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**Research Article**

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# Effect of conditions on the anodization of Zircaloy-4 in EDTA

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**ABSTRACT**

*Anodization of Zircaloy-4 in EDTA electrolyte has been studied under different anodizing conditions at room temperature. It has been observed that the change of current density and solvent has a marked influence on the kinetics of anodization. The kinetic parameters like rate of formation(dV/dt), ionic current efficiency(I]) and differential field of formation($F_D$) were calculated. The surface natures of the anodized films were studied from Scanning Electron Micrographs(SEM) under different anodizing conditions.*

**Keywords:** Zircaloy-4, anodization, ionic current efficiency and differential field.

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## INTRODUCTION

Zirconium alloys are used as structural material in water - cooled thermal reactors[1,2] Zircaloy-4, due to its lower cross-section for thermal neutrons and because of their relatively good corrosion resistance against water and steam used in water cooled reactors. Various authours[3-6] have studied the anodization of Zirconium alloys in different electrolytes.

In the present work, an attempt is made to study the effect of anodizing conditions like current density and solvent on the anodization of Zircaloy-4 in EDTA solution.

## EXPERIMENTAL SECTION

The high purity Zircaloy-4 specimens of 1$cm^2$ working area used in this study were obtained from Nuclear Fuel Complex, Hyderabad as gift samples. The nominal analysis of Zr-4 was Sn (1.44%), Fe (0.13%), Cr (0.07%) and remaining is Zirconium. The specimens were chemically polished in a mixture of 1 part of HF (49%), 3 parts of $HNO_3$ (70%) and 3 parts of distill water. and washed several times in double distill water. and dried. The anodizations were carried out using regulated power supply (DC) supplied by POWERTRONICS, Hyderabad. The thickness estimates of anodized film were made from capacitance measurements using digital capacitance meter supplied by DEVI ELECTRONICS, Hyderabad.

Zircaloy-4 specimens were used as anodic electrode while platinum foil of 20 $cm^2$ was used as cathode. The electrolyte used was EDTA. The anodizations were carried out using different current densities ranging from 2-32 mA/$cm^2$. The solvent effect was studied by using the solvents Ethylene Glycol, DMSO, n-Propanol, DMF and t-Butanol. All the solutions were prepared from reagent grade chemicals and deionized water. All anodization experiments were carried out at room temperature. After the experiment the specimens were washed in deionized water, dried and studied the surface nature of the film by SEM .

## RESULTS AND DISCUSSION

The anodization of Zircaloy-4 in EDTA electrolyte was studied under different anodizing conditions at room temperature. The kinetic parameters like rate anodization(dV/dt), ionic current efficiency(Ɪ]) and differential field($F_D$) were calculated from the plots of anodization voltage(V) vs time(t), reciprocal capacitance(1/C) vs. time(t) and reciprocal capacitance(1/C) vs. voltage(V).

### EFFECT OF CURRENT DENSITY

The kinetics of anodization of Zircoloy-4 in 0.05M EDTA solution was carried at different constant current densities i.e. 2-32 mA/cm$^2$ and at room temperature. The rate of anodization(dV/dt), current efficiency(Ɪ]) and differential field($F_D$) of formation were calculated from the plots (Fig. 1 - 3) and reported in the Table - 1. It has found that the increased in current density, increases the rate of anodization, ionic current efficiency and differential field. It is attributed due to the increase of ion migration with increase in current density[7]. It has observed that the surface nature of film has studied by taking Scanning Electron Micrograph(SEM). The films were smooth at low current density without breaks (Fig. 4 - 5).

