Breakdown Characteristics and Electronic Current Studies of Ta-Ta$_2$O$_5$-Electrolyte Systems.

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Abstract

Breakdown Characteristics and Electronic current data of tantalum oxide thin films in different electrolytes of various concentration and compositions have been studied . The effects of electrolyte concenteration, composition, Field Strength , temperature of bath and resistivity of the electrolyte have been discussed. A linear relation between breakdown voltage and logarithm of electronic current has been observed . The relation between electronic current and field strength is found to be same irrespective of film thickness of tantalum oxide film. The major factor contributing to te decrease in breakdown voltage with increasing electrolyte concentration is the increasing primary electronic current . The effect of electrolyte concentration, composition and resistivity on breakdown voltage has been discussed in terms of lkonoposov's electron injecting avalanche breakdown model of electrical breakdown. It has been found that with increase in temperature breakdown voltage decreases for same electrolyte concentration whereas it is independent of current density, field strength and topography of the specimen. It has been observed that during anodic oxidation the high field strength accelerates the electrons to an energy which is sufficient to free other electrons by impact ionization resulting in the multiplication of the avalanches and breaking the film at a critical voltage.

Introduction

The anodic oxide film on tantalum can be formed upto a maximum thickness beyond which the film breaksdown at a certain voltage designated as breakdown voltage. The breakdown voltages have been studied on different valve metals but the results obtained by different workers are at variance . This may be due to variation in the surface condition of different valve metals. The electrolyte concentration has a significant effect or the breakdown voltage value as this has been attributed to the resisitivity of the electrolyte solution. Since the mechanisms suggested to explain the breakdown phenomenon involve injection of electrons into the oxide film from the electrolyte, the role of electronic current needs to be examined more critically. A systematic study of the effect of electrolyte concentration , composition , resistivity and temperature of the bath on breakdown voltage and electronic current has been made due to its importance in capacitor technology.

Materials & Methods

Tantalum samples of 2 sq. cm area and with short tags were cut from tantalum sheets(99.9% purity) and the edges of the specimens were smoothened by abrading with a fine emery paper . The tantalum specimens were then dipped in KOH melt to clean the surfaces and finally washed with distilled water .The chemical polishing of these specimens was done by dipping ina freshly prepared etching mixture of 98% H_2SO_4 + 70% HNO_3 + 48% HF (5:2:2, V/V) for 3-5 s and the washed with distilled water. These specimens were then placed in boiling water for about 10 minutes to remove any remaining impurities from the surface of the specimens of tantalum. The tags of the specimens were covered with a thick anodic film in an electrolyte at which further anodisation on square portion of the specimen was to be carried out. The specimen thus prepared was placed in a glass cell and was connected to a platinum electrode which served as a cathode during anodic oxidation of tantalum . Anodic polarization of the specimens in different electrolytes was carried out at constant current adjusted through an electronically operated contant current generator. The supply of current was cut off by an electric control after the desired voltage of film formation is reached . The breakdown voltage studies were carried out in aqueous solution of sodium citrate , sodium oxalate and sodium chloride. The time for the passage of current for film formation through success interval voltages was recorded by electronic stop watch. Electronic current measurements at constant voltages through these films in various electrolytes of different concentrations were made. The field Strength was calculated by dividing the voltage at which the electronic current was measured by thickness of the film calculated using Faraday's law. The aqueous solutions were made with conductivity water and the electrolytic resistivities were measured using a digital conductivity bridge.

Results and Discussion

The anodic oxide films were grown on tantalum specimens in varying concentrations of aqueous solutions of sodium citrate , sodium oxalate and sodium chloride at 298 K. It is found that the films can be formed upto a certain maximum value of voltage beyond which any further increase in charge do not lead to change in the formation voltage . Hence there is a limit to film formation beyond which the film breaks down designated as breakdown voltage. Various criteria to identify electrical breakdown voltage were examined. These were i) Reaching of maximum voltage ii) The voltage at which gas evolution takes place iii) slowing down of voltage iv) The voltage at which audible cracking occurs. v) The voltage at which rapid fluctuation in voltage starts vi) The voltage at which sparking appears. It has been observed that at low current densities (5.0 and 10. Am^2) increase in the charge passed increases the voltage of formation upto a certain maximum value thereafter any further increase in charge doesn't lead to change in voltage of formation. Reaching of maximum voltage has been used as one of the criteria to measure breakdown voltage. However , at higher current densities no such maximum voltage is reached. Hence this criterion of identifying

breakdown voltage was not accepted. Rapid Voltage fluctuation was only occasionally observed . Gas evolution precede sparking but a low current densities gas evolution took place for a very long time before sparking starts. Hence at low current densities gas evolution is also not suitable criteria for identifying breakdown voltage. Slowing down of voltage which is also one of the criteria measure breakdown voltage has not been found useful beacuase the rate of slowing down decreases as the current density increase and ultimately it reaches almost a zero value in the region of voltage of interest. Audible cracking occurred at higher current densities and is not easily detectable at low current densities. Out of these various criteria of identifying breakdown voltage appearance of sparking was observed at all the current densities. Therefore, this criteria of appearance of sparking of identifying breakdown voltage was taken in all the electrolytes.

