Oxidation and Studies of Leakage Current of Aluminium Oxide Films

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Abstract

The rate controlling step during growth of aluminium oxide films is found to be ionic movement across the film and not at the metal/oxide interface. During anodic oxidation of aluminium, single barrier theory of Cabrera and Mott [6] is not found to be applicable. Dewald [2] theory of double barrier is found to explain the temperature independence of Tafel slopes. The data obtained during kinetics of growth of oxide film on aluminium shows that Dewald's theory which takes into account the space charge effect is found to be better than other theories of film growth. Electronic current also referred to as leakage current and anodic oxidation studies of aluminium oxide films in different electrolytes of various concentrations and compositions have been made. Anodic oxidation of aluminium has been done at different current densities and at varying field strength. It has been found that same relation between leakage current and field strength holds good irrespective of film thickness. A direct relation between leakage current and breakdown voltage has been observed. Steady leakage current data have been obtained at constant voltages through anodic oxide films on aluminium in contact with various electrolytes. The effects of electrolyte concentration, composition, field strength, temperature of the bath and resistivity of the contacting aqueous electrolyte on leakage current have been studied. The data have been examined critically by knowing the influence of above factors on breakdown. It is observed that increase in primary leakage current is the major factor contributing to the decrease in breakdown voltage with increase in electrolyte concentration.

I. Introduction

The study of anodic oxidation on valve metals such as tantalum, niobium, aluminium etc. has received considerable attention[1-6] because of the importance of such films in capacitor technology. It has been observed that the rate of increase of forming field with logarithm of ionic current density is independent of temperature during formation of aluminium oxide films in various electrolytes. Hence during anodic oxidation of aluminium, single barrier theory of Cabrera-Mott[6] is not applicable. Dignam's theory is capable of explaining temperature-independent Tafel slopes. The net activation energy and zero field activation energy is found to be independent of temperature. However, this approach did not take into account the space charge caused by the accumulation of charged ions in the oxide film. Dewald[2] theory of double barrier was able to explain the temperature-independence of Tafel Slope Therefore, during studies of growth of aluminium oxide films, the differences caused by different surface conditions were eliminated by using an improved method of surface preparation. When an oxide film is formed at a certain voltage of formation under constant current conditions and if the voltage is kept constant the growth of film causes a rapid decrease in the current and ultimately reaches a constant value. If the voltage is decreased the film growth stops and the entire current passing through the oxide film is electronic referred to as leakage current. Since the mechanisms suggested to explain the breakdown phenomenon involve injection of electrons into the film from the electrolyte, the role of leakage (electronic) current during growth of aluminium oxide films was examined. A linear relationship between logarithm of leakage current and breakdown voltage has been observed.

II. Materials and Methods

Aluminium samples (99.9% purity) of $2cm^2$ area were cut from a sheet of aluminium. The edges of the samples were abraded with fine emery paper to make them smooth. The samples were then   dipped in 10% NaOH solution for 2-3 s and then washed with distilled water to clean the surface. The chemical polishing of the samples 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 formed in 0.1M of the respective electrolyte in which further anodization has to be carried out. The sample thus prepared was placed in a glass cell and connected with a

platinum electrode which served as a cathode. The sample 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 3.565g cm^{-3} as reported by Tajima[8]. The field strength is 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 plot of field strength(E) versus reciprocal of temperature (1/T) for one current density pair (10.0,1.0 mAcm^{-2}) is shown in Fig.1. The plots of E versus 1/T are found to be linear and parallel irrespective of current density employed which shows that the difference of field strength at all temperatures for a given Current density pair is constant and hence the Tafel slope is independent of temperature. The Tafel slope at particular current density set was highly reproducible over a wide range of temperature. The Tafel slopes at other current density pairs were also calculated in the same manner. The values of Tafel slope at a particular current density pair were calculated using the field values obtained in all the repeat experiments. The mean values of Tafel slopes at various current density sets are given in Table 1. Since the Tafel slope was found to be be independent of temperature, applicability of Dewald's theory was attempted. It has been found during growth of   aluminium oxide films the field strength increases with current density but decrease with temperature for all the studied paired current densities. The plot of field strength versus reciprocal of temperature for one current density pair   (1.0 and10.0 mA/cm^2) is shown in Fig.1. Similar plots are obtained for other pairs of current density. The plots of field strength versus reciprocal of temperature are linear and parallel irrespective of current density which indicates that the difference of field strength at all temperatures for a given current density pair is constant and Tafel slope is non-dependent of temperature. At a particular temperature and at a particular current

