Electrical Breakdown and Anodic Oxidation Studies of Aluminium-Aluminium Oxide-Electrolyte Systems.

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Electrical breakdown voltage and anodic oxidation studies of aluminium oxide films in different electrolytes of various concentrations and compositions have been made. The effects of electrolyte concentration, 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 aluminium oxide film. The major factor contributing to the 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. Dewald's theory has been found to be more applicable during growth of aluminium oxide films, since it takes into account contribution of space charge in addition to surface charge as stated in Dignam's theory

I.   Introduction

The anodic oxide film on aluminium can be formed upto a maximum thickness beyond which the film breakdown at a certain voltage designated as breakdown voltage. The breakdown voltages have been studied on different valve metals such as tantalum, niobium 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 on the breakdown voltage value as this has been attributed to the resistivity 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. Different theories of ionic conduction during growth of aluminium oxide films have been studied.

II.   Materials & Methods

Aluminium specimens of 2 sq. cm area and with short tags were cut from aluminium sheets(99.9% purity) and the edges of the specimens were smoothened by abrading with a fine emery paper . The aluminium specimens were then dipped in 10./. NaOH solution for 2-3 sec and then washed with distilled water to clean the surface. The chemical polishing of these specimens was done by dipping in a freshly prepared etching mixture of O-phosphoric acid, sulphuric acid and nitric acid (75:25:5, V/V) at a temperature of 350-360K for 3-4 sec and then washed with distilled water and dried in a current of hot air. Final etching of the specimens was done just before anodization. The tags of the specimens were covered with a thick anodic film in an electrolyte in which further anodization 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 aluminium. . Anodic polarization of the specimens in different electrolytes was carried out at constant current adjusted through an electronically operated constant current generator. The supply of current was cut off by an electric control after the desired voltage of film formation is reached . The electrical breakdown voltage studies were carried out in various electrolyte solutions .The time for the passage of current for film formation through success

interval voltages was recorded by electronic stopwatch. 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. The density of oxide film was taken as 3.565 g cm^{-3} as reported by Tazima[22]

III.   Results and Discussion

The anodic oxide films were grown on aluminium specimens in varying concentrations of aqueous solutions of potassium carbonate , potassium chloride and sodium nitrate 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(1-4) 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 rate of film growth is uniform upto a certain maximum voltage of formation beyond which increase in the charge has no effect on formation voltage. 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 because 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 , the attainment of maximum voltage was observed in all the electrolytes studied and results were reproducible. Therefore, attainment of maximum voltage was chosen as a criterion for identifying breakdown voltage at all the current densities.

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 and 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

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

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 184.45,123.78 and 256.89 for aqueous solutions of potassium carbonate, potassium chloride and sodium nitrate, respectively and the corresponding values of intercepts of these curves gave the values $(V_B)_M$ as 346, 279 and 397 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 with resistivity of the electrolyte solution. However, the plots between breakdown voltage (V_B) and log (ρ) are found to be linear and hence a direct relation between (V_B) and log (ρ) can be represented by

$$V_B = a + b \log (\rho) \qquad \textbf{(2)}$$

Where a and b are constants with positive sign.

The values of constants 'a' and 'b' for potassium carbonate, potassium chloride and sodium nitrate were calculated from the intercepts and slopes of the linear plots between breakdown voltage and log ρ . The effect of field strength on

breakdown voltage was studied . The values of field strength at 298 K at current density of $100 Am^{-2}$ for 100 $molm^{-3}$ aqueous solutions of potassium carbonate, potassium chloride and sodium nitrate were found to be 5.67,5.34 and 5.96×10^8 Vm^{-1} , respectively. The corresponding values of breakdown voltage were 285,210 and 315 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 (3)

