

Kinetics and Current Efficiency Studies of Aluminium Oxide Films in Aqueous Electrolytes.

Dr.Parveen Katyal

Department of chemistry, S.D.(P.G) College, Panipat (Haryana)

E-mail :- pkkrtk@gmail.com

-----ABSTRACT-----

Kinetics and current efficiency data during growth of aluminium oxide films in various aqueous electrolytes of different concentrations and compositions have been evaluated. The kinetic 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 found to be independent of temperature. It is observed that entrance barrier energy is greater than the corresponding diffusion barrier energy which suggests that the rate- controlling step during anodic oxidation aluminium is the ionic movement across the film and not at the metal / oxide interface. The current efficiencies of such films are unity upto an electrolyte concentration of 100 mol m^{-3} . It is found that at higher electrolyte concentration the experimental mass-gain of aluminium specimen during anodization is greater than that expected for the formation of aluminium oxide on aluminium which implies that mass gain is due to incorporation of anions into the bulk of oxide film.

Keywords – Anodic Oxide, Films, Aluminium

I. Introduction

During growth of anodic oxide films on aluminium the views suggested by different workers regarding ionic conduction either within the film and/or at the interface as rate controlling step are at variance. Present investigation has been made to know the exact mechanism during growth of anodic aluminium oxide films in various electrolytes at different current densities at varying temperatures. Theories of ionic conduction during anodic oxidation of aluminium has been discussed. It has been found that the rate of increase of field strength with logarithm of ionic current density is independent of temperature during growth of oxide film on aluminium in various electrolytes which suggests that single barrier theory of Cabrera and Mott ⁵ is not applicable. The double barrier theory of Dewald ⁴ has been found to explain the temperature-independence of Tafel slopes. During growth of oxide films, the difference caused by different surface conditions has been eliminated. Current efficiencies of aluminium oxide films have been calculated in various aqueous electrolytes .

II. Material and Methods

Aluminium samples (2cm² in area) with a short tag were cut from aluminium sheet (purity 99.9%). The edges of the samples were abraded with fine emery paper to make them smooth. The surfaces of the samples were cleaned by dipping them in 10% NaOH solution for 2-3 sec and washing them with distilled water. The chemical polishing of these samples done by dipping them in a freshly prepared etching mixture of concentrated O- phosphoric acid , sulphuric acid and nitric acid in the ratio of 70:25:5 at 350-360K for 2-4sec. The samples were washed with distilled water and dried in a current of hot air. The samples were finally etched just before anodization. The tags of the samples were covered with a thick anodic film in an electrolyte in which further anodization was to be carried out. The samples were anodized at constant current density using an electronically operated constant current power supply. The supply of current was cut-off after the desired voltage of film formation is reached. The time for the passage of current for formation of film through successive intervals of voltage was recorded by an electronic timer. The thickness of the film was determined using Faraday law. The density of aluminium oxide film was taken as 3.56 g/cm³ as reported by Tajima⁶.

III. Results and Discussion

The linear plots between voltage of formation and time upto 165V shows that field strength is independent of film thickness. However, at higher voltages of formation, dependence of field strength on film thickness is observed. The plot of field strength against reciprocal of temperature at different current densities is shown in Fig.1. The values of slopes calculated from this plot shows its non-dependence on current density. The plot between field strength versus logarithm of current density at different temperatures is shown in Fig.2. The slopes of this plot show that it is independent of temperature which rules out the applicability of single barrier theory of Cabrera-Mott⁴. which suggests that Tafel slope is proportional to absolute temperature. Guntherschulze-Betz⁸ constants A & B (Eqn.1)

$$i = A \exp BE \quad \dots(1)$$

have been determined in presence of different electrolytes by least squares method at different temperatures. The values of 'B' are 5.02 X 10⁻⁶, 5.35 X 10⁻⁶ and 5.79 X 10⁻⁶ Vcm⁻¹ in aqueous solutions of calcium carbonate, lead chloride and nickel chloride , respectively. The values of constant B are almost of same magnitude in various electrolytes which shows that Tafel slope is independent of temperature. It is found that values of constant 'A' increase with increase in temperature . The values of constant 'A' calculated using Guntherschulze-Betz equation for calcium carbonate, lead chloride and nickel chloride are 2.107 X10⁻¹², 4.092X10⁻¹², 4.793 X 10⁻¹² at 303,318 and 333K, respectively. Similarly, values of constant 'A' at 298K are found to be 3.29X10⁻¹² and 4.16 X 10⁻¹² for calcium carbonate and lead chloride, respectively which shows its dependence on nature of the electrolyte. It is observed quadratic variation of field with ionic current density to explain the field and temperature dependence of Tafel slopes (Table1.)

