

## **Kinetics and Electronic Current Studies of Niobium Oxide Thin Films**

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### **Abstract**

*Ionic conduction studies of niobium oxide thin films in aqueous electrolytes over wide range of temperatures and current densities in various aqueous electrolytes have been made. The rate controlling step during growth of niobium oxide films is found to be ionic movement across the film and not at the metal/oxide interface. A single barrier theory of anodic growth of the film based on metal/oxide interface control as proposed by Cabrera and Mott<sup>6</sup> is not found to be applicable. As according to this theory, every ion which escapes from the metal sweeps right through the oxide and is not an activated process. This theory predicts a temperature dependent Tafel slope which is contrary to Young's<sup>12</sup> observations. Dignam<sup>5</sup> assumed quadratic variation of field with ionic current density and this model is capable of explaining temperature interdependent slopes. Verwey<sup>4</sup> considered the energy barrier for ion movement through the oxide bulk assumed to be in state of electrical neutrality, as the rate determining step. Dewald<sup>18</sup> theory of double barrier mechanism for the growth of anodic films which takes into account the space charge factor is found to explain the temperature independence of Tafel slopes. The exact picture of ionic conduction through anodic oxide thin films on metals and the exact nature of the dependence of Tafel slope has not been understood. The data obtained during kinetics of growth of oxide film on niobium shows that Dewald's theory which takes into account the space charge effect is found to be better than other theories of ionic conduction. Electronic current studies on niobium oxide thin films have been made at constant voltages in different aqueous electrolytes. The data have been obtained at varying concentrations, temperatures, current density, field strength, and resistivities of the electrolytes. The effect*

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*of above factors on electrical breakdown voltage have also been examined critically.*

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## **I. Introduction**

The aim of present investigation is to carry out a detailed study of ionic conduction mechanism during the growth of anodic oxide films on valve metals. Ionic conduction Studies over a wide range of current densities and temperatures have been made to develop a suitable growth model. 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 niobium oxide films in various electrolytes. Hence during anodic oxidation of niobium, single barrier theory of Cabrera-Mott<sup>6</sup> 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<sup>18</sup> theory of double barrier was able to explain the temperature-independence of Tafel Slope. Therefore, during studies of growth of niobium 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 current. Since the mechanisms suggested to explain the breakdown phenomenon involve injection of electrons into the film from the electrolyte, the role of electronic current during growth of niobium oxide thin films was examined.

## **II. Materials and Methods**

Specimens of niobium of  $2 \times 10^{-4} \text{m}^2$  area were cut from 99.9% pure sheet of niobium. The edges of the specimens were abraded with fine emery paper to make them smooth. The specimens were then dipped in KOH melt to clean the surface and finally washed with

distilled water. The chemical polishing of the specimens was done by dipping them in a freshly prepared mixture of 98% sulphuric acid+70% nitric acid+48% hydrofluoric acid in ratio of 5:2:2, v/v for 3-4 sec, washed with distilled water and then placed in boiling water for 10 minutes to remove any remaining impurities from the surface of the specimen. Finally the specimens were thoroughly washed with distilled water and dried in a current of hot air. The etching and drying process was repeated several times. The final etching of the specimens was done just before oxidation phenomenon. This method of surface preparation was found to give a better constant rate of film growth in the process of polarization of the anode under constant current density conditions than other methods. The working area of the specimen was defined by covering the tags of the specimens with a thick anodic film. Some oxide film was always formed on the square portion of the surface of the specimen due to creepage of the electrolyte during formation of thick film on the tag. The specimen prepared by above method was placed in a glass cell and connected with a platinum electrode which served as a cathode. A stirring arrangement in the cell avoided the heating effects, if any, produced by the passage of current through the cell. Anodic polarization of niobium was carried out under constant current conditions using constant current supply designed specifically for this purpose. The supply of current was cut off by an electronic control, after the desired voltage of formation was reached. The time for the passage of current for forming the film through successive intervals of voltage was recorded by an electronic timer. A constant voltage was set using a potentiostat and electronic current passed was measured. Of the various methods of identifying breakdown voltage like the attainment of maximum voltage, appearance of sparking, gas evaluation, the rapid voltage fluctuations, slowing down of voltage and audible cracking, the voltage at which gas evaluation started was found to be a superior method for identifying breakdown voltage at almost all the current densities studied although audible cracking was also taken one of the criteria at high current densities. The solutions were prepared in conductivity water and their electrolytic resistivities were measured using a digital conductivity meter. The density of the film was taken as  $4.36 \text{ g/cm}^3$  as reported by Holtzberg<sup>8</sup> The field strength is

calculated using the value of thickness and corresponding voltage of formation. The thickness of film formed in different electrolytes was calculate using Faraday law.

