

Current Efficiency, Dielectric Measurements & Ion Mobility Studies of Anodic Oxide Films Formed on Tantalum in Aqueous Electrolytes

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Current efficiencies, dielectric constants and ion mobilities of variously formed anodic oxide films on tantalum in the presence of various electrolytes such as citric, tartaric, acetic and hydrochloric acids have been evaluated. The current efficiencies of such films are unity upon an electrolyte concentration of 100 mol m^{-3} . However, at higher electrolyte concentration, the experimental mass-gain of the tantalum sample during anodization is greater than that expected for the anodic formation of Ta_2O_5 on tantalum, implying that mass-gain is probably due to the incorporation of anions into the films. The capacitances of such films depend on the concentration as well as nature of the aqueous electrolyte. The addition of chloride ions has been found to inhibit film growth, the effect being pronounced with increase in concentration of chloride ions. Only tantalum ions are mobile during the growth of tantalum oxide films.

The kinetics of growth of anodic oxide films formed on tantalum in aqueous electrolytes, and their breakdown characteristics have been reported recently by the authors¹⁻³. The present investigation is an extension of our earlier work¹⁻³, and has been undertaken in view of conflicting results^{4,15} of studies on current efficiencies, dielectric measurements and ionic mobilities of such anodic films.

Materials and Methods

Tantalum specimens ($32 \times 10^{-4} \text{ m}^2$ in area and 0.25 mm thick) with small tags were cut from tantalum sheets (purity 99.9%) mechanically and were chemically polished and anodically polarized in aqueous electrolytes (at a particular current density) as described earlier¹. Increase in weight of the tantalum specimen due to its anodic oxidation to tantalum oxide was used to calculate current efficiency. The capacitance and $\tan \delta$ measurements of the oxide films were made using an electrolytic capacitor bridge (BPL, India) at 1 KHz [$\tan \delta$, known as loss tangent or dielectric loss is the ratio of the voltage drop across the hypothetical series equivalent resistance (R_s) and capacitance (C_s). Also $\tan \delta = \omega C_s R_s$ where $\omega = 2\pi F$, F being the frequency]. Special care was taken to prevent the tags dipping into the electrolyte.

For ionic mobility measurements, two 0.25 mm thick tantalum specimens of different area, one of 169 mm^2 area (sample-I) and the other 100 mm^2 area (sample-II) were anodized upto identical formation voltage in 100 mol m^{-3} aqueous citric acid at a current density of 30 A m^{-2} and then paired together to get Ta, Ta_2O_5 , Ta sandwich geometry.

Perfect sealing of samples I and II was ensured by applying lacomite and Edward hard vacuum grease on the joints and the surfaces, except the outer surface of the sample II in the manner described earlier¹³. The effective geometric surface area after sealing was $1 \times 10^{-4} \text{ m}^2$.

All measurements were made in a well-stirred, electronically controlled, thermostatic bath maintained at $298\text{K} (\pm 0.5)$. The results reported are the mean of five repeat experiments. All the chemicals used were of AR(BDH) grade. The density of tantalum oxide film was taken as 793 kg m^{-3} as reported by Young¹⁵.

Results and Discussions

Current efficiency

The data for the experimental mass-gain (as a result of anodic oxidation), the calculated mass-gain due to oxidation (when current efficiency is unity) and the current efficiency (η) for the growth of oxide films in 10, 50, 100, 500 and 1000 mol m^{-3} aqueous citric acid at a current density of 50 A m^{-2} (when a particular amount of charge was passed) are reported in Table 1.