density the values of Tafel slope are calculated using the field strength values obtained in all the experiments. The values of Tafel slope at a particular pair of current density were highly reproducible over a wide range of temperature. As from the experiments done it is found that at a current density pair of 1.0mA/cm^2 and 10.0 mA/cm^2 at temperatures of 283,293,303,313 and 328K the values of Tafel slope are 3.03, 3.06, 3.04, 3.07and 3.04x10^{-7}Vm^{-1}, respectively. The values of Tafel slopes were also calculated for other pairs of current density as shown in Table1. As Tafel slope is found to be independent of temperature, Dewald's theory is found to be applicable during oxidation of aluminium. and it is further substantiated by the fact that space charge (δ) values calculated using Dewald's equation are found to be dependent mainly on exp. (-W/kT). The values of W(activation energy) are calculated from the plot of log(δ) versus reciprocal of temperature(Fig2.)for current density pairs of 0.5,5 1,10 and 2,20 mA/cm^2 and are found to be linear. The values of W are positive and decreases with current density. The values of activation energy (W) in aluminium oxide films using Dewald's theory are found to agree well with the values calculated Dignam[3] equation. Further, as it is found that Dewald's theory takes into account contribution of space charge in addition to surface charge as stated in Dignam's theory, the experimental data is explained more satisfactory using Dewald's theory during growth of aluminium oxide films.

Leakage current data for anodic oxide films grown on aluminium in different concentrations of zinc carbonate, ammonium bromide and potassium iodide has been obtained. The relation of electronic current with field strength in 0.1M solutions of zinc carbonate, ammonium bromide and potassium iodide are shown in in Fig.3. It is found that leakage (electronic) current (i_e) increase with field strength and the plot between log i_e versus E$^{1/2}$ are found to be linear. Similarly different concentrations of 0.01, 0.025, 0.05, 0.25 and 0.50M of each electrolyte were used. The plots of log i_e and E$^{1/2}$ were also found to be linear in all concentrations of different electrolytes. These observations suggest dependence of leakage current on field strength. The relation between leakage current and field strength can be represented by an equation

$i_e= \alpha_e \exp(\beta_e E^{1/2})$

where α_e and β_e are constants. Relation between leakage (electronic) current and field strength has been found in literature for very thin films[25]. The experimental data show similar relation for thick films of aluminium oxide which

suggests that for films of any thickness same relation between leakage current and field holds good. The values of slopes (β_e) and intercepts(α_e) are calculated by least - squares method (Table.2). It is observed that ae and be are dependent on concentration and composition of the electrolyte. The values of a_e increases with concentration of the electrolyte which suggests incorporation of anions into the oxide film at higher concentration. The leakage current for aluminium oxide films are measured at constant field and constant concentration of the electrolytes at different temperatures. It is found that leakage current increases with temperature and the plots of log i_e and reciprocal of temperature are found to be linear. It is further observed that electronic current at constant temperature and constant field through aluminium oxide films at different concentrations of various electrolytes increases with concentration of the electrolytes. The variations in the values of leakage current with concentration and composition of the electrolyte is due to the variation in the magnitudes of electrolytic resistivites of various electrolytes. It is further confirmed from the plots of log i_e and log(ρ) which are found to be linear. This dependence of leakage current on concentration can be represented by an equation

log i_e=a_e + b_e log (ρ)

where a_e and b_e are constants of dependence of leakage current on resistivity. It is found that constants a_e and b_e depend upon concentration and composition of the electrolyte. (Table.3). The plots (Fig. 4.) between log i_e and breakdown voltage (V_B) are found to be linear which implies dependence of V_B on leakage current and correlation between breakdown voltage and leakage current. From the data obtained for measuring leakage current at a certain voltage the values of impact ionization coefficient[7] are calculated knowing the field strength. The primary leakage current (i_O) can be calculated from the intercepts of the plots between log i_e and voltage V. It has been found that primary leakage current depends upon concentration and composition of the electrolyte. For a given electrolyte primary leakage current increases with increase in concentration of the electrolyte. Assuming that breakdown of film occurs when primary leakage current reaches a certain fraction of the total anodization current, it is possible to estimate the change in values of breakdown voltage with concentration and composition of the electrolyte. As the values of impact ionization coefficient are constant and are very high of the order of 10^4 provide a large impacts implying that the major factor contributing to decrease of breakdown voltage with concentration of the electrolyte is its increasing primary

leakage current. At a particular concentration the electrolyte which has high primary leakage current is associated with low breakdown voltage, which substantiates the role of primary leakage current in explaining the effect of electrolyte concentration on breakdown voltage.