The data for the experimental mass-gain as a result of anodic oxidation and the calculated mass-gain due to oxidation (when current efficiency is unity) for the growth anodic oxide in different concentrations of various electrolytes are reported in Table.2. At each electrolyte concentration current efficiency is found to be same irrespective of the charge passed. The experimental and calculated mass-gain are close to each other upto an electrolyte concentration of 100 mol m^{-3} when current efficiency is close to unity which implies that the entire current passed is ionic i.e.no fraction of electronic current is used for formation of film. It is observed that for higher concentrations of the electrolytes the experimental mass-gain is more than those calculated mass-gain. It is found that there is about 12% and 15% increase in mass-gain at concentration of 500 mol m^{-3} and 1000 mol m^{-3} , respectively in solution of calcium carbonate. Similar trends in mass-gain are observed for lead chloride and nickel chloride solutions at higher concentrations. The formation of higher oxides of aluminium has been ruled out as possible cause for observed mass-gain as no other stable aluminium oxide except Al_2O_3 has been reported in literature. The increase in mass-gain may be due to incorporation of anions into the oxide film and this is substantiated by the results reported earlier that the breakdown voltage of the films is affected by the incorporation of anions from the electrolytes into the film. Further, incorporation of other anions into oxide film has also been reported by other investigators^{7,8} which concludes that excess mass-gain is due to incorporation of anions into the bulk of oxide film.

Acknowledgment

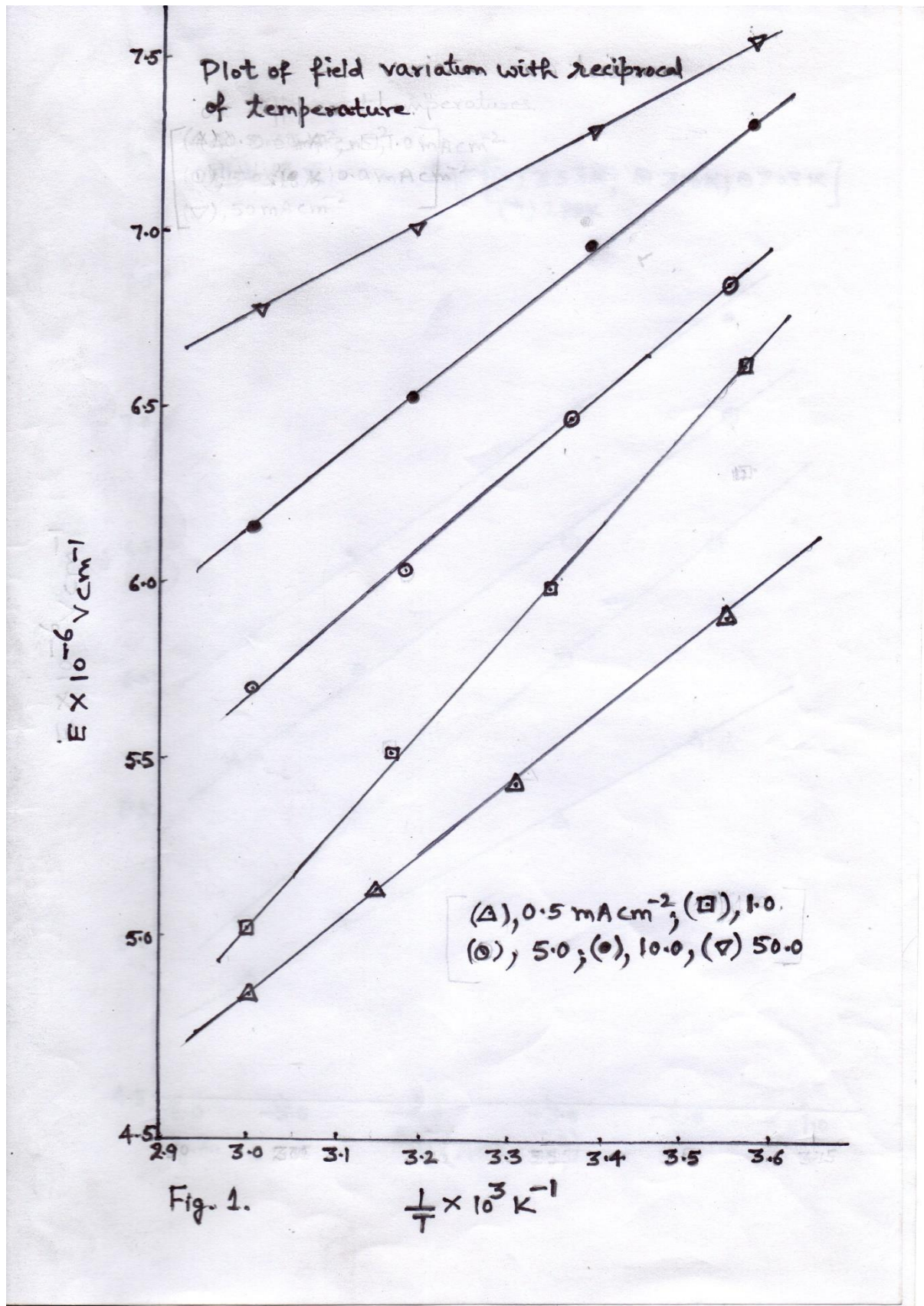
The author acknowledges University Grants Commission, New Delhi for the award of Research project.

