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# The half-Jump Distance and Height of Energy Barrier Studied in Different Constant Current Densities of Zircaloy-4 By Faraday 1st Law and it's Applications.

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***Abstract*--The Cabrera-Mott theory implies anodic polarization of zircaloy-4 is limited by the field – facilitated activated jumps of valve metal ions at the valve metal – oxide interface was originally proposed to interpret growth of anodic oxide films (coloured films) on planar valve metal surfaces. The growth kinetics of oxide film formed on zircaloy-4 in electrolyte diammonium oxalate concentation was at 0.1 mol dm$^{-3}$ as the anodic polarization was carried out in galvanostatic regime have been studied at constant current densities ranging from 8 to 16 mA.cm $^{-2}$ at room temperature in order to investigate the dependence of ionic current density on the field across the zirconia. The formation rate increased, faradaic yield increased and then slight decreased and differential field decreased and then increased were found with increase in the ionic current density for zirconia. The incorporation of anions at different constant current densities found to improve the growth kinetics of different colours covering entire oxide films on the surface of the valve metal upto the different breakdown voltages at different constant current densities. The kinetic results are calculated by Anodidation Rate, faradaic yield, and Differential Field from the conventional plots. A conventional linear plot of logarithm of ionic current density vs. Differential field and applying the Cabrera – Mott theory. The half – jump distance "a" and height of energy barrier "W" were deduced as 0.78 Å and 0.88eV.**

***Keywords*-- Anodic polarization, valve metal Zircaloy-4, electrolyte, different constant current densities, cabrera-mott theory, Faraday 1st law.**

## I. INTRODUCTION

Several research investigations have been dedicated to the anodic polarization of zircaloy-4 in differenr electrolytes ( acidic, basic or neutral). Their research aim based on the conditions under which they were carried out as well as the respective research results are quite diverse.

The theory advanced by Cabrera and Mott (1) on the basis of earlier work by Mott (2) to explain the rate of growth of oxide films on metals usually has been regarded as directly applicable to the case of anodic oxidation. When valve metals such as zirconium and its alloys like Zr – 2, Zr – 4, etc are anodically polarized, interference colored oxide films are formed. These smooth and mechanically perfect anodic films can act as dielectrics in capacitors. The phenomenon of anodic oxidation plays a basic role in micro-circuitry (3) and in thin film methods (4). Anodic oxide films formed on valve metals are useful in the field of electrical and electronic components (such as capacitors, resistors, dioxides and photo electric devices), corrosion protection and for decorative purposes. Applications of anodic films have been reviewed (5). Using the empirical relation proposed by Guntherschultze and Betz (6) were the first to investigate the kinetics and mechanism of the anodic oxidation of metals. The kinetics of anodic film formation on zirconium in various electrolytes has been reviewed (7). Vermilyea (8) has published data covering a range of temperatures, which dispute some of the predictions of the theory of Mott and Cabrera. Their theory predicts a logarithmic increase of forming field with current density (or rate of formation). Zirconium and its alloys have been studied for being used in the nuclear power industry and have been recently commercialized for its use in medical implants, especially for total knee and hip replacements after hydrothermally grown oxide (9). Zr and Zr alloys have greater strength, lower cytotoxicity and lower magnetic susceptibility than titanium (10). Zirconia is used as a dielectric layer in capacitors and as a passivation layer on metal surfaces (Google Search).

The scientific research aim is to describe the nano oxide film growth kinetics by using faraday 1st law and cabrera -mott theory.

In this research investigation, the ionic current density with various diffential field studies the effect of different constant current densities on the kinetic parameters of different anodization voltages of zircaloy-4 based on nanostructured oxide films have been obtained during anodic polarization experiments diammonium oxalate with 0.1 mol $dm^{-3}$ concentration by faraday 1st law and Cabrera – Mott theory to deduce the half – jump distance "a" and height of energy barrier "W".

Experiments will be conducted at various current densities to observe the exponential dependence of current density on differential field impressed across the oxide film to deduce and compare the kinetic parameters viz. Ai, Bi, "a" and "W".

