

Ion Mobility, Heat Treatment of Anodic Oxide Thin Films on Tantalum in Aqueous Electrolytes

Dr. Parveen Katyal

Department of Chemistry, S.D.(P.G) College, Panipat (Haryana)

Abstract

Studies on ions mobility during growth of tantalum oxide films , heat treatment and its effects on variously formed tantalum oxide thin films in different aqueous electrolytes have been made. The capacitance of tantalum oxide thin films depends on concentration and nature of the aqueous electrolyte. It has been observed that only tantalum ions are mobile during the growth of tantalum oxide thin films in various electrolytes. On heat treatment in air the oxide film becomes more conducting. The conductivity depends on the time period and temperature of heat treatment but it is independent of film thickness and nature of the electrolyte. Two different types of patterns of conductivity were observed before and after heating of anodic tantalum oxide thin films. One is associated with high conductance and low rate of change of capacitance with increase in temperature and second is associated with low conductance and high rate of change of capacitance with increase in temperature.

I. Introduction

Anodic oxidation on tantalum in various aqueous electrolytes and their breakdown voltage characteristics has already been reported by the author ¹⁻⁴ The present work is an extension of earlier investigations on tantalum oxide thin films. Ion mobility and heat treatment studies on tantalum oxide films have been made in various electrolytes and it has been found that the conductivity patterns before and after heating show similar trends and are of two types, one is associated with high conductance and low rate of change of capacitance with increase in temperature and the other is associated with low conductance and changes capacitance more rapidly with increase in temperature.

II. Materials and Methods

For ionic mobility measurements 0.25 mm thick tantalum samples were anodized upto identical formation voltage in 100 mol/m³ aqueous succinic acid at a current density of 50A/m². After anodization these tantalum samples were paired together to form tantalum/tantalum oxide/tantalum sandwich geometry. In this manner perfect sealing of the sample I and II was done except on the outer surface of the specimen II. The effective surface area for experimental purpose after sealing was 1 x 10⁻⁴ m². For heat treatment of tantalum oxide films, tantalum samples with small tags were cut from 99.9 % pure tantalum sheets

and the edges of the samples were abraded with fine emery paper to make them smooth. The samples were then dipped in Potassium hydroxide melt to clean the surface and finally washed with distilled water. The chemical polishing of these samples were done by dipping in a freshly prepared etching mixture of 98% H₂SO₄ + 70% HNO₃ +48% HF(5:2:2, V/V) for 3-5 s and then washed with distilled water. These samples were then placed in boiling water for about 10 minutes to remove any remaining impurities from the surface of the samples. The tag of the samples was covered with a thick anodic film in an electrolyte in which further anodization on square portion of the sample was to be carried out. The sample thus prepared was placed in a glass cell and was connected with a platinum electrode which served as cathode during the growth of oxide film. Anodization of the sample was carried out at constant current and the supply of the current was cut off by an electronic control after the desired voltage of formation was reached. The heating of the samples in air was done in a pre calibrated silica tube furnace. The density of the tantalum oxide film was taken as 7930 Kg/m³ as reported by Young⁷.