It has been observed that the values of the breakdown volatages are not constant for different electrolytes used and it is independent of current density at which the films are formed. Breakdown voltage (V_B) is found to decrease with the increase in electrolyte concentration and the linear plots between breakdown voltage at logarithms of concentration (fig.1) confirm this conclusion and hence the effect of concentration of electrolyte of electrical breakdown voltage can be represented by an equation of the form

$$V_B = (V_B)_M + n \log 1/c$$

where $(V_B)_M$ is the minimum value of breakdown voltage which will be obtained when log 1/c=0 i.e. c=1 mol dm^{-3} and n is a constant with a positive value. The values of 'n' calculated from the slopes of plots in Fig.1 were found to be 315.61 , 175.88 and 125.63 for aqueous solution of sodium citrate , sodium oxalate and sodium chloride, respectively and the corresponding values of intercepts of these curves gave the values $(V_B)_M$ as 435,310 and 255 V,respectively. At high electrolyte concentration large number of ions were available per unit concentration and hence the electrolyte possesses large electrolytic conductivity but low resistivity. The effect of electrolytic resistivity (ρ) on breakdown voltage was checked more directly by measuring the resistivities of electrolyte solution. It has been found that the values of breakdown voltage are low at high concentration of various electrolytes.The Breakdown voltage doesn't vary linearly eith resistivity of the electrolyte solution. However, the plots between breakdown voltage (V_B) and log (ρ) (Fig.2) are found to be linear and hence a direct relation between (V_B) and log (ρ) can be represented by

$$V_B = a + b \log (\rho)$$

Where a and b are constants with positive sign.

The values of contants 'a' and 'b' for sodium oxalate , sodium chloride and sodium citrate were calculated from the intercepts and slopes of the linear plots between breakdown voltage and log ρ (Fig.2) . The effect of field strength on breakdown voltage was studied . The values of field strength at 298 K at current density of 100Am^{-2} for 100 molm^{-3} aqueous solutions of sodium oxalate , sodium

chloride and sodium citrate were found to be 5.94,5.78 and 5.83 . 10^8 Vm^{-1} , respectively. The corresponding values of breakdown voltage were 310, 255 and 340 V .which suggests that breakdown voltage is independent of field strength. The effect of temperature on breakdown voltage was studied and it was found the breakdown voltage decrease slightly with the increase in temperature and the effect was more at lower electrolyte concentration . It is further observed that breakdown voltage is not affected by pH of the solution and it is also independent of the topography of the specimen.

An electron avalanche model can be proposed for explaining electrical breakdown voltage. According to this model the breakdown voltage results due to the conduction of avalanching in the bulk of the anodic film . During anodic polarization the anions of the electrolytes provide electrons which get injected into the conduction bands of the oxide film. Due to high field strength the electrons acquire very high energy which causes release of secondary electrons by impact ionization which results in the multiplication of avalanches and breaking of the film at a certain critical voltage. It has been observed that the electronic current (i_e) known as primary electronic current is injected from the electrolyte to the oxide conduction band. The high field strength accelerates these injected electrons to an energy which us sufficient to free other(Secondary) electrons by impact ionization so that an avalanche multiplication occurs which causes electrical breakdown when a certain critical current is reached . Therefore, the Breakdown voltage is related to electrical current and plots between log i_e versus V show that magnitude of electronic current increase with increase in electrolyte concentration. For the same concentration electronic current is found to vary with the composition of electrolyte. The variation of magnitude of electronic current may be due to variation in the electrolyte resistivities. The plots between logarithm of electronic current and electrolytic resistivity were found to be linear which shows that the dependence of electronic current on electrolyte concentration is due to the difference in the electrolyte resistivity. The relation between electronic current and electrolyte resistivity can be represented by