## II. Materials And Methods

Zircaloy-4 was of 98% nominal purity, supplied in the form of plate by Nuclear Fuel Complex [NFC], Hyderabad as gift sample. Thinning of Zircaloy-4 plate was done by Defence Metallergical Research Lab [DMRL], Hyderabad. Cutting of the thinned sheet was done at tools and techniques,Balanagar,Hyderabad. The chemical composition of zircaloy-4: 0.07 wt. % chromium; 0.23 wt. % iron; 1.44 wt. % tin and balance is zirconium.

In the scientific research work, the foil samples used were cut with the aid of a punch into flag-shaped specimens of 1 $cm^2$ working area on both side and 1½ cm long tag .The chemical polishing mixture consisted of acids such as HNO3, HF and water in a definite volume ratio of 3:3:1.

### *Anodic Polarization of Zircaloy-4 conditions*

The counter electrode was a sheet of Platinum (2x3 cm, weight 3.000 gm). The working electrode was the Zircaloy-4 sample. For anodizing, a double walled glass cell 100mL capacity was used. The experiments were performed in an electrolyte, 0.1M ammonium oxalate. All experiments were carried out at constant current densities ranging from 8 to 16 $mA.cm^{-2}$. The experimental procedure for the anodic polarization by faraday 1st law is given elsewhere [11].

## III. Results And Discussion

### *Kinetic measurements*

Specimen of zircaloy-4 was anodically polarized in 0.1 mol $dm^{-3}$ concentration (0.1M ammonium oxalate) of diammonium oxalate at a constant current density of $8mA.cm^{-2}$ and at room temperature.

The anodization time and the capacitance of the anodized film formed are measured at an interval of 10V by interrupting the constant current circuit. Thickness of the oxide film were estimated by capacitance measurements. The anodization voltage vs. anodization time plot Figure.1 was found to be linear up to the breakdown voltage. The breakdown voltage was observed to be different for zirconia ($ZrO_2$) at different constant current densities from 8 to 16 $mA.cm^{-2}$.

The effect of current density, the composition and concentration of electrolyte and the nature to the metal on the features of electrical breakdown and the value of breakdown voltage were studied. We detected the breakdown voltage as a visible spark.

The results have shown through conventional plots are linear and two portion linear up to break down voltage and the conventional plots are shown in Figures 1 to 12. From these plots the Anodization Rate, Faradaic Yield & Differential Field were estimated and are summarized in Table 1.

The dielectric strength of an oxide layer is often expressed in terms of the electric field at which the insulator is irreversibly damaged and lost its insulating properties. There are several test methods for measuring the breakdown parameters depending on the way the stress voltage or stress current are applied. We start with the most widely known technique, namely the voltage ramp. The voltage is ramped with a constant ramp rate dV/dt. While the current through the oxide is being measured, it increases towards higher voltage levels. When there is breakdown the curerent jumps to a high level and passes a pre-set current limit $I_{limit}$. The value of the violtage at which this happens is dedfined as the breakdown voltage. It should be noted that the actual current shape that can be measured is dependent on the sensitivity of the current meter. With a less sensitive instrument only the current jump is detected. Of course, this is sufficient for determining the breakdown voltage. Dividing the latter by the oxide thickness we obtain the breakdown field (provided no polysilicon depletion is necessary). Oxide breakdown has a strong statistical nature. In this and other breakdown techniques [12].