TABLE-1

Current density pair (mA/cm^2)	Tafel slope T X 10^{-7} (Vm^{-1})	Net activation energy W X 10^{19} (J)
5 , 0.5	2.39	0.522
10 , 1.0	2.42	0.513
20 , 2.0	2.46	0.502
30 , 3.0	2.49	0.491
40 , 4.0	2.54	0.482

TABLE-2

| Concentration of the electrolyte	α_e (Am^{-2})			$10^4 \beta_e$ (m$^{1/2}$ V$^{-1/2}$)		
	Zinc carbonate	Ammonium bromide	Potassium iodide	Zinc carbonate	Ammonium bromide	Potassium iodide
0.01 M	0.112	0.101	0.107	2.09	1.78	1.89
0.025 M	0.137	0.129	0.132	1.98	1.61	1.74
0.05 M	0.171	0.164	0.169	1.81	1.47	1.62
0.10 M	0.231	0.216	0.224	1.59	1.32	1.45
0.25 M	0.279	0.254	0.261	1.41	1.17	1.31
0.50 M	0.298	0.277	0.283	1.26	1.03	1.15

TABLE-3

Electrolyte	Constants of resistivity – breakdown voltage dependence		Constants of resistivity – Leakage current dependence	
	a_B (V)	b_B (V)	a_e (Am^{-2})	b_e
Zinc carbonate	301	189	2.97	0.214
Ammonium bromide	328	174	2.31	0.181
Potassium iodide	275	193	4.12	0.227