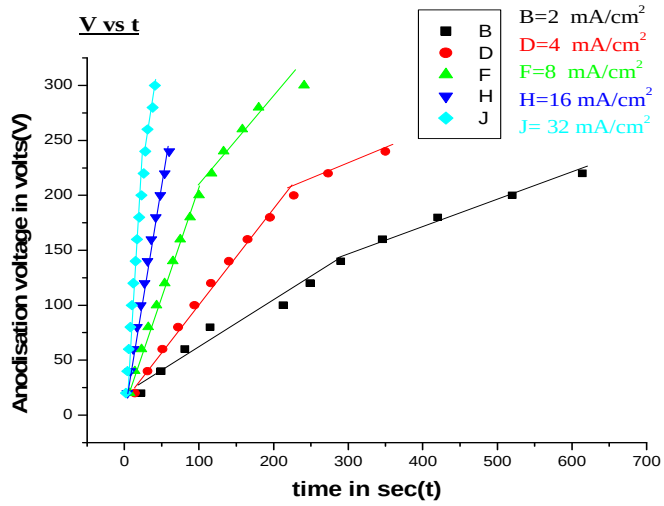


Fig-1.Plot of anodization voltage(V) as a function of time(t) at different current densities

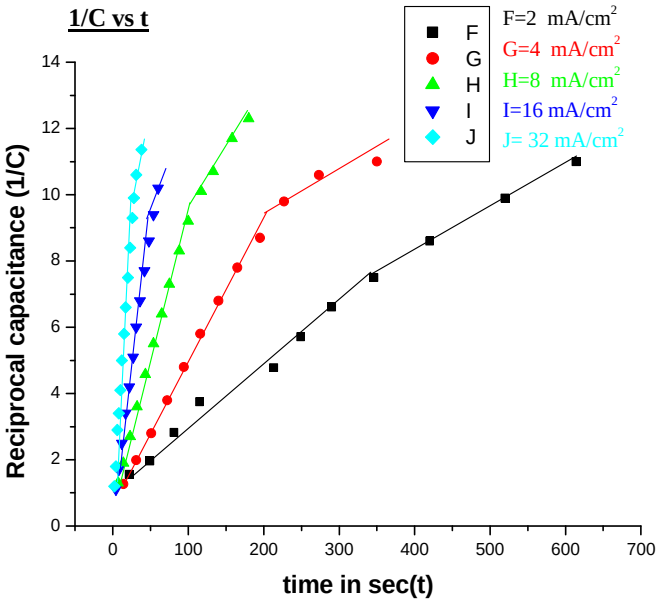


Fig-2. Plot of reciprocal capacitance(1/C) as a function of time(t) at different current densities

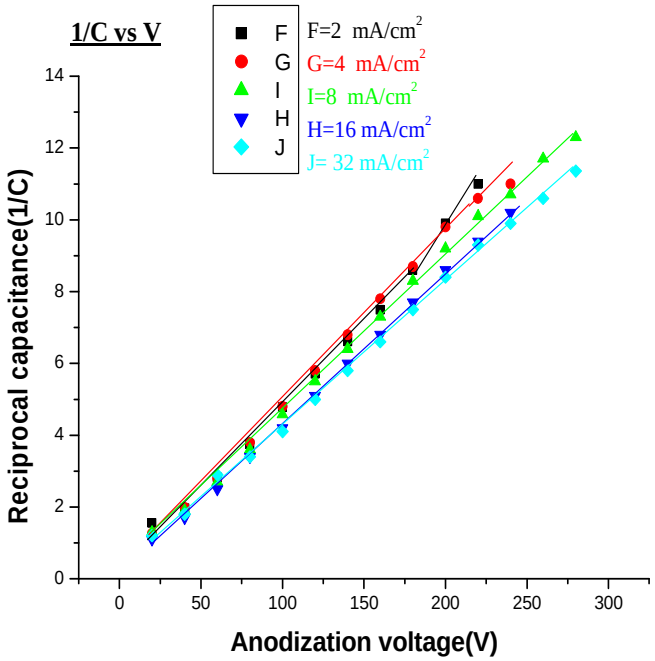


Fig-3.Plot of reciprocal capacitance(1/C) as a function of voltage(V) at different current densities