### **III. Results and Discussion**

Data for anodic polarization of niobium under constant current conditions in aqueous solutions of magnesium sulphate, aluminium sulphate and magnesium nitrate have been obtained. The plot of field variation with ionic current density( $i$ )in aqueous solution of magnesium sulphate at different temperatures of formation is shown in Fig.1. The Tafel slope,  $\delta E/\delta \ln i$  calculated from Fig.1 is observed to be independent of temperature. Such an observation rules out the applicability of single barrier theory of Cabrera-Mott<sup>6</sup> to such films because according to this theory, the Tafel slope should be proportional to absolute temperature. Guntherschulze-Betz<sup>15</sup>(constants A and B (using  $i = A \exp BE$ ) have been determined by the method of least squares at varying temperatures and in different electrolytes. It has been found that there are not much significant variations in the values of B with temperature of the aqueous electrolytes. The near constant value of B explain independence of Tafel slope with temperature. The value of B, however, vary with the nature of electrolyte. The mean values of constant B over the studied range of temperature are  $3.94 \times 10^{-8}$ ,  $3.17 \times 10^{-8}$  and  $3.56 \times 10^{-8} \text{mV}^{-1}$  in the presence of magnesium sulphate, aluminium sulphate and magnesium nitrate, respectively. Using these mean values of B and taking the mean temperature, the values of half jump distances (using  $B = aq/kT$ ) were calculated for different electrolytes studied. The values of A increase with the increase in temperature for each of the aqueous electrolytes. The increase in the value of constant A with temperature may be due to increase in the number of active sites. The values of constant A also depend upon the nature of the electrolyte used e.g., the values of A in aqueous solution of magnesium sulphate and aluminium sulphate at 298K are  $0.73 \times 10^{-8}$  and  $2.79 \times 10^{-8} \text{Am}^{-2}$ , respectively.. The higher values of A in the presence of aluminium sulphate may be due to more number of ions available. It appears that there may be correlation between the pre-exponential factor A and the number of ions at the metal surface and hence with the number of active sites.

These active sites change with the change in temperature. Dignam<sup>7</sup> theory justified quadratic variation of field with ionic current density to explain the field and temperature dependence of Tafel slopes. The values of net activation energy were calculated using Dignam theory and it is found to vary with the nature of the electrolyte but are independent of current density. Small variations in the values of activation energy were observed with temperature. The values of  $i_0$  were calculated (using  $i_0 = i \exp(-W(E)/kT)$ ) and it is found that  $i_0$  is temperature dependent. The values of  $i_0$  were also found to change with change in current density and nature of the electrolyte. It appears that increase in temperature causes increase in activation distance from the mean position and there is appreciable contribution of the quadratic term. Though there is an appreciable contribution of quadratic term yet various parameters of Dignam theory are found to be temperature dependent which were assumed to be temperature independent by Dignam. Hence Dignam's approach does not explain experimental data satisfactorily. This may be probably due to the neglect of space charge caused by accumulation of charged ions in the film and the pre-history of the specimens. Therefore, the effect of space charge in the oxide film has been examined and the differences caused by different surface conditions have been eliminated by using an improved method of surface preparation as described in the experimental part. The double barrier theory of Dewald which is an extension of the oxidation theory of Cabrera-Mott considers the effect of space charge in the oxide film which develops if the time required for an excess interstitial ion to move from one side of the film to the other is not very much smaller than the time required for the ion to cross the interface. The fundamental basis of his treatment of the case was that the metal ions are the only source of net space charge. In Cabrera-Mott theory, the space charge was considered to be negligible which led electric field strength to be function of thickness in the oxide film. Further, according to Cabrera-Mott theory the Tafel slope should be proportional to absolute temperature whereas Dewald proposed his theory to account for almost temperature independent Tafel slope. 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. Since the Tafel slope was found to be independent of temperature, applicability of Dewald's theory was attempted. It has been found during growth of niobium oxide films the field strength increases with current density but decrease with temperature for all the studied paired current densities. 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 current densities  $5.0\text{mA/cm}^2$  and  $50.0\text{mA/cm}^2$  and at temperatures of 275, 290, 305, 318 and 333K the values of Tafel slope are 2.74, 2.77, 2.67, 2.69 and  $2.75 \times 10^{-7} \text{Vm}^{-1}$ , respectively. The values of Tafel slopes were also calculated for other pairs of current density and were found to be almost constant. As Tafel slope is found to be independent of temperature, Dewald's theory is found to be applicable during oxidation of niobium. and it is further substantiated by the fact that space charge ( $\delta$ ) 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  $\log(\delta)$  versus reciprocal of temperature for current density pairs of 1, 10 and 3, 30 and  $5, 50\text{mA/cm}^2$  and are found to be linear. The values of W are positive and decreases with current density. The values of activation energy (W) in niobium oxide thin films using Dewald's theory are found to agree well with the values calculated Dignam 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