III. Results and Discussions

Tantalum samples I and II were anodized at film formation voltages of 60, 80 and 100V in 50 mol/m³ succinic acid at a current density of 100 A/m² and their capacitances before sealing were measured and found to be 2.81,2.07,1.39 for sample I and 1.68,1.06,0.87 F x 10⁻⁶ for sample II at the above film formation voltages respectively. In the combined assembly the capacitance of both samples I and II are same (0.88,0.65 and 0.49 x 10⁻⁶ F at 60,80 and 100 V respectively) and the values are in proportion to their reduced areas of 1 x 10⁻⁴ m² , and the assembly acts as one unit. The tag of the sample I in each of the paired assembly was connected to the positive end of the constant current supply and the sample II which was earlier anodized upto 60 , 80 and 100 V paired assemblies was further anodized upto 120, 160 and 200 V respectively. The capacitances of these paired systems were again measured taking specimen I and II in the circuit respectively and it was found that the capacitances of samples I and II were almost same(0.65,0.48 and 0.34 x 10⁻⁶ F at 120,160 and 200V respectively and this ensured that complete sealing of sample I and II and no possibility of electrolyte creeping into the oxide film. The magnitudes of the capacitances were further reduced due to further formation of oxide film. The assembly of samples I and II was dismantled and then the capacitances of the separated sample I and II were measured as also those of the outer and the inner surfaces of both the samples after applying locomite to the other side. The capacitance of the sample I after separation was found to be 2.79, 2.09 and 1.37 x 10⁻⁶ F at 60,80 and 100V respectively and before sealing were identical indicating that sample I remain unaffected. The capacitances per m² for both the inner and outer surfaces of sample I were found to be 0.87,0.66 and 0.50 x 10⁻² F/m² at film formation voltages of 60,80 and 100V respectively while the corresponding values for the inner surface of sample II were 0.89,0.68 and 0.48 x 10⁻² F/m². The magnitudes of the capacitance per m² for sample I compare well with those of the inner surface of sample II which concludes that the sandwiched oxide film is not affected. Further anodization of the separated sample I increases the film formation voltage immediately and it attains the voltage of the film already present on it i.e. film formation voltage (Fig 1). This implies that there is no possibility of oxygen ion

moving through the electrolyte to sample I to produce layers inside the existing oxide layers. The field of tantalum oxide film between samples I and II of this experiment remains unchanged and tantalum ions produced as sample I are transported to sample II through the tantalum oxide and then to solution to produce fresh layers on the outer surface of the sample II which shows that only tantalum ions are mobile during the growth of tantalum oxide film. The normal rate of anodization compare well with the anodization rate during this experiment.

(II) Heat treatment of tantalum oxide thin films in various electrolytes.

Samples of tantalum were anodized in 250 mol m^{-3} aqueous solutions of sodium citrate, succinic acid and sodium oxalate at a current density of 100 Am^{-2} up to 50, 100, 150 and 200 V. These anodized specimens were Separately heated in a tube furnace in the presence of air at a constant temperature for different intervals of time. The sample were allowed to cool and taken out & there capacitances measured in the respective aqueous solutions of succinic acid, orthophosphoric acid & ammonium hydrogen phosphate at room temperature ($298 \pm 0.5 \text{ K}$). from the plots of littance versus time of heating films formed up to different formation voltages (50, 100, 150 & 200 V in Succinic acid) at a fixed temperature, it is observed that while there is no appreciable change in the value of capacitance with time at room temperature, the capacitance of each of the film increases with the duration of heating. Which shows that on heating the films become more conducting. The change in capacitance is more for 50V film and decreases as the voltage film formation increases after heating for about 1.5 hours. However, after long time periods these differences disappear and films become equally conducting irrespective of voltage of film formation. Similar trends were shown by the films formed in other aqueous electrolytes. It is further observed that capacitances before and after heating for long hours in different electrolytes are affected by heat treatment to the same extent which concludes that effect of heat treatment on tantalum oxide films is independent of the nature of the electrolyte. Similarly on heating the oxide film formed at different temperatures for a fixed interval of time, It is observed that capacitances of the oxide film did not change when these were heated up to temperature of about 600 K. (Table.1) and above this temperature, the capacitances increased almost linearly with rise in temperature of heating as shown in Fig. (2) From the plots of capacitance versus temperature in various electrolyte it is observed that conductivity profile across the tantalum oxide film is of to types, one which is associated with high conductance and smaller rate of change of capacitance with temperature, and the other associated with low conductance and higher rate of change of capacitance with temperature. The conductivity patterns for both heated and unheated specimens of tantalum oxide films show similar trends. It appears that on heating of oxide films the conductivity results from the extraction of oxygen from tantalum oxide by tantalum and causing oxygen deficiency in the oxide film. In the presence of air, when oxygen deficiency reaches oxide – air, interface it renders oxygen to flow into the film. The flow of oxygen maintains the oxide composition both at the tantalum-tantalum oxide and tantalum oxide-air interfaces and is independent of the nature of the electrolyte. Heat treatment of the oxide films in air makes them more conducting.