Log i_e = log a_e +b_e log ρ

Where a_e and b_e are constants of dependence of electronic current on resistivity. The plots between logirthm of electronic current and breakdown voltage were also found to be linear which suggests strong relation between the electronic current and breakdown voltage.
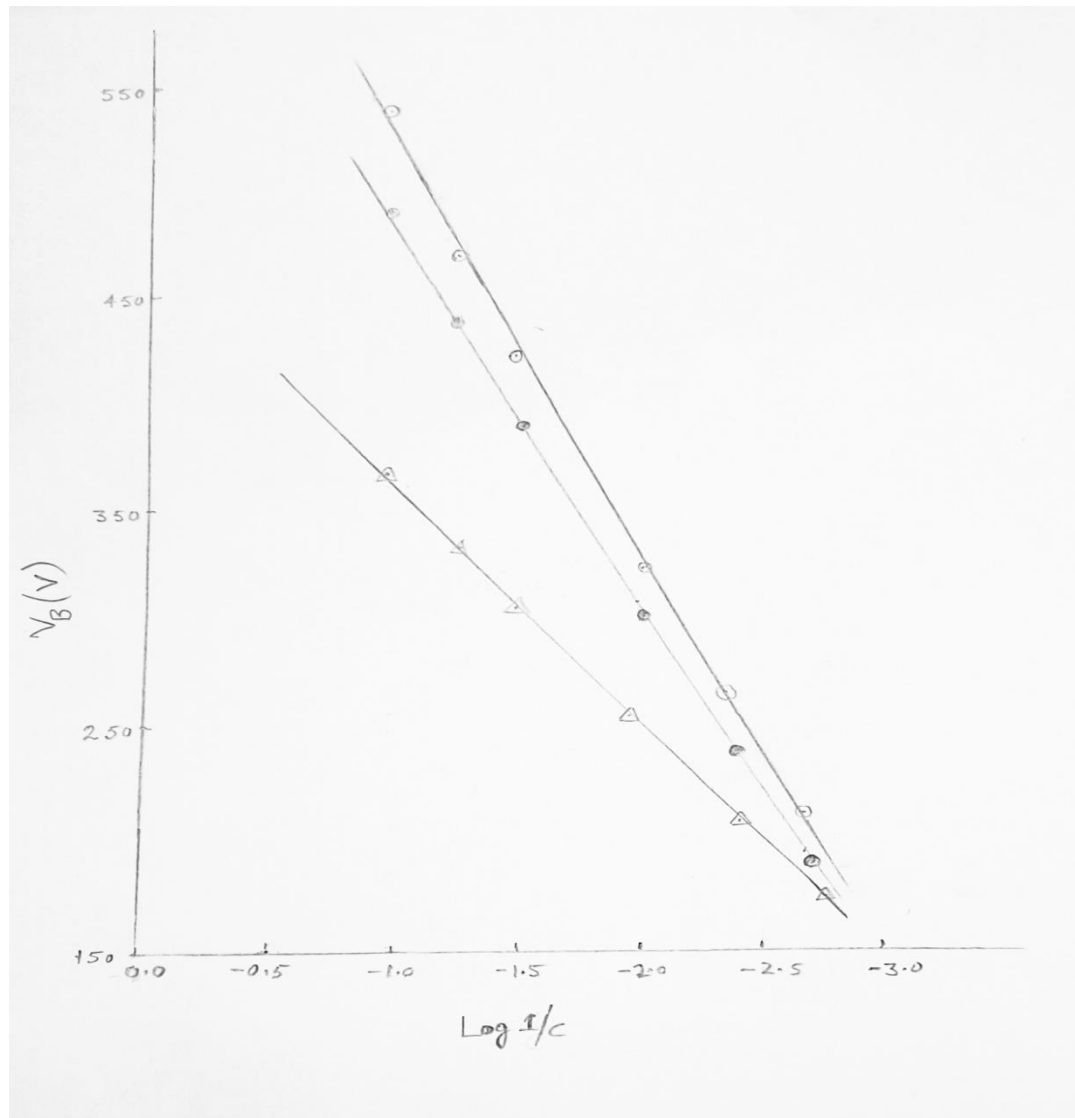
Acknowledgement:

TABLE-1

Values of breakdown voltage (V_B) and electrolytic resisitivity of different electrolytes:-