data obtained during growth of niobium oxide thin films is explained more satisfactory using Dewald's theory. Next, breakdown voltage studies were made in various aqueous electrolytes at different current densities and concentrations. It was observed that the plots of breakdown voltage against concentrations of various electrolytes are linear upto concentration of 0.1M, thereafter, with further increase in electrolyte concentration only small decrease in the values of breakdown voltage are obtained and it tends to acquire a certain minimum value. These observations point to an exponential decrease of breakdown voltage with increase in electrolyte concentration and linear plots were obtained between breakdown voltage and logarithms of reciprocal of concentration confirmed it. At high electrolyte concentration a large number of ions are available per unit concentration and hence the electrolyte possess large conductivity but low resistivity suggesting a direct relation between breakdown voltage and electrolytic resistivity. Electronic current data for anodic oxide films grown on niobium in different concentrations of magnesium sulphate, aluminium sulphate and magnesium nitrate has been obtained. The relation of electronic current with field strength in 100molm<sup>-3</sup> solutions of magnesium sulphate, aluminium sulphate and magnesium nitrate was studied. It was found that electronic current ( $i_e$ ) increase with field strength and the plot between  $\log i_e$  versus  $E^{1/2}$  were found to be linear. Similarly different concentrations of 1,10,25,50,250 and 500 molm<sup>-3</sup> 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 electronic current on field strength. The relation between electronic current and field strength can be represented by an equation.

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

where  $\alpha_e$  and  $\beta_e$  are constants. Relation between electronic current and field strength has been found in literature for very thin films<sup>25</sup>. The experimental data show similar relation for oxide films on niobium which suggests that for films of any thickness same relation between electronic current and field holds good. The values of slopes ( $\beta_e$ ) and intercepts ( $\alpha_e$ ) are calculated by least-squares method (Table.1). It is



observed that  $a_e$  and  $b_e$  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 electronic current of niobium oxide films are measured at constant field and constant concentration of the electrolytes at different temperatures. It is found that electronic 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 niobium oxide films at different concentrations of various electrolytes increases with concentration of the electrolytes. The variations in the values of electronic current with concentration and composition of the electrolyte is due to the variation in the magnitudes of electrolytic resistivity of various electrolytes. It is further confirmed from the plots of  $\log i_e$  and  $\log(\rho)$  which are found to be linear. This dependence of electronic current on concentration can be represented by an equation

$$\log i_e = a_e + b_e \log(\rho)$$

where  $a_e$  and  $b_e$  are constants of dependence of electronic current on resistivity. It is found that constants  $a_e$  and  $b_e$  depend upon concentration and composition of the electrolyte.(Table2.)The plots(Fig.2.) between  $\log i_e$  and breakdown voltage ( $V_B$ ) are found to be linear which implies dependence of  $V_B$  on electronic current and correlation between breakdown voltage and electronic current. From the data obtained for measuring electronic current at a certain voltage the values of impact ionization coefficient<sup>7</sup> are calculated knowing the field strength. The primary electronic 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 electronic current depends upon concentration and composition of the electrolyte. At a particular concentration the electrolyte which has high primary electronic current is associated with low breakdown voltage, which substantiates



the role of primary electronic current in explaining the effect of electrolyte concentration on breakdown voltage. For a given electrolyte primary electronic current increases with increase in concentration of the electrolyte. Assuming that breakdown of film occurs when primary electronic 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 electronic current.