Acknowledgement :

The author acknowledges University Grants Commission, New Delhi for the award of a Research Project.

TABLE – 1

Capacitances of films formed at formation voltages of 50 and 100 V in various electrolytes before & after 5 hours of heating.

Electrolyte	Film formation Voltage (V)	Capacitances (10^6 F)	
		Before heating	After Heating
Sodium Oxalate	50	9.75	10.70
	100	4.65	5.05
Succinic Acid	50	8.60	9.20
	100	3.95	4.35
Sodium Citrate	50	9.90	11.40
	100	4.70	5.15

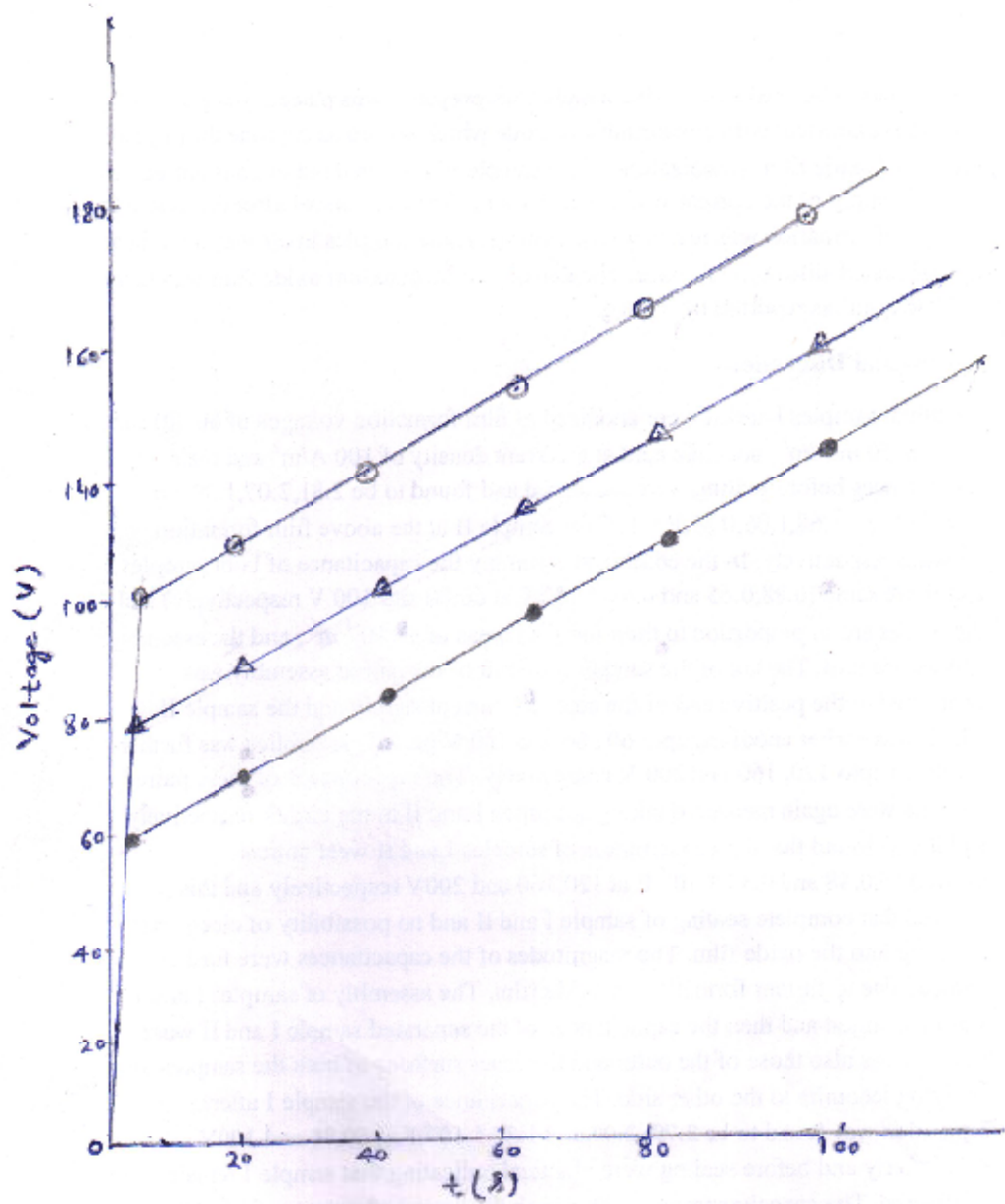


Fig. 1- Variation of formation voltage versus time of anodization for Ta_2O_5 of various thicknesses
[(●) 60 V; (Δ) 80 V; (○) 100 V]

