# Breakdown Voltage and Electronic Current Studies of Anodic Aluminium Oxide Films In Aqueous Electrolytes

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### Abstract

*Electrical breakdown and electronic current data of aluminium oxide films in various electrolytes of different concentrations and compositions have been obtained. The above studies have also been made as a function of field strength and current density at which the oxide filmsare formed. Breakdown voltage and electronic current depend on electrolyte concentration, nature of the electrolyte, composition, temperature and resistivity of the solution. However, it is independent of current density used for film formation, film strength, topography of the specimen. The effect of the electrolyte concentration, composition and resistivity on breakdown voltage has been explained in terms of Ikonopisov's electron injecting avalanche breakdown model. Breakdown voltage is affected only anions of the electrolyte. It is found that during anodic polarisation, the electrons from the anions of the electrolyte get injected into the conduction bands of the oxide films which increases with the concentration of the electrolyte. These incorporated anions result in the formation of traps. The electrons are thermally excited continuously from the traps into the conduction band and electronic equilibrium is maintained by the continuous injection of the electrons from the electrolytes. 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 of the film when a critical voltage is reached. The major factor contributing to the decrease in breakdown voltage with increasing in electrolyte concentration is its increase in primary electronic current. The exact model of electrical breakdown voltage during anodic oxidation of aluminium has been made.It has been found that of the various methods for identifying breakdown voltage, the attainment of maximum voltage is chosen as a criterion for identifying breakdown voltage in aluminium oxide films.*

## I. Introduction

During anodic oxidation of valve metals there is a limit to thickness of the oxide film beyond which the film breaks down. The voltage at which the oxide film reaches this critical thickness is referred to as the electrical breakdown voltage. It is observed that the results obtained and the mechanisms suggested for electrical breakdown are at variance. There is no uniform criterion for identifying breakdown voltage. The behaviour of breakdown voltage in the presence of aqueous electrolytes is different from that in the presence of dry electric. A systematic study of the effect of electrolyte concentration, composition and resistivity on the breakdown voltage has been carried out. Relationship between electronic current and breakdown voltage has been observed. Such studies are of great importance because of their utility in capacitor technology and other anodization phenomenon. These observations suggest the imperative need for further research in this area.

## II. Materials and Methods

Specimens of aluminium (99.9% purity) of $2 \times 10^{-4} m^2$ area were cut from a sheet of aluminium and the edges of the specimens were abraded with fine emery paper to make them smooth. The surfaces of these specimens were cleaned by dipping them in 10% NaOH solution for 2-3 s and then washed with distilled water. The chemical polishing of the specimens was done by dipping in a freshly prepared etching mixture of O-phosphoric acid, sulphuric acid and nitric acid in the ratio of 70:25:5 at a temperature of 350-360 K for 2-4 sec followed by washing in distilled water and drying in a current of hot air. The final etching was done just before anodization. The tags of the specimen was covered with a thick anodic film in an electrolyte in which anodization has to be carried out. The specimen thus prepared was placed in a glass cell and connected with a platinum electrode which served as a cathode. The specimen of aluminium was anodized at constant current in different electrolyte solutions. The current source used was an electronically controlled power supply unit which can cut off current supply after the desired voltage of film formation was reached. The time for the passage of current for forming film through successive intervals of voltage was recorded by a timer. A constant voltage was set using a potentiostat and electronic current passed was measured. Of the various methods of identifying breakdown voltage, the attainment of maximum voltage was found to be a superior method. The solutions were prepared in conductivity water and there electrolytic resistivities were measured using a digital conductivity

meter. The thickness of the film formed in various electrolytes was determined using Faraday law. The density of the film was taken as 3565 $Kgm^{-3}$ as reported by Tajima[4]. Field strength was calculated using the value of thickness and corresponding formation voltage. All data refer to 298+- 0.5K unless otherwise stated.