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**TABLE-1**

Concentration of the electrolyte Molm <sup>-3</sup>	$\alpha_e$ (Am <sup>-2</sup> )			$10^4 \beta_e$ (m <sup>1/2</sup> V <sup>-1/2</sup> )		
	Magnesium sulphate	Aluminium sulphate	Magnesium nitrate	Magnesium sulphate	Aluminium sulphate	Magnesium nitrate
10	0.123	0.114	0.102	2.09	1.78	1.89
25	0.156	0.134	0.121	1.98	1.61	1.74
50	0.191	0.165	0.143	1.81	1.47	1.62
100	0.221	0.196	0.187	1.59	1.32	1.45
250	0.265	0.232	0.213	1.41	1.17	1.31
500	0.304	0.286	0.255	1.26	1.03	1.15

**TABLE-2**

Electrolyte	Constants of resistivity – Breakdown voltage dependence		Constants of resistivity – Electronic current dependence	
	$a_B$ (V)	$b_B$ (V)	$a_e$ (Am <sup>-2</sup> )	$b_e$
Magnesium sulphate	329	204	3.21	0.232
Aluminum sulphate	343	236	3.72	0.266
Magnesium nitrate	364	254	4.79	0.289

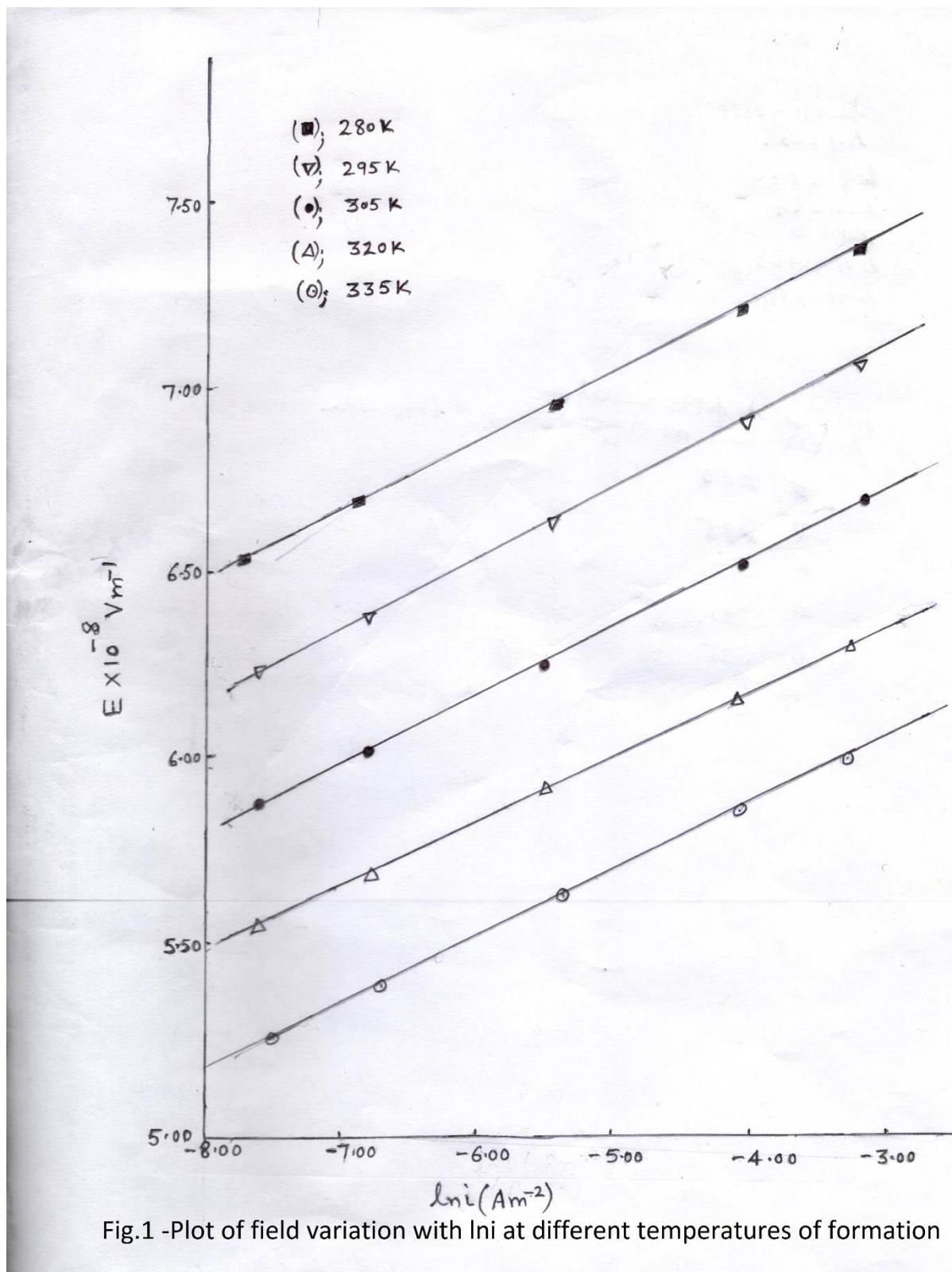
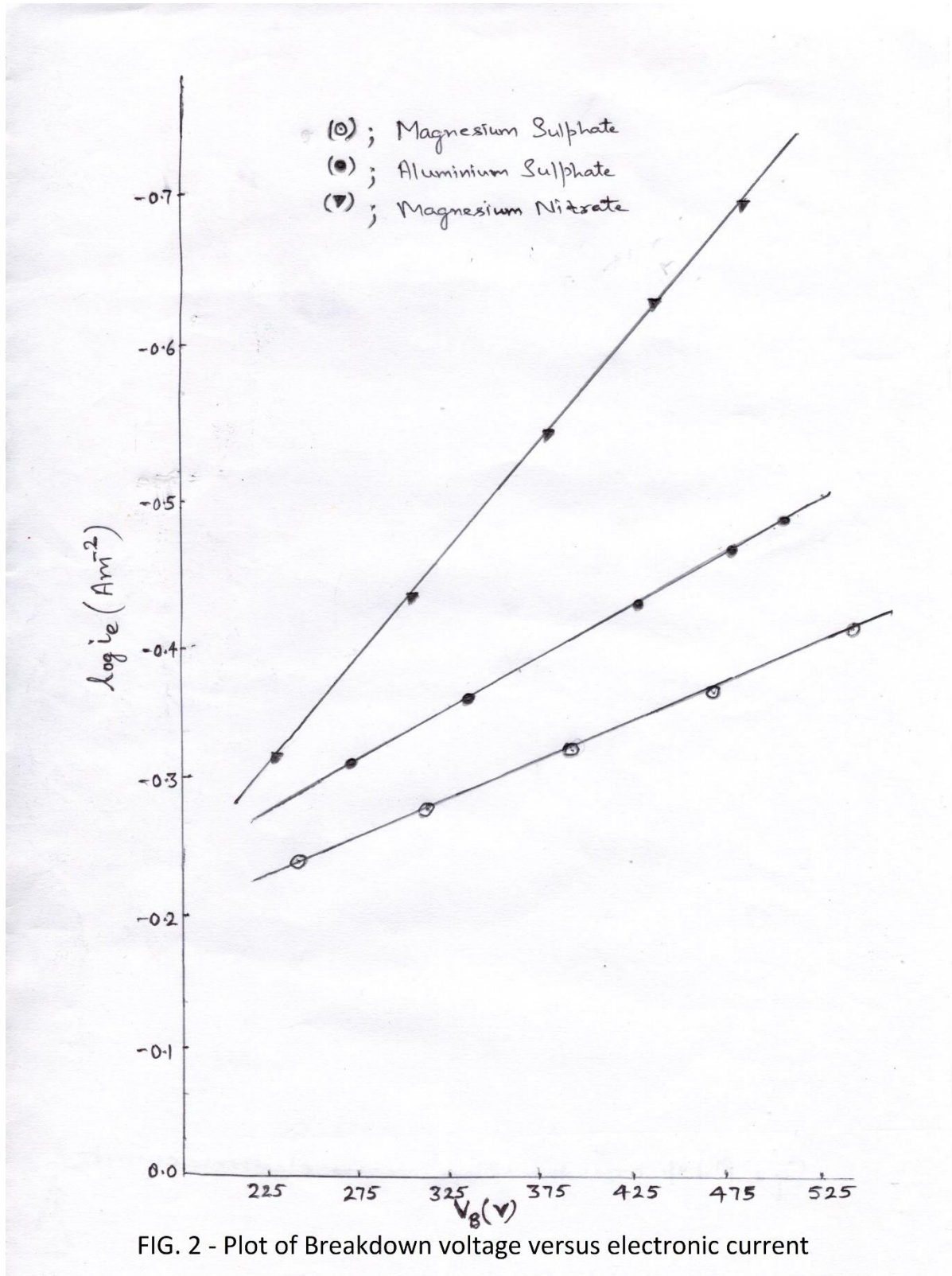