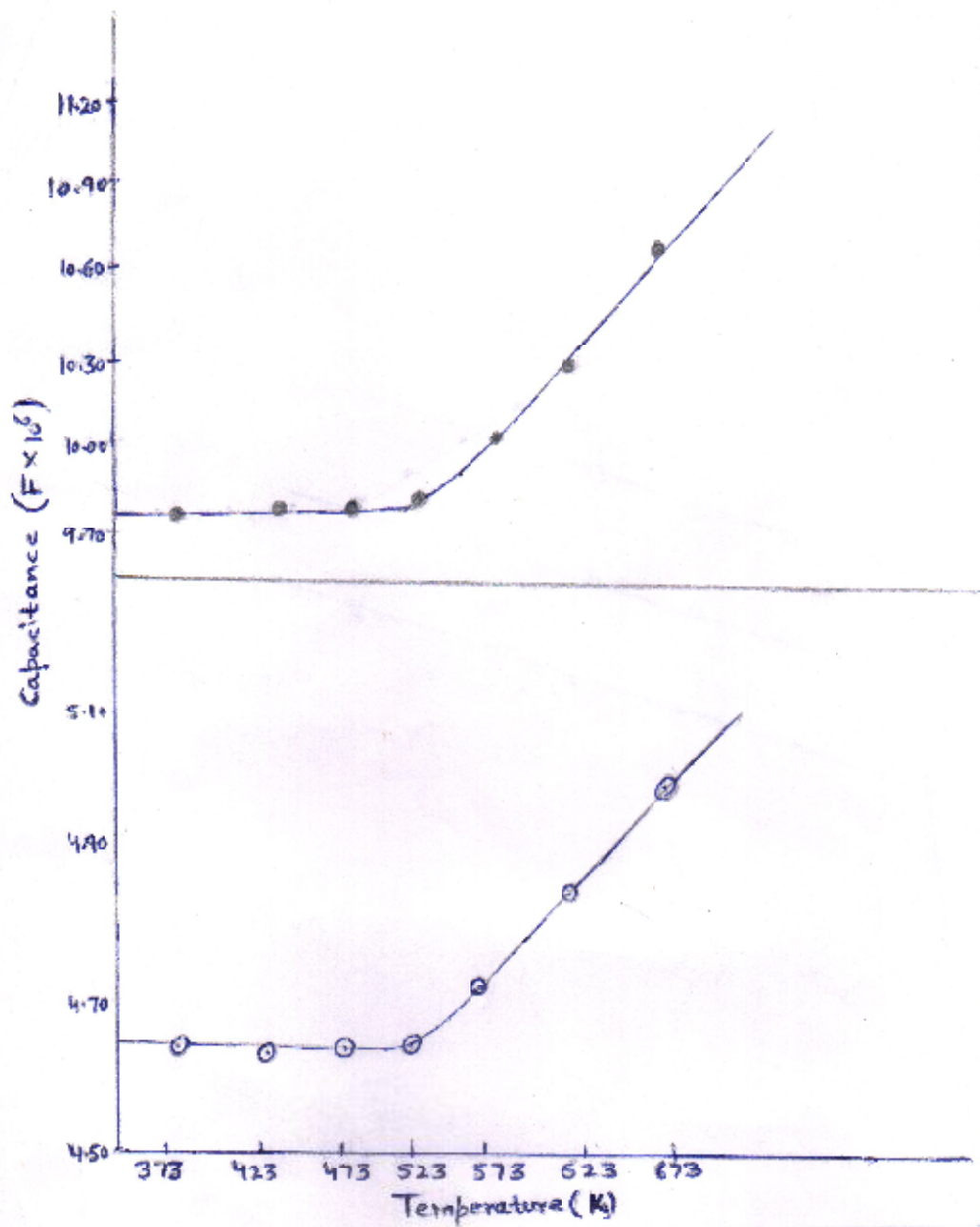


Fig. 2- Plot of variation of capacitance with temperature for Ta₂O₅ films formed upto film formation voltages of 50 and 100 V in sodium oxalate.

REFERENCES

- [1]. K.C.Kalra and Parveen Katyal. Thin solid Films, 201 (1991) 203
- [2]. R. K. Nigam, K C Kalra and P. Katyal, Indian J Chem., 26A (1987)17.
- [3]. R. K. Nigam, K C Kalra and P. Katyal, Indian J Chem., 25A (1986)1080.
- [4]. R. K. Nigam, K C Kalra and P. Katyal, Indian J Chem., 26A (1987)819.
- [5]. I. Montero, J.M.A lbella & J.M. Martinez- Duart,J.Electrochem.Soc. , 132(1985)814.
- [6]. Kaiyang Zeng, Furong Zhu, Jianqiao Hu Lu, Shen Kerran Zhang and Hao Gong,Thin Solid Films, 443(2003) 60
- [7]. L.Young., Proc. R. Soc., London, A244 (1958)41
- [8]. R.Jayakrishnan and G.Hodes, Thin Solid Films,440(2003) 19
- [9]. J.M.Albella, I.Montero & J.M.Martinez-Duart, Electrochim Acta,32(1987)255.
- [10]. S.Ikonopisov, Electrochim Acta, 22(1977)1077.
