of electronic current is used for formation of film. It is observed that for higher concentrations of the electrolytes the experimental mass-gain is more than those calculated mass-gain. It is found that there is about 8% and 10% increase in mass-gain at concentration of 0.5M and 1.0M respectively in solution of ammonium sulphate. Similar trends in mass-gain are observed for cadmium chloride and ammonium nitrate solutions at higher concentrations. The formation of higher oxides of tantalum has been ruled out as possible cause for observed mass-gain as no other stable tantalum oxide except Ta_2O_5 has been reported in literature. The increase in mass-gain may be due to incorporation of anions into the oxide film and this is substantiated by the results reported earlier that the breakdown voltage of the films is affected by the incorporation of anions from the electrolytes into the film. Further, incorporation of other anions into oxide film has also been reported by other investigators^{8,9} which concludes that excess mass-gain is due to incorporation of anions into the oxide film.

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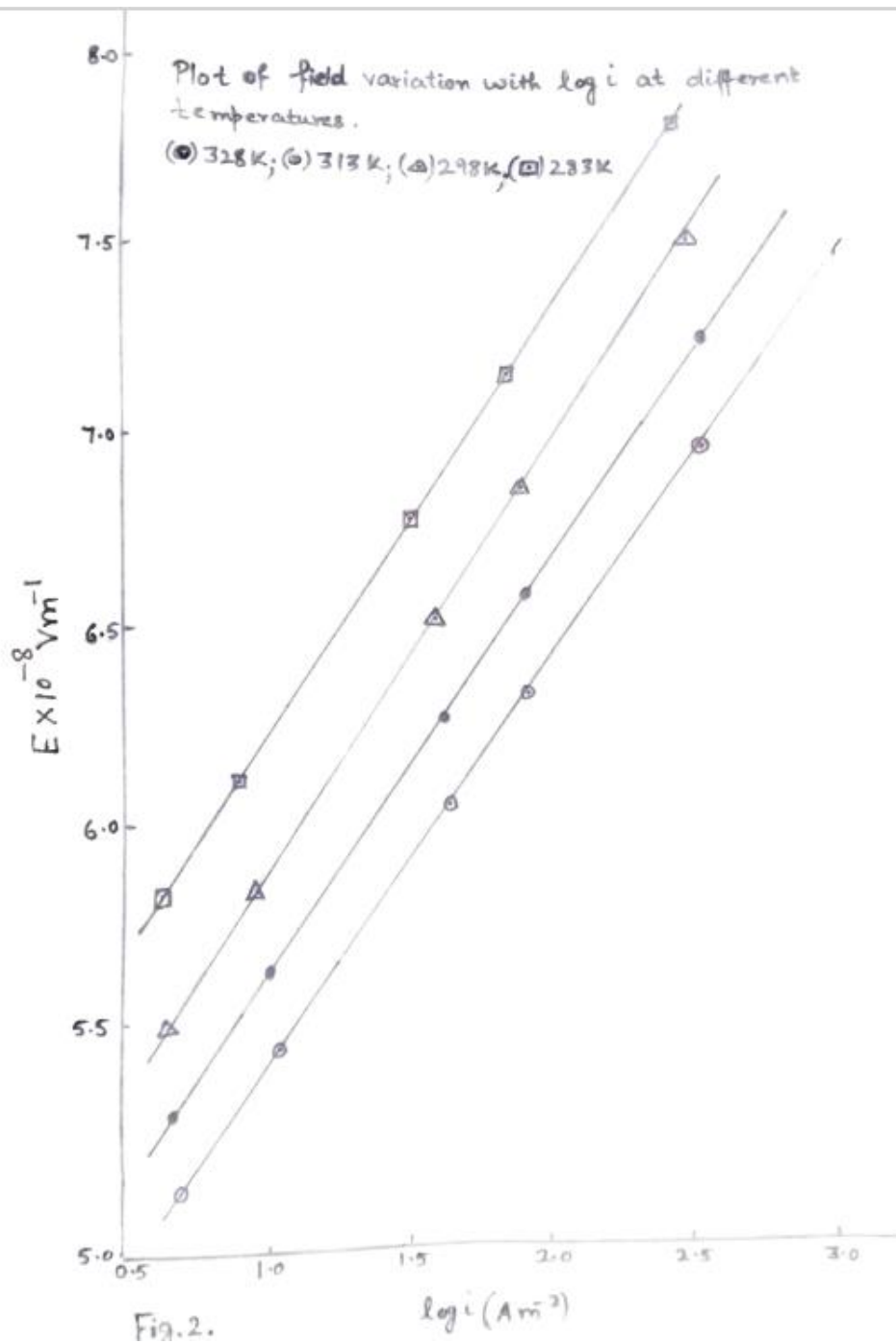
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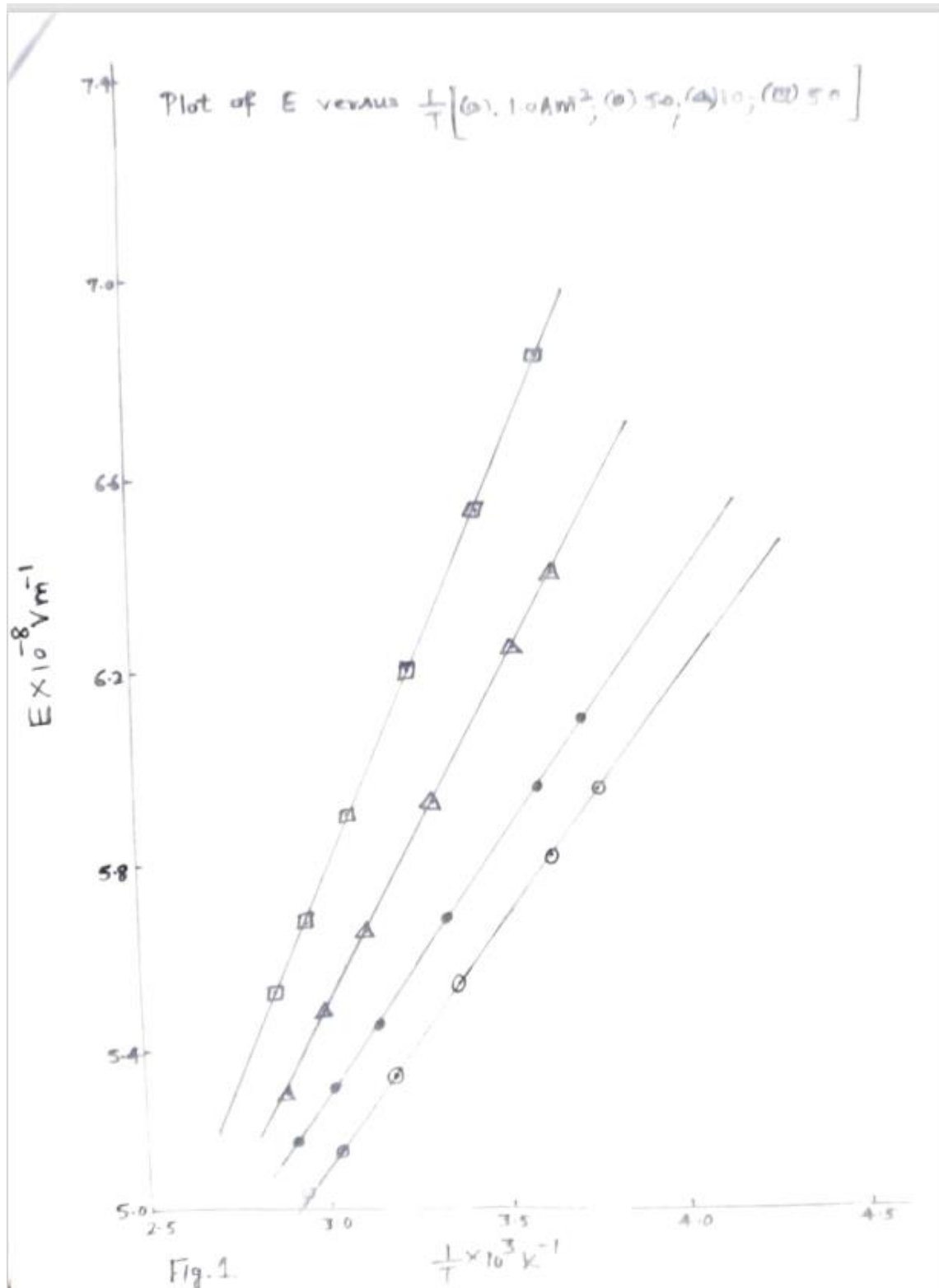
Table.1

