The Effect of Added Ions and Dielectric Measurements of Aluminium Oxide Films in Aqueous Electrolytes

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Abstract

Dielectric measurements and systematic study of film growth on aluminium in different electrolytes has been made when varying amounts of different ions are added. The effect of halide ions added during growth of anodic oxide thin films on aluminium and their capacitances and dielectric constants in various electrolytes have been studied. Studies on effect of HF concentration and oxide thickness on rate of dissolution have been made. Capacitance data for the oxide films formed upto various formation voltages in different electrolytes have been obtained. The relation between capacitance and thickness of oxide film has been established. The effects of concentration and nature of the electrolyte on capacitance have been studied.

I.   Introduction

Dielectric measurements are of a great value for producing good quality capacitors[2-4]. Further, the knowledge of capacitance measurements also finds use in determining oxide film thickness. The determination of oxide film thickness on a substrate depends on various factors, like the type of oxide produced, the electrical double layer capacity at the oxide/electrolyte interface, the dielectric constant of the oxide film etc. The uniform thickness oxide film on metal in metal-metal oxide-electrolyte system can be likened to a system present in a parallel plate capacitor. This can provide a method of evaluating dielectric constants of oxide films. The effect of chloride ions on the capacitance of aluminium oxide films formed in zinc nitrate has been studied. It has been found that the capacitance of the film increases with the increase in amount of chloride ions added.

II.   Materials and Methods

The preparation of anodic oxide film on metal is very sensitive to the method of preparation of surface of the specimen and precautions are required. Therefore, to obtain reproducible results the following experimental method was used.

Aluminium specimens (2×10^{-4} in area) with short tags were cut from a sheet of aluminium (99.9% purity). The edges of the specimens were abraded with fine emery paper to make them smooth. The specimens were then dipped in 10% NaOH solution for 2-3sec to clean

the surface and finally with distilled water. The chemical polishing of these specimens were done by dipping them in a freshly prepared mixture of concentrated O-phosphoric acid, sulphuric acid and nitric acid in the ratio of 70:25:5 at 350-360K for 2-4 seconds, washed with distilled water and then dried in a current of hot air. The etching and drying procedure was repeated just before anodization. This method of surface preparation was found to give a better constant rate of growth in the process of polarization of anode under constant current density.The working area of the specimen was defined by covering the tags of the specimens with a thick anodic film in an electrolyte in which further anodization on square portion of the specimen was to be carried out. In this way no anodization on the tag took place during anodic oxidation of the electrode and the working area is the square surface area of the specimen. The specimens prepared by the above method were placed in a glass cell and connected to a platinum electrode which served as a cathode in oxide film formation process. Anodic oxidation of aluminium was carried out under constant current conditions. 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 film through successive intervals of voltage was recorded by an electronic timer. The dielectric measurements of the oxide films of various thicknesses on aluminium specimens ($16 \times 10^{-4} m^2$ area) in different electrolytes of varying concentrations were made using a capacitor bridge. The mixtures of hydrochloric acid and zinc nitrate were made in different molar ratios .The effect of chloride ions in different mixtures was studied. The effect on the rate of dissolution was studied in various concentrations of aqueous hydrofluoric acid solutions and their capacitances were measured after different intervals of time. The thickness of the film formed in different electrolytes was determined using Faraday law. The density of the film was taken as 3.565 g/cm^3 as reported by Tazima[5].

III.   Results and Discussion

Capacitance data for the oxide films formed upto various formation voltages in 0.25M aqueous zinc nitrate at a current density of 0.5 mAcm^{-2} were obtained. The plot of reciprocal capacitance(1/C) per m^2 versus thickness per m^2 calculated using Faraday law is found to be linear which indicates that the film is uniformly formed with constant field and reciprocal capacitance can be taken as a measure of thickness of the oxide film formed in aqueous electrolyte. The effect of concentration of the electrolyte was studied by forming films of various voltages in .01,.05,0.1,and 0.5M oxalic acid (Table.1) The plots of 1/C per m^2 versus V for each electrolyte concentration are linear (Fig1.)and show a higher value of 1/C for a film formed at lower electrolyte concentration. The capacitance data were also obtained for the films formed in 0.25 Mammonium carbonate, nickel sulphate, succinic acid and cadmium nitrate and the plots of 1/C per m^2 versus V were found to be linear and their slopes calculated by least squares method are reported in Table.2. The data for a 100V film (Table 2.) show the dependence of capacitance on the nature of the electrolyte. The dielectric constants were calculated using the capacitance formulae for a parallel plate capacitor. i.e

$C = \mu A \mu_0 / d.$ (1)

Where μ is the dielectric constant of the oxide film, μ_0 is permittivity of the free space, A is the area of the specimen (used as a counter electrode) and 'd' is the thickness of the oxide film.

