

Formation of Anodic Oxide Films on Tantalum in Presence of Ultraviolet Radiations & Heat Treatment of Anodic Tantalum Oxide Films

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The data obtained during the growth of anodic oxide films on tantalum indicate higher values of rates of growth, constant A (of Guntherschulze-Betz equation) and Tafel slopes in the presence of UV radiations than those in the absence of radiations. However, the values of constant B (of Guntherschulze-Betz equation), half-jump distances and breakdown voltages are lower in the presence of UV light. Faster rate in the presence of UV is probably due to increased number of mobile ions per unit volume and decreased width of potential energy barrier. Stimulated ionic movements due to UV radiations cause breakdown of films at lower voltages. Heat treatment of the oxide films in air makes these more conducting. This effect depends on the time period and temperature of heat treatment but is independent of film thickness and nature of electrolyte. The conductivity patterns before and after heating show similar trends and are of two types: One is associated with high conductance and lower rate of change of capacitance with increase in temperature and the other is associated with low conductances and changes capacitance more rapidly with increase in temperature. The hypothetical break temperature is independent of the nature of electrolyte or treatment.

The growth kinetics, breakdown characteristics, current efficiencies, dielectric measurements and ion-mobility studies of aqueous anodic oxide films on tantalum have been reported recently by the authors¹⁻⁴. Film formation on valve metals under UV radiations has also received much attention⁵⁻¹¹. However, the data obtained and the views expressed are at variance.

The properties of anodic oxide films undergo change when heated in vacuum¹³⁻¹⁷ but the effect of heating anodized tantalum in air has not received much attention and needs further probing. The trends in the conductivity profile during heat treatment also require investigation. In this paper are presented the results of ionic conduction study of anodic oxide films formed on tantalum at constant current density and very high-field strength in the presence and absence of UV radiations.

Materials and Methods

Tantalum specimens ($16 \times 10^{-4} \text{ m}^2$ in area) with small tags were cut from 99.9% Ta sheets and their surfaces prepared in the manner described earlier¹. The specimens thus prepared were placed in glass cells containing aqueous electrolyte and were surrounded by platinum gauzes which served as cathodes. The assembly was then put in a photochemical reactor (Srinivasan-Griffin-Rayonet Type, Popular Traders, India) and anodic polarization was carried out at a particular current density using constant current generator

(General Electronics, India) as reported earlier¹. The temperature during these measurements was $305 \pm 1 \text{ K}$.

The heating of the samples in air was done in a pre-calibrated silica tube furnace. The capacitances before and after heating the oxide films were measured at 1 kHz using an electrolytic capacitor bridge (BPL, India) in the respective aqueous electrolyte taking special care that the tags did not dip into the electrolyte. For studying conductivity profile the cell was kept in an ultracryostat (model MK 70, GDR) and the liquid used was 38% H_2SO_4 . Such an arrangement allowed temperature variation from 248 to 298 K. The density of the tantalum oxide film was taken as 793 kg m^{-3} as reported by Young¹⁸. All the chemicals used were of AR (BDH) grade.

Results and Discussion

A. Formation of aqueous oxide films in presence and absence of UV radiations

Anodic oxide films were formed in 100 mol m^{-3} aqueous solution separately in citric, tartaric and acetic acids at various current densities (6.25, 12.50, 62.5 and 125 A m^{-2}). The plots of voltages of film formation (V) in aqueous citric acid versus time (t) for which charges were passed are shown in Fig. 1 and are linear up to a film formation voltage of 200 V and thereafter there was deviation from linearity. Similar trends were also observed in tartaric and acetic acids. The rates of formation (dV/dt) were lower in the absence of

Table 1 – Constants A & B, Tafel Slopes, Half-Jump Distances and Breakdown Voltages of Various Formed Oxide Films in Presence and Absence of UV Radiations

Electrolyte	A $\text{Am}^{-2} \times 10^8$	B $\text{mV}^{-1} \times 10^8$	Tafel slope $\text{Vm}^{-1} \times 10^{-7}$	Half jump distance, nm	Breakdown voltage, V
Citric acid	16.11(0.41)*	3.01(3.77)	3.46(2.63)	0.158(0.199)	340(365)
Tartaric acid	38.10(3.40)	2.82(3.41)	3.52(2.38)	0.148(0.185)	350(375)
Acetic acid	0.82(0.07)	3.50(4.02)	2.67(1.89)	0.185(0.212)	420(460)

* Values in parentheses are for the systems in the absence of UV radiations.

