

Breakdown voltage and electronic current studies of aluminium-aluminium oxide-electrolyte systems

K C Kalra*, Parveen Katyal & Rakesh Bhardwaj

Department of Chemistry, Maharshi Dayanand University, Rohtak (Haryana) 124 001

Received 18 October 1989; revised 8 January 1990; rerevised and accepted 22 March 1990

Breakdown voltages and electronic current data (at constant voltage) of anodic aluminium oxide films in contact with different aqueous electrolytes of varying concentrations and compositions have been obtained at 298K. 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 Ikonopisov electron injecting avalanche model of electrical breakdown [*Electrochim Acta*, 22 (1977) 1077]. The major factor contributing to the decrease in breakdown voltage with increasing electrolyte concentration is the increasing primary electronic current. Breakdown voltage decreases with increase in temperature. Addition of ferrous ions to the electrolyte decreases the breakdown voltage, the effect being pronounced at higher concentrations.

During anodic polarization, there is a limit to the thickness of the oxide film beyond which the film breaks down. The voltage at which this phenomenon occurs is referred to as the breakdown voltage. The breakdown voltages have been studied in the case of aluminium and other valve metals, but the results obtained by different workers are at variance¹⁻⁸. This may be due to variation in surface conditions in different investigations. Moreover, a systematic study of the effect of electrolyte concentration, composition, resistivity and temperature of the bath on breakdown voltage has not been carried out so far. Such studies are of great importance because of their utility in capacitor technology. This prompted us to take up the title investigation.

Materials and Methods

Aluminium specimens ($2 \times 10^{-4} \text{m}^2$ in area) with short tags were cut from a sheet of aluminium (99.9% purity). The edges of the specimens were polished with emery paper to make them smooth. The specimens were dipped in 10% NaOH solution for 2-3 sec and then washed with distilled water to clean the surface. The chemical polishing of the specimens was done by dipping them in a freshly prepared etching mixture of concentrated ortho-phosphoric, sulphuric acid and nitric acids in the ratio of 70:25:5 at 350-360K for 2-4 sec. The samples were washed with distilled water and dried in a current of hot air. The final etching was

done just before anodization. The tags of the specimens were covered with a thick anodic film formed in 500 mol m^{-3} of the respective electrolyte. The specimens thus prepared were placed in glass cells and were surrounded by platinum gauzes which served as cathodes.

Anodic polarization of aluminium was carried out at constant current, adjusted through an electronically operated constant current generator (General Electronics, Ambala Cantt). The supply of current was cut-off by an electronic control after the desired voltage of film formation was reached. The time for the passage of current for the film formation at different voltages was recorded by an electronic timer ($\pm 0.01\text{s}$) (ECI, Hyderabad). The attainment of maximum voltage was chosen as a criterion for identifying breakdown voltage (V_B). During the process of anodization, the potential of the oxide electrode was measured with respect to platinum electrode. The potentials mentioned in the text are overpotentials. The contribution of the electrolytic resistance to the measured voltage was negligible. Electronic current measurements at constant voltages were made using a potentiostat. The thickness of the film was determined using Faraday's law. All the chemicals used were of AR(BDH) grade. The solutions were prepared in conductivity water and their electrolytic resistivities were measured using a conductivity meter (Naina Electronics, India). The density of the film was taken as 3565 Kg m^{-3} as reported by Tajima⁹.