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

On anodization, metals can undergo a variety of oxidation reactions like anodic oxide growth, oxygen evolution, anodic dissolution and oxidation of solute components of the electrolyte. Of the several possible accompanying reactions, which will be the predominant one depends on a variety of factors .Among most important of these factors are the electrode kinetic features of the surface film which is almost always formed on the electrode surface during these oxidation reactions. The growth of anodic oxide film is essentially a problem in ionic conduction at high field strength complicated by the presence of two interfaces i.e metal/oxide and oxide solution at which transfer process must occur. Anodic oxide films can be formed on valve metals by any of three methods (I)at constant current,(ii) at constant voltage (iii) be a sequence of constant current and constant voltage. It is a complete description of state that a film was formed at certain ionic current density to given overpotential in a given solution and temperature, on a crystal face of the metal of known purity and given mode of surface preparation. During the formation at constant voltage (overpotential) the current falls continuously until the leakage current predominates or recrystallization starts. A steady state in theory is never reached since although the current changes only slowly, the time required to pass the charge necessary to obtain the steady state is very long. Consequently, to obtain the steady state, anodic oxidation was done at constant current. Most of theories of kinetics of growth of anodic oxide films on metals assume the rate controlling step of ionic conduction either with in the film and /or at the interfaces . Considering the cation- mobile system, where Movement of these cations depends on the electric field strength across the oxide film, the two situations where ionic charge transfer is possible are I) high field conduction, where it is assumed that the electric field strength is high enough to prevent movement of cations against the field direction ii)low field conduction, where it can no longer be assumed that movement of cations against the field direction is negligible. Since the electric field strengths lie in the range of $10^8 Vm^{-1}$,these fields being regarded as sufficient to prevent ions movement against the field direction, high field ionic conduction is

considered to be operative. Cabrera and Mott [21] visualized that rate controlling step is when the ions move across the metal/oxide interface and thus every ion escaping from the metal is swept right through the oxide is not an activated process and the ionic transport is supposed to be controlled at the boundary.Guntherschuze and Betz[10] have shown that the average field strength' E 'and current density 'i' under steady conditions are related by an equation

$$I = A \exp BE \qquad (4)$$

Where A and B are constants. In order to understand the process that could lead to such an expression for ionic current, an analogy can be drawn to a simple electrochemical reaction .In an electrochemical reaction, charge transport is controlled by the step which has the highest potential energy with respect to the rate controlling step. Data for anodic polarization on aluminium in different electrolytes at various temperatures and current densities have been obtained (Table 2&3) .The plot of voltage of formation and time is found to be linear upto a film formation voltage of 160V and become concave towards the time axis at higher formation voltages. The linear plots upto formation voltage of 160V showed the constancy of field strength independent of film thickness. However, at higher formation voltages ,the dependence of field strength on film thickness is observed. The plot of thickness versus voltage of formation at 298K in potassium carbonate are shown in Fig.2. Similar plots were obtained for aqueous solution of potassium chloride and sodium nitrate. The plot of field strength versus logarithm of current density at different temperatures at varying current densities in various electrolytes are found to be linear and parallel (Fig.3), indicating that Tafel slope is independent of current density. Similarly, Tafel slope is observed to be independent of temperature in all the electrolytes studied. The mean values of Tafel slopes at various current density pairs are almost constant. It has been found that during growth of aluminium oxide films, the field strength increases with current density but decrease with temperature(Table.2 and 3) for all the studied pair of current densities. Similarly the plots of E versus 1/T are linear irrespective of current density employed which indicates that the difference of field strength at all temperatures for a given pair of current density is constant and Tafel slope is non- dependent of temperature. Such an observation rules out the applicability of single barrier theory of Cabrera-Mott to such films because according to this theory, the Tafel slope should be proportional to absolute temperature. Gunthershultz - Betz constants A and B using equation (4)

have been determined by the method of least squares at varying temperatures and in different electrolytes. There are not much significant variations in the values of B with temperature of the aqueous electrolytes. The near constant values of 'B' explain the independence of Tafel slope with temperature. At a particular temperature and current density, the values of Tafel slope were calculated using values of field strength and these values of Tafel slopes were highly reproducible over a wide range of temperature As Tafel slope is found to be independent of temperature, Dewald's theory[23] is found to be applicable during growth of aluminium oxide films. The values of activation n energy calculated for different current density pairs are found to be positive and it decrease with current density. These values of activation energy calculated using Dewald theory are found to agree well with Dignam theory[20] .Further it has been observed that Dewald theory takes into account contribution of space charge in addition to surface charge as stated in Dignam theory suggesting that Dewald theory is more applicable during growth of aluminium oxide films.

