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Breakdown voltage and electronic current studies of tantalum–tantalum oxide electrolyte systems

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Breakdown voltages and electronic current data (at constant voltage) of anodic tantalum oxide films in contact with aqueous, as well as non-aqueous, electrolytes of varying concentrations and compositions have been obtained at 298 K. Both breakdown voltage and electronic current depend on electrolyte concentration, resistivity and composition. A linear relation between breakdown voltage and logarithm of electronic current has been observed. The effect of electrolyte concentration, composition and resistivity on breakdown voltage has been discussed in terms of the Ikonopisov electron injecting avalanche model of electrical breakdown. The values of the parameters for impact ionization coefficient (α) and primary electronic current (j_0) have been evaluated. The major factor contributing to the decrease in breakdown voltage with increasing electrolyte concentration is the increasing primary electronic current.

1. Introduction

During anodic polarization, there is a limit to the thickness of oxide films beyond which the film breaks down. The voltage at which this phenomenon occurs is referred to as the breakdown voltage. Such studies are of great importance because of their utility in capacitor technology. This subject has received attention but the results obtained and the views expressed are at variance [1–10]. Ikonopisov [2] proposed a theoretical model of electrical breakdown in which he assumed the occurrence of the injection of electrons onto the conduction band: the electrons were then accelerated by the anodization electric field causing avalanche multiplication. Albella and coworkers [1, 3, 4] have extended Ikonopisov's model to explain the details of breakdown phenomena. Since these models are based on injection of electrons, or electrons in the form of anions, into the oxide film, it envisages an important role for the electronic current. 'How is breakdown voltage related to electronic current?' and 'How are both breakdown voltage and electronic current affected by the concentration and composition of electrolytes?' These questions formed the determining objectives for the present study.

2. Experimental details

Square tantalum specimens ($2 \times 10^{-4}\,m^2$) in area and 0.25 mm thick) with short tags were cut from tantalum sheet (99.9% purity) and the edges of these samples were made smooth by abrading with a fine emery paper. The surfaces of the samples were cleaned by dipping them in molten KOH and the chemical polishing of the specimens was done in a mixture of concentrated sulphuric, nitric and hydrofluoric acids in the ratio of 5 : 2 : 2, respectively, for 3–5 s. The samples, after washing, were placed in boiling water for about 10 min to remove any remaining impurities from the surface of the sample. The specimen, thus prepared, was placed in a glass cell and was surrounded by platinum gauze which served as a cathode. Anodic polarization of the sample up to a desired formation voltage was carried out at a constant current density ($100\,A\,m^{-2}$) in electrolyte solutions (250 ml) using an electronically operated constant generator. Anodization was performed in aqueous solutions of formic acid (HCOOH) and butyric acid (C_3H_7COOH) in deionized water (electrolyte conductivity = $0.5 \times 10^{-4}\,\Omega^{-1}\,m^{-1}$); and in solutions of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) in a solvent which was prepared by mixing formic acid and ethyl alcohol in the ratio of 2 : 1. Breakdown voltage values (breakdown voltage, V_B = cell voltage *minus* the voltage drop across the electrolyte at the first visible spark) were obtained in the respective electrolyte solutions. The appearance of 'first spark' was the criterion employed for identifying the breakdown voltage: this identifying decision was found to give good reproducibility and sensitivity. For measuring electronic current, the anodization of Ta was carried out at a constant current density in an electrolyte solution of known concentration until the cell voltage was slightly greater (~ 10 V) than 300 V in the case of aqueous formic acid and butyric acid and 200 V in the case of non-aqueous ammonium dihydrogen phosphate solutions. The voltage was maintained constant at 300 V (200 V in case of non-aqueous solution) and readings from a potentiostat (as well as a microammeter) were noted. A slow decrease in the magnitude of current, which ultimately reached a constant value after about 1 h, was noted. This constant value is referred to as the 'electronic current'. Then, after decreasing the voltage by 20 V and holding it constant, the procedure for

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Table 1. Values of the constants of dependence of electrolyte concentration and resistivity on breakdown voltage and electronic current