**Table-1**

| S.No | Current density ($mA/cm^2$) | Rate of Anodization (dV/dt), V $s^{-1}$ | Differential Field($F_D$) (MV/cm) | Current efficiency (Ƞ %) |
|---|---|---|---|---|
| **1** | 2 | 0.416 | 4.85 | 86.85 |
| **2** | 4 | 0.86 | 4.94 | 87.23 |
| **3** | 8 | 2 | 5.31 | 87.75 |
| **4** | 16 | 5.6 | 5.53 | 89.14 |
| **5** | 32 | 8.33 | 5.60 | 90.03 |

**SEM:**

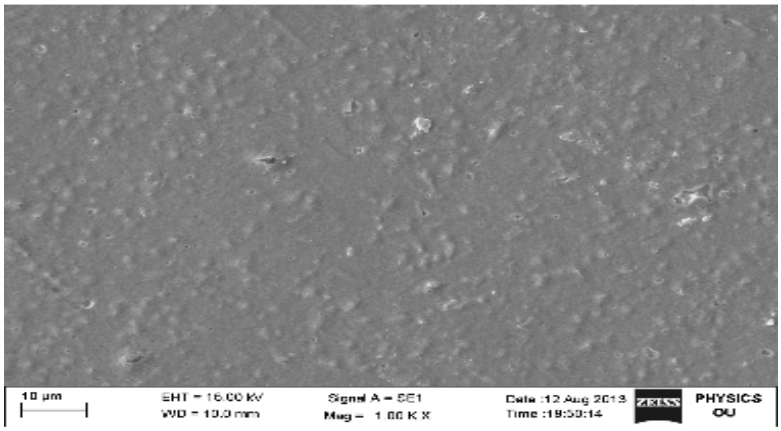


**Fig-4(2 $mA/cm^2$)**

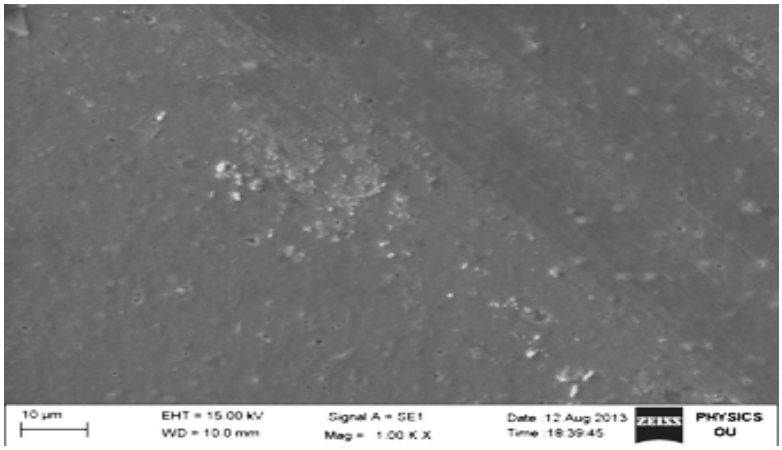


**Fig-5(32 mA/cm$^2$ )**

**EFFECT OF SOLVENT**

The kinetics of anodization of Zircaloy-4 in 0.05M EDTA electrolyte was carried out by using 20% of aquo - organic solvents at a constant current density of 4 mA/cm$^2$ and at room temperature. The kinetic parameters were estimated from the relevant plots (Fig. 6 - 8) and reported in the table - 2. It was observed that the rate of anodization, current efficiency and differential field found to changes with change of solvent, it may be due to the change in dielectric constant of the medium[8,9]. The films formed in aqua - organic medium acts as better electrolytic capacitors[10].

