Kinetics and Breakdown Voltage Studies of Tantalum - Tantalum Oxide - Electrolyte Systems

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Abstract
Steady state kinetic data and breakdown voltage studies of anodic oxide thin films on tantalum in various aqueous electrolytes have been obtained. The above data has been obtained at different current densities, field strength, temperature, composition, concentration and resistivity of the Electrolytes. These studies have been made by eliminating the difference of film growth caused by different surface conditions. The rate of increase of field strength with logarithm of ionic current density is independent of temperature. The data show same relation between electronic current and field holds irrespective of film thickness. A direct relation between electronic current and breakdown voltage has been observed. The maximum thickness reached during the growth of Anodic oxide film on tantalum and other metals is limited by electrical breakdown. The effect of electrolyte concentration on breakdown voltage can be explained in terms of Ikonopisov electron injecting avalanche model. The major factor contributing to the decrease in breakdown voltage with increase in electrolyte concentration is its increasing primary electronic current. The values of the parameters for impact ionization coefficient and primary electronic current have been evaluated. Appearance of sparking is found to be superior method for identifying breakdown voltage during formation of Tantalum oxide films. It has been found field strength is independent of film thickness up to certain formation voltage and at higher formation voltages, the dependence of field strength on film thickness was observed.

Introduction
During growth of Anodic oxide films on Tantalum in aqueous electrolytes it has been found that rate of increase of field with logarithm of Ionic current is independent of temperature. When an oxide film is formed at a constant current density up to a certain formation voltage and if the voltage is kept constant, the film growth causes a rapid decrease of current and ultimately reaches a constant value. If the voltage is lowered, the film growth stops and the current passes through the film is entirely electronic. The practical limit to the maximum thickness of oxide reached in anodization process is given by breakdown voltage across the film. It is found that concentration of the electrolyte has a significant effect on the breakdown voltage and this has been attributed to the resistivity of the electrolyte solution. Since the mechanism suggested to explain the breakdown phenomena involves injection of electrons into the film

from the electrolyte, the data have been examined critically by taking into effects of field strength, temperature, composition, concentration and resistivity of the electrolyte.

Materials and Methods

Specimens of tantalum ($2 \times 10^{-4} \, m^2$) with small tags were cut from 99.9% pure tantalum sheets and the edges of the specimens were abraded with fine emery paper to make them smooth. The specimens were then dipped in potassium hydroxide melt to clean the surface and finally washed with distilled water. The chemical polishing of these specimens was done by dipping in freshly prepared etching mixture of 98% H_2SO_4 + 70% HNO_3 + 48% HF (5:2:2, V/V) for 3-5 seconds and then washed with distilled water. Thereafter, the specimens were placed in boiling water for about 10 minutes to remove any remaining impurities from the surface of the specimens. The tags of the specimens were covered with a thick 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 the growth of oxide film. Anodic polarization of specimens was carried out at constant current and the supply of current was cut off by an electronic control after the desired formation voltage was reached. Before anodization, the tags of the specimens were covered with a thick anodic film in their own electrolyte solutions so that oxidation takes place only at the working area of the specimens. Experiments under galvanostatic conditions were performed up to breakdown voltage in aqueous solutions of potassium nitrate, magnesium chloride and lead nitrate. The solutions were made with conductivity water and their electrolytic resistivities were measured using a digital conductivity bridge. The time for passage of current for formation of film through successive intervals of voltage was recorded by an electronic timer. The density of tantalum oxide film was taken as 7930 kg/m^3 as reported by Young[8] for calculating thickness of the oxide film.

Results and Discussion.

The plot of voltage of formation against time during growth of oxide film on tantalum in various concentrations of potassium nitrate are shown in Fig.1.These plots were found to be linear up to certain voltage of formation indicating that field strength is independent of film thickness up to certain formation voltage thereafter dependence of field strength on film thickness is observed. Similar data was obtained for other aqueous electrolytes. It is found that oxide films can be grown up to certain maximum value of voltage beyond which any further increase in charge does not lead to change in voltage of formation. This maximum value of formation voltage referred to as breakdown voltage is difficult to be identified. Therefore, various criteria to identify breakdown voltage were examined. These were (1) the voltage at which rapid fluctuation in voltage starts, (2) reaching of maximum voltage, (3) slowing down of voltage, (4) the voltage at which gas evolution takes place, (5) the voltage at which sparking appears, (6) the voltage at which audible cracking takes place. It was observed that gas evolution preceded sparking but at low current densities gas evolution takes place for a very long time before sparking starts. Therefore, at low current densities gas evolution was not chosen as criteria for identifying breakdown voltage. Slowing down of voltage as a criterion is not found to be useful because the rate of slowing down (dV/dt) decreases as current density increases and ultimately it reaches almost a zero value in the region of voltage of interest. Audible cracking occurs at current densities higher than 10