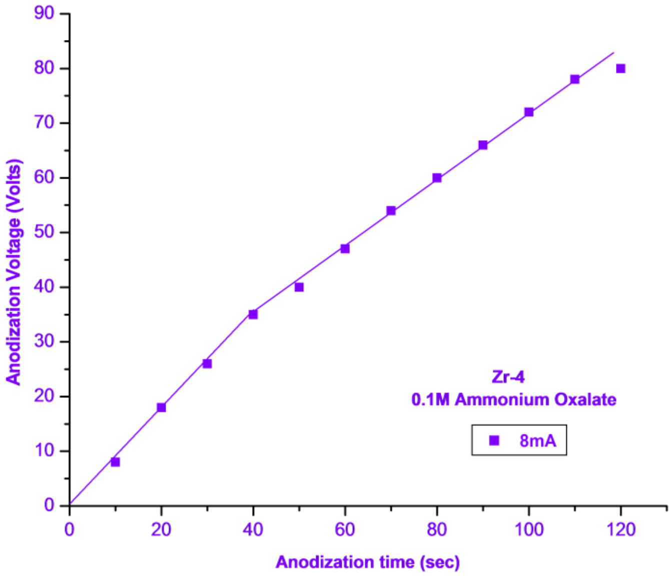

Fig 1. Plot of anodization voltage as a function of anodization time.

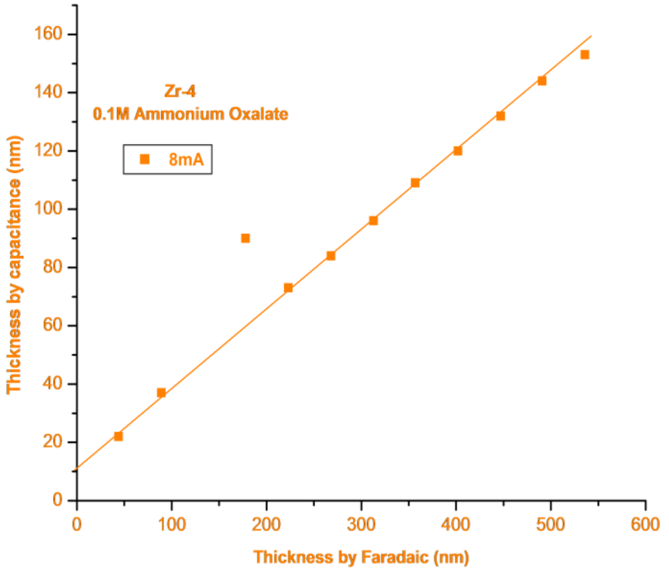

Fig 2. Plot of thickness by capacitance as a function of faradaic.

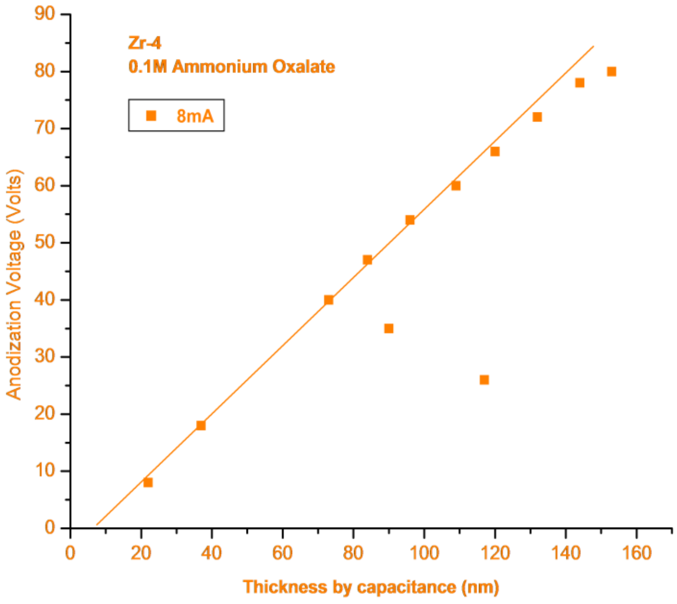

Fig 3. Plot of anodization voltage as a function of thickness by capacitance.