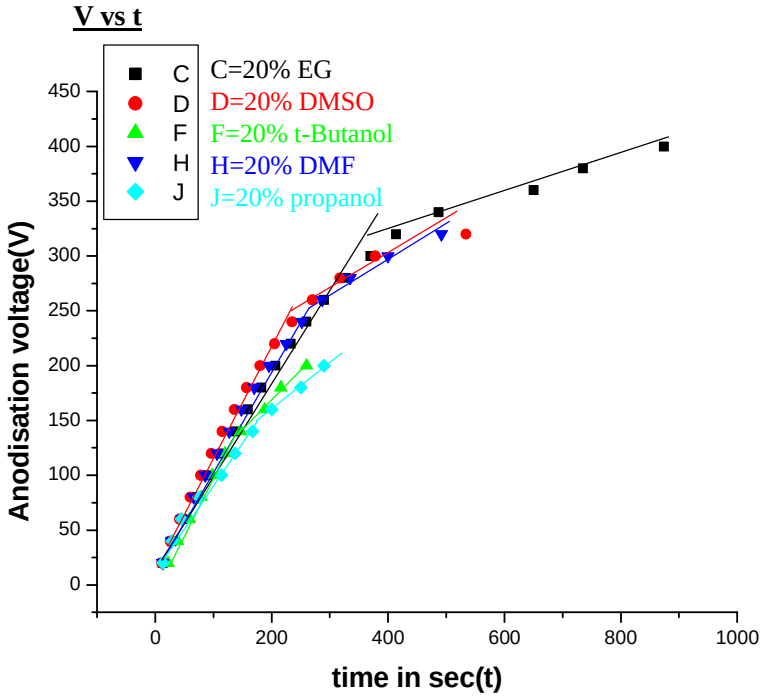


Fig-6:Plot of anodization voltage as a function of time in aquo- organic solvents

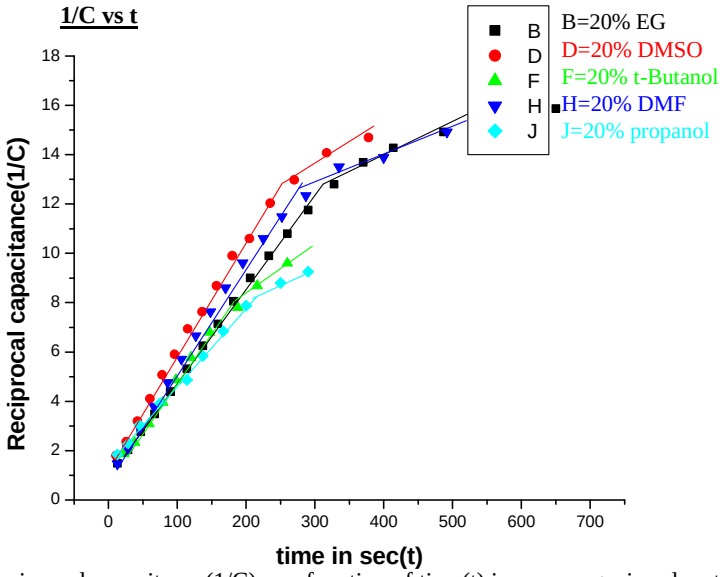


Fig-7: Plot of reciprocal capacitance(1/C) as a function of time(t) in aquo-organic solvents

