

Galvanostatic Breakdown Voltages of Anodic Oxide Films Formed on Tantalum in Aqueous Electrolytes

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Received 11 April 1986; accepted 24 July 1986

The breakdown voltage (V_B) is found to be independent of current density used for film formation, field strength, topography of the specimen and pH of the electrolyte solution. However, it depends upon the nature of the electrolyte, concentration of the solution and temperature employed. Only anions of the electrolyte influence the V_B . It appears that during anodic polarisation the electrons from the anions of the electrolyte get injected into the conduction bands of the film. Due to high field strength the electrons acquire very high energy and cause release of secondary electrons, resulting in the multiplication of avalanches and hence breaking the film. Of the various methods of identifying V_B , the appearance of sparking is found to be a superior method.

The anodic oxide film on a valve metal can be formed upto a certain maximum value of voltage designated as breakdown voltage (V_B) beyond which sparking appears and the film breaks down¹⁻⁹. The appearance of visible sparking¹, slowing down of voltage², attainment of maximum voltage³, occurrence of audible cracking⁴ and rapid voltage fluctuation⁵ have been variously used by different workers to identify V_B . Burger and Young⁶ reported that the electrical break down was triggered by conduction through electrolyte-filled fissures and flaws in the oxide film. Yahalom and Hoar⁷ suggested that the breakdown resulted by the incorporating of ions into the film from the electrolyte. Alwitt and Vijn⁵ expressed the view that the breakdown was controlled by the electrochemical reactions at the electrolyte/oxide interface and also depended on the solid state properties of the oxides. Ikonopisov⁸ suggested a theoretical model to explain breakdown.

It appears that the results obtained and the mechanisms suggested for electrical breakdown are at variance. There is no uniform criterion for identifying breakdown voltage (V_B). Further, the behaviour of V_B in the presence of an electrolyte is different from that in the presence of a dry dielectric⁹. This is of value in the capacitor technology and other anodization phenomena. These observations suggest the imperative need for further research in this area and hence the title investigation.

Materials and Methods

Samples of tantalum (99.9% purity) of $2 \times 10^{-4} \text{m}^2$ area were prepared as described in an earlier communication¹⁰. The experimental set-up and the procedure for anodic polarization have been reported elsewhere¹⁰. The voltage at which sparking appeared was

taken as the breakdown voltage (V_B). All the chemicals used were of AR (BDH) grade. The solutions were prepared in conductivity water and their electrolytic resistivities were measured using a digital conductivity meter, type NDC 732 (Naina Electronics, India).

Results and Discussion

The plots of voltage at which the oxide film on tantalum was formed versus the time for which anodic polarization was carried out in 0.1 mol dm^{-3} aqueous oxalic acid solution at varying current densities (5, 10, 50, 100, 500, 1000 Am^{-2}) and 298 K are shown in Fig. 1. At low current densities (5 and 10 Am^{-2}), increase in the charge passed increases the voltage of formation upto a certain value (maximum value) thereafter any further increase in charge does not lead

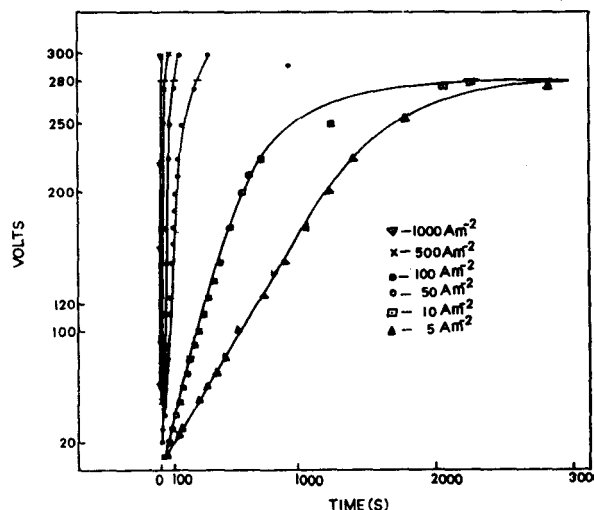


Fig. 1—Variation of voltage of formation with time at 298 K at different current densities