Am^{-2} and is not easily detectable at low current densities. Reaching of maximum voltage has not been used as criterion to measure breakdown voltage because at higher current densities (500 and 1000 Am^{-2}) no such maximum voltage is reached. Therefore, this criterion was not chosen for identifying breakdown voltage. It is found that sparking appears at all the current densities and at low current densities, voltages at which sparking appears is close to maximum voltage. Hence, for identifying breakdown voltage, appearance of sparking is chosen as a criterion (as it occurs at all current densities) during growth of tantalum oxide films. The plots of breakdown voltage against current densities in various aqueous solutions of potassium nitrate, magnesium chloride and lead nitrate are linear with zero slopes which indicates that breakdown voltage is independent of current density at which the oxide films are formed. The variation in voltage of formation with time during which charge is passed at different current densities in 100 $molm^{-3}$ aqueous solution of potassium nitrate at 298 K are plotted in Figure 2. Similar plots were obtained for aqueous solutions of magnesium chloride and lead nitrate. The plots are found to be linear up to a film formation voltage of 225V and become concave towards the time axis at higher voltages of formation. The effect of electrolyte concentration on breakdown voltage was studied and it was observed that the plots of breakdown voltage versus concentrations of various electrolytes are linear up to concentration of 100 $molm^{-3}$,thereafter, with further increase in electrolyte concentration only small decrease in the values of breakdown voltage is 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 the linear plots between breakdown voltage and logarithms of reciprocal of concentration as shown in Figure 3 confirmed it. Therefore, the effect of concentration on V_B can be represented by equation 1:

$$V_B = a_c + b_c \log 1/c \qquad (1)$$

Where a_c and b_c are constants whose values are reported in Table 2. At high electrolyte concentrations large number of ions are available per unit concentration and hence the electrolyte possesses large electrolytic conductivity but low resistivity. The low values of V_B obtained for high electrolyte concentration possessing low resistivity suggest a direct relation between breakdown voltage and electrolytic resistivity. The effect of concentration on breakdown voltage was checked more directly by measuring electrolytic resistivities of solutions of potassium nitrate, magnesium chloride and lead nitrate. No linear relation was found between breakdown voltage and resistivity of the electrolyte. However, the plots of breakdown voltage and logarithm of electrolyte resistivity are linear and their relation can be represented by equation 2:

$$V_B = a_b + b_b \log(\rho) \qquad (2)$$

Where a_b and b_b are constants. The values of constant a_b and b_b for potassium nitrate, magnesium chloride and lead nitrate are given in Table 2. Breakdown voltage is found to be independent of pH of the solution. This was confirmed from V_B values of aqueous solutions of potassium nitrate, magnesium chloride and lead nitrate. The values of breakdown voltage decreases only slightly with the increase in temperature and the decrease in breakdown voltage was more at lower Electrolyte concentration. The

decrease in V_B with increase in temperature is due to decrease in electrolytic resistivity at higher temperature. The values of field strength at 298 K for 100 molm^{-3} aqueous solutions of potassium nitrate, magnesium chloride and lead nitrate are found to be 5.69, 6.34 and 5.82 × 10^8 Vm^{-1}, respectively. The corresponding values of breakdown voltage are 245, 330 and 235 V, respectively. This clearly showed non-dependence of field strength on breakdown voltage. Further it was observed that breakdown voltage does not change with topography of the specimen, as checked by taking various samples of different topography which suggests that breakdown voltage is not triggered by conduction through fissures and flaws on the surface of the specimens. Next, it is found that breakdown voltage values are closer to each other in case of aqueous solutions of potassium nitrate and lead nitrate (Table1) which suggests that breakdown voltage is only affected by anions of electrolyte solutions. These anions of the electrolytes get injected into the conduction bands of the oxide film during anodic polarization. These incorporated anions results in the formation of traps which being in electronic equilibrium with the electrolyte. Further it can be concluded that the electrons are thermally excited continuously from traps into conduction band o and equilibrium is maintained by the continuous injection of electrons from the electrolyte. At a critical voltage, due to high field strength the electrons acquire very high energy and cause release of secondary electrons by impact ionization, which results into avalanche multiplication and breaking of the oxide film.