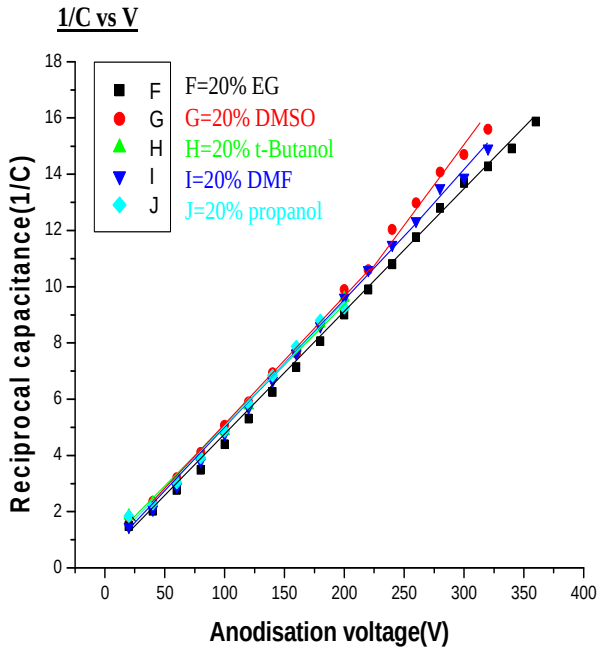


Fig-8:Plot of reciprocal capacitance(1/C) as afunction of anodization voltage(V) in aquo-organic solvents

**Table-2:**

| S.NO | 80% EDTA + 20% organic solvent | Rate of anodization (dV/dt), V $s^{-1}$ | Differential field($F_D$) (MV/cm) | Current efficiency (Ƞ %) |
|---|---|---|---|---|
| **1** | **20% Ethylene glycol** | 0.77 | 4.9 | 71.27 |
| **2** | **20% DMSO** | 0.96 | 4.87 | 81.25 |
| **3** | **20% Propanol** | 0.95 | 4.97 | 68.25 |
| **4** | **20% DMF** | 1 | 4.16 | 85.8 |
| **5** | **20% t-Butanol** | 0.72 | 5.45 | 60.45 |