At each electrolyte concentration current efficiency was found to be the same irrespective of the charge passed. The experimental and calculated mass-gains are close to each other upto an electrolyte concentration of 100 mol m^{-3} (i.e. current efficiency is close to unity) implying that the entire current passed is ionic (and no fraction is electronic) and has been used for the film formation. However, the experimentally observed mass-gains were greater than those calculated by about

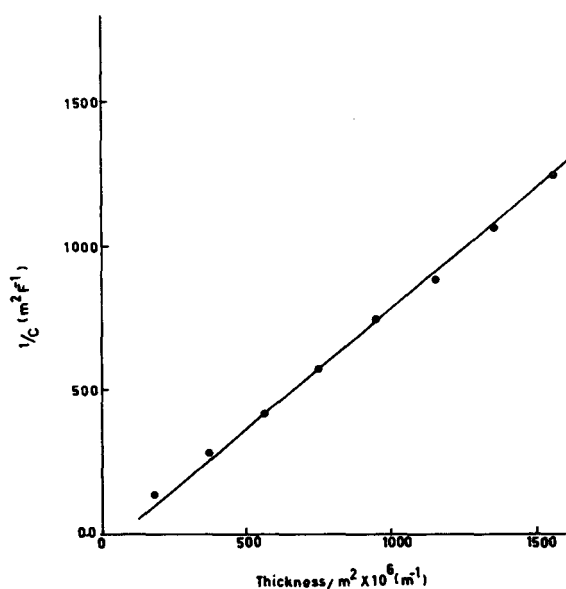
Table 1—Experimental and Calculated Mass-Gains and Current Efficiencies for Formation of Oxide Films on Tantalum in Aqueous Electrolytes at Different Charges

Electrolyte	Concentration (mol m ⁻³)	Charge C × 10 ³	Mass-gain (kg × 10 ⁹)		Current efficiency
			Exp.	Calc.	
Citric acid	10	8320	681	690	0.987
do	50	4000	330	332	0.994
do	100	9280	764	769	0.993
do	500	4320	380	358	1.051
do	1000	8640	801	716	1.118
Tartaric acid	100	4000	331	332	0.997
do	1000	17760	1680	1472	1.141
Acetic acid	100	18400	1520	1526	0.996
do	1000	9440	862	783	1.101
Hydrochloric acid	100	4800	393	398	0.987
do	1000	9920	889	882	1.082

6 and 12% respectively at 500 and 1000 mol m⁻³ citric acid concentrations. The data in tartaric, acetic and hydrochloric acids as electrolytes also showed similar trends (Table 1). The data indicate an excess equivalent to 14, 10 and 8% respectively over the calculated mass-gain due to oxidation in 1000 mol m⁻³ tartaric, oxalic and hydrochloric acids. Experimental error and formation of higher oxides of tantalum have been ruled out as the possible causes for the observed mass-gain since experiments were repeated five times and the excess mass-gain obtained was highly reproducible ($\pm 2\mu\text{g}$), and in literature formations of no other stable tantalum oxide, except Ta₂O₅ has been reported. The only possibility is the incorporation of anions into the oxide film and this is substantiated by the results reported in our earlier communication² that the breakdown voltage of the films is affected by the incorporation of anions (and not cations) from these electrolytes. Further, the incorporation of anions such as P, Cl, S and F into the oxide film has been reported by other workers^{4,5} and this also suggests that the enhanced mass-gain is most probably due to the incorporation of anions into the oxide films.

Dielectric measurements

Capacitance data for the oxides films formed upto various formation voltages (V) in 100 mol m⁻³ aqueous citric acid at a current density 50 A m⁻² were obtained. The plot of reciprocal capacitance (1/C) per m² versus thickness per m² calculated using Faraday's law, is linear (Fig. 1), indicating that the film is uniformly formed with constant field and 1/C can be taken as a measure of thickness of the oxide film formed in aqueous electrolyte. The effect of concentration of

Fig. 1—Plot of 1/C per m² versus thickness per m² for anodic oxide films in aqueous citric acid.

the electrolyte was studied by forming films of varying voltages in 10, 100 and 1000 mol m⁻³ citric acid. The plots of 1/C per m² versus V at each electrolyte concentration are linear (Fig. 2) and show a higher value of 1/C for a film formed at lower electrolyte concentration. The plots of tan δ versus V for these films are given in Fig. 3. As expected tan δ decreases with the increase in voltage of formation at each electrolyte concentration. The values of tan δ are higher at lower electrolyte concentration. The capacitance data were also obtained for the films formed in 100 mol m⁻³ tartaric, acetic, oxalic and hydrochloric acids and the plots of 1/C per m² versus V are linear and their

