JCBPS; Section C; May 2025 to July 2025, Vol. 15, No.3; 221-228. E- ISSN: 2249 –1929
[DOI: 10.24214/jcbps.C.15.3.22108]

Journal of Chemical, Biological and Physical Sciences

An International Peer Review E-3 Journal of Sciences

International scientific indexing (ISI) Impact Factor (2024-2025) 03.362

*Available online at*www.jcbsc.org

Section C: Physical Sciences

CODEN (USA): JCBPAT Research Article

Nano Studies of Incorporation of Halide anions to Zircaloy-4 and Zirconia by Faraday 1st law, it's Application's

Dr J. Padmaja[1]*, Dr V. Nathanial[2], Dr Ch. Venkateswarlu[3], and Prof Ch. Anjaneyulu (Rtd)[4].

[1]Faculty Of Chemistry, IGNOU (Nizam College), Basheerbagh, Osmania University, Hyderabad-500001, Telangana, India.

[2]Department Of Physics, University College of Science, Osmania University, Hyderabad-500007, Telangana, India.

[3]Department Of Physics, Nizam College, Basheerbagh, Osmania University, Hyderabad-500001, Telangana, India.

[4]Department Of Chemistry, University College of Science, Osmania University, Hyderabad-500007, Telangana, India.

Received: 05 April 2025; **Revised:** 18 May 2025; **Accepted:** 26 May 2025

Abstract: Nano studies of added halide ions in 0.1M ammonium oxalate to zircaloy-4 have been investigated by faraday 1st law through anodic polarization technique (galvanostatic technique). Kinetics of anodic polarization of zircaloy-4 have been studied at a constant current density of 8 $mA.cm^{-2}$ at room temperature. Thickness estimates were made from capacitance data and faradaic data in nanometers. The anodization voltage; Thickness of Capacitance,Thickness of Faradaic; anodization rate, faradaic efficiency and field strength were calculated based on the plots. Kinetics of anodic polarized zirconia oxide coloured films was observed by the addition of millimolar concentration of anions (Cl-, Br-, I-). By the incorporation of halide ions on the zirconia samples was better improved by the investigatation of research sqamples. The anodization rate, faradaic efficiency and field strength investigated. Zirconium based alloys are used as structural material in

water-cooled thermal reactors. Zirconia as one of the important oxide materials, exhibits excellent properties including low thermal conductivity, high thermal expansion, good thermal stability, fine mechanical strength, good fracture toughness and high thermal shock resistance. In the last decade, the whole scientific community achieving great advances in nano technology of research progress [nanomaterials] in different research fields of nanoscience which has [zirconia nanomaterials] numerous applications as Nano catalysts, Nano sensors, adsorbents, oxygen sensors, fuel cells, biological materials, automobile parts and thermal barrier coatings on metal components. Zirconia materials have also been employed in medical and orthopedic. ZrO2 nanoparticles have found uses in solid oxide fuel cell.

Keywords: Anodic polarization technique, Zircaloy-4, zirconia, faraday 1st law, Faradaic efficiency, field strength, incorporation of halide anions and its applications.

1.INTRODUCTION

Zirconium based alloys are used as structural material in water-cooled thermal reactors [1, 2]. Zirconia as one of the important oxide materials, exhibits excellent properties including low thermal conductivity, high thermal expansion, good thermal stability, fine mechanical strength, good fracture toughness and high thermal shock resistance [3]. Thus, zirconia has been used in abroad range of applications as catalysts / catalyst support [4], oxygen sensors [5], fuel cells [6], biological materials [7], automobile parts and thermal barrier coatings on metal components [8]. ZrO_2 (zirconia) is a material of great technological importance having good natural color, high strength, transformation toughness, high chemical stability, excellent corrosion resisting material, and chemical and microbial resistance [9,10].

ZrO_2 nanoparticles have found uses in solid oxide fuel cells [11]. Zirconium has an atomic number of 40 and has distinctive physical and chemical properties like titanium [12]. Zirconium alloys are used in nuclear power plants for example as fuel cladding [13]. Sastry and Draper [14] studied the effect of chloride ions on the kinetics of anodization of zirconium in 0.1M KOH and observed that there is a consistent ratio of 10: 1 of [OH^-]: [Cl^-], above which the voltage sustained by any film already formed fell almost to zero and further anodization was not found to be possible.