Results and Discussion

The anodic oxide films were grown on aluminium samples at a current density of 100 A m^{-2} in varying concentrations of aqueous ortho-phosphoric acid, ammonium dihydrogen phosphate and sodium potassium tartrate at 298 K. The plots of voltage (V) at which the oxide films were formed against time (t) for which current was passed are shown in Fig. 1 for ortho-phosphoric acid system. Similar plots were obtained for other electrolytes as well. It was found that the films could be formed upto a certain maximum value of voltage beyond which any further increase in charge did not lead to change in the voltage of formation. Thus, there is a limit to film formation beyond which the film breaks down, i.e., a critical thickness of the oxide film is reached. The voltage at which this occurs is referred to as the breakdown voltage (V_B). The attainment of maximum voltage was chosen as a criterion for identifying breakdown voltage (V_B) in aluminium oxide films. The appearance of first spark, which was taken as a criterion¹⁰ for identifying breakdown in Ta_2O_5 film, was not found to be a suitable criterion in the present case as it was not uniformly observed in all the electrolytes. The results of the breakdown voltage for the anodic oxide films formed in 10, 50, 100, 250 and 500 mol m^{-3} (and in certain cases 1000 mol m^{-3}) aqueous solutions of ortho-phosphoric acid, ammonium dihydrogen phosphate and potassium sodium tartrate are shown in Fig. 2. The values of breakdown voltage show an appreciable decrease with increase in concentration of the electrolytes upto a certain concentration. Thereafter, for any increase in concentration there is only a very small decrease in breakdown value and ultimately it tends to acquire a certain minimum value. The plots between breakdown voltage and log of electrolyte concentration were found to be linear. Thus, the effect of electrolyte concentration on breakdown voltage can be represented by the equation.

$$V_B = a_c - b_c \log C \quad \dots (1)$$

where a_c and b_c are the constants of dependence of breakdown voltage on electrolyte concentration; the values of these constants are reported in Table 1. A high electrolyte concentration means high conductance or low electrolytic resistivity and since the values of V_B are low at high concentration this suggests a direct relationship between V_B and electrolytic resistivity (ρ). The data presented in Table 2 indicate that the relationship between V_B and ρ is not linear; however, V_B versus $\log \rho$

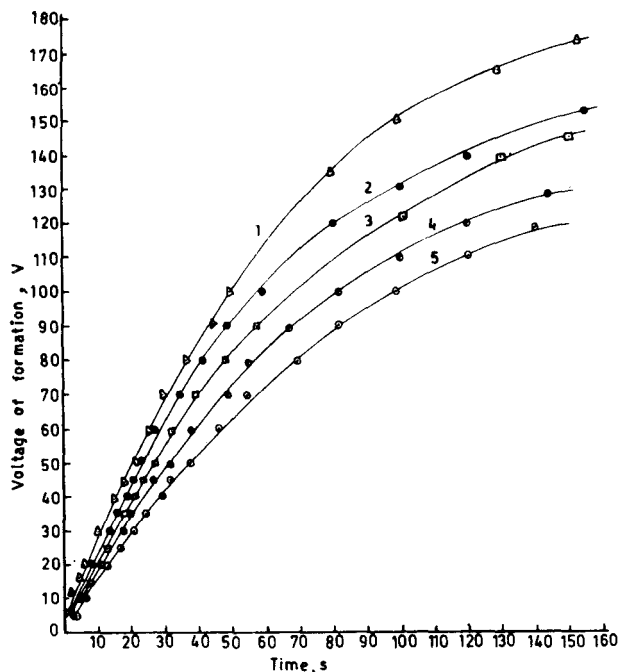


Fig. 1—Variation of voltage of formation with time at 298 K at different concentrations in aqueous ortho-phosphoric acid. [(1) 10 mol m^{-3} ; (2) 50; (3) 100; (4) 250; (5) 500]

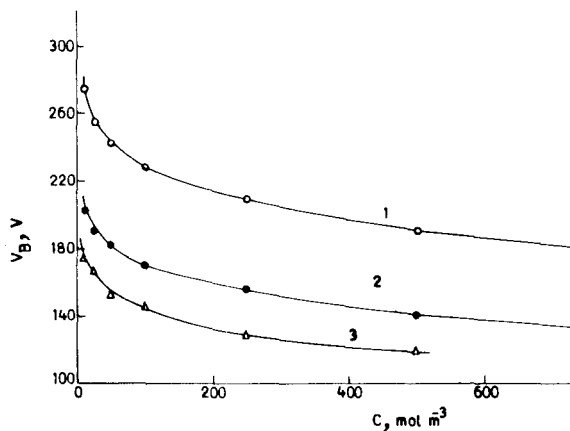


Fig. 2—Plot of breakdown voltage (V_B) versus electrolyte concentration in different aqueous electrolytes. [(1) potassium sodium tartrate; (2) ammonium dihydrogen phosphate; (3) ortho-phosphoric acid]

plots were found to be linear suggesting that the dependence of breakdown voltage on electrolytic resistivity can be represented by the equation,

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

where a_B and b_B are the constants of dependence of breakdown voltage on electrolytic resistivity.