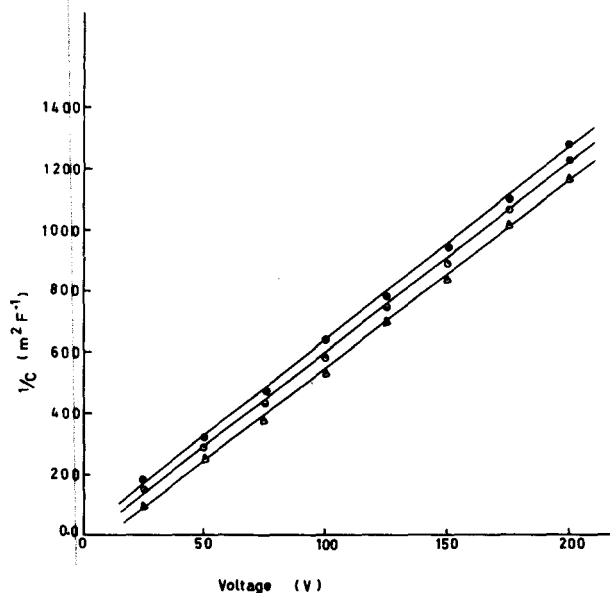


Fig. 2—Variation of $1/C$ per m^2 with voltage of formation (V) for anodic oxide films on tantalum at varying concentrations of aqueous citric acid [(●) 10 mol m^{-3} ; (○) 100 ; (△) 1000].

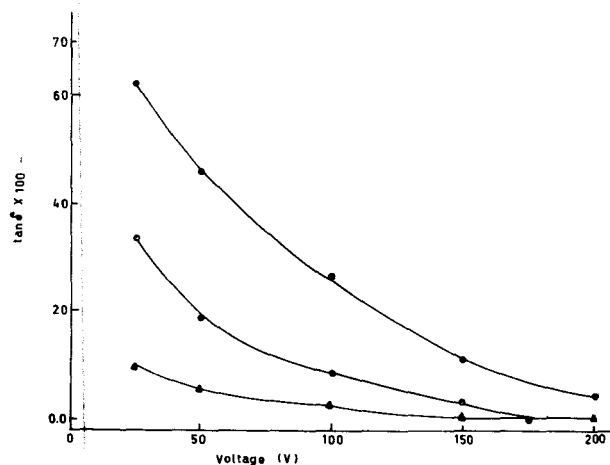


Fig. 3—Variation of dielectric loss factor ($\tan \delta$) with voltage of formation for anodic oxide films on tantalum at varying concentrations of aqueous citric acid. [(●) 10 mol m^{-3} ; (○) 100 ; (△) 1000].

slopes obtained by the method of least squares are reported in Table 2. The typical data for a 50V film (Table 2) show dependence of capacitance on the nature of the electrolyte.

The dielectric constants were calculated using the capacitance formulae for a parallel plate capacitor in the manner described below:

The capacitance (C) is defined by Eq. (1)

$$C = \frac{\epsilon A \epsilon_0}{d} \quad \dots (1)$$

where ϵ is the dielectric constants of the oxide film, ϵ_0 is the permittivity of the free space ($8.85 \times 10^{-12} \text{ Fm}^{-1}$), A is the area of the specimen (used as a counter electrode) and d is the thickness of the oxide film. At a constant current density, d increases linearly with voltage and becomes equal to βV where β is the anodization constant. Substituting βV for d in Eq. (1) we get

$$C = \frac{\epsilon A \epsilon_0}{\beta V} \quad \dots (2)$$

putting $A = 1 \text{ m}^2$ and rearranging Eq. (2), we get

$$\frac{1}{C} = \frac{\beta V}{\epsilon \epsilon_0} \quad \dots (3)$$

The plot of $1/C$ versus V is linear with the slope $= \beta / \epsilon \epsilon_0$. If the anodization constant is known then from the slope ϵ can be calculated. Anodization constants were calculated from the anodization data using Faraday's law and are reported in Table 2. Using the slopes of $1/C$ per m^2 versus V plots and the anodization constants (Table 2), the dielectric constants were calculated. The results reported in Table 2 show dependence of dielectric constant on the nature as well as the concentration of the electrolyte.