Contacting electrolyte	*Constants of resistivity-electronic current dependence*		*Constants of electrolyte concentration-breakdown voltage dependence*		*Constants of resistivity-breakdown voltage dependence*	
	Log (a_e) ($A m^{-2}$)	b_e	a_c (V)	b_c (V)	a_B (V)	b_B (V)
Aqueous formic acid	0.743	0.507	697.5	125.0	225.2	245.7
Aqueous butyric acid	0.919	0.358	610.0	112.5	12.8	253.6
Non-aqueous ammonium dihydrogen phosphate	0.586	0.511	507.1	119.6	200.3	233.3

noting the electronic current was repeated as described above. Similarly, the electronic currents were measured at other constant voltages and in other electrolyte solutions. Each experimental observation was repeated four times taking a fresh electrolyte solution each time. The thicknesses of the films were calculated using the Faraday law and the field strengths were calculated using the thickness values and corresponding voltage to formation. The tantalum oxide density was taken as 7930 $kg\,m^{-3}$ as reported by Young [14]. The conductance of the electrolyte solutions were measuring using a digital conductivity bridge. The chemicals used were of Aldrich. All data refer to an ambiant temperature of 298 ± 0.5 K.

3. Results

Breakdown voltages, V_B, obtained at varying concentrations of aqueous formic and butyric acids and non-aqueous ammonium dihydrogen phosphate solutions are shown in Fig. 1. The breakdown voltage decreases with increasing electrolyte concentration and varies linearly with logarithm of reciprocal concentration. Thus the effect of electrolyte concentration on breakdown voltage can be represented by

$$V_B = a_c + b_c \log (1/C) \qquad (1)$$

where a_c and b_c are constants whose values are reported in Table 1. The low values of V_B obtained for high electrolyte concentration possessing low resistivity suggest a direct relation between breakdown voltage and electrolyte resistivity (ρ). The effect of concentration on V_B was checked more directly by measuring the resistivities of solutions. The plots of breakdown voltage and logarithm of electrolyte resistivity are linear (Fig. 2) and their relation can be represented as

$$V_B = a_B + b_B \log \rho \qquad (2)$$

where a_B and b_B are constants whose values are also given in Table 1.

The results of electronic current (at constant temperature and field strength) through Ta_2O_5 films in contact with varying concentrations of the electrolytes show that the magnitude of the electronic current (j_e) increases with electrolyte concentration and for the same concentration, electronic current varies with the composition of the electrolyte (Fig. 3). The variations in the magnitude of electronic currents with electrolyte

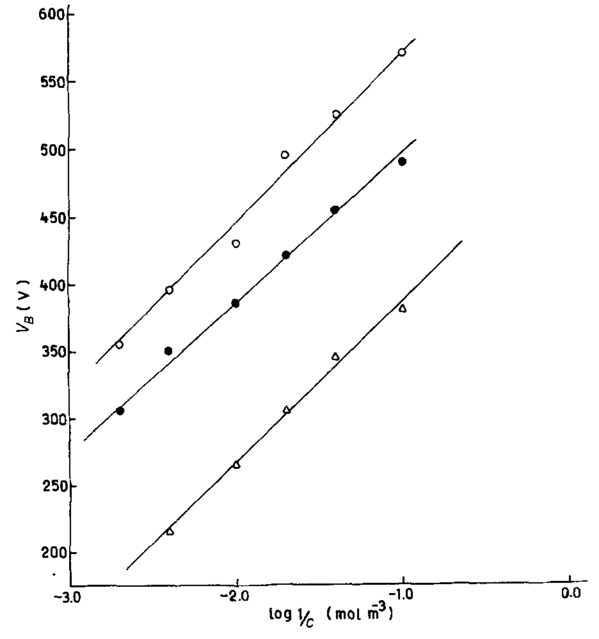

Fig. 1. Plot of breakdown voltage (V_B) against logarithm of reciprocal of electrolyte concentration. Key: (○) Aqueous formic acid; (●) aqueous butyric acid; (△) non-aqueous ammonium dihydrogen phosphate.