**SEM:**

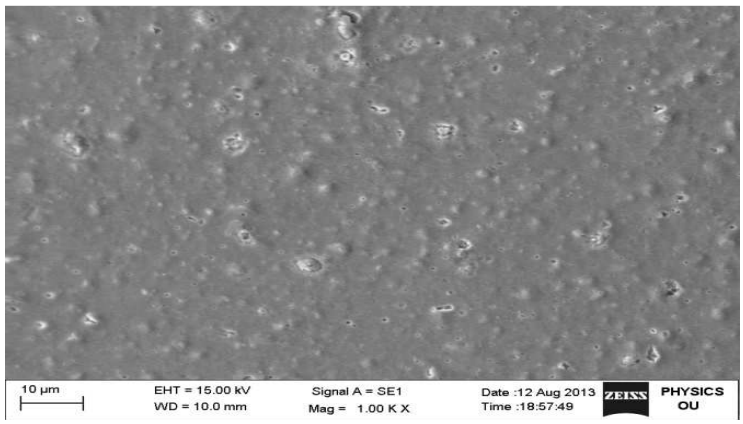


**Fig-9(20% EG)**

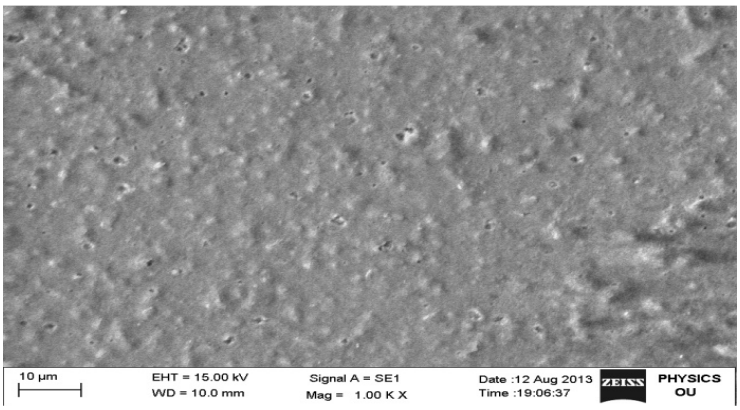


**Fig-10(20% DMSO)**

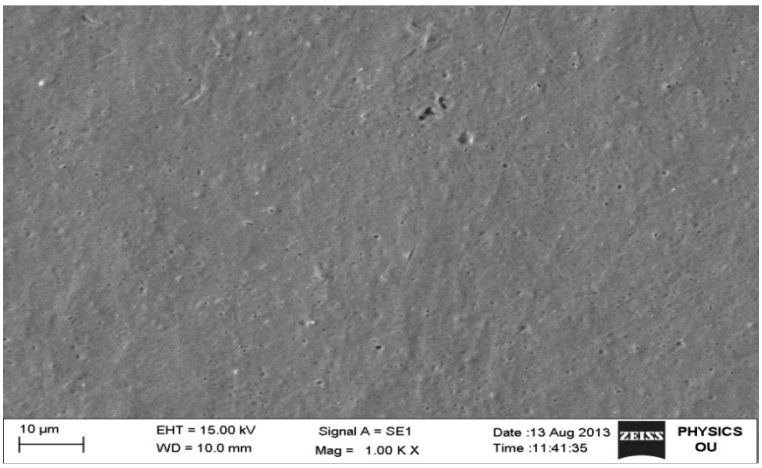


**Fig-11(20% Propanol)**

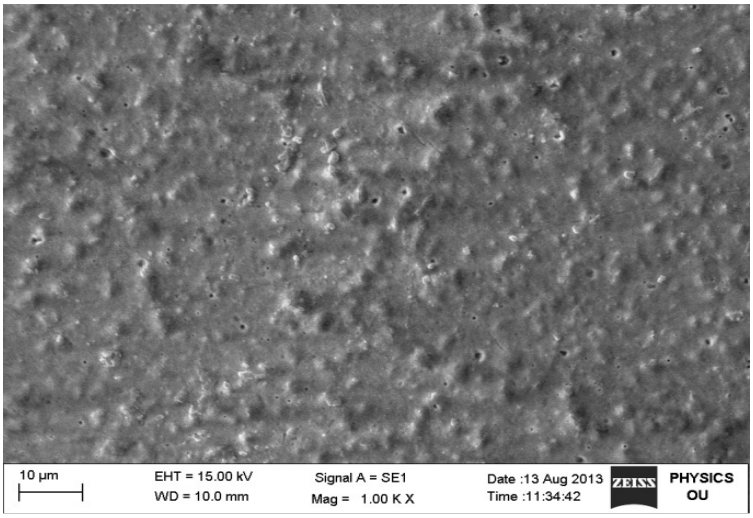


**Fig-12(20%DMF)**

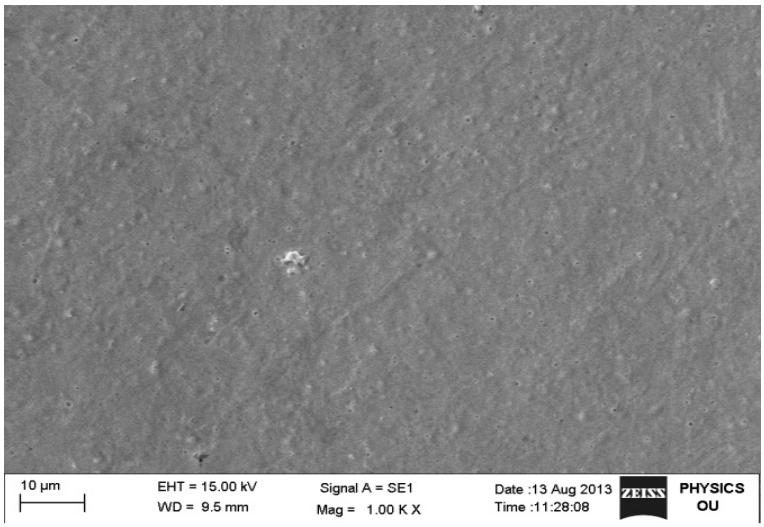


**Fig-13(20% t-Butanol)**

## CONCLUSION

The increase of current density increases the rate of anodization and efficiency of anodization. The change of solvent from aqueous to aquo - organic solvent has a marked influence on the kinetics of anodization of Zircaloy - 4 in EDTA solutions at room temperature.

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