to change in voltage of formation. This maximum voltage³ has been used as one of the criteria to measure V_B . However, at higher current densities no such maximum voltage is reached at least in the vicinity of reported breakdown values. Hence this criterion cannot be accepted as a measure of V_B . Slowing down of voltage which is also one of the criteria² to measure V_B , has not been found useful because the rate of slowing down (dV/dt) decreases as the current density increases and ultimately it reaches almost a zero value (as indicated by the curvature in the plot) in the region of voltage of interest. Further, at each current density sparking occurred. The voltages at which sparking occurred are shown on each curve in Fig. 1 by a horizontal line. Since the appearance of sparking occurred at all current densities in the same region and further at low current densities (5 and 10 Am^{-2}) the sparking voltages were close to the maximum voltage, the appearance of sparking was taken as a measure of V_B . Audible cracking⁴ occurred at current densities $> 10 \text{ Am}^{-2}$ and was not easily detectable at low current densities. Rapid voltage fluctuation was only occasionally observed. Gas evolution preceded sparking but at low current densities gas evolution took place for a very long time before sparking started. Hence at low current densities gas evolution is also not better than sparking as a criterion for identifying V_B . The order of sequence of events which took place during the process of breakdown is summarised as under:

At low current densities
(5 and 10 Am^{-2})

Slowing down of voltage; reaching of maximum voltage; gas evolution staying for a longer period and sparking.

At moderate current densities
(50 and 100 Am^{-2})

Slowing down with much less rate; gas evolution staying for a smaller period; sparking and audible cracking.

At high current densities
(500 and 1000 Am^{-2})

Gas evolution instantaneously leading to sparking; audible cracking.

The plots of breakdown voltage (V_B) versus current density for 0.1 mol dm^{-3} aqueous solutions of oxalic, citric, tartaric and acetic acids are shown in Fig. 2. The linear plots (Fig. 2) with zero slopes indicate non-dependence of V_B on current density. However, the values of V_B are not constant for various electrolytes used. The results of breakdown voltages obtained at varying concentrations of aqueous oxalic, citric and acetic acids are shown in Fig. 3. In each case V_B shows a linear decrease with increase in electrolyte concentration upto 0.1 mol dm^{-3} . Thereafter, with further

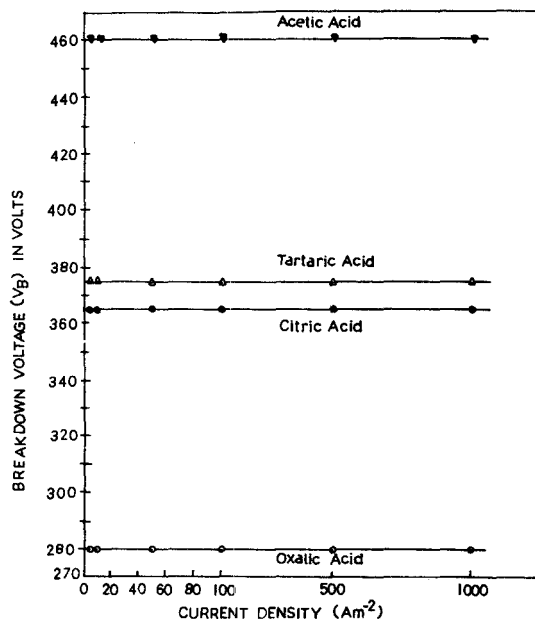


Fig. 2—Plot of breakdown voltage (V_B) versus current density at 298 K.

(Scale along abscissa—From 0 - 100 Am^{-2} ; $1 \text{ cm}^2 = 20 \text{ Am}^{-2}$.
From 100 - 1000 Am^{-2} , $1 \text{ cm}^2 = 100 \text{ Am}^{-2}$)

