



Growth Kinetics of Faraday 1st law by Cabrera Mott theory of zirconia its Biomedical Applications

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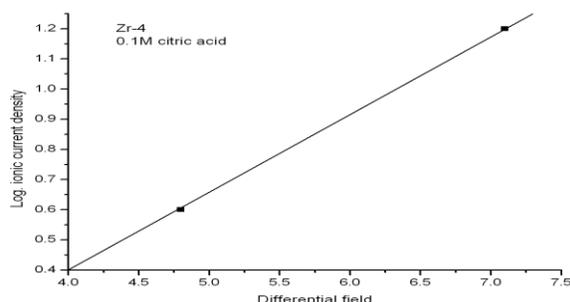
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Highlights

- Galvanostatic technique favoured to coloured thin films of Zircaloy-4
- The growth kinetics of zirconia studied at constant current densities
- Investigated the ionic current density on differential field strength
- The half – jump distance and height of the energy barrier deduced by Cabrera – Mott theory.
- Graphical Representation



Abstract:

Anodic polarization of zircaloy-4 implies the Cabrera-Mott theory is limited by the field-facilitated activated jumps of the metal ions at the metal-oxide interface was originally proposed to interpret growth of thin oxide coloured films on plane metal surfaces. The growth kinetics of Zircaloy-4 have been studied by Faraday 1st law in 0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid at constant current densities ranging from 8 to 20 mA.cm² at room temperature in order to investigate the dependence of ionic current density on the field across the zirconia. Thickness of the oxide coloured films was estimated from capacitance data. The formation rate, faradaic efficiency and differential field were found to increase with increase in the ionic current density for coloured zirconia. Investigated the Growth kinetics of different anodization voltages shown colour zirconia formed on the surface of entire thin oxide film by the citrate anions. A 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.

Keywords: Zircaloy-4, 0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid, Anodic polarization by Faraday 1st law, Cabrera-Mott theory, constant current densities.

Introduction

Among the various available materials zirconium dioxide is observed as potential material for biomedical applications due to its superior bio-compatibility, good compression resistance (2000MPa), good viability of cell culture good opacity and radio pacifying capacity showcasing its diverse applications in bone and tissue regeneration, orthopaedic implants as well as bone resorption. bone tissue regenerative modifications accompanied with coating of zirconium dioxide on metal alloys. zirconium dioxide is also recorded for exhibiting enhanced mechanical properties as well as biocompatibility in hip orthoplastyas well as bone implants. it also serves application in bone cement to provides adhesion between the biomedical implants [1].

Zirconium alloys for biomedical applications are received increasing attention due to their two unique properties: 1) the formation of an intrinsic bone-like apatite layer on their surfaces in body environments, and 2) better compatibility with magnetic resonance imaging (MRI) diagnostics due to their low magnetic susceptibility, as well as their overall excellent biocompatibility, mechanical properties, and bio-corrosion resistance [2].

Zirconia is in evidence as a dental biomaterial and it is the material of choice in contemporary restorative dentistry. it has been applied as structural material for dental bridges, crowns, inserts, and implants mostly because of its biocompatibility, high fracture toughness, and radiopacity [3].

The theory advanced by Cabrera and Mott [4] on the basis of earlier work by Mott [5] 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 [6] and in thin film methods [7]. 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 [8]. Guntherschultze and Betz [9] 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 [10]. Vermilyea [11] 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 [12]. Zr and Zr alloys have greater strength, lower cytotoxicity and lower magnetic susceptibility than titanium [13]. These advantageous properties make Zr and its alloys good promising candidates as materials in orthopaedic surgery.

In the current research work, to study the effect of constant current densities on the anodic polarization of zirconium oxide anodic layer on zircaloy-4 in 0.1M 2-hydroxy-1,2,3- propane tricarboxylic acid (citric acid) by Faraday 1st law and Cabrera – Mott theory to deduce the half – jump distance (a) and height of energy barrier (W)

Materials and Methods

Zircaloy-4 was of 98% nominal purity, supplied in the form of plate by **Nuclear Fuel Complex, Hyderabad** as gift samples. Thinning of this Zr-4 plate was done by **Defence Metallurgical Research Lab, Hyderabad**. Cutting of the thinned sheet was done at **tools and techniques, 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 present work, the foil samples used were cut with the aid of a punch into flag-shaped specimens of 1 cm² working area on both side and 1 ½ 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.

2.1 Electrochemical conditions

The counter electrode was a sheet of Platinum (2x3 cm, weight 3.000 gm). The working electrode was the Zr-4 sample. For anodizing, a double walled glass cell 100mL capacity was used. The experiments were performed in an electrolyte, 0.1M 2-hydroxy-1,2,3- propane tricarboxylic acid. All experiments were carried out at constant current densities ranging from 8 to 20 mA.cm⁻². The experimental procedure for the anodic polarization by faraday 1st law is given elsewhere [14]. The kinetic results calculated are formation rate in Vs⁻¹, faradaic efficiency (η) % from the conventional plots V vs. t, D_c vs. D_F. The Cabrera – Mott theory to deduce the half – jump distance (a) in Å and height of energy barrier (W) in eV.