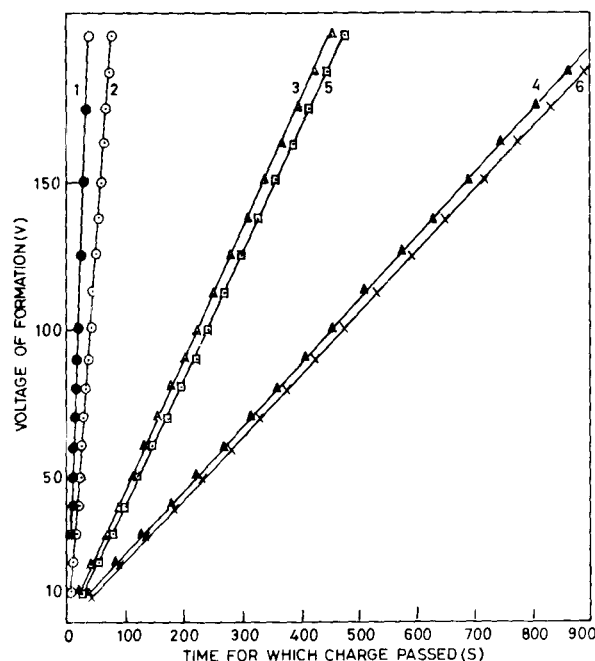


Fig. 1 – Variation of voltage of formation with time at different current densities for the films formed in citric acid [(1) 125.0 A m^{-2} ; (2) 62.50 ; (3) 12.5 and (4) 6.25 in presence of UV radiations; (5) 12.5 A m^{-2} and (6) 6.25 in the absence of UV radiations]

UV radiations than those observed in the presence of UV radiations (Fig. 1). The values of breakdown voltage (V_B) obtained in 100 mol m^{-3} citric, acetic and tartaric acids in the presence of UV radiations (Table 1) are lower than those obtained in their absence. The values of V_B (in the presence of UV radiations) decrease with increase in electrolyte concentrations (e.g. the values of V_B in 100 mol m^{-3} citric and acetic acids are 340 and 420 V while the corresponding values in 500 mol m^{-3} acids are 295 and 385 V). The plots of field strength (E) versus \log (current density) in the case of citric, tartaric and acetic acids are linear. Thus, the dependence of field on current density in the presence of UV radiations can be represented by Guntherschultze-Betz equation,

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

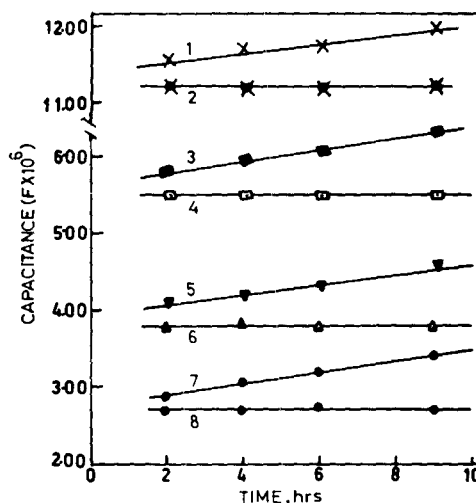


Fig. 2 – Variation of capacitance with time for the films formed up to different voltages in citric acid before and after heating [(1) Heated 25 V; (2) unheated 25 V; (3) heated 50 V; (4) unheated 50 V; (5) heated 75 V; (6) unheated 75 V; (7) heated 100 V; (8) unheated 100 V.

where A and B are constants. The values of constants A and B were evaluated both in the presence and absence of UV radiations and the results are presented in Table 1. The A -values are dependent on the nature of electrolyte and are higher in magnitude in the presence of UV radiations than those in their absence. Higher A -values indicate larger number of mobile ions per unit volume. The higher A -value in citric acid than that in acetic acid may be due to higher dissociation constant of citric acid (8.7×10^{-4}) than that of acetic acid (1.8×10^{-5}). The B -values show only small changes in different electrolytes; however, the B -values are lower in the presence of UV radiations. Using $B = qa/kT$ (ref. 19) (where q is the charge on Ta_2O_5 and can be taken as $5e$, k is the Boltzmann constant, T is the temperature and a is the half-jump distance between lattice points), the values of a were calculated (Table 1). The results show that a -values are higher in the presence of UV radiations than those in their abs-