Fig.1 -Plot of field variation with  $\ln i$  at different temperatures of formation



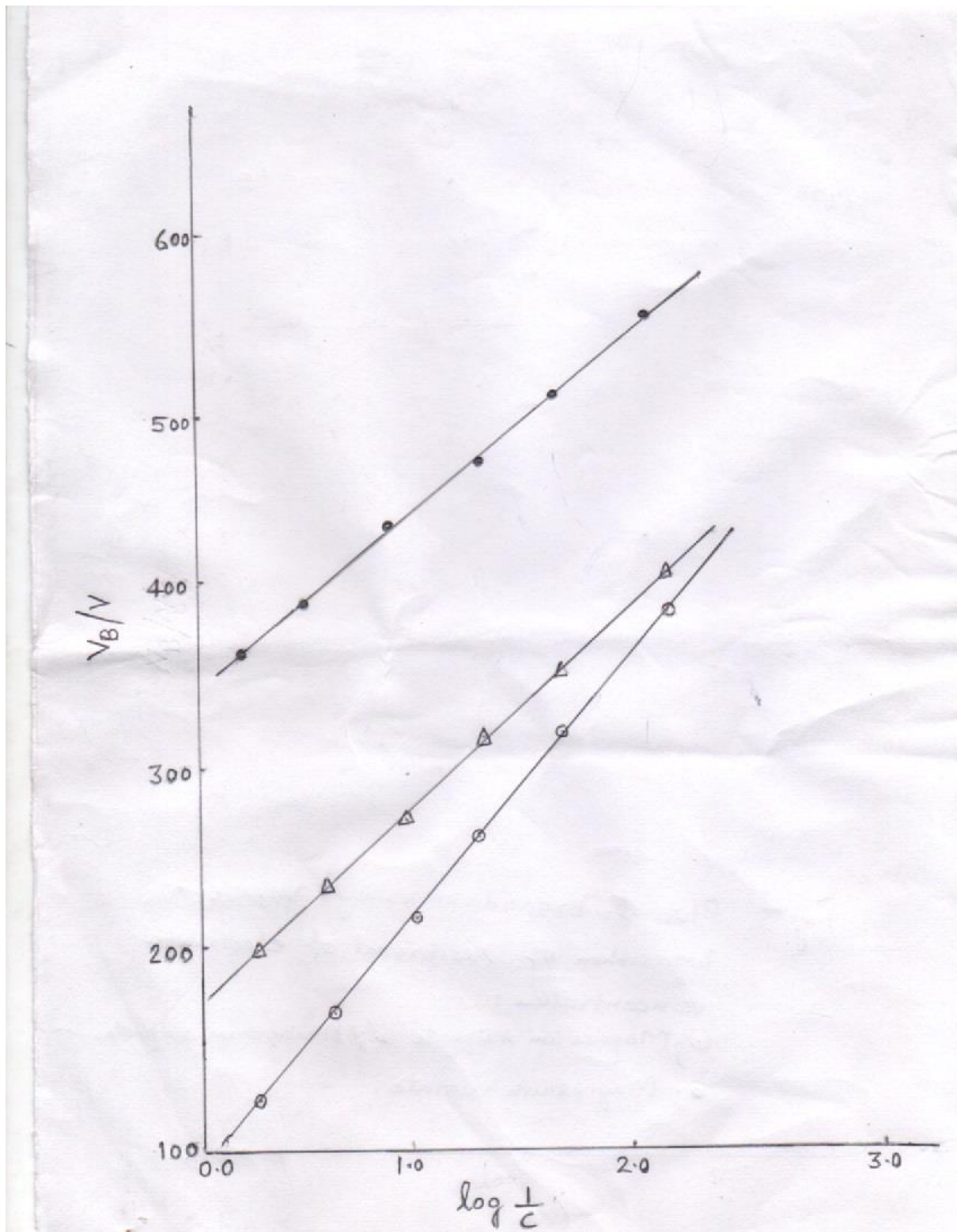


Fig 3: Plot of breakdown voltage versus logarithm of reciprocal of electrolyte concentration. (○); Magnesium sulphate, (△); Aluminium sulphate (●); Magnesium nitrate.



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