### III.    Results and Discussion

The effect of electrolyte concentration on the rate of growth of aluminiumoxide films at a current density of 100 $Am^{-2}$ in varying aqueous solutions of Tri-sodium citrate, sodium tartrate and sodium oxalate was studied. It is observed that rate of film growth is uniform upto a certain maximum voltage of formation beyond which increase in charge has no effect on formation voltage. The attainment of maximum voltage was observed in all the electrolytes studied and results were reproducible. Appearance of sparking as in the case of tantalum oxide films was not found to be a suitable criterion. Therefore, attainment of maximum voltage was chosen as a criterion for identifying breakdown voltage ($V_B$) in aluminium oxide films. The results of breakdown voltage for anodic oxide films grown on aluminium in different concentrations of tri-sodium citrate, sodium tartrate and sodium oxalate are shown in Fig.1. Breakdown voltage decreases with increase in electrolyte concentration upto a certain concentration thereafter, for any increase in concentration there is very small decrease in breakdown voltage value and ultimately it tends to acquire a certain minimum value. These observations point to a exponential decrease of $V_B$ with increase in electrolyte concentration and therefore to further check it , the values of $V_B$ were plotted against log[concentration]$^{-1}$ (Fig.1). Linear plots in Fig.1 confirm this conclusion and hence the effect of concentration of electrolyte on $V_B$ can be represented by an equation (1)

$$V_{B=}(V_B)_M+ n \log 1/c \qquad (1)$$

Where $(V_B)_M$ is the minimum value of breakdown voltage which will be obtained when log 1/c = 0 that is C = 1 mol $dm^{-3}$ and n is constant with positive value. The values of $(V_B)_M$ can be calculated from the intercepts of plots in Fig.1 and corresponding values of 'n' from the slopes of these curves and were 132.89, 116.27 and 49.83 for tri-sodium citrate , sodium tartrate and sodium oxalate, respectively. At high concentrations, large number of ions are available per unit concentration and hence the electrolyte possess large electrolytic conductivity but low resistivity. The low values of $V_B$ obtained at high electrolyte concentration suggest a direct relation between breakdown voltage and resistivity. The effect of electrolytic resistivity ($\rho$) on breakdown voltage was studied by measuring the resistivities of aqueous solutions (Table-1) and it was found that breakdown voltage did not vary linearly with ($\rho$). However, when the values of $V_B$ were plotted against log ($\rho$), linear plots were obtained suggesting dependence of $V_B$ on electrolytic resistivity can also be represented by equation (2)

$$V_{B =} a + b \log (\rho) \qquad (2)$$

where a and b are constants. The values of 'a' fortri-sodium citrate, sodium tartrate and sodium oxalate were obtained from the intercepts of linear plots as 244, 192 and 171 V, respectively. The corresponding values of 'b' were found to be 235, 405 and 106, respectively. It was also observed that there is decrease in breakdown voltage with increase in temperature due to decrease in electrolytic resistivities with increase in temperature.Further ,studies of electronic current in different electrolyte concentrations were made and the result show that the magnitude of electronic current ($i_e$) increase with increase in electrolyte concentration (Fig.3). For the same concentration, $i_e$ is found to vary with composition of the electrolyte. The variation of magnitude of electronic current with concentration is due to the variation in their electrolyti c resitivities.The plots between logarithm ofelectronic current and electrolytic resistivityare found to be linear (fig.3).This clearly shows that dependence of electronic current on electrolyte concentration is due to the difference in the electrolytic resistivity.The relation between electronic current and electrolytic resistivity is given by an equation

logie =  log ae +be log($\rho$)     (3)