Results

Anodic Polarization Studies

0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid (zircaloy-4)

Voltage time- thickness relationship

Specimens of zircaloy-4 were separately polarized galvanostatically in 0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid (citric acid) at a constant current density of 8 mA.cm⁻² and at room temperature. The anodization voltage vs. anodization time plot **Fig.1** consist of three straight lines intersecting at 47 volts and further intersecting at 115volts was found to be linear with a curve upto the breakdown voltage. The breakdown voltage was observed to be 142V for zircaloy-4. the calculated formation rate and faradaic efficiency are found to be 0.8V.s⁻¹ and 58.53%. The plots of anodization voltage vs anodization time, thickness by capacitance (ΔD_c) vs. thickness by faradaic (ΔD_F) and thickness by capacitance vs. anodizing voltage for zircaloy-4 are were drawn and observed to be linear up to break down voltage and plots are shown in **Fig. 1, 2 and 3**. From these plots the formation rate, faradaic efficiency, differential field were increased, estimated and are summarized in **Table 1**.

Dependence of ionic current density on the field of formation Anodic polarization were carried out separately in 0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid or citric acid at constant current densities ranging at 8 & 20 mA.cm⁻² to investigate the exponential dependence of the ionic current density on the field across the anodized oxide films. the anodic polarize4d zirconia plot at 20mA.cm⁻², anodization voltage vs. anodization time has two linear portions intersected. the potential further increased upto the break down voltage. The formation rate, faradaic efficiency and differential field were found to increase with the increase in the ionic current density for zircaloy-4. The plots of anodizing voltage vs. anodization time, reciprocal capacitance vs. anodization time are shown in **Fig. 4 and 5**. The details are summarized in **Table-1**. The plots of log. ionic current density vs. differential field gave fairly a linear relationship as shown in **Fig-6**.

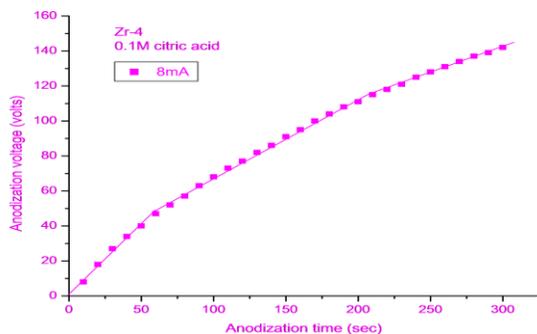


Figure. 1: Plot of anodization voltage as a function of anodization time.

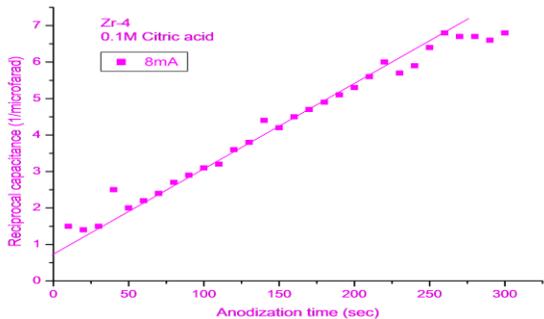


Figure. 2: Plot of thickness by capacitance as a function of faradaic.