The effect of halide ions, mainly fluoride and iodide ions, upon the kinetics of anodic oxide films formed on zircaloy-4 and niobium in 0.1M sulphamic acid, 0.1M ferrous ammonium sulphate, 0.1M LiOH were examined and it was known [15] that the presence of relatively small concentration of halide ions in the electrolyte change the efficiencies of the film growth.

Archibald and Leach [16] observed that fluoride ions in the surface preparation or in subsequent anodizing of zirconium have a profound effect upon the stresses in the zirconium oxide anodic layer. They found that by a suitable choice of surface preparation, anodizing electrolytes and growth rate, anodic oxide film could be grown on the surface of zirconium, having tensile, compressive or effectively zero stress.

In the research work, the report of the results of the nano studies of the zircaloy-4 material (sample) in 0.1 M ammonium oxalate at 8mA.cm-^{2}. The incorporation of added anions (iodides, bromides and chlorides)on the surface of the zirconia coloured oxide films have been investigated based on the calculation of the anodization rate, faradaic efficiency and field strength of anodic polarized coloured zirconia.

2.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 Metallergical Research Lab, 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 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 1 ½ cm long tag .The chemical polishing mixture consisted of acids such as HNO_3, HF and water in a definite volume ratio of 3:3:1.

2.1. Electrochemical Conditions: The counter electrode was a sheet of Platinum [10] (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 research experiments were performed in an electrolyte, 0.1 M ammonium oxalate and incorporation of halide anions (chlorides, bromides and iodides) in 0.001M concentration.

All experiments were carried out at a constant current density of 8 $mA.cm^{-2.}$ The experimental procedure for the anodic polarization by faraday 1st law is given elsewhere [17]. The kinetic results calculated are anodization rate in Vs^{-}, faradaic efficiency (η) %, and field strength (**$MV.cm^{-1}$**) from the conventional plots V vs. t; Dc vs. DF and V vc Dc.

3.RESULTS AND DISCUSSION

Anodic polarization of zircaloy-4 experiments was done in various electrolytes like ammonium oxalate, potassium iodide, potassium bromide and potassium chloride. The anodization rate, the faradaic efficiency and field strength was calculated.

3.1. Effect of substitution (kinetic studies): The kinetics of zircaloy-4 anodized in 0.1 M ammonium oxalate. The incorporation of anions was studied in 0.1 M ammonium oxalate as 0.001M potassium iodide, potassium bromide and potassium chloride to check whether there was enhancement in the kinetics of coloured oxide film formation.

3.2.Effect of added halide anions [chloride ions, bromide ions and iodide ions]: The effects of Cl^{-}, Br^{-} and I^{-} on the formation of anodic films are well known. Various molar proportions of halide solutions added to 0.1M ammonium oxalate and the kinetics of anodic polarization were investigated. We were observed excellent colour oxide film formation on zircaloy-4 and on zirconia due to increase in potential at constant current density **$8mA.cm^{-2}$.**

When anodic polarization experiments were carried out on zircaloy-4 in **0.1M ammonium oxalate + 0.001M halide ion solutions**, it was observed that an increase in the kinetics with chloride ions with increase in colour film formation, there is no pitting corrosion on a valve metal surface [zirconia] with iodide ions, bromide ions and chloride ions. The plots of anodization voltage vs. anodization time measured in volts and seconds, thickness by capacitance vs. thickness by faradaic measured in nanometers and anodization voltage vs. thickness by capacitance measured in volts and nanometers and are shown in **Figures1 and 2** estimates result of anodization rate, **Figures 3 and 4** estimates result of faradaic efficiency and **Figures** 5 and ,6 estimates result of differential fields. The estimated results of the anodization rate[18], faradaic efficiency and differential fields are summarized in the **Tables 1 and 2**.

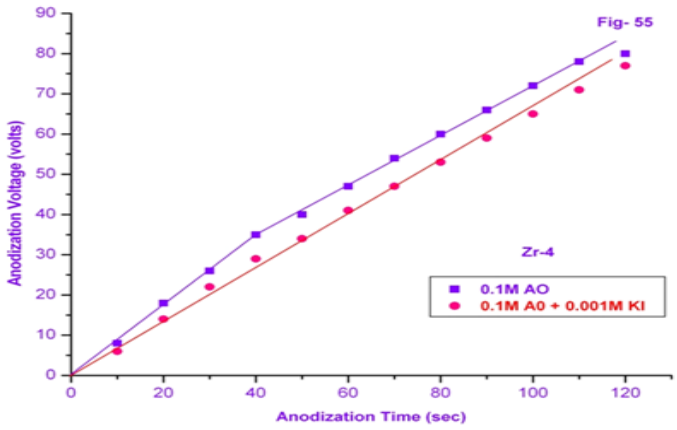


Fig.1: Plot of anodization voltage(volts) as a function of anodization time(seconds) in anion solutions