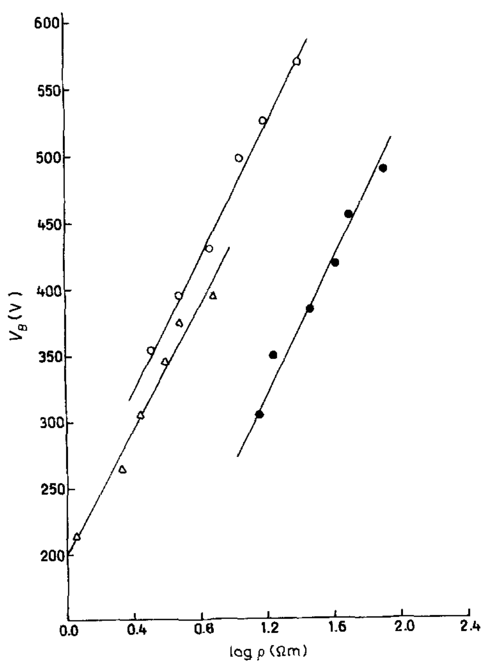

Fig. 2. Effect of electrolytic resistivity on breakdown voltage (V_B against log ρ). Key as in Fig. 1.

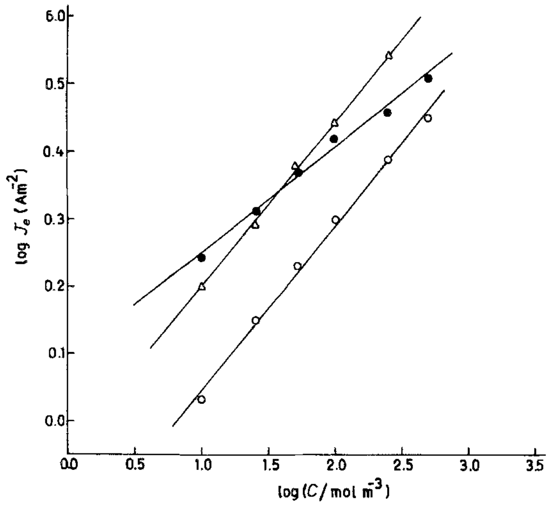

Fig. 3. Effect of electrolyte concentration on electronic current (log j_e against log C). Key as in Fig. 1.

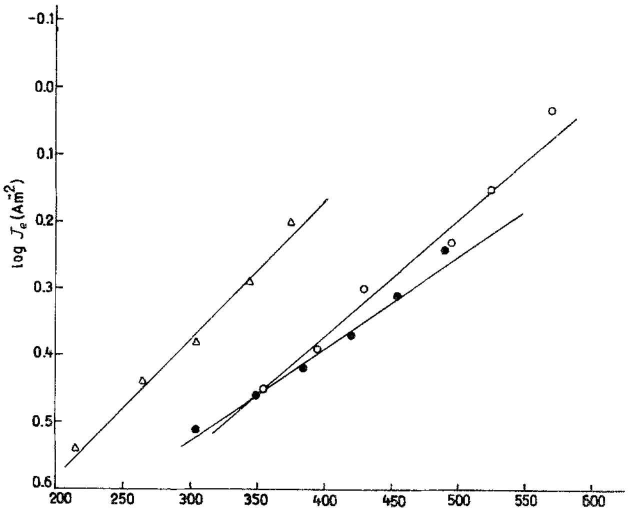

Fig. 5. Relation between electronic current and breakdown voltage. Key as in Fig. 1.

concentration and composition may be due to the variations in the values of the resistivities. The plots of log j_e against ρ are found to be linear (Fig. 4) and the relation between electronic current and electrolytic resistivity is

$$\log j_e = \log a_e + b_e \log \rho \qquad (3)$$

where a_e and b_e are constants and are given in Table 1. The dependence of breakdown voltage (V_B) on electronic current is indicated by the linear plots of log j_e versus V_B (Fig. 5). This suggests a strong correlation between the electronic current and the breakdown phenomenon. The electronic current density (j_0), injected into the conduction band of the oxide film from the electrolyte/oxide interface, increases exponentially according to an avalanche process [1–4]. Therefore, the electronic current density at the anode should be given by

$$j_e = j_0 \, e^{\alpha d} \qquad (4)$$

where α is the impact ionization coefficient and d is the distance travelled by the primary electrons on their way to the anode. As a first approximation it may be assumed that d is equal to the total oxide thickness and, during anodization at constant current, the oxide thickness increases linearly with the voltage, i.e. $d = \beta V$, where β is the anodization constant and is equal to the reciprocal of the field, i.e., $1/E$.