Table 2 – Capacitances of Films Formed at Formation Voltages of 25 and 50 V in Various Electrolytes Before and After Heating for 9 hr at 748 K

Electrolyte	Film formation voltage (V)	Capacitance ($F \times 10^6$)	
		Before heating	After heating
Citric acid	25	11.20	11.95
	50	5.50	6.30
Tartaric acid	25	10.40	11.05
	50	5.20	5.90
Acetic acid	25	10.90	11.55
	50	5.35	6.00
Sulphuric acid	25	11.00	11.70
	50	5.40	6.10

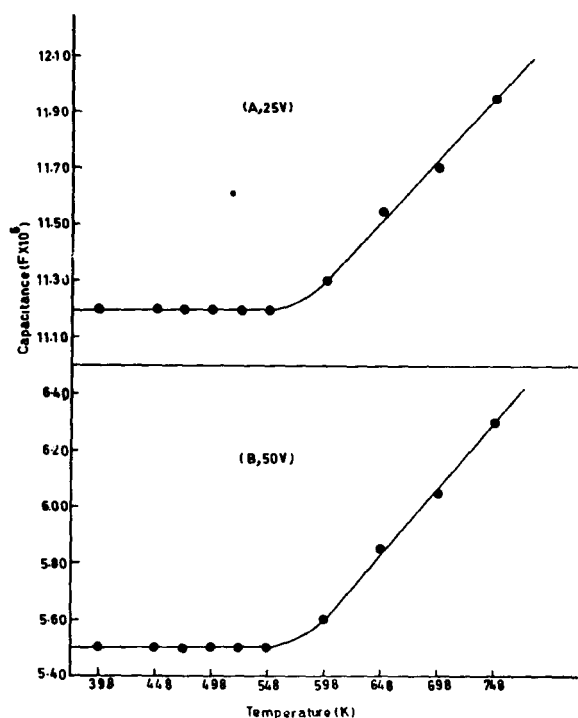


Fig. 3 – Variation of capacitance with temperature for the films formed upto film formation voltages of 25 and 50 V in citric acid.

ence. The Tafel slopes ($\partial E/\partial \ln i$) were calculated from the linear plots of field strength (E) versus \log (current density) and the results are given in Table 1. The Tafel slopes for films formation induced by UV radiations are higher than those in their absence.

Irradiation with UV mainly produces an electronic photocurrent. Since the applied current is fixed, irradiation results in an enhanced rate of growth of oxide films as observed above. Hence irradiation should stimulate ionic conduction even in the presence of large ionic currents and, therefore, higher rates of growth of anodic films are

observed for films grown in the presence of UV radiations at all current densities. It appears that in the presence of UV radiations there is an increase in the number of mobile ions per unit volume and this causes an increase in the rate of growth in the presence of UV radiations (Table 1). The faster growth rate in the presence of UV light may also be due to decrease in the width of the potential energy barrier and this is substantiated by the observed decrease in half-jump distances (a). Since the ionic movement is stimulated in the presence of UV radiations, the maximum film formation is reached at relatively lower voltages and this explains the observed lower breakdown voltages in the presence of UV radiations.

Heat treatment of anodic tantalum oxide films

Tantalum specimens were anodically polarised in 100 mol m^{-3} aqueous citric, tartaric, acetic and sulphuric acids (at a current density of 50 Am^{-2}) up to 25, 50, 75 and 100 V. These anodically oxidized samples after washing were separately heated in a tube furnace in the presence of air at a constant temperature for different intervals of time. The specimens were allowed to cool and taken out and their capacitances measured in the respective aqueous solutions at room temperature ($303 \pm 1 \text{ K}$). The plots of capacitance versus time of heating films formed up to different formation voltages (25, 50, 75 and 100 V in citric acid) at a fixed temperature (748 K) are shown in Fig. 2. The corresponding plots between capacitance after the same interval of time (equal to time of heating) at room temperature are also included in Fig. 2. The plots show that while there is no appreciable change in the values of capacitance with time at room temperature, the capacitance of each of the film increases with the duration of heating. Thus heat treatment makes the films more conducting. After 2 hr, the change in capacitance is more for a 25-V film and decreases as the voltage of film formation (i.e. thickness) increases. However, after longer time periods these differences disappear and films become equally conducting irrespective of film thickness. Similar trends were shown by the films formed in other acids. The capacitances, before and after heating for 9 hr, for the films formed in different electrolytes are given in Table 2. The results show that the variously formed films are affected by heat treatment to the same extent and hence the effect of heat treatment on oxide films is independent of the nature of the electrolyte.