The breakdown voltage data were obtained at three different temperatures 298, 323 and 348 K in 100 mol m^{-3} aqueous solution of ortho-phosphoric acid and ammonium dihydrogen phosphate

Table 1—Values of the dependence of electrolyte concentration and resistivity on breakdown voltage as well as electronic current

Contacting electrolyte	Electrolyte concentration-breakdown voltage dependence		Resistivity-breakdown voltage dependence		Resistivity-electronic current dependence	
	a_c (V)	b_c (V)	a_B (V)	b_B (V)	$\log(a_c)$ (A m ⁻²)	b_c
Ortho-phosphoric acid	217	37.50	139	48.5	1.390	0.900
Ammonium dihydrogen phosphate	242	36.92	159	50.0	-0.019	0.809
Potassium sodium tartrate	321	46.00	240	61.3	—	—

Table 2—Values of breakdown voltages and electrolytic resistivities in varying concentrations of different electrolytes

Electrolyte	Concentration (mol m ⁻³)	Electrolyte resistivity (Ω m)	Breakdown voltage (V)
Ortho-phosphoric acid at 298 K	10	5.682	175
	25	3.021	165
	50	1.972	153
	100	1.224	145
	250	0.647	128
	500	0.412	118
Ortho-phosphoric acid at 323K	100	0.906	83
Ortho-phosphoric acid at 348K	100	0.823	22
Ammonium dihydrogen phosphate at 298 K	10	12.500	205
	25	5.050	190
	50	2.840	181
	100	1.562	170
	250	0.696	156
	500	0.412	140
	1000	0.259	123
Ammonium dihydrogen phosphate at 323 K	100	0.566	140
Ammonium dihydrogen phosphate at 348 K	100	0.377	113
Potassium sodium tartrate at 298 K	10	4.545	275
	25	2.109	258
	50	1.105	243
	100	0.647	228
	250	0.335	210
	500	0.210	190
	1000	0.141	168
Potassium sodium tartrate at 323 K	100	0.476	215

(Table 2). These show a decrease in breakdown voltage with increase in temperature. This may be due to a decrease in resistivities (Table 2) with increase in temperature.

The effect of the presence of ferrous ions in the aqueous electrolyte solutions was studied by pre-

paring mixed solutions of $\text{FeSO}_4 + 200 \text{ mol m}^{-3} \text{H}_3\text{PO}_4$ in the ratio of 1:80, 1:40, 1:20 and 1:10. The breakdown voltages were found to be 132, 120, 90 and 43V respectively. The value of V_B in 200 mol m^{-3} ortho-phosphoric acid was 133 V. Thus, breakdown value decreases when ferrous

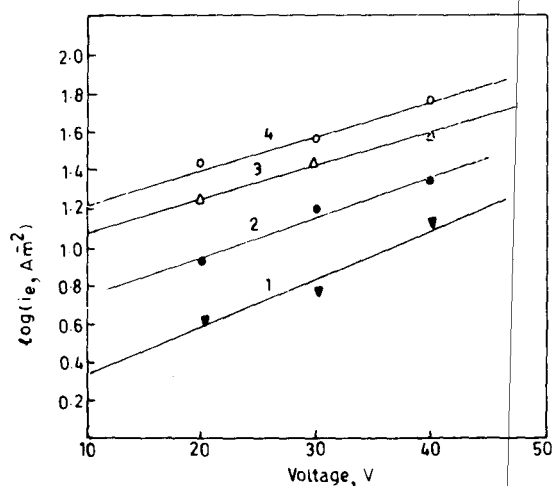


Fig. 3—Plot of logarithm of electronic current ($\log i_e$) versus voltage (V) at different concentrations in aqueous ortho-phosphoric acid. [(1) 50 mol m^{-3} ; (2) 100; (3) 250; (4) 500]

ions are added to ortho-phosphoric acid. The values of $\log \rho$ for these solutions were 0.118, 0.112, 0.100 and 0.082 Ωm showing that the linear relation of breakdown voltage and electrolytic resistivity fails in this case. These observations suggest that the structure of Al_2O_3 /electrolyte interface undergoes some changes in the presence of ferrous ions and hence affects the breakdown voltage.