Substituting for d in Equation 4, then

$$j_e = j_0 \, e^{\alpha\beta V} \qquad (5)$$

and, from Equation 5

$$\alpha = \frac{1}{\beta V} 2.303 \log (j_e/j_0) \qquad (6)$$

or

$$\alpha = \frac{2.303E}{V} \log (j_e/j_0) \qquad (7)$$

Knowing the field (E), the primary electronic current (j_0) and the electronic current at a particular constant voltage (j_e), the impact ionization coefficient can be evaluated from Equation 7. Values for j_0 were obtained from the intercepts of the linear plots of log j_e against

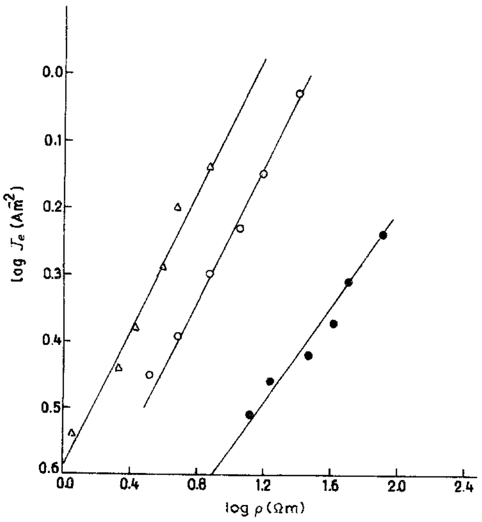

Fig. 4. Variation of electronic current (log j_e) with logarithm of electrolytic resistivity (log ρ). Key as in Fig. 1.

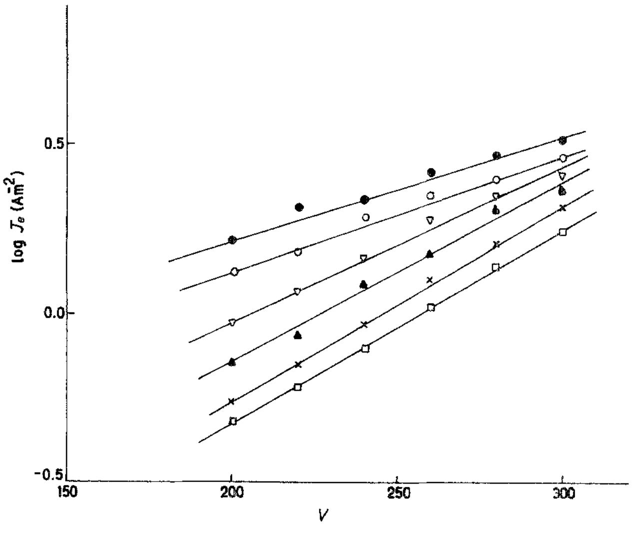

Fig. 6. Plot of logarithm of electronic current (log j_e) against Voltage (V) at different concentrations in aqueous butyric acid. Key: (□) 10, (x) 25, (▲) 50, (▽) 100, (○) 250, and (●) 500 mol m^{-3}.

*Table 2. Parameters of electrical breakdown of tantalum oxide films in varying concentrations of different electrolytes**

Electrolyte concentration ($mol\,m^{-3}$)	Impact ionization coefficient (α) ($\times 10^{-4}\,cm^{-1}$)	Primary electronic current (j_0) ($A\,m^{-2}$)	Breakdown voltage (V_B) (V)	Electrolytic resistivity (ρ) ($\Omega\,m$)
Aqueous formic acid				
10	8.02	0.003	570	25.16
25	6.96	0.008	525	15.62
50	6.83	0.011	495	11.18
100	4.97	0.049	430	7.25
250	4.82	0.068	395	4.77
500	3.95	0.149	355	3.23
Aqueous butyric acid				
10	5.98	0.036	490	81.61
25	6.18	0.038	455	50.33
50	5.62	0.062	420	41.17
100	4.87	0.113	385	29.22
250	3.54	0.292	350	17.42
500	3.17	0.417	305	14.38
Non aqueous ammonium dihydrogen phosphate				
1	12.18	0.011	395	7.55
10	7.25	0.088	380	4.76
25	6.13	0.170	345	3.94
50	6.24	0.199	305	2.74
100	5.20	0.348	265	2.16
250	4.99	0.474	215	1.11