Acknowledgment

Table 1: Electrical Breakdown Voltages (VB) and Electrolytic Resistivity Values for Various Aqueous Electrolyte Solutions

Concentration	Potassium Nitrate		Magnesium Chloride		Lead Nitrate	
(Moles/Litre)	Breakdown Voltage (V)	Electrolytic Resistivity (Ω cm)	Breakdown Voltage (V)	Electrolytic Resistivity (Ω cm)	Breakdown Voltage (V)	Electrolytic Resistivity (Ω cm)
0.01	410	448.1	555	285.3	390	349.2
0.025	345	339.0	460	191.8	335	276.3
0.05	290	283.7	415	140.9	275	204.1
0.10	245	101.3	330	51.0	235	81.3
0.25	225	47.6	280	26.1	215	33.9
0.50	170	30.8	235	18.9	160	20.8

Table 2: Values of the Constants of Dependence of Electrolyte Concentration and Resistivity on Breakdown Voltage

Contacting Electrolyte	Electrolyte Concentration - Breakdown Voltage Dependence		Resistivity - Breakdown Voltage Dependence	
	a_c (V)	b_c (V)	a_b (V)	b_b (V)
Potassium Nitrate	289.6	206.3	178.2	87.5
Magnesium Chloride	267.8	182.4	203.7	115.2
Lead Nitrate	297.3	213.7	186.4	93.7

Fig.1.

Fig.2.