Table 2—Dielectric Measurement Data for Variously Formed Tantalum Oxide Films in Aqueous Electrolytes

Electrolyte	Concentration (mol m^{-3})	Capacitance of a 50V film ($\text{F} \times 10^6$)	Anodization constant (β) ($\text{mV}^{-1} \times 10^{10}$)	Slope of $1/C$ versus V plots ($\text{F}^{-1} \text{m}^2 \text{V}^{-1}$)	Dielectric constant
Tartaric acid	100	10.4	15.72	6.17	28.8
Acetic acid	100	10.9	16.31	6.16	28.9
Oxalic acid	100	10.6	15.48	6.05	28.9
Hydrochloric acid	100	10.8	16.00	6.22	29.1
Citric acid	10	10.2	15.95	6.25	28.8
do	100	11.2	15.92	6.20	29.0
do	1000	12.3	15.85	6.12	29.3

The effect of chloride ions on the capacitance of Ta_2O_5 formed in 100 mol m^{-3} citric acid was studied by measuring the capacitances of the films in the mixed solutions of hydrochloric and citric acids in the molar ratios of 1:1200, 1:120, 1:12 and 1:2.4. The capacitance of the film increased with the increase in the amount of chloride ions. The plots of $1/C$ per m^2 versus voltage of film formation are linear (Fig. 4). The slopes of these linear plots decrease from 6.20 to 5.30, 4.30, 3.95 and $3.45 \text{ m}^2\text{F}^{-1}\text{V}^{-1}$ when the concentration of hydrochloric acid is increased successively. The corresponding dielectric constants are found to increase from 29.0 to 33.9, 41.8, 45.6 and 52.2, respectively.

Direct anodization of tantalum was also carried out in all the mixed solutions. It is found, though the maximum film formation voltage is 365V in citric acid yet the films could be formed only upto 340, 320, 280 and 220V respectively in the respective mixed solutions containing chloride ions in increasing concentration. It appears that during the growth of tantalum oxide film in the presence

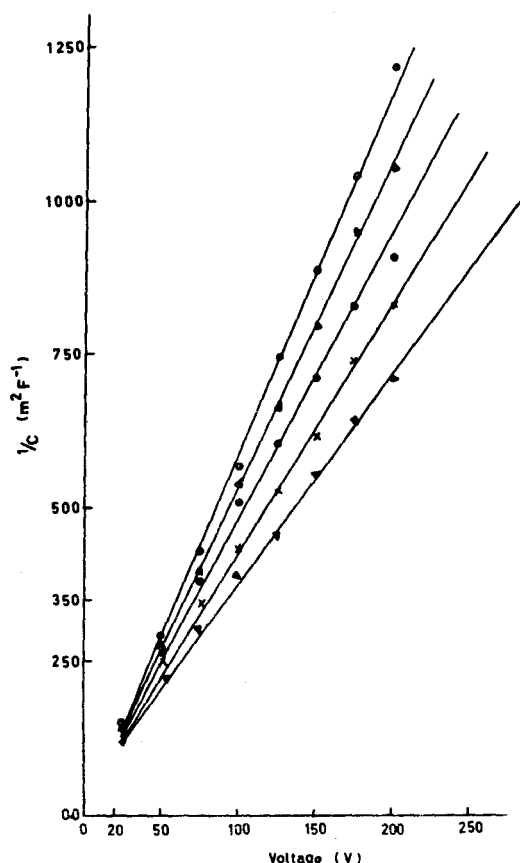


Fig. 4—Effect of chloride ion concentration on anodic oxide film growth on tantalum. [(\circ) 100 mol m^{-3} citric acid; mixed solution of hydrochloric acid and citric acid in the molar ratios of (\blacktriangle) 1:1200; (\bullet) 1:120 (\times) 1:12; (\triangle) 1:2.4].