whereae and be are constants of dependence of electronic current on resistivity. The values of log aeand be   were determined from the intercepts and slopes of log ie versus log($\rho$) and are found to bedependent on electrolyte composition. The plots between logarithm of electronic current and breakdown voltage are also found to be linear which suggests co-relation between the elecroniccurrent and breakdown voltage.An electron avalanche model may be proposed for explaining electrical  breakdown.According to this model an electronic current (ie), known as primary electronic current  is injected from the electrolyte to the oxicde conduction band. 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 at a critical voltage.
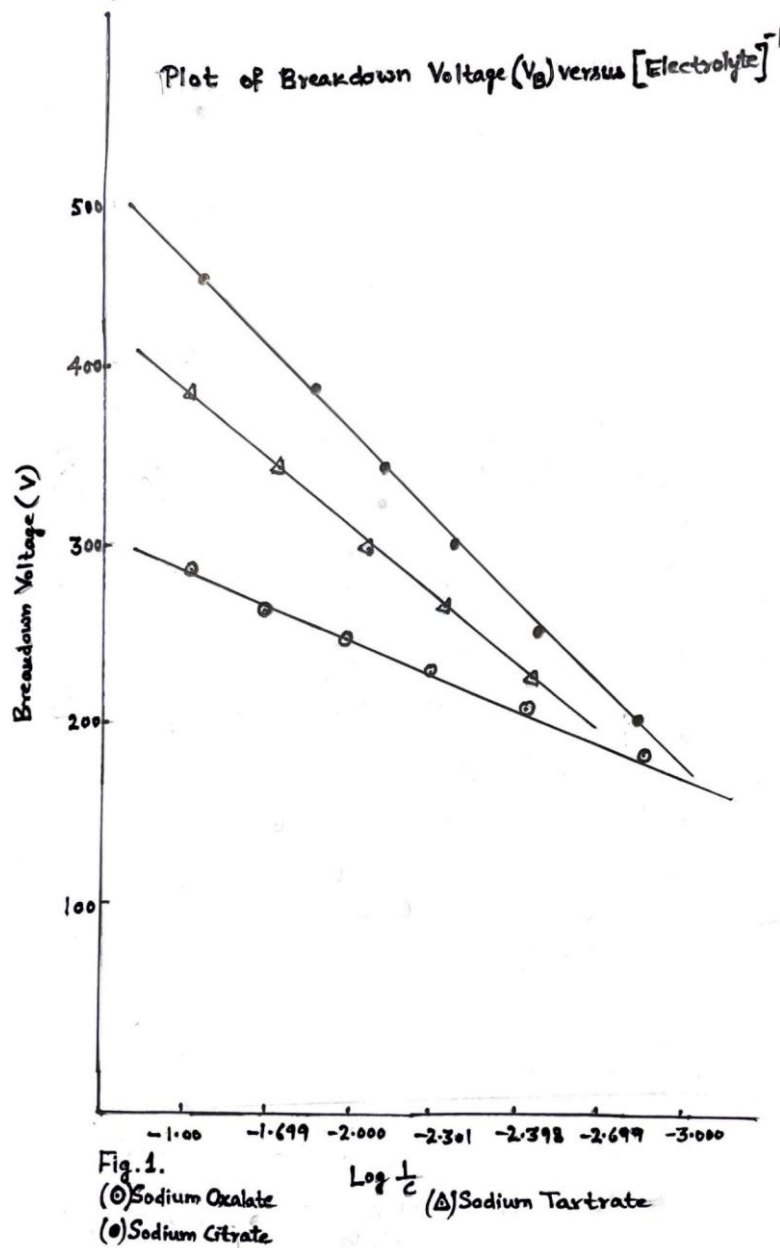
**Acknowledgement**

**TABLE-1**

Values of breakdown voltages ($V_B$) and electrolytic resistivity in varying concentration of different electrolytes

| Concentration (mol m⁻³) | Sodium Tartrate | | Sodium Oxalate | | Tri - Sodium Citrate | |
|---|---|---|---|---|---|---|
| | Breakdown voltage (V) | Electrolytic resistivity (ΩM) | Breakdown voltage (V) | Electrolytic resistivity (ΩM) | Breakdown voltage (V) | Electrolytic resistivity (ΩM) |
| 10 | 385 | 6.667 | 290 | 5.263 | 480 | 4.373 |
| 50 | 350 | 2.985 | 270 | 4.822 | 390 | 3.225 |
| 100 | 320 | 1.538 | 255 | 2.672 | 350 | 2.195 |
| 200 | 285 | 1.274 | 240 | 2.171 | 310 | 1.986 |
| 250 | 250 | 1.107 | 205 | 1.665 | 265 | 1.732 |
| 500 | 220 | 0.886 | 190 | 1.318 | 230 | 1.092 |



Plot of Breakdown Voltage ($V_B$) versus [Electrolyte]⁻¹

Fig.1.
(⊙)Sodium Oxalate
(●)Sodium Citrate
(Δ)Sodium Tartrate

Plot of Breakdown Voltage ($V_B$) versus electrolytic resistivity.