The effect of temperature of heating was studied next by heating the oxide films formed at different

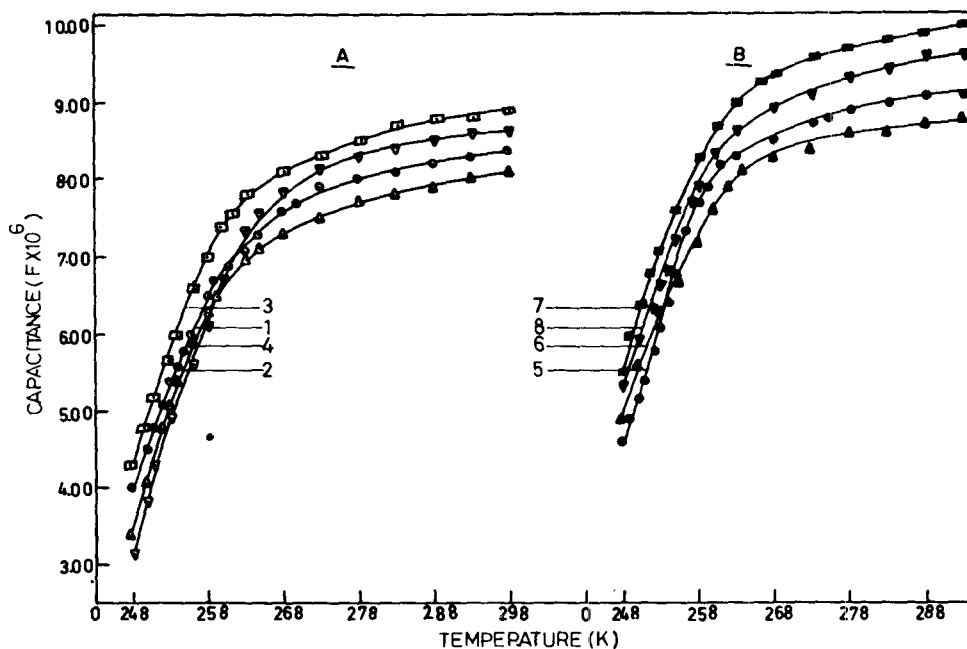


Fig. 4 - Variation of capacitance as a function of temperature for heated and unheated oxide films formed in various electrolytes. [(A) Unheated - (1) citric acid; (2) tartaric acid; (3) acetic acid; (4) sulphuric acid. (B) Heated - (5) citric acid; (6) tartaric acid; (7) acetic acid; (8) sulphuric acid]

temperatures upto 748 K for a fixed interval of time (9 hr). It was not possible to work beyond this temperature (748 K) as the films got damaged. The plots of capacitance versus temperature of heating for the oxide films formed in citric acid upto formation voltages 25 and 50 V are shown in Fig. 3 (A, B). The capacitances of the oxide films did not change when these were heated up to about 575 K. However, beyond this temperature, the capacitances increased almost linearly with rise in temperature of heating. Similar trends were shown by the films formed in other acids.

The conductivity profile across the Ta_2O_5 film was studied by measuring the capacitance of heated as well as unheated oxide samples as a function of temperature in 38% H_2SO_4 in the temperature range of 248 and 298 K. The plots of capacitance versus temperature for films formed in citric, tartaric, acetic and sulphuric acids are shown in Fig. 4. The plots show the conductivity profile to be of two 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 samples show similar trends. Our results on conductivity profile do not agree with those of Smyth and Tripp¹². This may be probably due to non-

availability of data to Smyth and Tripp in a wide range of electrolytes. The hypothetical break temperature (obtained by extrapolating the linear portions of the capacitance-temperature plot) was independent of nature of electrolyte or treatment. It appears that during heat treatment the conductivity results from the extraction of oxygen from Ta_2O_5 by Ta and hence 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. Oxygen flow maintains the oxide composition both at the Ta/ Ta_2O_5 and Ta_2O_5 /air interfaces and is not affected by the nature of the electrolyte.

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