At a constant current density, 'd' incrases linearly with voltage and becomes equal to βV where β is the anodization constant. By substituting βV for 'd', Equation.1 becomes

$$C = \mu A \mu_0 / \beta V. \qquad (2)$$

Putting $A = 1 m^2$ and rearranging Eqn.2

$$1/C = \beta V / \mu \mu_0. \qquad (3)$$

The plot of $1/C$ versus V is linear with the slope equal to $\beta/\mu\mu_0$. If the value of anodization constant is known then from the slope, μ can be calculated. Anodization constants were calculated from anodization data using Faraday law and are reported in Table.2. Using the slopes of $1/C$ per m^2 versus V plots and the anodization constants (Table.2), the dielectric constants were calculated and the results reported in Table.2 show dependence of dielectric constant on the nature and concentration of the electrolyte.

The effect of chloride ions on the capacitances of aluminium oxide films formed in 0.25M zinc nitrate was studied by measuring the capacitances of the films in the mixed solutions of hydrochloric acid and zinc nitrate in various molar ratios of 1:600, 1:60, 1:6 and 1:2. The data show that the capacitance of the film increases with the increase in the amount of chloride ions .The plots of reciprocal capacitance per m^2 versus the voltage at which the films are formed are found to be linear (Fig. 2). The slopes of these plots decrease when the concentration of hydrochloric acid is increased successively. The corresponding dielectric constants are found to increase as the concentration of hydrochloric acid increases. Direct anodization of aluminium was carried out in all the mixed solutions. It is found that though the maximum voltage upto which the films could be formed is 330V in zinc nitrate solutions yet the films could be formed upto 305,285,250 and215V respectively in the respective mixed solutions containing chloride ions in increasing concentration. It appears that during the growth of aluminium oxide films in the presence of chloride ions aluminium metal combines with chloride ions giving an adsorbed film of aluminium chloride which then undergoes partial dissolution providing Al^{+3} ions in the solution. The released aluminium ions can combine with the chloride ions in anodic charge transfer. In the presence of higher concentration of chloride ions, the chloro- complex of aluminium is formed more efficiently thereby inhibiting the growth of oxide film[5]. The rate of film dissolution was studied next measuring the capacitance of 100V film formed in 0.25M solution of zinc nitrate in2.5M and 5.0M aqueous hydrofluoric acid solutions at various intervals of time(t) and the plots of $1/C$ per m^2 versus time (t) show that the film dissolved more readily in 5.0M than in 2.5M HF, as the time periods required for dissolution of half of the film in 5.0M and 2.5M HF are 165 and 240 seconds, respectively. The rate of dissolution is very fast upto a stage when half the film dissolves and thereafter it slows down. Similar trends in the rate of dissolution are found for a film of 200V formation and since, this film has larger thickness, it requires more time to reduce to half its original thickness. It appears that when aluminium oxide film is put in concentrated hydrofluoric acid, a surface layer of aluminium fluoride is formed which dissolves completely in concentrated HF and hence causes dissolution of the film.

Acknowledgment

Table 1

Variation of capacitance with electrolyte concentration for aluminium oxide films formed at different voltages.

Area of the Al specimen – 16 x 10^{-4} m^2

Electrolyte concentration	.01M	0.05M	0.1M	0.5M
Formation Voltage (V)	Capacitance (Fx10^6)	Capacitance (Fx10^6)	Capacitance (Fx10^6)	Capacitance (Fx10^6)
10	29.3	36.4	40.7	46.2
30	21.7	33.2	37.8	41.9
50	18.4	30.8	32.5	37.4
70	14.2	26.4	28.3	33.8
90	11.8	21.9	24.9	30.4
110	8.9	18.7	21.8	27.6
130	6.7	15.8	19.3	24.7
150	4.9	12.9	15.6	21.4
170	3.5	9.6	12.9	19.7
190	2.4	7.4	9.4	16.2
210	1.5	5.6	6.9	13.1

Table 2

Dielectric measurement data for variously formed aluminium oxide films in aqueous electrolytes