TABLE-1

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

Concentration (moles/lt.)	Potassium carbonate		Potassium chloride		Sodium nitrate	
	Breakdown voltage (V)	Electrolytic resistivity (Ω cm)	Breakdown voltage (V)	Electrolytic resistivity (Ωcm)	Breakdown voltage (V)	Electrolytic resistivity (Ωcm)
.01M	355	517.2	320	347.8	390	446.1
.025M	315	405.7	295	165.6	345	239.6
.o5M	290	276.5	275	107.9	335	143.4
.10M	240	89.8	230	56.7	285	75.2
.25M	205	67.5	190	29.5	225	44.7
.50M	180	34.7	170	17.6	195	23.6

TABLE – 2

Current density- 10.0Am^{-2}			
Temperature (K) 298		Temperature (K) 328	
Voltage of formation (V)	Field E X 10^{-8} (Vm^{-1})	Voltage of formation (V)	Field E X 10^{-8} (Vm^{-1})
10	5.82	15	5.43
30	5.76	25	5.45
45	5.84	40	5.41
65	5.78	60	5.42
80	5.81	85	5.44
95	5.75	105	5.45
110	5.80	125	5.40
125	5.79	140	5.43
155	5.76	160	5.42

TABLE – 3

Current density- 5.0Am^{-2}			Current density- 10.0Am^{-2}	
Voltage of formation (V)	Charge Q X 10^3 (C)	Field E X 10^{-8} (Vm^{-1})	Voltage of formation (V)	Field E X 10^{-8} (Vm^{-1})
10	48	5.63	10	5.91
20	97	5.61	20	5.96
30	147	5.64	30	5.93
40	198	5.66	40	5.95
50	242	5.63	50	5.92
60	289	5.61	60	5.96
70	342	5.62	70	5.92
80	401	5.65	80	5.91
90	462	5.61	90	5.95
110	534	5.67	110	5.94
130	615	5.62	130	5.90
150	672	5.63	150	5.93