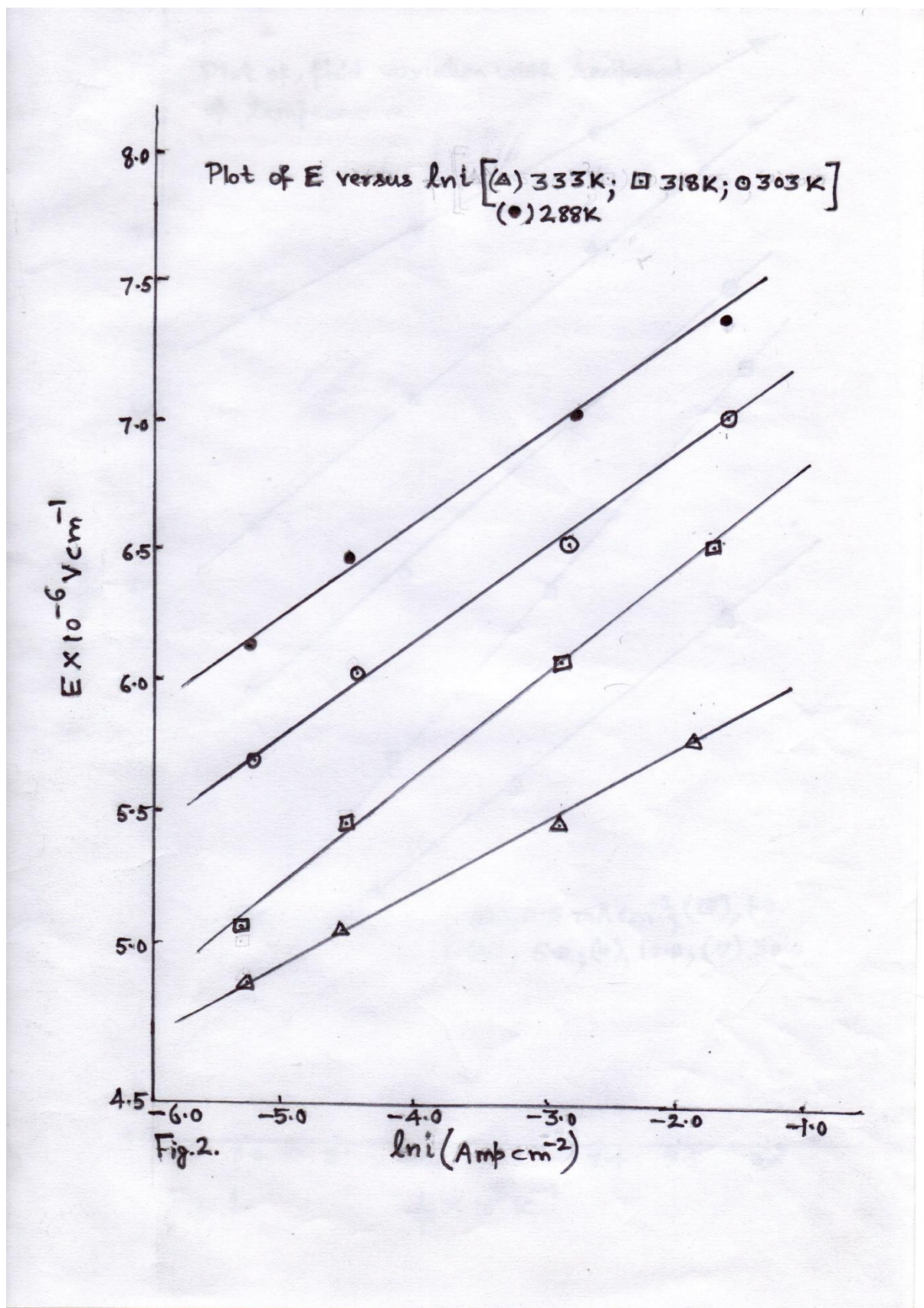
Table.1

Temperature (K)	E X 10⁻⁶(Vcm⁻¹) Current density – 0.5mA/cm²	E X 10⁻⁶ (Vcm⁻¹) Current density – 1.0 mA/cm²	E X 10⁻⁶(Vcm⁻¹) Current density – 5.0mA/cm²	E X 10⁻⁶ (Vcm⁻¹) Current density - 10.0mA/cm²	E X 10⁻⁶ (Vcm⁻¹) Current density - 50.0mA/cm²
288	5.97	6.34	6.80	7.27	7.49
303	5.49	5.97	6.42	6.95	7.21
318	5.12	5.53	6.07	6.45	6.89
333	4.79	5.01	5.69	6.14	6.63

Table.2

Concentration	Mass-Gain		Current efficiency
mol m ⁻³	Exp.	Cal.	
10	496	501	0.990
20	522	527	0.991
50	551	556	0.991
100	588	594	0.990
250	777	685	1.134
500	1079	949	1.136
1000	1246	1107	1.125





REFERENCES

- [1]. K.C.Kalra and Parveen katyal J.Applied Electrochemistry, 21 (1991) 729
- [2]. K.C.Kalra and Parveen Katyal. Thin solid Films, 201 (1991) 203
- [3]. J.M.Albella, I.Montero&J.M.Martinez-Duart, ElectrochimActa,32(1987)255.
- [4]. J.F Dewald , J. electrochem Soc, 102 (1955) 1.
- [5]. N Caberera & N.F Mott , Rep Prog Phys,12 (1948) 163.
- [6]. S.Tajima,N.baba&T.Mori,Elect-rochim Acta,9(1964)1509
- [7]. R.K.Nigam, K.C.Kalra&ParveenKatyal,Indian J. Chem. 26A (1987)