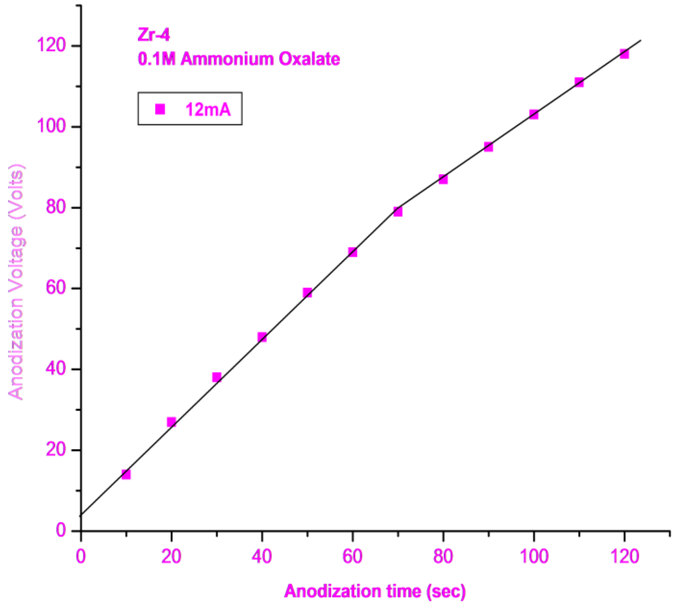

Fig 4. Plot of anodization voltage as a function of anodization time.

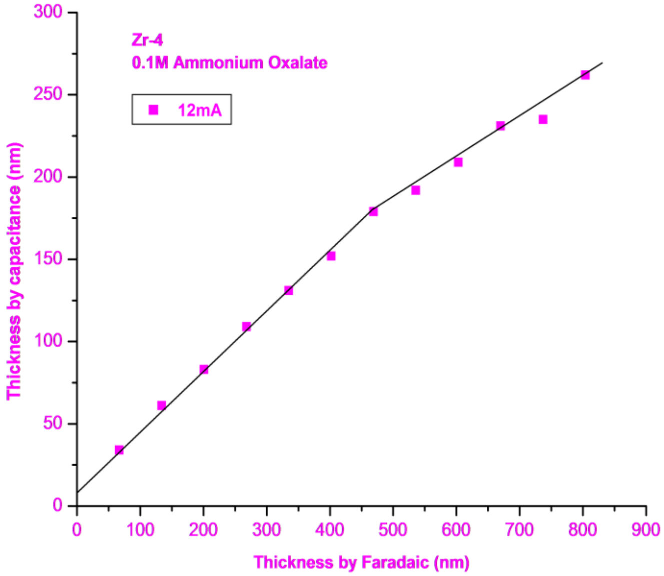

Fig 5. Plot of thickness by capacitance as a function of faradaic.

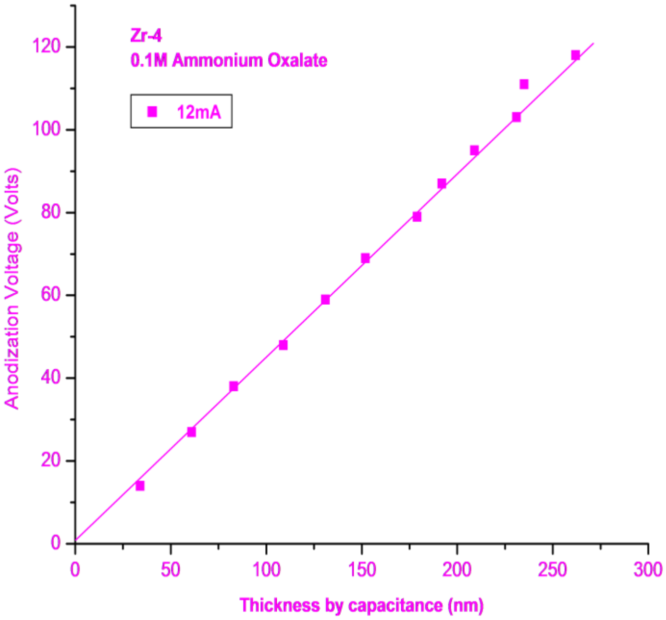

Fig 6. Plot of anodization voltage as a function of thickness by capacitance.

