



Effect of Aquo-glycolic Media and Added Anions on the Anodization of Zircaloy-4 in Sulphamic Acid

VIPLAV DUTH SHUKLA* and CH. ANJANEYULU

Department of Chemistry
University College for Women, Osmania University, Koti, Hyderabad, India

*Department of Chemistry
BJR Govt. Degree College, Bazarghat, Nampally, Hyderabad, India
drviplove@gmail.com

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Abstract: Anodization of zircaloy-4 in 0.1 M sulphamic acid has been carried out. Kinetics of anodic oxidation of zircaloy-4 has been studied at a constant current density of 8 mA/cm^2 and at room temperature. Thickness estimates were made from capacitance data. The plots of formation voltage vs. time, reciprocal capacitance vs. time, reciprocal capacitance vs. formation voltage and thickness vs. formation voltage were drawn and rate of formation, current efficiency and differential field were calculated. The addition of solvent (ethylene glycol) showed better kinetic results. For 25%, 50% and 75% aquo-glycolic media, the dielectric constant values are low leading to a marked improvement in the kinetics. In 80% ethylene glycol, though the dielectric constant value of solution is less, the kinetics was slow which may be attributed to the fact that the electrolyte becomes highly non-polar. Improvement in the kinetics of oxide film formation was observed by the addition of millimolar concentration of anions (CO_3^{2-} , SO_4^{2-} , PO_4^{3-}). The presence of phosphate ions improved the kinetics of anodization to better extent.

Keywords: Zircaloy-4, Anodization, Formation rate, Current efficiency, Aquo-glycolic media, Anion impurities

Introduction

Zirconium based alloys are used as structural material in water-cooled thermal reactors^{1,2}. Zircaloy-4 is an alloy of 98% pure zirconium with other trace impurities. Zircaloy-4, due to their low cross section for thermal neutrons and because of their relatively good corrosion resistance against water and steam used in water cooled reactors. Anodization of zirconium alloys have been studied in some electrolytes³⁻⁶.

In the present work, we report the results of our studies on the anodization of zircaloy-4 in 0.1 M sulphamic acid and the effect of solvent (ethylene glycol) and also the effect of added anion impurities (phosphates, sulphates and carbonates). We have calculated the formation rate, current efficiency and differential field of formation of zircaloy-4.

Experimental

Zircaloy-4 was of 98% nominal purity, supplied in the form of annealed sheet by Nuclear Fuel Complex, Hyderabad as gift samples. 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 2 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.

For anodizing, a closed cell of 200 mL capacity was used. The cathode used was a platinum foil of 20 cm² superficial area to make the double layer capacitance as large as possible. Electrolytes used were 0.1 M sulphamic acid in 25%, 50% and 75% aquo-glycolic mixtures, the solvent being ethylene glycol and the added anionic impurities were PO₄⁻³, SO₄⁻² and CO₃⁻² in 0.001 M concentration.

All experiments were carried out at a constant current density of 8 mA.cm⁻². The experimental procedure for the anodization is given elsewhere⁷. The kinetic results calculated are formation rate in Vs⁻¹, current efficiency (η) % and differential fields of formation (F_D) in MV cm⁻¹ from the conventional plots V vs. t, 1/C vs. V and 1/c vs. t.

Results and Discussion

Anodization of zircaloy-4 was done in various electrolytes (acidic, basic and neutral). The formation rate, the current efficiency and the differential fields were calculated.

Effect of substitution

The kinetics of zircaloy-4 anodization in 0.1 M sulphamic acid was better. The effect of solvent and added anionic impurities was studied in 0.1 M sulphamic acid to check whether there was enhancement in the kinetics of film formation^{8,9}.

Effect of solvent

Anodization of zircaloy-4 in 0.1 M sulphamic acid was performed by mixing various proportions of ethylene glycol to the aqueous solution (25%, 50% and 75%). There was an improvement in the kinetics as given in Table 1. The relevant plots are shown in Figures 1&2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors¹⁰. These facts support the current results obtained in aquo-organic mixtures of 0.1 M sulphamic acid. It can be explained on the basis of decrease in the dielectric constant of the medium (Table 2).

In solutions of low dielectric constant there is less chance of ion-dipole interactions (solvent-ion interactions), which do not interfere in the oxide film formation. However, the ions in the high dielectric constant solutions, interact with oxide ions responsible for oxide film formation due to high solvation with water molecules. In such solutions, the kinetics are poor. The kinetics are better in low dielectric constant solutions. For 25%, 50% and 75% aquo-glycolic media, the dielectric constant values are low leading to a marked improvement in the kinetics¹¹. The oxide film formed on the zircaloy-4 consists of two discrete layers in 0.1 M sulphamic acid were disappeared and made to a single layer in presence of ethylene glycol.