- [8]. A. GuntherSchulze&H.Betz, Z Phys, 92 (1934) 367.
- [9]. K.C. Kalra, ParveenKatyal&K.C.Singh, Thin solid films, 177(1989) 35
- [10]. S.Ikonopisov, ElectrochimActa, 22(1977)1077.
- [11]. I. Montero, J.M.A Ibella& J.M. MartinezDuart,
- [12]. J.Electrochem.Soc.,132(1985)814.
- [13]. KaiyangZeng, Furong Zhu, Jianqiao Hu Lu, Thin Solid Films, 443(2003) 60.
- [14]. R.Jayakrishnan and G.Hodes, Thin Solid Films,440(2003) 19
- [15]. V.Kadary&N.Klein, J.Electrochem. Soc., 127(1980)139.
- [16]. J. yahalom& J. Zahavi, ElectrochimActa, 15(1970) 429
- [17]. Kim and S.M.Rossnagel, Thin Solid Films,441 (2003) 317
- [18]. G.C.Wood&C.Pearson, Corros. Science,7 (1967) 119
- [19]. F.J.Burger&J.C.wit, J. Eletrochem Soc., 118 (1971) 2039
- [20]. O. NilsenH.Fjellvag and A.Kjekshus, Thin Solid Films,444(2003)44
- [21]. G.Machado, Thin Solid Films,489(2005) 124
- [22]. H. Kim and S.M. Rossngel, Thin Solid Films,441 (2003) 311
- [23]. F.Qin, N.P. Magtoto, M.Garza and J.A. Kelber, Thin Solid Films(2003)807
- [24]. Arsova.et.al., Journal of Solid State Electrochemistry,11 (2007)209.