Ikonopisov¹ proposed an electron avalanche model for explaining electrical breakdown. According to him, an electronic current (i_e), known as primary electronic current, is injected from the electrolyte to the oxide conduction band. The high field strength present there can accelerate these 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. Thus, breakdown voltage is related to electronic current, and hence electronic currents (i_e) through aluminium oxide films in contact with varying concentrations of aqueous ortho-phosphoric acid at constant voltage (V) were measured.

The plots of $\log i_e$ versus V are shown in Fig. 3. The results show that the magnitude of electronic current increases with increase in electrolyte concentration. For the same electrolyte concentration, electronic current is found to vary with the composition of electrolyte. Electrolyte concentration is related to electrolytic resistivity and for the same concentration of the electrolyte, the electrolyte resistivity is a function of electrolyte composition. The variation of magnitude of electronic current may be due to variation in their electrolyte resistivities.

The plots between logarithm of electronic current and electrolytic resistivity were found to be linear. This clearly 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 is given by

$$\log i_e = \log a_e + b_e \log \rho \quad \dots (3)$$

where a_e and b_e are constants of dependence of electronic current on resistivity. The values of $\log a_e$ and b_e were determined from the intercepts and slopes of $\log i_e$ versus $\log \rho$ plots and were found to be dependent upon the electrolyte composition. The plots between logarithm of electronic current and breakdown voltage were also found to be linear. This suggests a strong co-relation between the electronic current and breakdown voltage. According to Ikonopisov, the constants a_B and b_B at constant temperature, composition, concentration and current density are given by the relations,

$$a_B = \frac{\epsilon_m}{re} (\log i_B - \log a_e) \quad \dots (4)$$

$$b_B = \frac{2.303 \epsilon_m b_e}{re} \quad \dots (5)$$

where ϵ_m is a threshold energy for impact ionization, r is a recombination constant, i_B is the value of the electronic current at a thickness sufficient for oxide destruction, e is the electronic charge and a_e and b_e are the constants of the dependence of electronic current on resistivity. The constants r and ϵ_m are specific only for the anodized metal and the quantity b_e is characterized by the injection of electrons from the electrolyte into the oxide film. From Eq. (5) we get,

$$b_B/b_e = \frac{2.303 \epsilon_m}{re} \quad \dots (6)$$

Since the experiments were performed at constant temperature and current density the ratio b_B/b_e should be constant for any two electrolytes. The ratio b_B/b_e was determined for ortho-phosphoric acid and ammonium dihydrogen phosphate and was found to be 54 and 61, respectively. The ratio is reasonably constant. Thus, Ikonopisov electron avalanche model explains the effect of electrolyte resistivity on the electrical breakdown voltage.

The primary electronic current (i_0), injected into the conduction band of the oxide film from the

Table 3—Values of impact ionization coefficient (α), field (E) and primary electronic current (i_0) at different electrolyte concentrations

[Current density = 100 A m^{-2} , temp = 298K]

Concentration (mol m^{-3})	$\alpha \times 10^{-5}$ (cm^{-1})	i_0 (A m^{-2})	$E \times 10^{-8}$ (V m^{-1})
Electrolyte = Ortho-phosphoric acid			
500	1.04	10.965	2.663
250	1.24	7.943	3.162
100	1.73	3.467	3.748
50	2.59	1.236	4.401
Electrolyte = Ammonium dihydrogen phosphate			
500	6.99	0.083	8.434
250	7.96	0.035	9.201
100	9.17	0.015	10.121

electrolyte/oxide interface, increases exponentially according to avalanche process. Therefore, electronic current (i_e) could be given by,

$$i_e = i_0 e^{\alpha d} \quad \dots (7)$$

where α is the impact ionization coefficient and d is distance travelled by the primary electrons on their way to anode. As a first approximation, one can assume d to be equal to total oxide thickness. During anodization, at constant current, the oxide thickness increases linearly with the voltage; hence,

$$d = \beta V \quad \dots (8)$$

where β is the anodization constant and is equal to the reciprocal of the field ($1/E$), i.e.