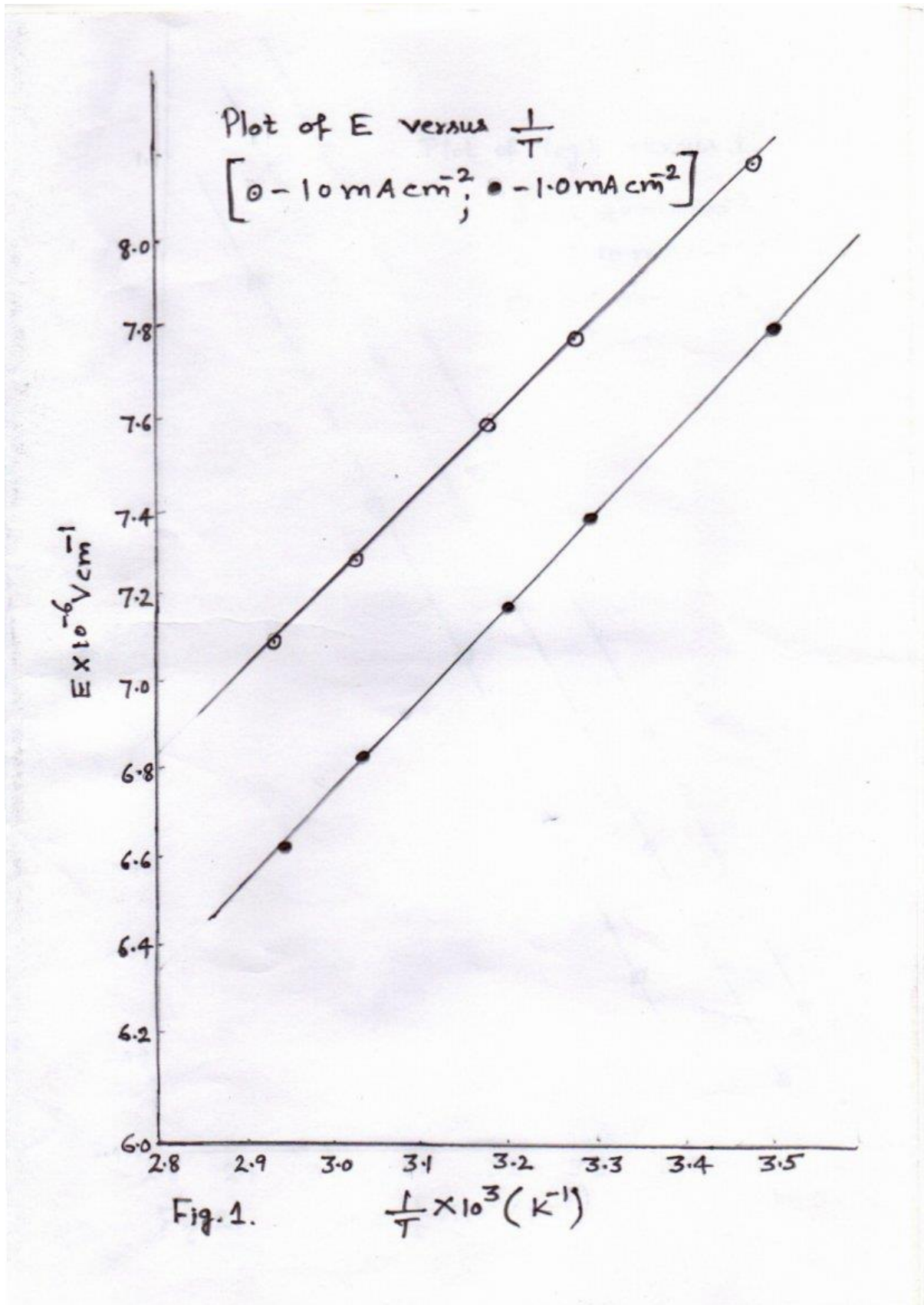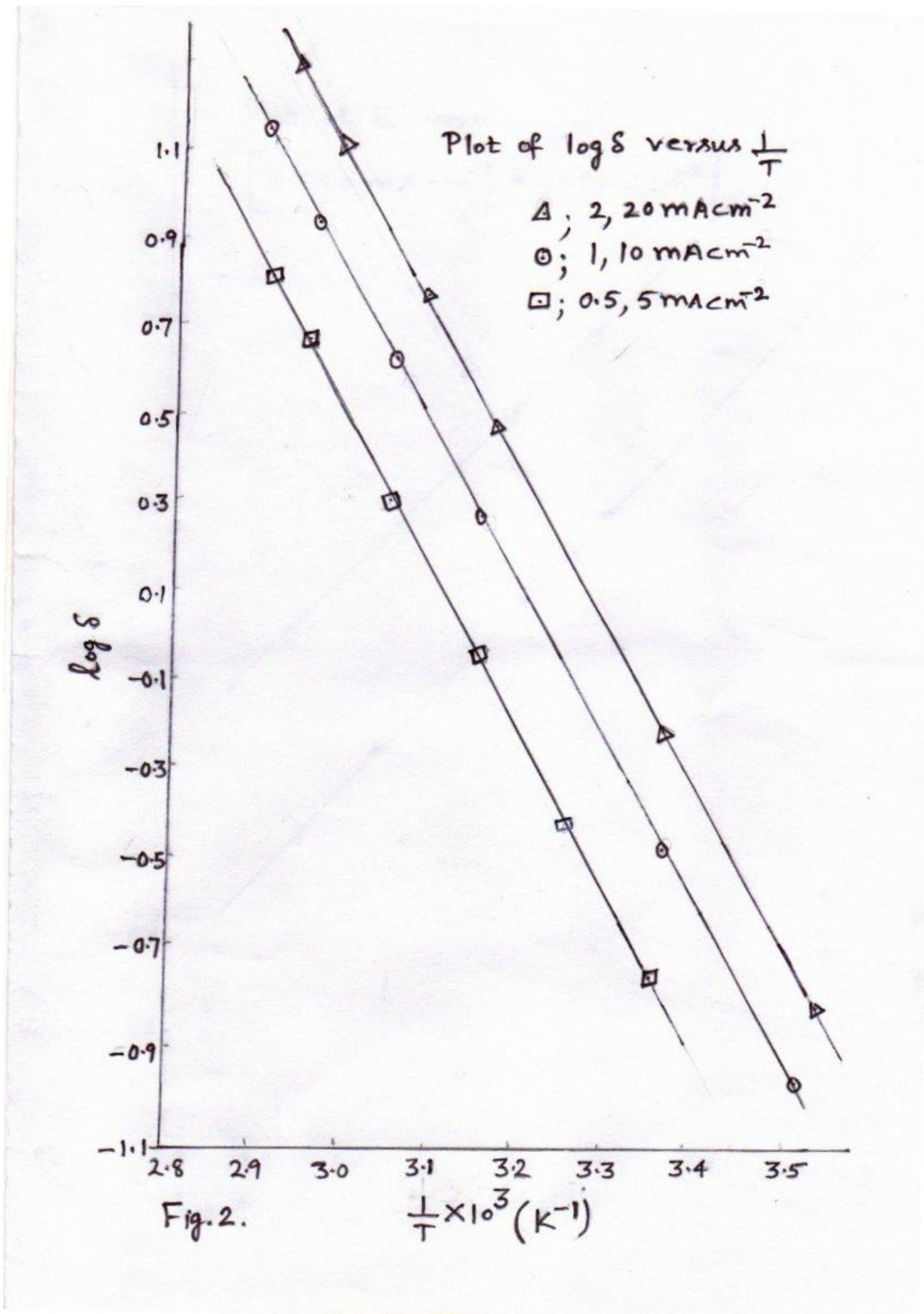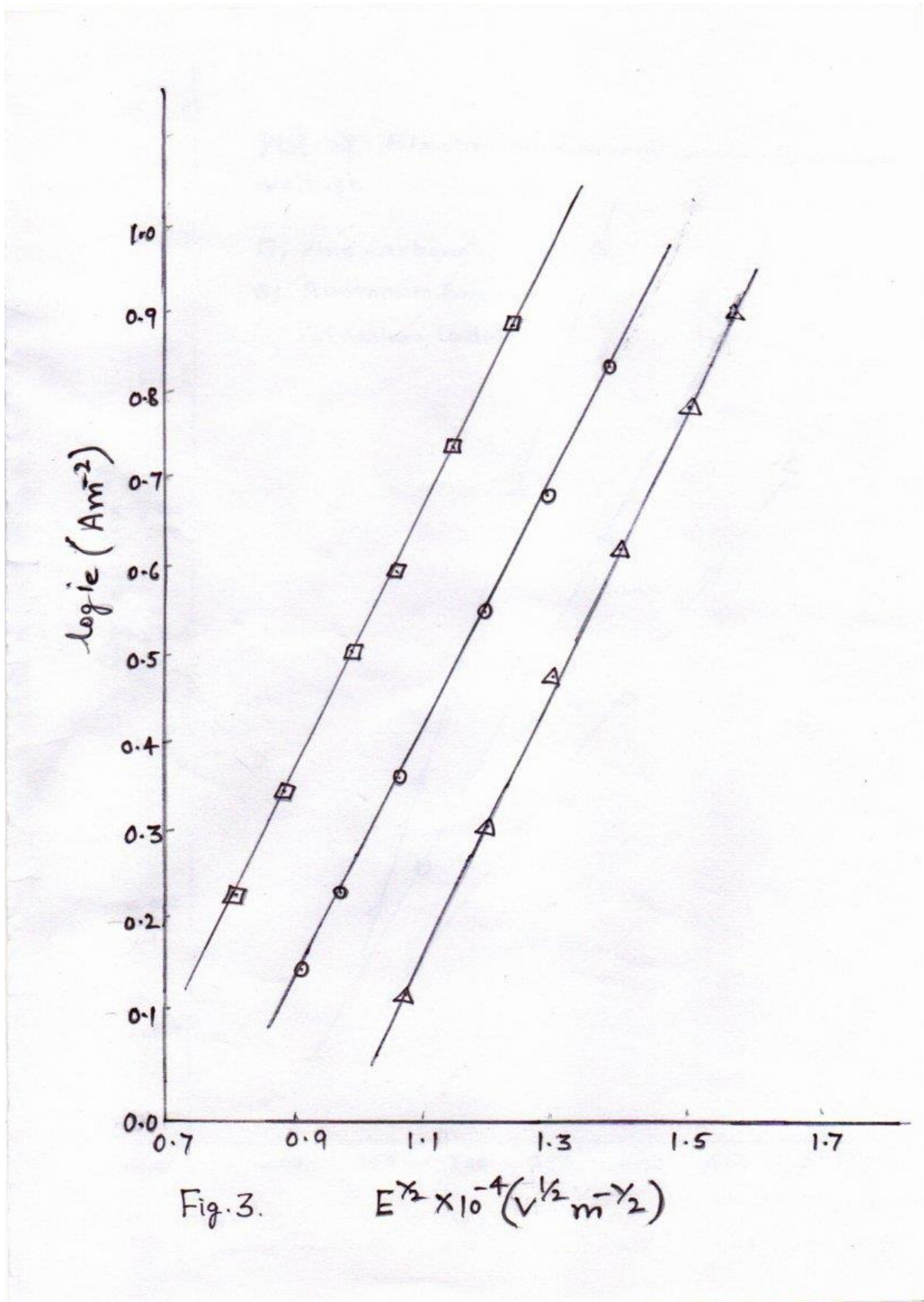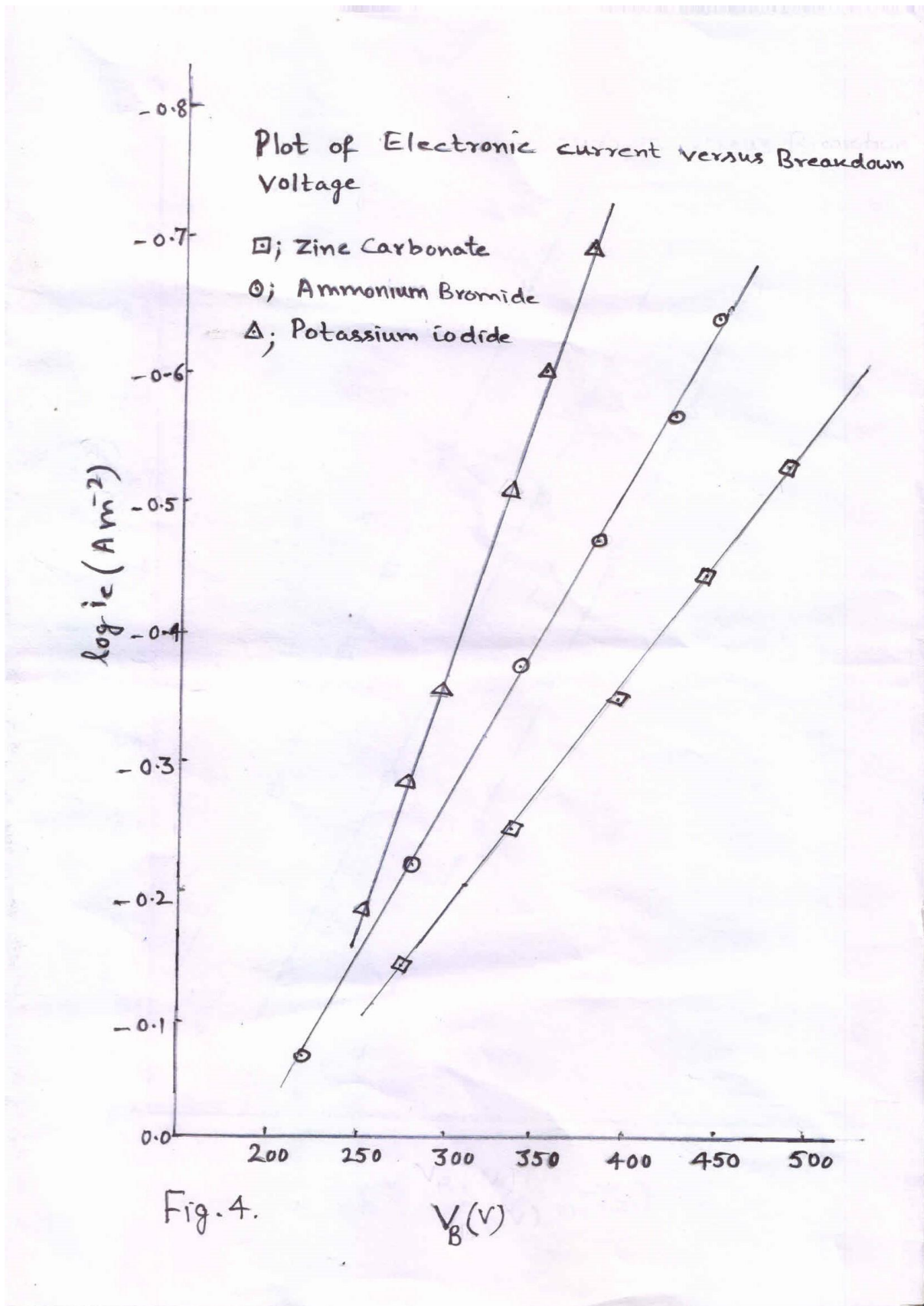
Fig. 1.

Fig.2.

Fig. 3. $E^{1/2} \times 10^{-4} (V^{1/2} m^{-1/2})$

Fig.4.

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