of chloride ions tantalum metal combines with chloride ions giving an adsorbed film of tantalum chloride ($TaCl_5$) which then undergoes partial dissolution providing Ta^{+5} ions in solution. The released tantalum ions can combine with the chloride ions in the solution giving rise to a stable chloro-complex of tantalum (of the type $Ta_5Cl_a^{(a-5)-}$) which does not dissociates and thus prevents further participation of chloride ions in the anodic charge transfer. At higher chloride ion concentration, the chlorocomplex of tantalum is formed more efficiently, thereby inhibiting the growth of oxide film. A similar observation has been recorded earlier¹².

The rate of film dissolution was studied next by measuring the capacitance of a 50 V film (formed in 100 mol m^{-3} citric acid) in 5,400 and $10,800 \text{ mol m}^{-3}$ aqueous hydrofluoric acid solutions at various intervals of time (t) and the plots of $1/C$ per m^2 versus t are shown in Fig. 5. The film dissolves more readily in $10,800 \text{ mol m}^{-3}$ than in $5,400 \text{ mol m}^{-3}$ HF; for instance, the time periods required to dissolve half of the film in $10,800$ and $5,400 \text{ mol m}^{-3}$ HF are 205 and 275 sec., respectively. The rate of dissolution is very fast upto a stage when half the film dissolves and thereafter it slows down. Similar trends in the rate of dissolution are found for a 100 V film (Fig. 5), and since this film has larger thickness, it requires larger time to reduce to half its original thickness. It is most likely that when Ta_2O_5 film is put in concentrated hydrofluoric acid, a surface layer of tanta-

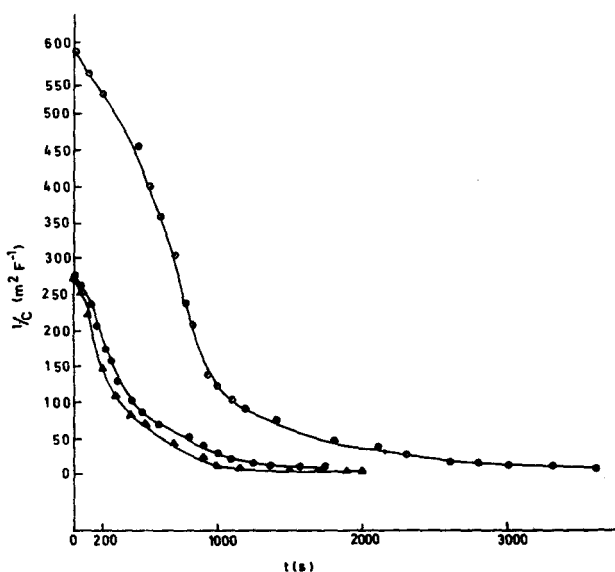


Fig. 5—Rate of dissolution of anodically formed film on tantalum in hydrofluoric acid. [(\circ) 100V in 5400 mol m^{-3} hydrofluoric acid; (\bullet) 50V in 5400 mol m^{-3} hydrofluoric acid; and (\triangle) 50V in 10800 mol m^{-3} hydrofluoric acid].

lum fluoride (TaF_5) is formed which dissolved completely in conc HF and hence causes dissolution of the film.