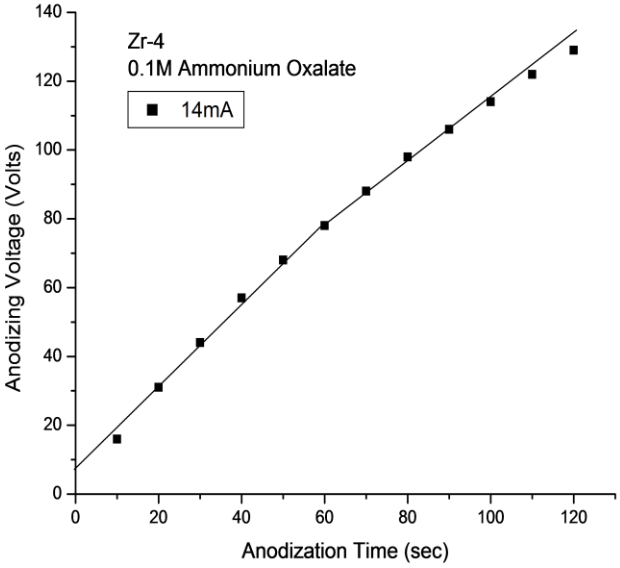

Fig 7. Plot of anodization voltage as a function of anodization time.

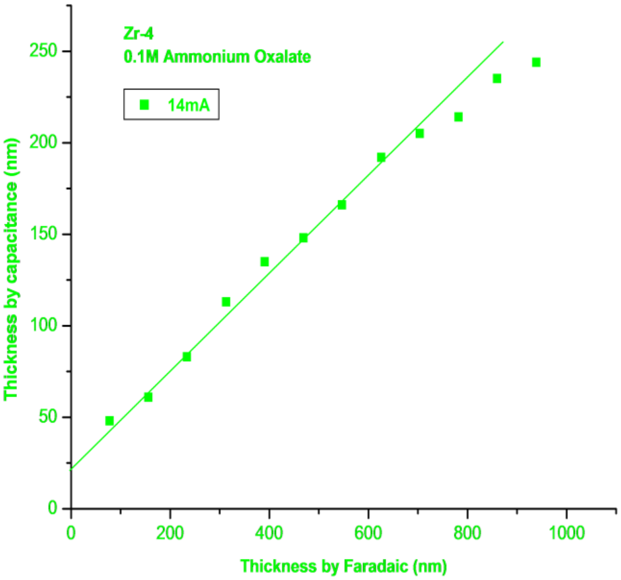

Fig 8. Plot of thickness by capacitance as a function of faradaic.

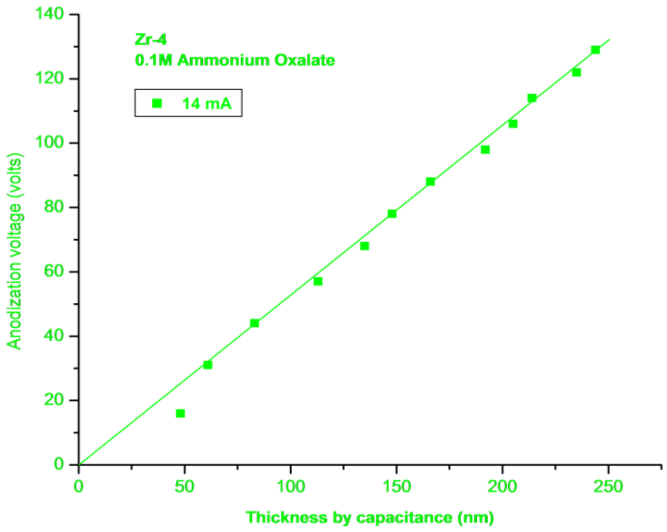

Fig 9. Plot of anodization voltage as a function of thickness by capacitance.