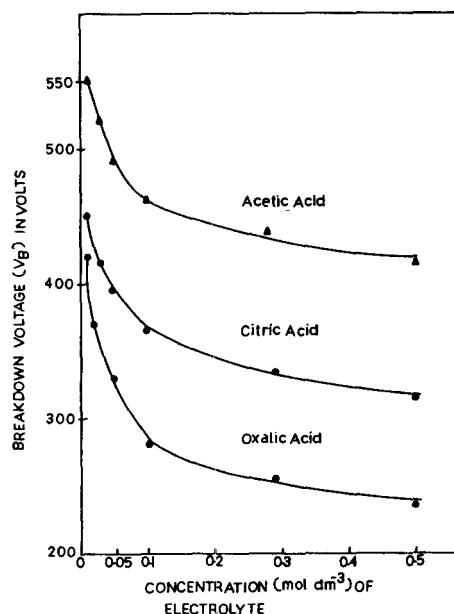
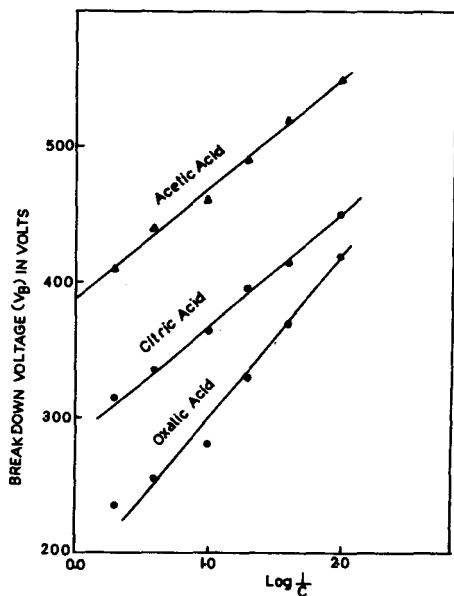


Fig. 3—Plot of breakdown voltage (V_B) versus electrolyte concentration in aqueous medium

increase in electrolyte concentration only small decrease in the values of V_B is obtained and it tends to acquire a certain minimum value. These observations point to an exponential decrease of V_B with increase in electrolyte concentration and, therefore, to check it further the values of V_B were plotted against $\log[\text{electrolyte}]^{-1}$ (Fig. 4). Linear plots in Fig. 4 confirm this conclusion and hence the effect of concentration of


 Fig. 4—Plot of breakdown voltage (V_B) versus $\log [\text{electrolyte}]^{-1}$

electrolyte on breakdown voltage can be represented by an equation of the form (1)

$$V_B = (V_B)_m + n \log 1/c \quad \dots (1)$$

$(V_B)_m$ is the minimum value of breakdown voltage which will be obtained when $\log 1/c = 0$, i.e. $c = 1 \text{ mol dm}^{-3}$ and n is a constant with a positive value. The intercepts of plots in Fig. 4 gave the values of $(V_B)_m$ for acetic, citric and oxalic acids as 386, 282, and 228 V respectively. The corresponding values of n from the slopes of these curves were 82, 84 and 125 respectively. At high electrolyte concentrations large number of ions are available per unit concentration and hence the electrolyte possesses large electrolytic conductivity but low resistivity. The low values of breakdown voltages obtained at high electrolyte concentrations (possessing low resistivities) suggest a direct relation between V_B and resistivity.

The effect of electrolytic resistivity (ρ) on V_B was checked more directly by measuring the resistivities of aqueous solutions. It was found that V_B did not vary linearly with ρ . However, when the values of V_B were plotted against $\log (\rho)$, linear plots were obtained and hence a relation between V_B and ρ can be represented by Eq. (2).

$$V_B = a + b \log \rho \quad \dots (2)$$

where a and b are constants with positive sign. The values of a for acetic, citric and oxalic acids were obtained from the intercepts of the linear plots (V_B versus $\log \rho$), as 246, 278 and 332 V respectively. The corresponding values of b were found to be 187, 171 and 169 respectively.