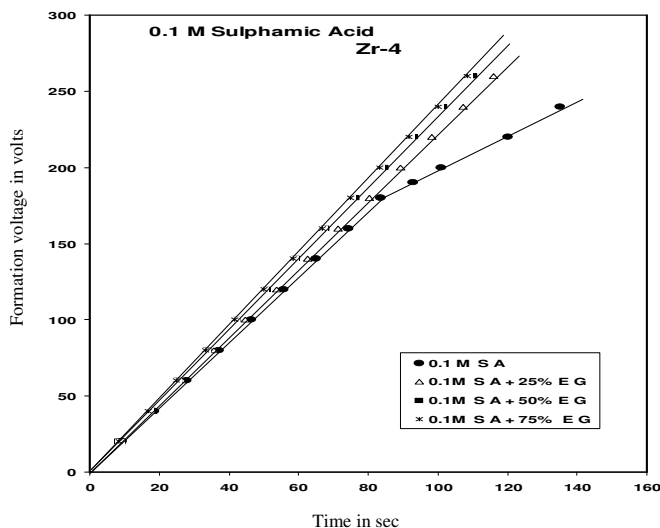


Figure 1. Plot of formation voltage as a function of time in aquo-glycolic solution

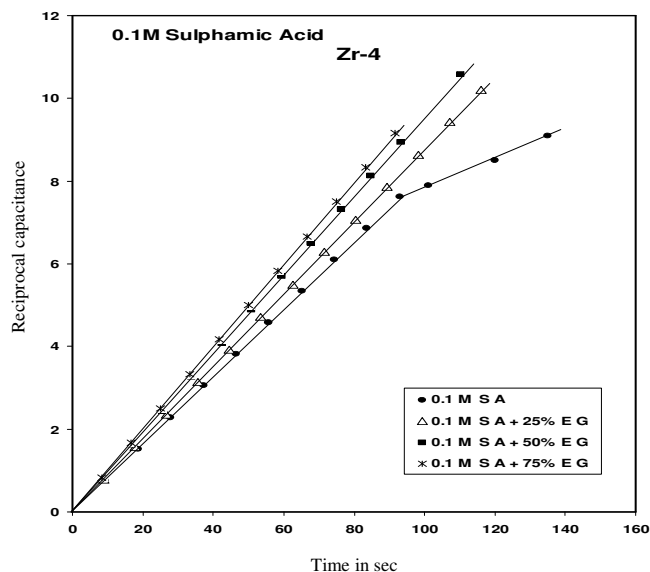


Figure 2. Plot of reciprocal capacitance as a function of time in aquo-glycolic solution

Table 1. Effect of solvent on the anodization of zircaloy-4 in 0.1M sulphamic acid

Electrolyte	Formation Rate, $V \cdot s^{-1}$	H, %	F_D in, $MV \cdot cm^{-1}$
0.1 M SA	2.15	80.23	6
0.1 M SA + 25 % EG	2.24	80.3	5.82
0.1 M SA + 50 % EG	2.36	80.5	5.64
0.1 M SA + 75 % EG	2.39	80.25	5.5

SA = Sulphamic acid, EG= ethylene glycol, η = current efficiency; F_D = differential field of formation

Table 2. Variation of dielectric constant as a function of solution composition

EG, %	Dielectric constant
0	80
25	72.8
50	69.2
75	57.8

EG= ethylene glycol

A further increase in the percentage of ethylene glycol to 80% results in non-uniformity in the film formation, which may be attributed to the fact that the electrolyte becomes highly non-polar due to the addition of more ethylene glycol. At high ethylene glycol concentrations, the mobility of the oxide ions (Which form the oxide film) decreases. Hence, in 80% ethylene glycol solution, the kinetics are slow. Though the dielectric constant value of the >80% ethylene glycol solution is less, there is still poor film formation. This can be explained on the basis of the highly non-polar nature of the medium, which plays a major role in the anodization process.

Effect of added anion impurities

Experiments were carried out in 0.1 M sulphamic acid + 0.001 M SO_4^{2-} , PO_4^{3-} , CO_3^{2-} anions to check the effect of the added anions. The addition of phosphates, sulphates and carbonates resulted in improvement of the kinetics. The presence of phosphate ions improved the kinetics of anodization to better extent. It is observed that the oxide film formed on the alloy consisting of two discrete layers in 0.1M sulphamic acid appear as a single layer in presence of added anion impurity. The results are given in Table 3 and the plots are shown in Figures 3&4.

Table 3. Effect of added anion impurities

Electrolyte	Formation rate, V.s^{-1}	η , %	F_D in, MV.cm^{-1}
0.1 M SA	2.15	80.23	6.00
0.1 M SA + 0.001 M CO_3^{2-}	2.49	89.70	6.20
0.1 M SA + 0.001 M SO_4^{2-}	2.52	98.72	5.70
0.1 M SA + 0.001 M PO_4^{3-}	2.60	97.50	5.96

SA = Sulphamic acid; η = current efficiency; F_D = differential field of formation.