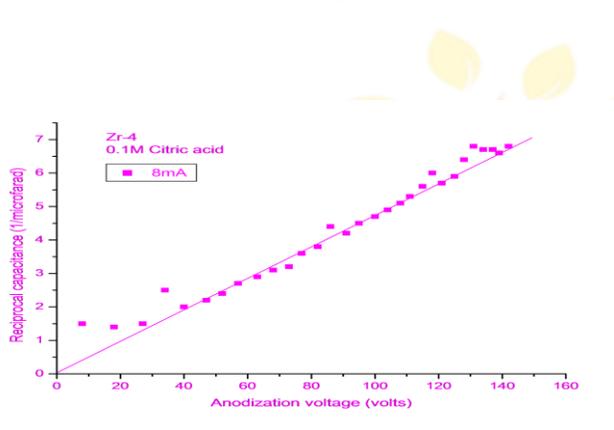


Figure. 3: Plot of thickness by capacitance as a function of anodization voltage

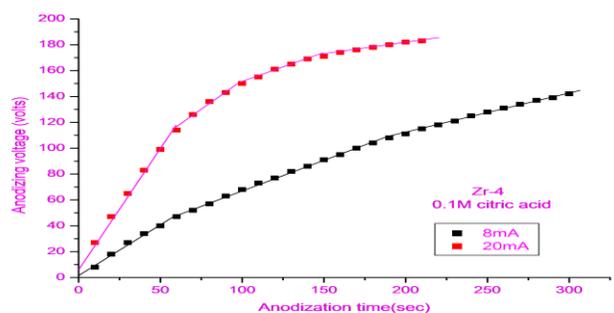


Figure. 4: plot of anodization of voltage as a function of anodization time

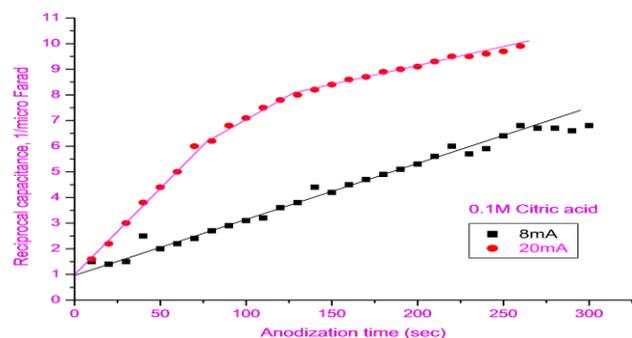


Figure.5: Plot of reciprocal capacitance as a function of anodization time

Table-1 Anodized oxide films formed on zircaloy-4 in 0.1M citric acid.

Current density, mA.cm ⁻²	Formation rate V.s ⁻¹	Faradaic efficiency η (%)	Ionic current density, mA.cm ⁻²	Log.ionic current density, Log. i _i	Differential field, F _D (MV.cm ⁻¹)
8	0.8	58.53	4.682	0.670	4.872
20	1.74	95.58	19.11	1.281	7.156

Discussion

4.1 Growth kinetics

4.1.1. Ionic current density on differential field strength.

The growth kinetics involves the study of variation of differential field with the ionic current density and calculation 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 present study it was assumed that the highest energy barriers are situated at the interfaces and the Cabrera-Mott type theory is applicable. The **Fig- 3**, show the variation of log. ionic current density with differential field of formation for anodization of zircaloy-4 in 0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid or citric acid, **Table-1**, illustrates the details of influence of current density on kinetic results. Applying Cabrera Mott theory, therefore using equations with $n = 1.212 \times 10^{15}$ ions / cm², $\nu = 10^{13}$ Hz, $q = 2e$ for zircaloy-4 (the assumption of limiting saturation value for the concentration of active sites for the anodic oxide growth at a surface), the kinetic parameters of high field ionic condition are deduced.

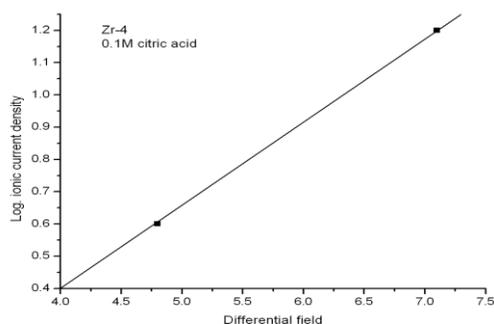


Figure. 6: Plot of variation of log. ionic current density with differential field.

A sketch is given in Fig. 5 (not to scale). It is assumed that the total film formed consists of two discrete layers with differential fields 4.87 and 7.15MV/cm for zircaloy-4, across P₁ and P₂ layers respectively. The voltage across the system can be calculated and compared with that experimental value. ($V = Fp_1 Dp_1 + Fp_2 Dp_2$). The value obtained for zircaloy-4 is in agreement with the experimentally observed value.

This can be explained by the electron current/ ionic current ratio which may not be constant throughout the range of polarization. It is possible that the ionic current predominates during the oxide film formation. As the thickness of oxide film increases, crystallization may start and this increases the defect character of the oxide. Hence the electron current increases and oxygen evolution occurs on grain boundaries and lattice imperfections. The increase in electron current and oxygen evolution leads to chemical oxidation at pores and when the crystalline oxide formation becomes complete the electron current decreases again and oxygen evolution ceases. At this stage electrical conduction through oxide is

mainly ionic, and the thickness starts to increase again till the breakdown finally occurs. The changes observed in the faradaic efficiency with the thickness can also attributed to the changes observed in the differential field of formation.

Based on the above trends in the kinetic results, a highly speculative mechanism has been proposed. Initially a thin compact oxide film formed up to 47V, beyond this potential it is assumed that the anions of 2-hydroxy-1,2,3-propane tricarboxylic acid are adsorbed at metal sites. As a result the thickness of oxide increases suddenly. In the successive steps, oxidation of the adsorbed compound formally can occur by electrochemical reaction with water or more probably bifunctionally in an heterogeneously catalysed reaction with surface-oxide species discharged from the solvent. Under some conditions, unoxidized dehydrogenated carbon residues can build up on the electrode surface and cause inhibition.

CONCLUSIONS

Anodic oxide film formation in the electrolyte 0.1M 2-hydroxy-1,2,3-propane tricarboxylic acid or citric acid found to improve the kinetic results, formation rate, faradaic efficiency and differential field with the current density. The addition of anions found to improve the growth kinetics of different colours covering entire thin films on the surface at different break down voltages. 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) height of the energy barrier (W) are found to be 1.09\AA , 0.94eV respectively. Zirconia is in evidence as a dental biomaterial and it is the material of choice in contemporary restorative dentistry. zirconium dioxide is also recorded for exhibiting enhanced mechanical properties as well as biocompatibility in hip orthoplastyas well as bone implants. it also serves application in bone cement to provides adhesion between the biomedical implants.

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