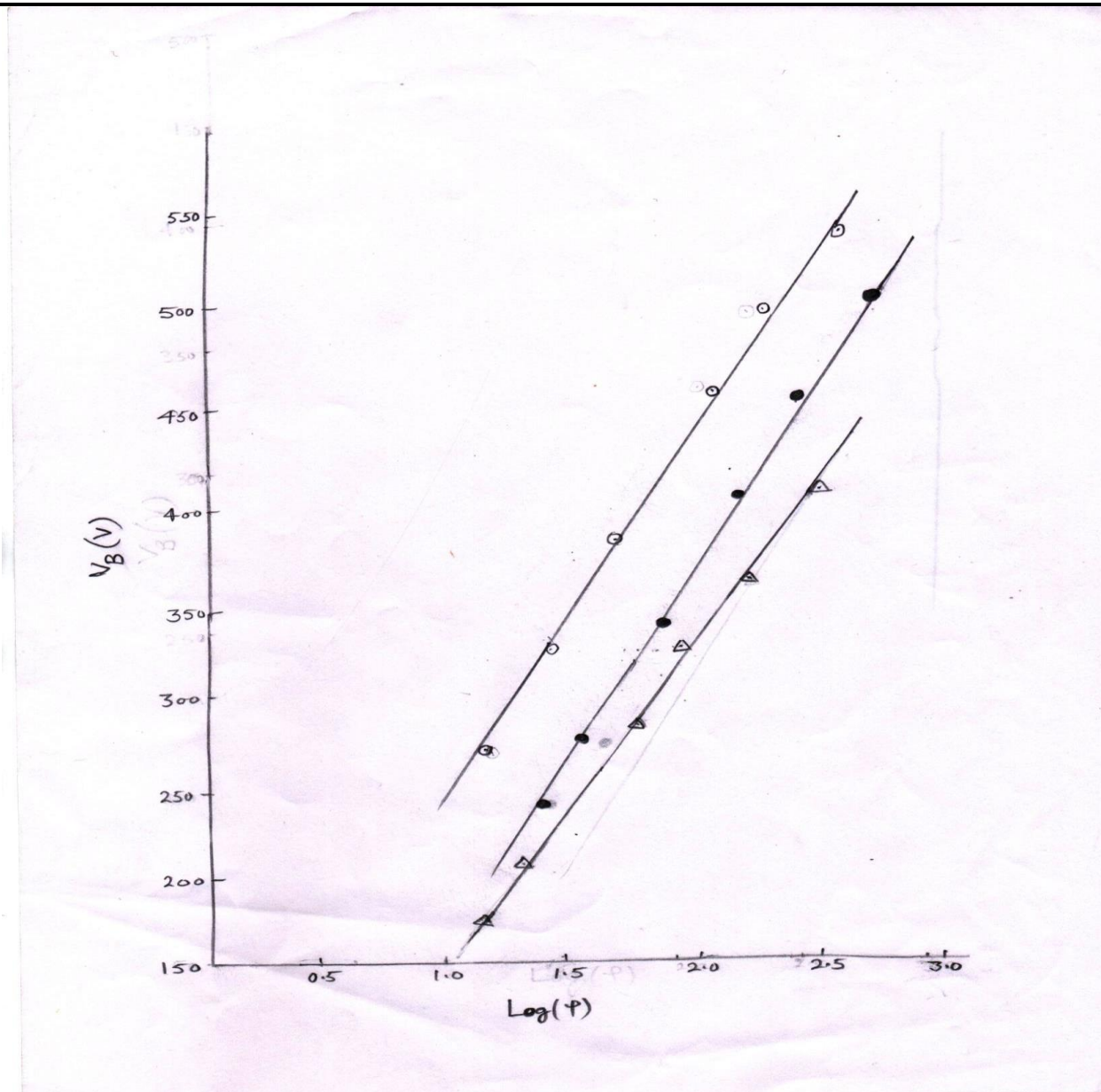| Concentration (mol m^{-3})	Sodium oxalate		Sodium Chloride		Sodium Citrate	
	Breakdown voltage (V)	Electrolytic resistivity (ΩM)	Breakdown voltage (V)	Electrolytic resistivity (ΩM)	Breakdown voltage (V)	Electrolytic resistivity (ΩM)
10	505	526.32	365	135.14	540	476.19
25	440	411.56	340	79.46	475	208.33
50	395	294.12	315	35.71	435	120.48
100	310	66.67	255	11.36	340	71.42
250	240	45.45	205	6.71	270	41.67
500	185	25.64	170	3.23	205	23.26

$(\triangle)$ Sodium Chloride $(\odot)$ Sodium Citrate

$(\bullet)$ Sodium oxalate

Fig.1 – Plot of Breakdown voltage (V_B) Versus log electrolyte [Concentration]$^{-1}$

(△) Sodium Chloride   (☉) Sodium Citrate

(●) Sodium oxalate

Fig.2 – Plot of Breakdown voltage (V_B) Versus electrolytic resistivity

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