 Table 1—Experimental Values of Breakdown Voltage (V_B), Electrolytic Resistivity and pH for Various Aqueous Electrolyte Solutions

Electrolyte	V_B (V)	Electrolytic resistivity (Ωm)	pH
0.1 mol dm^{-3} at 298 K			
Oxalic acid	280	0.49	1.38
Citric acid	365	3.25	2.17
Acetic acid	460	16.57	2.89
Tartaric acid	375	2.64	2.10
Sodium oxalate	290	0.65	7.20
Sodium citrate	240	0.62	8.04
Sodium acetate	310	2.13	7.36
0.05 mol dm^{-3}			
Oxalic acid at 298 K	330	0.91	1.55
Oxalic acid at 338 K	300	0.62	—
0.5 mol dm^{-3}			
Oxalic acid at 298 K	235	0.27	0.87
Oxalic acid at 338 K	225	0.19	—

Since pH is an important property of acid solutions, it was considered worthwhile to check the effect of varying pH on V_B . The plot of V_B versus pH for aqueous oxalic acid solutions was linear. However, the value of V_B in the presence of sodium oxalate which has a very high pH came out to be close to that in oxalic acid. Thus though the pH value changed from 1.38 (for oxalic acid) to 7.2 (for sodium oxalate) there was only a small change (from 280 to 290 V) in V_B values. This strongly indicates that V_B is independent of the pH of the solution. This was further confirmed from the V_B values in aqueous solutions of acetic and citric acids and their sodium salts (Table 1).

The V_B values were also obtained at two different temperatures (298 and 338 K) for two different concentrations (0.05 and 0.5 mol dm^{-3}) of oxalic acid, and the values are reported in Table 1. The values of V_B decreased only slightly with the increase in temperature and the decrease in the value of V_B was more at lower electrolyte concentration (0.05 mol dm^{-3}). The decrease in V_B value with increase in temperature was due to decrease in electrolytic resistivity at higher temperature. A relatively larger decrease at low electrolyte concentration was due to large decrease in the resistivity (Table 1).

The effect of field strength on V_B was studied. The values of field strength at 298 K (current density 50 Am^{-2}) for 0.1 mol dm^{-3} oxalic and citric acids were found to be 6.46×10^8 and $6.36 \times 10^8 \text{ Vm}^{-1}$, respectively. The corresponding values of V_B were 280 and 365 V. This clearly showed non-dependence of field strength on V_B . Further, though the values of field strength at 298 K for oxalic acid at current densities 5,

10, 50 and 100 Am^{-2} were 5.77, 5.98, 6.46 and $6.68 \times 10^8 \text{Vm}^{-1}$, respectively the values of V_B did not change as the current density increased. This again confirmed non-dependence of field on V_B , atleast in the range of present study.

Ten samples of tantalum with varying degrees of topography were prepared and the breakdown voltages in 0.1 mol dm^{-3} aqueous solution of oxalic acid measured. It was found that V_B did not change with the change in topography of the specimen. Since the samples with varying topography would have varying degrees of flaws and fissures and since V_B is independent of the topography, the suggestion⁶ that V_B is triggered by conduction through fissures and flaws cannot be accepted.

The V_B values in 0.1 mol dm^{-3} solutions of oxalic acid and its sodium salt were found to be 280 and 290, respectively (Table 1). This showed that only anions affected V_B . However, the values of V_B for citric and acetic acids decreased from 365 to 240 and from 460 to 310 V respectively when their sodium salts were used (Table 1). The decrease in V_B values was not due to the change of cations but due to the decrease in the values of resistivity when the acids were changed into their sodium salts, e.g. in the case of citric acid the value of resistivity decreased from 3.25 to 0.62 while the corresponding value for acetic acid decreased from 16.57 to 2.13 Ωm . Using the values of resistivity of sodium oxalate, sodium citrate and sodium acetate, the V_B values were computed from the linear plots of V_B versus $\log \rho$ and the values obtained were 296, 244 and 305 V respectively. These computed values are very close to the experimental values of V_B in the pres-

ence of sodium oxalate (290 V), sodium citrate (240 V) and sodium acetate (310 V). Hence it may be concluded that only anions (and not the cations) influence the V_B value.

It appears that the breakdown voltage results because of the conduction of avalanching in the bulk of anodic film. During anodic polarization the anions of the electrolytes provide electrons which are injected into the conduction bands of the film. Due to high field strength the electrons acquire very high energy and cause release of secondary electrons by impact ionization, resulting in the multiplication of avalanches and breaking of the film. This view is close to the view expressed earlier⁸.

Acknowledgement

One of the authors (PK) thanks the CSIR, New Delhi for the award of a junior research fellowship.

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