Area of the Al specimen – 16 x 10^{-4}m^2

Electrolyte	Concentration	Capacitance of a 100V film (Fx10^6)	Anodization constant β (mV^{-1}x10^{10})	Slope of 1/C versus voltage plots (F^{-1}m^{2}V^{-1})	Dielectric Constant
Ammonium carbonate	0.25M	24.2	19.81	8.12	32.1
Nickel sulphate	0.25M	23.9	20.42	8.06	31.9
Succinnic acid	0.25M	24.1	19.98	8.17	32.2
Cadmium nitrate	0.25M	24.0	20.16	8.10	32.0
Zinc nitrate	0.01M	9.8	19.27	8.21	32.2
--do--	0.05M	19.1	19.34	8.25	32.0
--do--	0.10M	21.7	19.21	8.19	31.9
--do--	0.50M	29.4	19.30	8.29	32.4

Variation of $1/c$ per m^2 with formation voltage (V) for aluminium oxide films at varying concentrations of aqueous zinc nitrate.
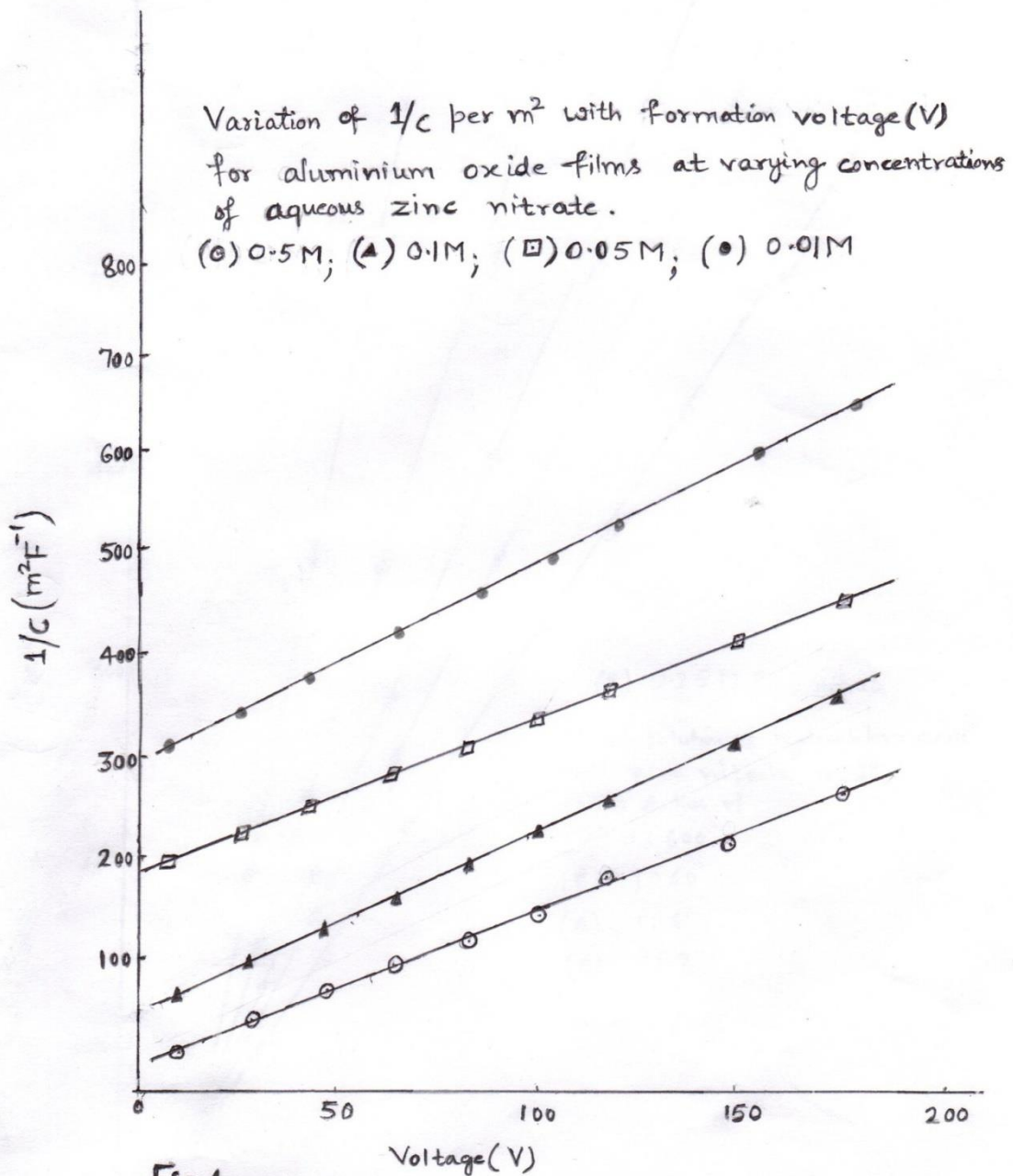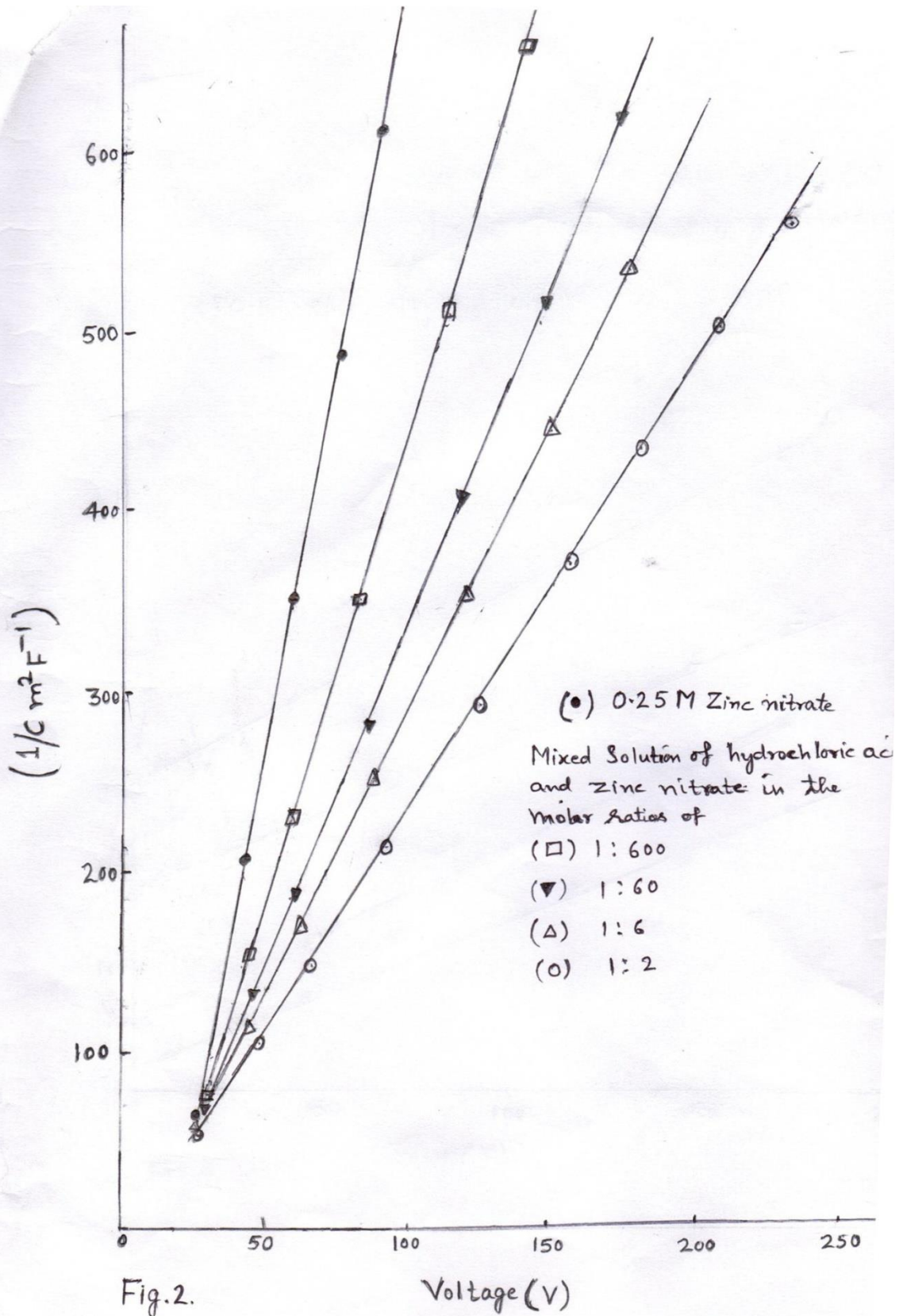
(⊙) 0·5 M; (▲) 0·1M; (▣) 0·05M; (●) 0·01M

Fig.1.

Fig.2.

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