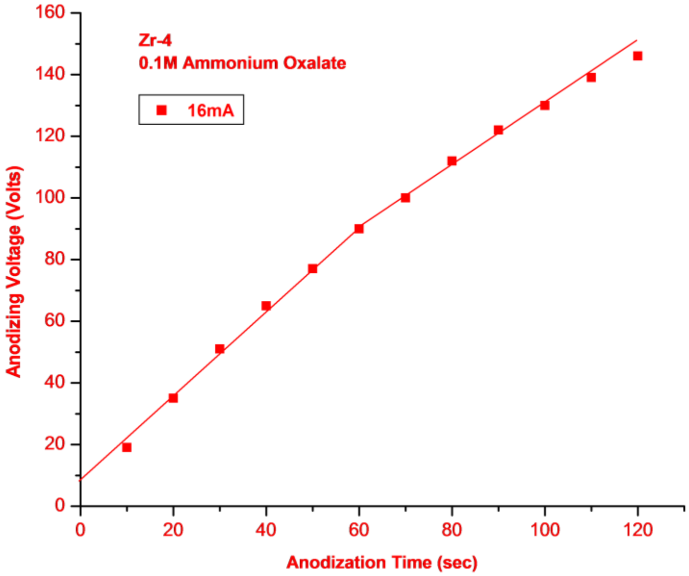

Fig 10. Plot of anodization voltage as a function of anodization time.

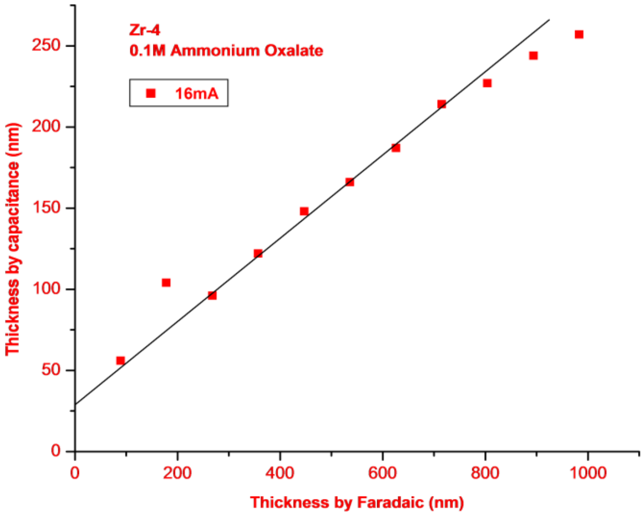

Fig 11. Plot of thickness by capacitance as a function of faradaic.

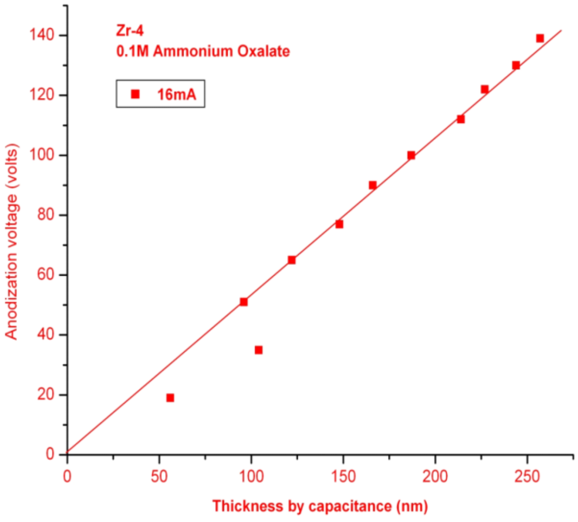

Fig 12. Plot of anodization voltage as a function of thickness by capacitance.

**Table: I**
**Anodic film formed on zircaloy-4 in 0.1 mol dm$^{-3}$ diammonium oxalate.**

| Constant Current Density mA.cm$^{-2}$ | Anodization Rate V.s$^{-1}$ | Faradaic Yield η (%) | Ionic Current Density mA.cm$^{-2}$ | Log.Ionic Current Density, Log.$i_i$ | Differential Field,$F_D$ MV.cm$^{-1}$ |
|---|---|---|---|---|---|
| 8 | 0.72 | 53.72 | 4.544 | 0.657 | 5.669 |
| 12 | 1.2 | 65.66 | 7.879 | 0.896 | 5.0 |
| 14 | 1.3 | 65.82 | 9.214 | 0.964 | 5.256 |
| 16 | 1.4 | 60.66 | 9.705 | 0.986 | 5.384 |