Fig.2.

(●) Sodium Citrate; (▲) Sodium Tartrate; (◉) Sodium Oxalate

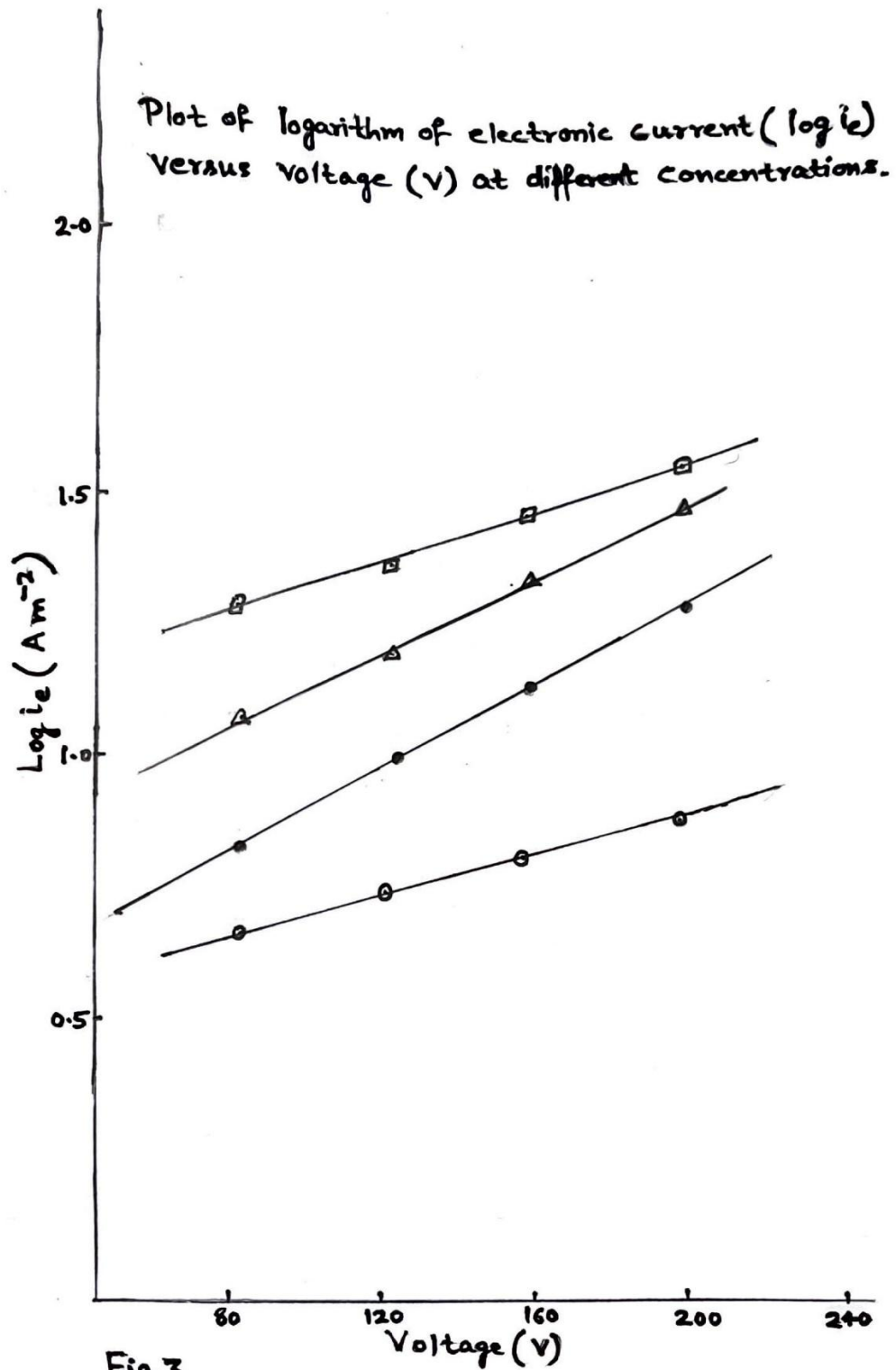Plot of logarithm of electronic current ( log $i_e$ ) versus voltage (v) at different concentrations.
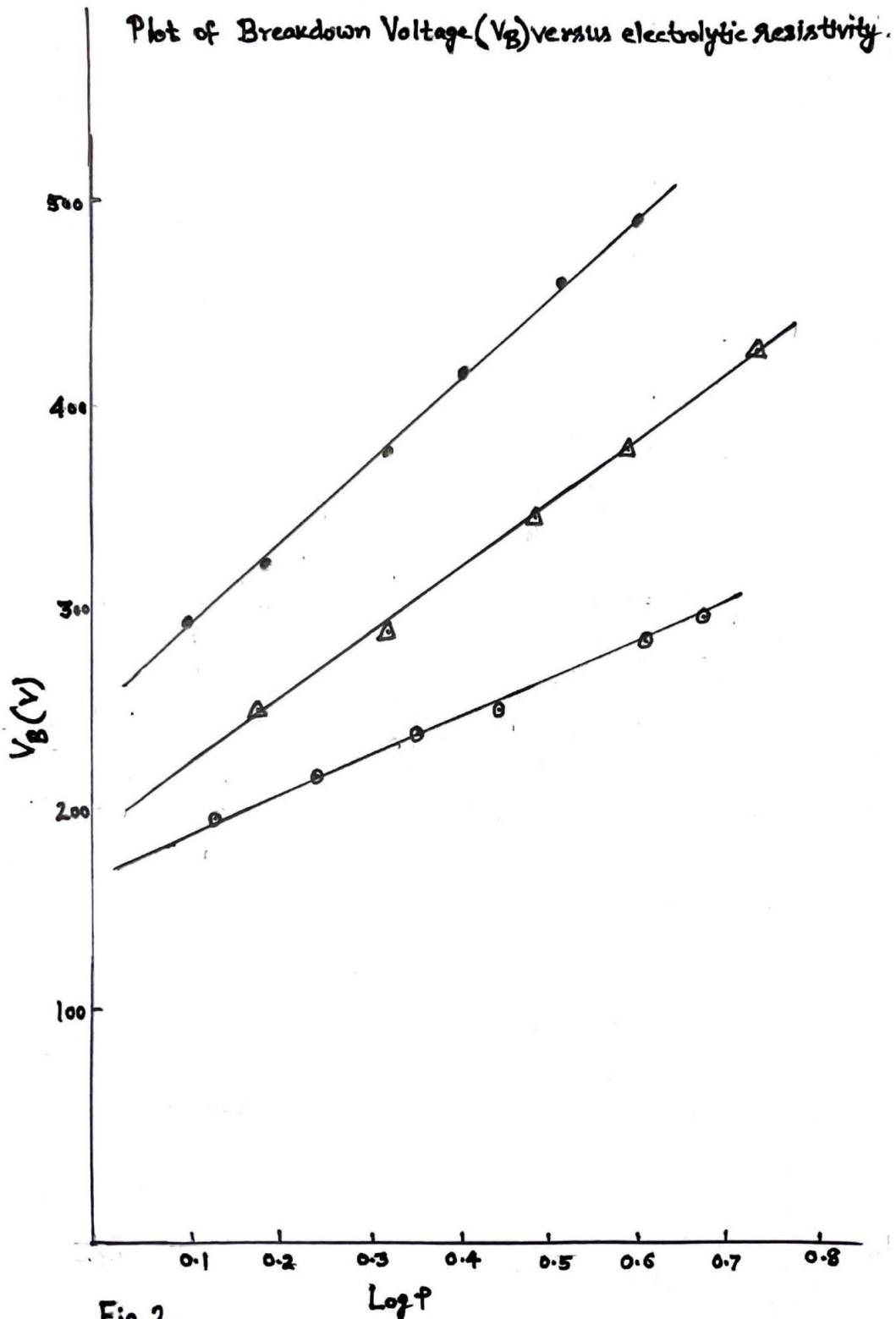
Fig.3.
[(⊙)100 mol m⁻³ ; (●)200 ; (△)300 ; (▣)400 ]

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