- [11]. K.C.kalra, Parveen Katyal, K.C. Singh & Rakesh Bhardwaj, J.Electrochem Soc., India 410 (1992) 33.
- [12]. V.Kadary & N.Klen, J.Eletrochem Soc., 127(1980)139.
- [13]. .A. GuntherSchulze & H.Betz, Electrolyte Kundensaporen, (herbert Cram, Berlin) 1952
- [14]. J. yahalom & J. Zahavi, Electrochim Acta, 15(1970) 429.
- [15]. Kim and S.M.Rossnagel, Thin Solid Films,441 (2003) 317
- [16]. G.C.Wood & C.Pearson, Corros. Science,7 (1967) 119
- [17]. R.S.Alwitt & A.K.Vijh, J Electrochem. Soc., 116(1969) 388
- [18]. F.J.Burger & J.C.wit, J. Eletrochem Soc., 118 (1971) 2039
- [19]. O. Nilsen H.Fjellvag and A.Kjekshus, Thin Solid Films,444(2003)44
- [20]. Arsova.et.al., Journal of Solid State Electrochemistry,11 (2007) 209
- [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 EI-Haleem, Thin Solid Films, 441 (2003) 06
- [24]. K.C.Kalra and Parveen katyal J.Applied Electrochemistry, 21 (1991) 729
- [25]. K.C Kalra and Parveen Katyal.
- [26]. J.Electrochem.Soc.18, 165 (1990)