The increase in the kinetics when 0.001 M of PO_4^{3-} is added to 0.1 M sulphamic acid can be explained by the firm incorporation of phosphate ions into the layers of the oxide films¹². Added anions get incorporated between the ionic vacancy sites of the metal oxide films and reduce the height of the energy barrier of the movement of ions from one ionic site to another, thereby increasing the current. This incorporation increases the current efficiency with much ionic current getting utilized for film formation, which implies better kinetic results.

On the other hand, by the addition of CO_3^{2-} and SO_4^{2-} , there is a little improvement in the kinetics, which implies that certain anions have favorable high influence on the kinetics of oxide film formation. Such ions that are capable of interstitial occupation in the film lattice increase the kinetics.

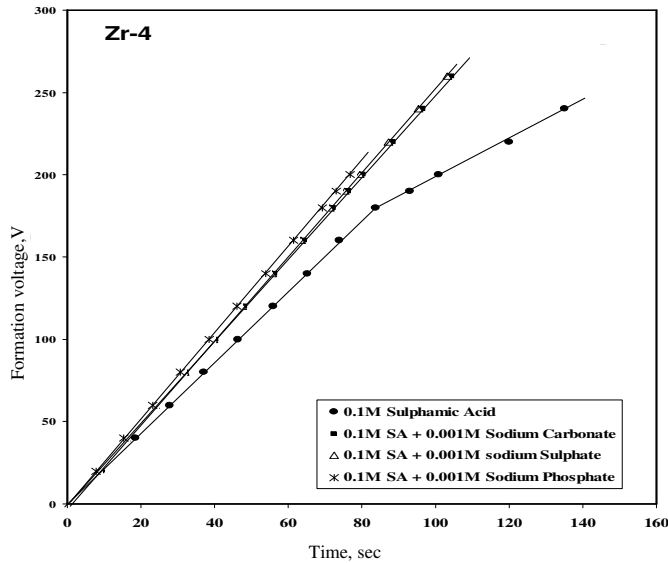


Figure 3. Plot of formation voltage as a function of time in anion impurity solution

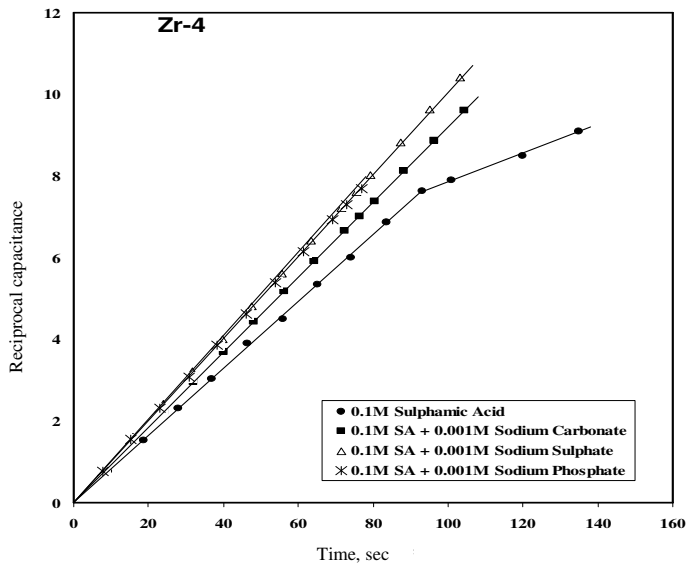


Figure 4. Plot of reciprocal capacitance as a function of time in anion impurity solution

Conclusion

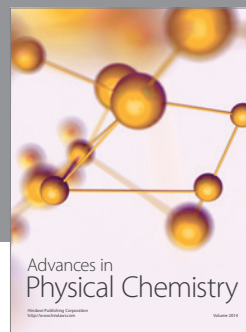
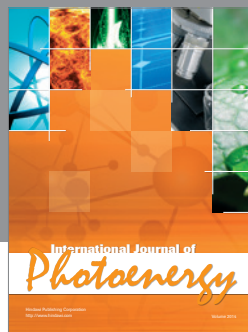
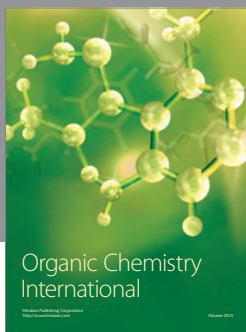
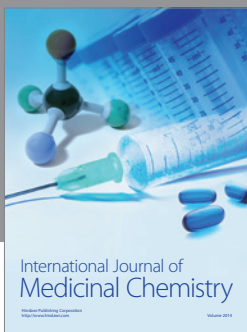
For the anodization of zircaloy-4, the kinetics (formation rate, current efficiency) are better in 0.1 M sulphamic acid with aquo-glycolic media and added anion impurities. Use of aquo-glycolic media with up to 75% ethylene glycol showed improvement in the kinetics. Addition of phosphate anions in 0.001 M concentration showed improvement in the kinetics. For the anodization of zircaloy-4 it can be concluded that the oxide film formed on the alloy consists of two discrete layers in 0.1 M sulphamic acid and they are made to a single layer in presence of ethylene glycol and added anion impurity.

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