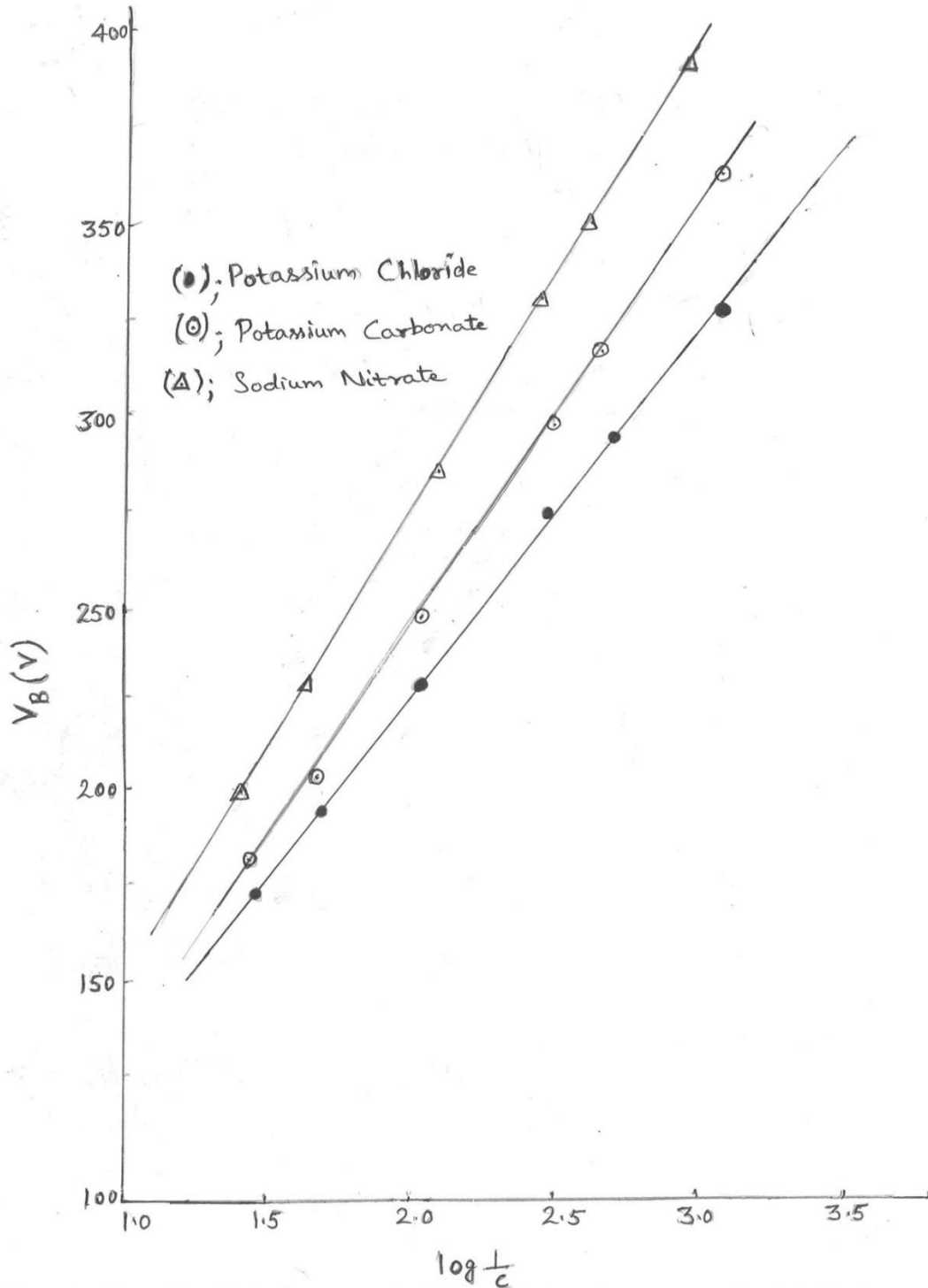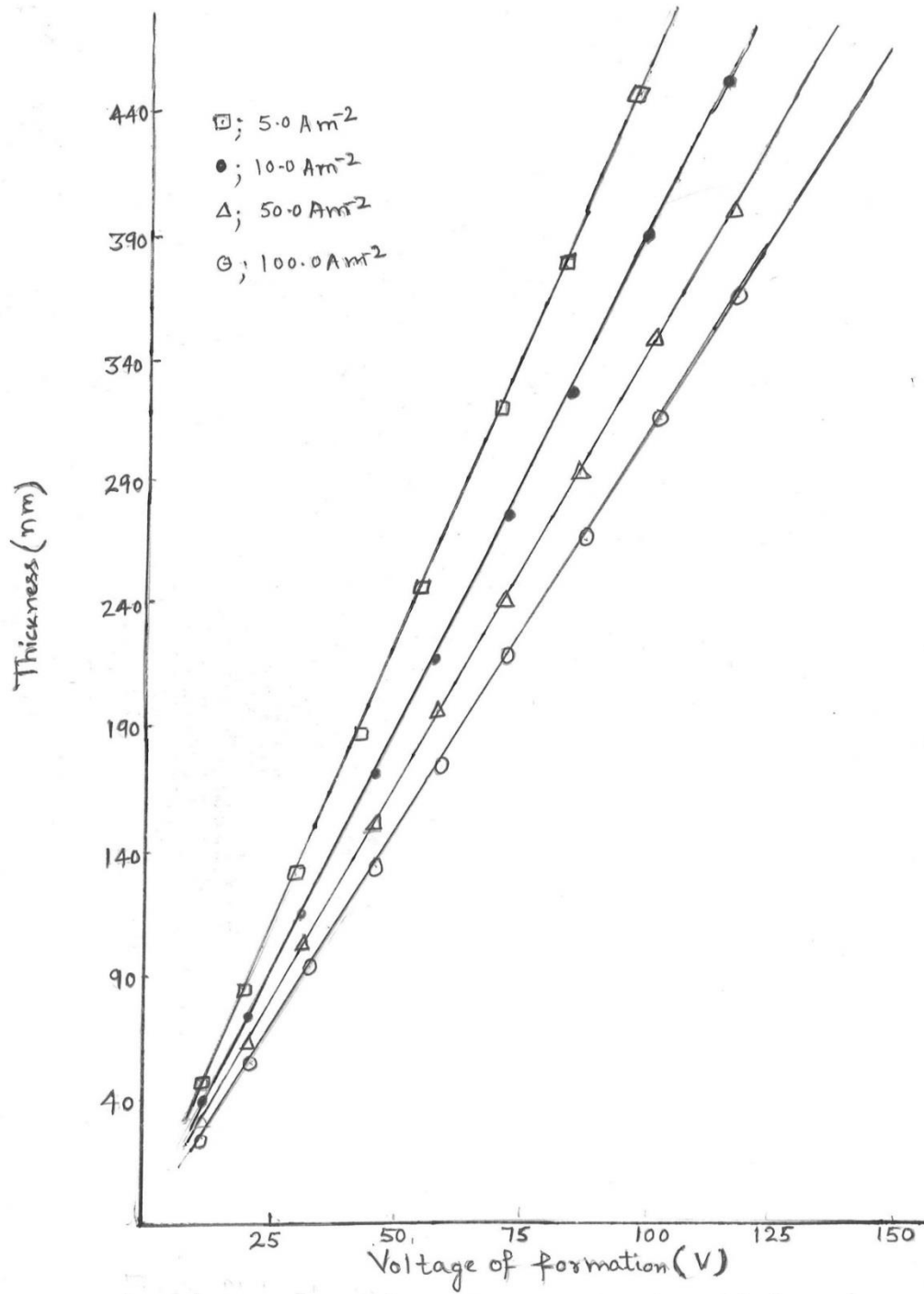**Fig. 1 - Plot of breakdown voltage (V$_B$) Vs Logarithm of Resiprocol of electrolyte concentration (log 1/C)**