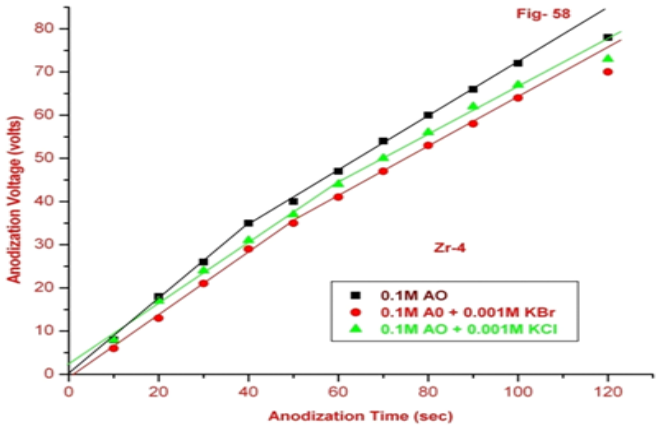


Fig.2: Plot of anodization voltage(volts) as a function of anodization time(seconds) in anion solutions.

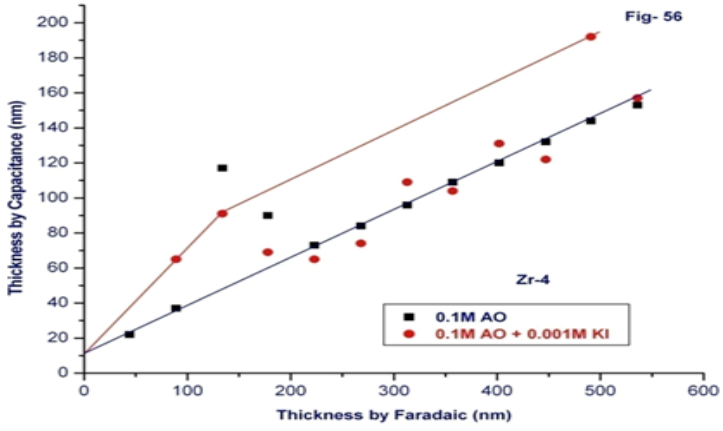
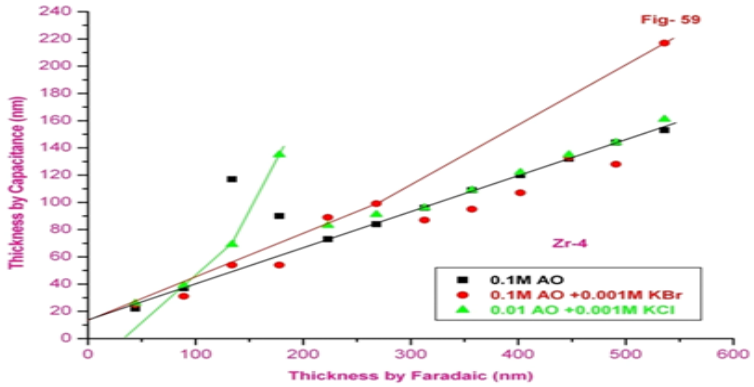


Fig .3: Plot of thickness by capacitance(nm) as a function of thickness by faradaic(nm) in anion solutions.



.Fig.4:. Plot of thickness by capacitance(nm) as a function of thickness by faradaic(nm) in anion solutions

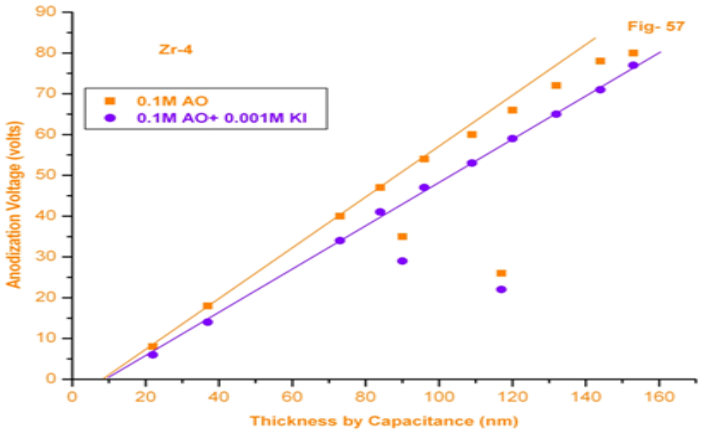


Fig.5: Plot of anodization voltage(Volts) as a thickness by capacitance(nm) in anion solutions