Plot of breakdown voltage (V_B) versus logarithm of reciprocal of electrolyte concentration (log 1/c)
(⊚) Potassium Nitrate (◉) Magnesium Chloride
(△) Lead Nitrate
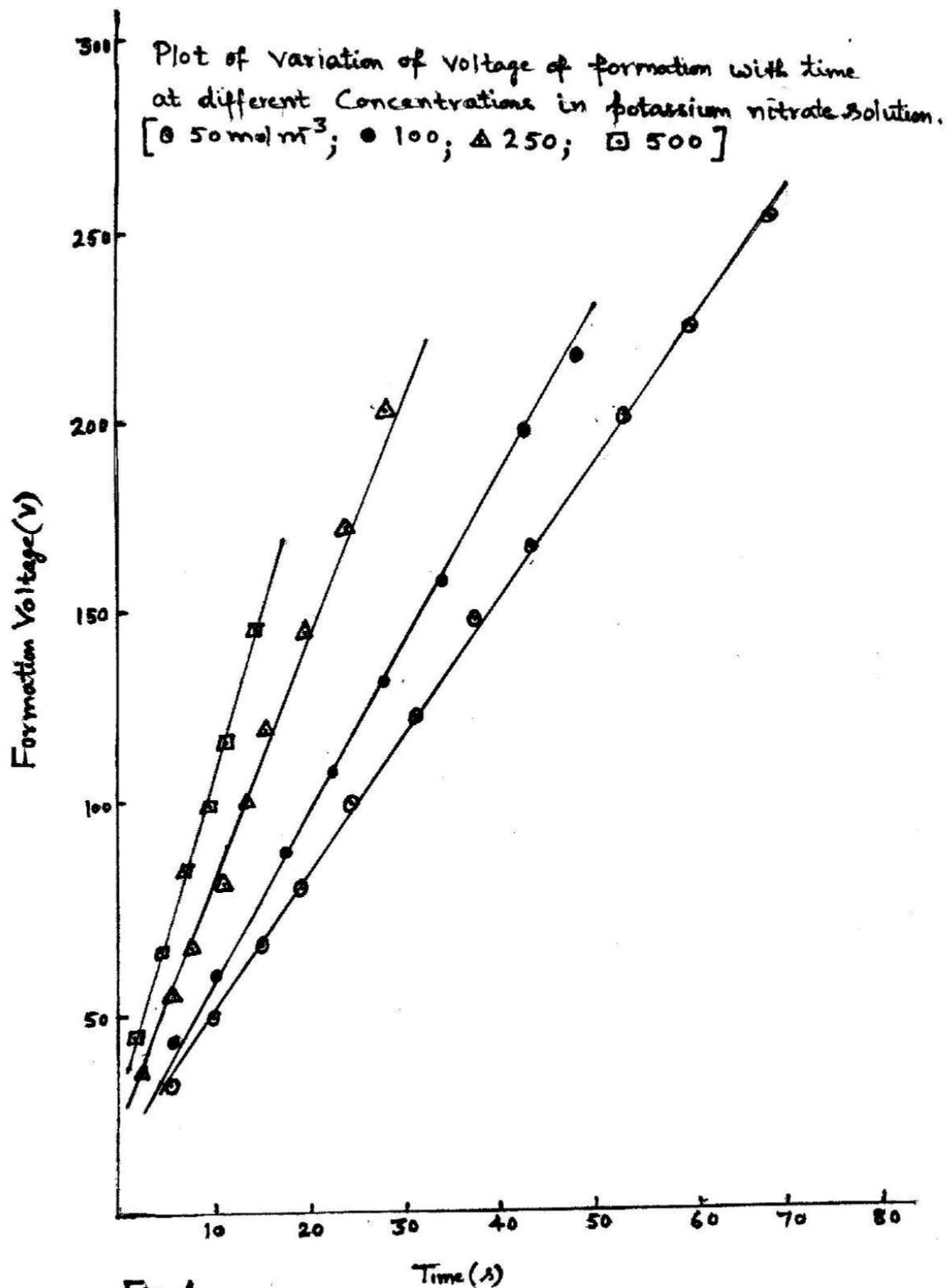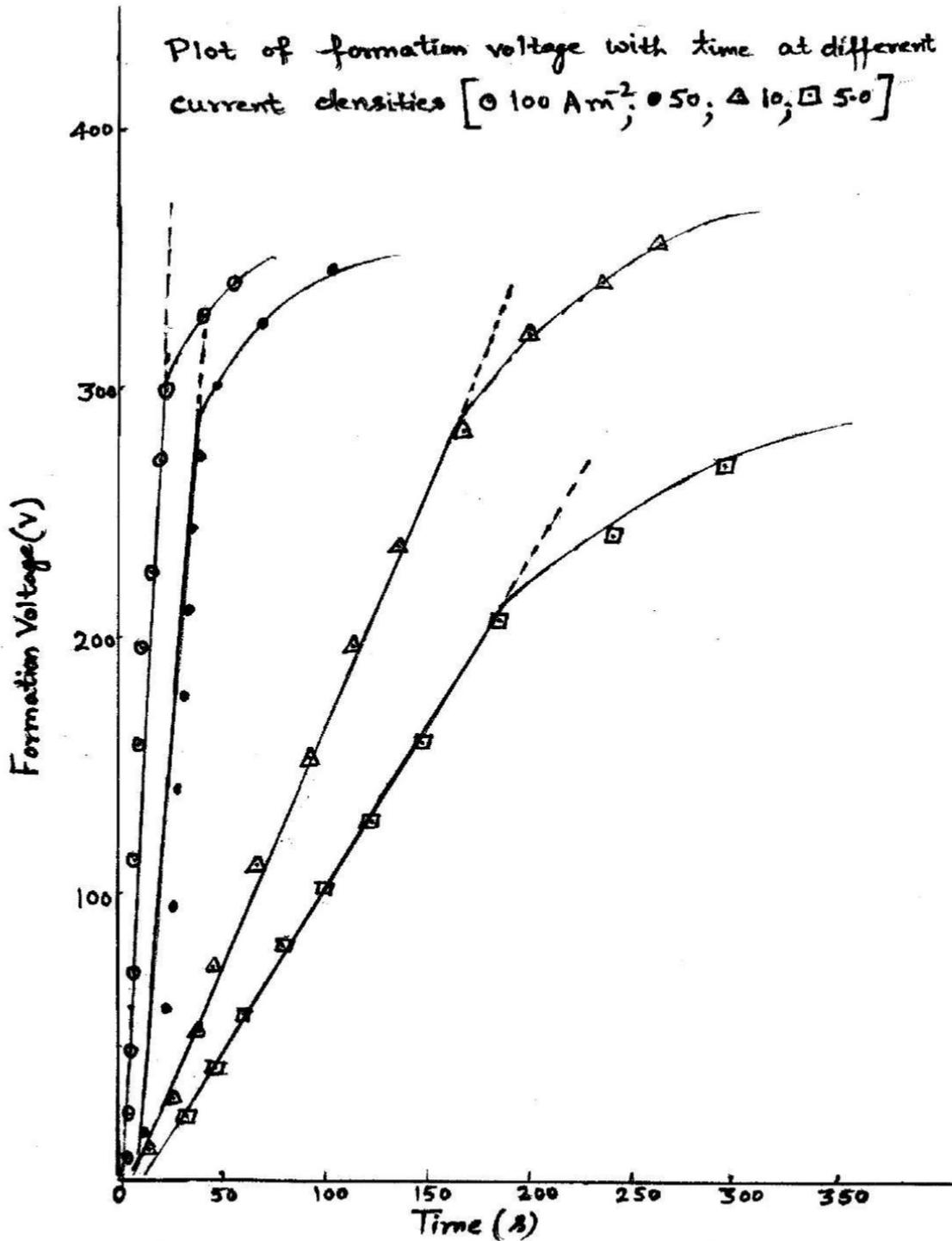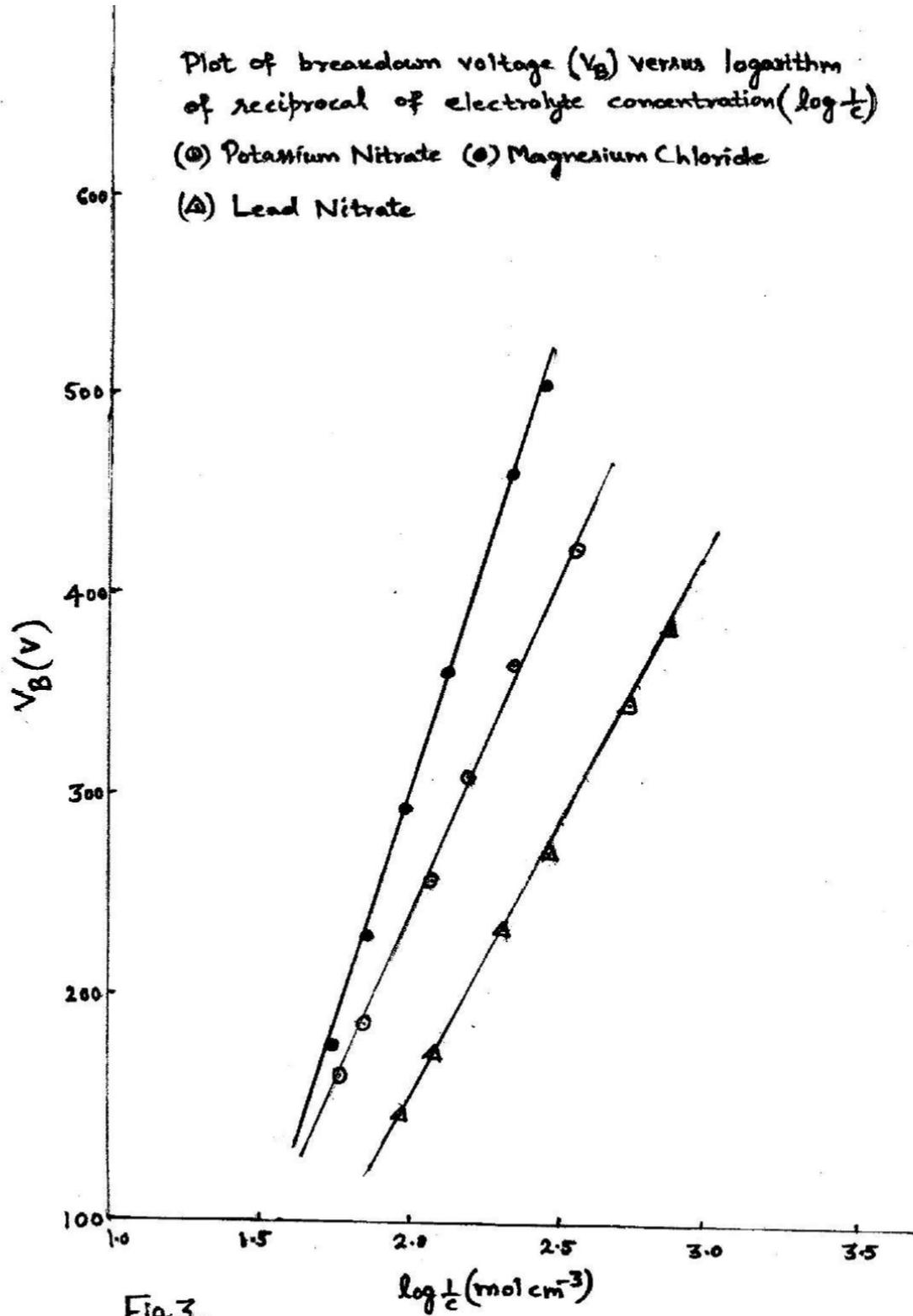
Fig.3.

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