Temperature (K)	E X 10⁻⁸ (Vm⁻¹) Current density - 5.0Am⁻²	E X 10⁻⁸ (Vm⁻¹) Current density - 10.0Am⁻²	E X 10⁻⁸ (Vm⁻¹) Current density - 50.0Am⁻²	E X 10⁻⁸ (Vm⁻¹) Current density - 100.0Am⁻²	E X 10⁻⁸ (Vm⁻¹) Current density - 500.0Am⁻²
283	5.78	6.12	6.76	7.18	7.85
298	5.45	5.80	6.48	6.82	7.47
313	5.29	5.58	6.22	6.54	7.29
328	5.15	5.37	5.95	6.26	6.91

Table.2

Concentration	Mass-Gain		Current efficiency
	Exp.	Cal.	
0.01M	741	748	0.991
0.02M	796	802	0.993
0.05M	842	849	0.992
0.10M	892	901	0.990
0.25M	1009	1132	1.122
0.50M	1248	1415	1.134
1.00M	1365	1691	1.154





REFERENCES

- [1]. K.C.Kalra and Parveenkatyal *J. Applied Electrochemistry*, 21 (1991) 729
- [2]. K.C.Kalra and ParveenKatyal. *Thin solld Films*, 201 (1991) 203
- [3]. J.M.Albella, I.Montero&J.M.Martinez-Duart, *ElectrochimActa*,32(1987)255.
- [4]. N Caberera & N.F Mott , *Rep Prog Phys*,12 (1948) 163.
- [5]. J.F Dewald , *J. electrochem Soc*, 102 (1955) 1.
- [6]. L.Young., *Proc. R. Soc., London*, A244 (1958)41
- [7]. A. GuntherSchulze&H.Betz, *Z Phys*, 92 (1934) 367.
- [8]. R.K.Nigam, K.C.Kalra&ParveenKatyal,*Indian J. Chem.* 26A (1987)
- [9]. K.C. Kalra, ParveenKatyal&K.C.Singh, *Thin solid films*, 177(1989) 35
- [10].S.Ikonopisov, *ElectrochimActa*, 22(1977)1077.
- [11].I. Montero, J.M.A Ibella& J.M. MartinezDuart,
- [12].*J.Electrochem.Soc.*,132(1985)814.
- [13].KaiyangZeng, Furong Zhu, Jianqiao Hu Lu, *Thin Solid Films*, 443(2003) 60.
- [14].R.Jayakrishnan and G.Hodes, *Thin Solid Films*,440(2003) 19
- [15].V.Kadary&N.Klen, *J.Eletrochem Soc.*, 127(1980)139.
- [16].J. yahalom& J. Zahavi, *ElectrochimActa*, 15(1970) 429
- [17].Kim and S.M.Rossnagel, *Thin Solid Films*,441 (2003) 317
- [18].G.C.Wood&C.Pearson, *Corros. Science*,7 (1967) 119
- [19].F.J.Burger&J.C.wit, *J. Eletrochem Soc.*, 118 (1971) 2039
- [20].O. NilsenH.Fjellvag and A.Kjekshus, *Thin Solid Films*,444(2003)44
- [21].G.Machado, *Thin Solid Films*,489(2005) 124
- [22].H. Kim and S.M. Rosssngel, *Thin Solid Films*,441 (2003) 311
- [23].A.S. Mogoda and T.M. Abd El-Haleem, *Thin Solid Films*, 441 (2003) 06
- [24].Arsova.et.al., *Journal of Solid State Electrochemistry*,11 (2007)209
- [25].F.Qin, N.P. Magtoto, M.Garza and J.A. Kelber, *Thin Solid Films*(2003)807