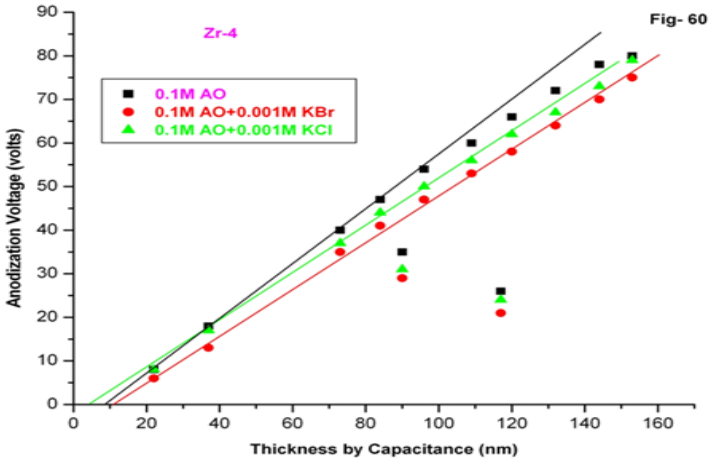


Fig.6: Plot of anodization voltage(Volts) as a thickness by capacitance(nm) in anion solutions**.**

Table-1: Anodized oxide films formed on zircaloy-4 in 0.1M AO and 0.1M AO + 0.001M KI.

Electrolyte	Formation rate dVs/dt ($V.s^{-1}$)	Faradaic efficiency η (%)	Differential field F_D ($MV.cm^{-1}$)
0.1M AO	0.72	56.8	5.669
0.1MAO+0.001M KI	0.66	>100	5.555

AO=Ammonium oxalate, KI=Potassium iodide.

Table-2: Anodized oxide films formed on zircaloy-4 in 0.1M AO; 0.1M AO + 0.001M KBr and 0.1M AO + 0.001M KCl

Electrolyte	Anodization rate dV/dt($V.s^{-1}$)	Faradaic efficiency η (%)	Differential field F_D($MV.cm^{-1}$)
0.1M AO	0.72	56.8	5.669
0.1MAO+0.001M KBr	0.7	67.16	5.402
0.1MAO+0.001M KCl	0.8	>100	6

AO=Ammonium oxalate, KBr=Potassium bromide, KCl=Potassium chloride

3.3. Experiments were carried out in 0.1 M ammonium oxalate + 0.001M [Chlorides, bromides and iodides] anions to check the effect of the added anions on zirconia: We have investigated without pitting corrosion on the surface of zirconia when oxalate ions occurred and when we added (halide anions) to zirconia, explained due to incorporation of halide anions in to the layers of the zirconia oxide films (sample). Added halide anions get incorporated between the ionic vacancy sites of the zirconia oxide films and reduce the height of the energy barrier of the movement of halide anions from one ionic site to another ionc site, there by current will be increased due to this chloride ions anodization rate is increased resulted in improvement of the kinetics of anodic polarization to better extent.

It is observed that the anodic oxide films formed on the zirconium alloy consisting of two discrete layers in 0.1M ammonium oxalate appear as a single layer due to the presence of added anions. The results are given in Table 1, and 2, and the plots are shown in Figures 55,56,57,58, 59 and 60. This incorporation of halide anions increases the faradaic efficiency with much ionic current getting utilized for zirconia film formation, which implies better kinetic results.

CONCLUSION

For the anodic polarization of zirconia, the kinetics is better in 0.1 M ammonium oxalate and added chloride ions. Kinetics of anodic polarized coloured zirconia oxide films was observed by the addition of millimolar concentration of anions measured in nanometers (iodides, bromides and chloride ions). For the anodized zirconia it can be concluded that the oxide film formed on the surface of zirconium alloy(zircaloy-4) consists of two discrete layers in 0.1M ammonium oxalate and they appear as a single layer in the presence of incorporation of halide anions on zirconia. Anodization rate increased only by incorporation of chloride anions to zirconia [**0.8($V.s^{-1}$)].** faradaic efficiency [**>100[η (%)] increased** more than hundred due to the incorporation of iodide anions and