* Oxidation current density: $100\,A\,m^{-2}$.

V. Such plots for only one electrolyte (butyric acid) are shown in Fig. 6. The primary electronic currents were found to depend both on electrolyte concentration and composition and, for a particular electrolyte, increase with increasing electrolyte concentration (Table 2). The value of impact ionization coefficients were calculated at all the concentrations and the results are presented in Table 2.

4. Discussion

As shown above, breakdown voltage depends on electrolyte resistivity and the relevant relation is given in Equation 2. Ikonopisov [2] derived such a relation from his theoretical model of electrical breakdown. In the Ikonopisov model of avalanche breakdown an electronic current is injected from the electrolyte to the oxide conduction band. The high field strength there accelerates the injected electrons to an energy which is sufficient to free other (secondary) electrons by impact ionization so that an avalanche multiplication can occur which causes electrical breakdown when a certain critical current is reached. In the Ikonopisov theoretical equation, the constants a_B and b_B (at constant temperature, composition, concentration and current density) are given by

$$\begin{aligned} a_B &= \frac{\varepsilon_m}{re}(\log j_B - \log a_e) \\ b_B &= \frac{2.303}{re}\varepsilon_m b_e \end{aligned} \tag{8}$$

where ε_m is the energy which is sufficient to free other electrons by impact ionization, r is the recombination length, e is the electronic charge, j_B is the value of the electronic current at a thickness sufficient for oxide destruction, and a_e and b_e are the constants of the dependence of electronic current on resistivity. The constants ε_m and r are specific only for the anodized metal and the quantity b_e characterizes the injection of electrons from the electrolyte into the oxide film. From Equation 8 we get

$$\frac{b_B}{b_e} = \frac{2.303\varepsilon_m}{re} \tag{9}$$

The constant b_e determines the injection of electrons from the electrolyte into the oxide. Since ε_m (a threshold energy for the impact ionization), and r (a recombination length) are specific only for the anodized metal, thus b_B/b_e = constant. Thus, since the experiments were carried out at constant temperature and current density, then the ratio of b_B/b_e is constant for any two electrolytes. This ratio was determined and the values for aqueous formic acid, butyric acid and non-aqueous ammonium dihydrogen phosphate solutions were found to be 485, 708 and 457, respectively. The order of the values is reasonably constant which shows that the effect of electrolyte concentration (resistivity) on the breakdown voltage can be explained satisfactorily in terms of Ikonopisov's electron injecting model.

According to Albella and coworkers [1], it is possible to make an estimation of the variation of breakdown voltage with the electrolyte concentration and composition if it is assumed that the breakdown appears when the avalanche current j_0 reaches a certain fraction Z of the total anodization current, j_1. Under these conditions the breakdown voltage satisfies the equation

$$j_0 \exp(\alpha\beta V_B) = Zj_1 \tag{10}$$

or

$$V_B = \frac{2.303E}{\alpha} \log (Zj_1/j_0) \quad (11)$$

If α decreases with increasing electrolyte concentration, it will mean an increased V_B at high electrolyte concentration. However, the experimental values showed a decrease with increasing electrolyte concentration. Therefore, α is not a major factor contributing towards change in the breakdown voltage value with increase in the electrolyte concentration; it is the increase in primary electronic current (j_0) which is a major factor contributing towards the decrease of V_B with increase in the electrolyte concentration. Further, at a particular concentration, aqueous formic acid, which has a lower primary electronic current than butyric acid, is associated with a higher breakdown voltage, thus emphasizing the role of the primary electronic current in explaining the effect of composition on breakdown voltage.

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