*Dependence of ionic current density on the field strength of formation*

Anodic polarization were carried out separately in 0.1 mol dm$^{-3}$ diammonium oxalate at constant current densities ranging from 8 to 16mA.cm$^{-2}$ to investigate the exponential dependence of the ionic current density on the field across the anodic oxide film. The potential further increased up to the breakdown voltages at different constant current densities. The parameter differential field, also known as the CABRERA-MOTT FIELD, which describes the electric field across the anodic polarized oxide layer its growth. The cabrera-mott field plays very important role in the field-assisted migration of valve metal ions across the interface between the valve metal and the growing oxide layer. This is a key mechanism in the growth of anodic oxide coloured films. The details are summarized in Table 1. The plot of log. ionic current density vs. Field Strength gave fairly linear relationship as shown in Figure 40.

Anodic films formed in suitable conditions have versatile applications as resistors, dielectrics, reflectors, rectifiers, semiconductors and photoanodes etc [13].

## IV. DISCUSSIONS

*Growth Kinetics Dependence of ionic current density on differential field strength of zirconia*

The time dependence of the thickness of the $ZrO_2$ layer growing on top of a zirconium alloy is usually, described as $kt^n$ where k is a rate constant and n is typically smaller than 0.5, i.e the rate is Sub-parabolic [14].

Guntherschultze and Betz[12] were the first to establish empirically, that under steady state and high field conditions, the ionic current density ( $i_i$ ) and electrical field strength ( F ) are related through the exponential law [6].

$$\mathbf{i_i = A_i \exp (B_i F) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)}$$

The temperature dependent constants Ai and Bi were found comparing with Cabrera-Mott equarion[1]. Where **'$A_i$'** and **'$B_i$'** are temperature dependent constants for a particular metal. Cabrera and Mott **[1]** proposed that ionic current density, "$i_i$", could be written as

$$\mathbf{i_i = n\,vq \quad \exp \quad [-(W-qaF/kT)] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)}$$

where 'n' is the surface density of mobile ions i.e, the number of cations per square cm of the metal surface able to undergo anodic transfer into the film, 'ν' is the vibrational frequency of a moving ion, i.e, the number of chances the ion may jump the energy barrier at the metal/oxide interface if it has sufficient energy, 'W' is the height of energy barrier at the metal/oxide interface over which the ion must pass in order to enter the oxide bulk.

Verwey[15] considered the energy barrier for ion movement through the oxide bulk as being the rate determining step and obtained an equation of an identical nature.

$$\mathbf{i_i = 2an\,vq \exp [-(W-qaF)/kT] \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)}$$

where 'n' is the number of mobile ions per unit volume and ' ν ' is their vibrational frequency.

Comparing equations (1) and (2) it can be seen that

$$\mathbf{A_i = n\,vq \exp (-W/kT) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)}$$

$$\mathbf{B_i = qa/kT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)}$$

The growth kinetics involves the study of ionic current density with variation of differential field and calculations of kinetic parameters, half jump distance "a" and height of the energy barrier "W" assuming the rate determining step lies at the interfaces or within the bulk of the oxide.

In the research investigation we assumed that the energy barriers are situated at the interfaces and the cabrera-mott theory is applicable.

The figure 40. shown the variation of log.ionic current density with differential field of formation for anodic polarization of zirconia in Table.2 illustrates the details of influence of current densities on kinetic growth results.

The value of half jump distance "a" deducted in this electrolyte for zircaloy-4 is smaller than the mean separation of oxygen ion in $ZrO_2$ [1.66A°]. At the same time, the value of "a" is comparable to the half lattice parameter of the cubic modification for ZrO2 in Table-2 : Phases identified determined by XRD [16]. The high value of "a' found in the electrolyte diammonium oxalate/ ammonium oxalate could be due to the migration of oxygen ions via interstices, grain boundaries etc, however, the mean jump distance could be more than the interatomic distance. Young [17, 18] accounted for this and for the temperature independence described, to the linear variation of activation distance with the field,

$$a = \alpha - (\beta) F \text{.........................................} (6)$$

Where α and β are both positive constants.