chloride anions on the surface of zirconia coloured oxide films and when compared with incorporation of oxalate dianions on the surface of zircaloy-4; incorporation of bromide anions on the surface of zirconia coloured anodic oxide film decreased anodization rate [**0.66 ($V.s^{-1}$)**. Differential field strength increased [**6($MV.cm^{-1}$)]** due to the incorporation of chloride anions on the surface of the zirconia which acts as coloured coatings for anodic oxide films.Added halide anions get incorporated between the ionic vacancy sites of the zirconia coloured oxide films and reduce the height of the energy barrier of the movement of halide anions from one ionic site to another ionc site, there by current will be increased due to this chloride anions anodization rate is increased resulted in improvement of the kinetics of anodic polarization to better extent. Zirconium based alloys are used as structural material in water-cooled thermal reactors. Zirconia as one of the important oxide materials, exhibits excellent properties including low thermal conductivity, high thermal expansion, good thermal stability, fine mechanical strength, good fracture toughness and high thermal shock resistance In the last decade, the whole scientific community achieving great advances in nano technology of research progress [nanomaterials] in different research fields of nanoscience which has [zirconia nanomaterials] numerous applications as Nano catalysts, Nano sensors, adsorbents, oxygen sensors, fuel cells, biological materials, automobile parts and thermal barrier coatings on metal components. Zirconia materials have also been employed in medical and orthopedic. ZrO2 nanoparticles have found uses in solid oxide fuel cell

REFERENCES

1. C.D.Williams, Atomic Energy of Canada Limited Report, AECL 1969; 3456.
2. C.D.Williams, Reactor Technol 1970; 13: 147.
3. J.R.Kelly &I . Denry, Stabilized zirconia as a structural ceramic: An overview. Dent. Mater,2008, 24, 289-298.
4. J.Gosianska, M. Ziolek, E. Gibson & M. Daturi, Meso-macroporous zirconia modified with niobia as support for platinium — Acidic and basic properties. Catal. Today 152, 33-41 (2010).
5. D.A.Ward & E.I.Ko, Preparing Catalytic Materials by the Sol- Gel Method. Ind. Eng. Chem. Res. 1995,34, 421-433.
6. C. Viazzi, J.P. Bonino & F.Ansart, Synthesis by Sol-gel route and Characterization of Yttria Stabilized Zirconia coatings for thermal barrier applications. Surf. Coat. Technol.2006, 201, 3889-3893.
7. G.Korotcenkov, S.D. Han. & J.R.Stetter, Review of Electro Chemical Hydrogen Sensors. Chem. Rev. 2009,109, 1402-1433.
8. P.F.Manicone, P.R. bmmetti & L. Raffaelli, An overview of zirconia ceramics: Basic properties and clinical applications. J. Dent. 35, 819-826 (2007).
9. A. Hirvonen, R. Nowak, Y. Yamamota, T. Sekino and K. Niihara, Fabrication, structure, mechanical and thermal properties of zirconia — based ceramic nano composites, Journal of the European Ceramic Society. 2006,26,8,1497-1505, https://doi.org/ 10.1016/ j.jeurceramsoc. 2005.03.232,2-s2.0-32644441862.
10. J.C. Ray, D.W. Park and W.S. Ahn, Chemical synthesis of stabilized nanocrystalline zirconia powers, Journal of Industrial and Engineering Chemistry, (2006) 12, no.1, 142-148, 2-s2.0-31944446596.

11. S.Park. J.M.Vohs and R.J.Gorte , Direct oxidation of hydrocarbons in a solid-oxide fuel cell, Nature,2000, 404, no.6775, 265-267, https://doi.org/10.1038/35005040,2-s2.0-0034673637.
12. M. Shahid, E. Ferrand, E. Schreck, C. Dumat, Behaviour and impact of Zirconium in the Soil-Plant System: Plant uptake and Phytotoxicity. In Reviews of Environmental Contamination and Toxicology: whitacre., D., Ed.; Springer: New York, NY, USA, 2013; Volume 221. [Google Scholar].
13. Christian PROFF thesis,2011.
14. K.S. Sastry and P.H.G. Draper, J. Electrochem. Soc., India,1975, 24, 173.
15. K.S. Sastry, Ph.D. Thesis, London,1971,
16. L.C.R.Archibald and J.S.Leach, Electrochim Acta.,1977, 22.
17. F. Arifuku, C. Iwakura , Yoneyama H and Tamura H, Denki Kagaski,1978, 46:19.
18. J. Padmaja thesis, 2013.

*** Corresponding author: Dr J. Padmaja**

Faculty Of Chemistry, IGNOU (Nizam College), Basheerbagh, Osmania University, Hyderabad-500001, Telangana, India

Online publication Date: 27.05.2025