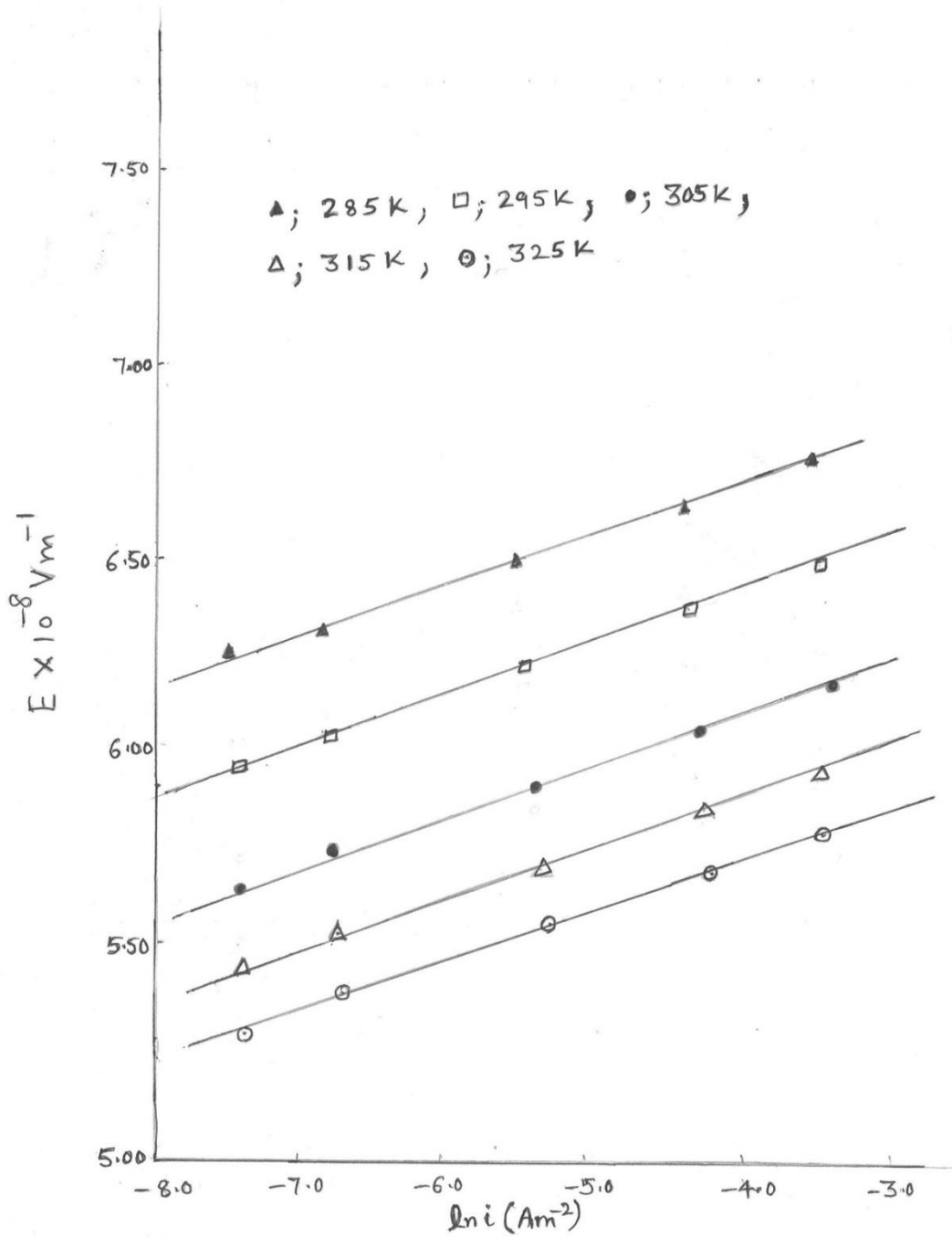Fig-2 - Plot of thickness vs voltage of formation for various current densities at 298 K

Fig.3 - Plot of field variation with lni at different tempertures of formation

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