$$i_e = i_0 e^{\alpha \beta V} \quad \dots (9)$$

or

$$\alpha = \frac{2.303}{\beta V} \log \frac{i_e}{i_0} \quad \dots (10)$$

$$\alpha = \frac{2.303 E}{V} \log \frac{i_e}{i_0} \quad \dots (11)$$

The values of the primary electronic current (i_0) were obtained from the intercept of the linear $\log i_e$ versus V plots (Fig. 3). The primary electronic current increases with electrolyte concentration and is dependent upon the composition of the electrolyte. The values of α were calculated using Eq. 11; these were found to be dependent on elec-

trolyte concentration as well as composition (Table 3).

Following Ikonopisov¹, Albella *et al.*² stated that it is possible to make an estimation of the variation of the breakdown voltage with the electrolyte concentration and composition. If one assumes that the breakdown appears when the avalanche current (or primary current, i_0) reaches a certain fraction Z of the total anodization current (i_t), then the breakdown voltage will satisfy the equation,

$$i_0 \exp(\alpha \beta V_B) = Z i_t \quad \dots (12)$$

$$V_B = 2.303 \frac{E}{\alpha} \log \frac{Z i_t}{i_0} \quad \dots (13)$$

According to Eq. (13), breakdown voltage should depend on field strength (E), impact ionization coefficient (α) and primary electronic current (i_0). The values of both E and α decrease with increase in concentration and the ratio E/α (i.e. the mean free path of the electrons) does not undergo much change with electrolyte concentration. Therefore, the major factor contributing to the decrease in breakdown voltage with electrolyte concentration is its increasing primary electronic current.

Thus, the effect of concentration of the electrolyte on the breakdown voltage can be explained in terms of electron injecting model of Ikonopisov. There is evidence in literature⁷ that anions get incorporated into the oxide film. Therefore, it appears that electrons in the form of anions get incorporated into the aluminium oxide film. These incorporated anions most probably result in the formation of traps which are in electronic equilibrium with the electrolyte. The electrons are probably thermally excited continuously from traps into the conduction band and electronic equilibrium is maintained by the continuous injection of electrons from the electrolyte. The high field strength accelerates these electrons to an energy which is sufficient to free other electrons by impact ionization, so that avalanche multiplication occurs and causes breakdown when a certain critical current is reached.

Acknowledgement

Dr. Parveen Katyul thanks the CSIR, New Delhi for the award of a research associateship.

References

- 1 Ikonopisov S, *Electrochim Acta*, 22 (1977) 1077.
- 2 Montero I, Albella J M & Martínez-Duart J M, *J electrochem Soc*, 132 (1985) 814.

- 3 Yahalom J, *Proc Symp on Oxide-electrolyte interfaces*, edited by R S Alwitt (Electrochemical Society, Princeton NJ) 1973 p 288.
- 4 Albella J M, Montero I & Martinez-Duart J M, *Thin Solid Films*, 125 (1985) 57.
- 5 Kadary V & Klein N, *J electrochem Soc*, 127 (1980) 139.
- 6 Ikonopisov S & Elenkov N, *J electroanal Chem*, 86 (1978) 105.
- 7 Tajima S, *Electrochim Acta*, 22 (1977) 995.
- 8 Albella J M, Montero I, Fernandez M, Gomez Aleixandre C & Martinez-Duart J M, *Electrochim Acta*, 30 (1985) 1361.
- 9 Tajima S, Baba N & Mori T, *Electrochim Acta*, 9 (1964) 1509.
- 10 Kalra K C, Katyal P & Singh K C, *Thin Solid Films*, 177 (1989) 35.