The equation for an ionic current density would thus involve a quadratic function of the electrical field strength "F", with the first and second order terms in "F" acting in opposite directions,

$$i_i = n\, vq \exp [-(W - q\, \alpha\, F + q\, \beta\, F^2 ) /k\, T] \text{...............} (7)$$

i.e, the slope of $\log.i_i$ vs. F plots varied as expected with temperature in an exponential manner but was not independent of field. The anomaly in previous determination was due to the calculation of mean slope over a fixed range of ionic current density.

The values of **$A_i$ , $B_i$, W and a** deduced for zirconia in diammonium oxalate concentation was at 0.1 mol $dm^{-3}$ (0.1M AO) are found. The difference in the field of formation to grow films[19]. Plots of the logarithm of formation rate vs. logarithm of the current density are fairly linear. From linear plots of logarithm of ionic current density vs. differential field and applying the cabrera-mott theory, the half-jump distance and the height of the energy barrier are deduced and compared.[20].

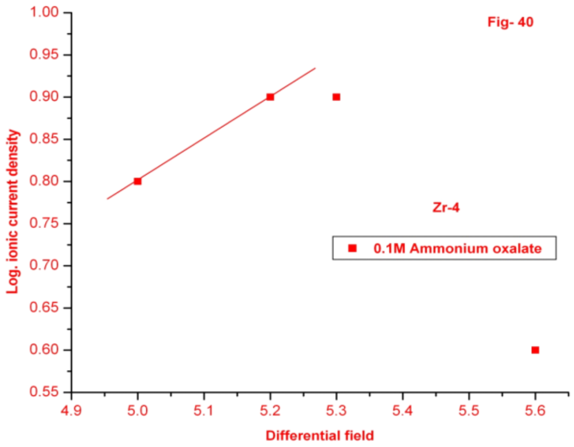

**Fig 40. Plot of variation of log.ionic current density vs. differential fiield.**

**Table II**
**Estimation of kinetic parameters of field ion conduction (Control by Oxide/ Electrolyte barrier).**

| Electrolyte | Ai<br>$mA.cm^{-2}$ | Bi<br>$cm.V^{-1}$ | W<br>eV | a<br>Å |
|---|---|---|---|---|
| 0.1mol $dm^{-3}$ diammonium oxalate | $3.83 * 10^{-4}$ | $0.61*10^{-6}$ | 0.88 | 0.78 |

## V. CONCLUSION

Oxide films investigated in the electrolyte 0.1 mol $dm^{-3}$ diammonium oxalate[0.1M ammonium oxalate] found to improve the kinetic results analyzed in Table 1. Faraday 1st law governs the formation of zirconia oxide films with the faradaic yield percentage is increased indicates the percentage of current used for film growth kinetically improved due to increase of constant current density. Capacitance measure determines the zirconia store electrical energy, effectively it conduct charge. Anodization rate estimates the thickness of zirconia oxide films, faradaic yield evaluates the electrical charge transfer estimated good yield and differential field with different constant current densities from 8 to 16 $mA.cm^{-2}$. Oxalate coated zirconia exhibits much higher capacitance. On the basis of the evidence available the rate determining step is considered to be situated at the oxide/electrolyte interface, and CABRERA-MOTT THEORY is applied to the growth kinetics. The deduced value of half jump distance "a" and height of the energy barrier "W" are investigated to be as 0.78A° and 0.88eV. zirconia is considered a "high-k" dielectric material i.e it has a relatively high dielectric constant.zirconia is using in nuclear industry and in natural science[physics, chemistry, geology and biology]. Anodic films formed in suitable conditions have versatile applications as resistors, dielectrics, reflectors, rectifiers, semiconductors and photoanodes etc.

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