Ion mobility studies

The specimens I and II were anodized at film formation voltages of 30, 40 and 50V in 100 mol m^{-3} citric acid at a current density of 30 A m^{-2} and their capacitances before sealing were measured and found to be 1.92, 1.44, 1.15 (for specimen I) and 1.14, 0.85, $0.68 \text{ F} \times 10^{-6}$ (for specimen II) at the above film formation voltages respectively. In the combined assembly the capacitance of both specimens I and II are the same ($0.57, 0.43, 0.34 \times 10^{-6} \text{ F}$ at 30, 40 and 50V respectively) and the values are in proportion to their reduced areas of $1 \times 10^{-4} \text{ m}^2$, and the assembly acts as one unit (area $1 \times 10^{-4} \text{ m}^2$). The tag of the specimen I in each of the paired assembly was connected to the positive terminal of the constant current generator and the specimen II which was earlier anodized upto 30, 40 and 50V paired assemblies was further anodized upto 60, 70 and 80V, respectively. The capacitances of these paired systems were again measured taking samples I and II in the circuit respectively. The capacitances of specimens I and II were again found to be the same ($0.30, 0.26$ and $0.22 \times 10^{-6} \text{ F}$ at 60, 70 and 80V respectively) and this ensured complete sealing of I and II and no possibility of the electrolyte creeping through the oxide. The magnitudes of capacitances were further reduced due to further formation of the film. The assemblies were dismantled by dissolving lacomite in acetone and washing with conductivity water. The capacitances of separated specimens I and II were measured as also those of the outer and inner surfaces of both the specimens after applying lacomite to the other side. The capacitances of the specimen I after separation ($1.90, 1.42, 1.17 \times 10^{-6} \text{ F}$ at 30, 40 and 50V, respectively) and before sealing were identical indicating that specimen-I remained unaffected. The capacitances per m^2 for both the inner and outer surfaces of the specimen-I were 0.56, 0.42 and $0.35 \times 10^{-2} \text{ F m}^{-2}$ at film formation voltages of 30, 40 and 50V respectively while the corresponding values for the inner surface of the specimen-II were 0.57, 0.43 and $0.34 \times 10^{-2} \text{ F m}^{-2}$. The magnitudes of capacitance per m^2 for the specimen I compare well with those of the inner surface of the specimen-II. This implies that the sandwiched oxide film is not affected. Further anodization of the separated specimen-I increases the film formation voltage immediately and the film formation voltage attains the

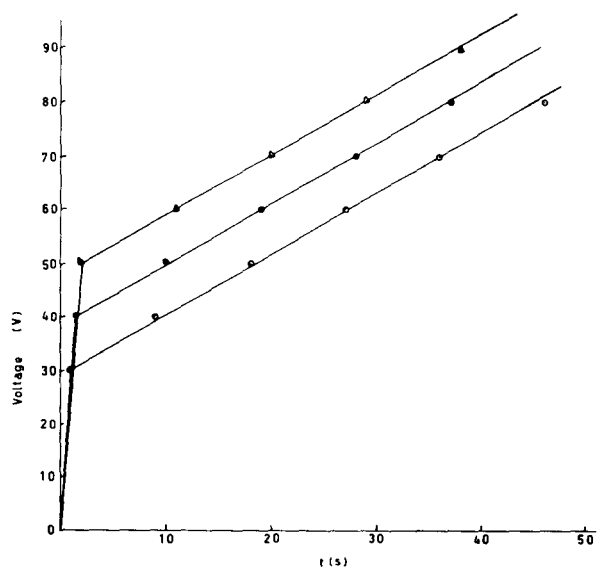


Fig. 6—Plot of variation of voltage of formation versus time of anodization for tantalum oxide films of various thicknesses [(○) 30V; (●) 40V; (△) 50V].

voltage of the film already present on it (Fig. 6). This shows that there is no possibility of oxygen ion moving through the electrolyte to specimen-I to produce layers inside the existing oxide layers. The normal rate of anodization compare well with the anodization rate during this experiment. This indicates that the field of Ta_2O_5 film between specimens I and II of this experiment remains unchanged and tantalum ions produced at specimen I are transported to specimen-II through the tantalum oxide (where the field is constant) and then to solution to produce fresh layer on the outer surface of the specimen-II. Thus it can be concluded that only tantalum ions are mobile during the growth of Ta_2O_5 film.

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