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Kinetics of Anodic Oxidation of Niobium in 0.1M L-Ascorbic acid: Solvent and Temperature effects.

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ABSTRACT

Anodization of Niobium in 0.1M L-Ascorbic acid has been carried out. Kinetics of anodic oxidation of Niobium has been studied at a constant current density of 8 mA.cm^{-2} and at room temperature. The plots of formation voltage vs. time, and reciprocal capacitance vs. time were drawn. From these plots, formation rate, current efficiency and differential field were calculated. The Addition of Solvent (Ethylene glycol at various concentrations) to the aqueous solution of L-ascorbic acid showed improvement in the kinetic results. The surface morphology of the anodic films was also studied by Scanning Electron Micrographs (SEM). Kinetics was studied at different temperatures ranging from 273K to 333K at a constant current density of 8 mA.cm^{-2} . It was observed that kinetic results were found to be increasing linearly with the decrease in temperature.

Key words: Anodization, formation rate, current efficiency, differential field, Niobium, SEM.

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INTRODUCTION

Metals such as Niobium, Zirconium & its alloys, Tantalum, Titanium etc. can be anodized to give thin, uniform & relatively flaw free oxide films, which are stable chemically & mechanically. Anodic oxide films formed on Niobium are useful in the field of electrical and electronic components (capacitors, resistors, diodes, photoelectric devices etc.), corrosion protection & for decorative purposes. Several other applications have been investigated by others [1-5].

In the present work, the kinetics of anodic oxidation of Niobium in aqueous solution of 0.1M L-Ascorbic acid & aquo-glycolic media in various proportions (v/v) of water-ethylene glycol mixtures ranging from 0 to 80% Ethylene glycol are studied. Scanning Electron Microscopic studies was also carried out to observe the changes in the surface morphology of the anodic films formed. An attempt was also made to study the kinetics at various temperatures ranging from 273K to 333K at a constant current density of 8 mA.cm^{-2} .

EXPERIMENTAL

Niobium was of 99.5% purity, supplied in the form of annealed sheet by NFC, Hyderabad as gift samples. In the present work, the foil samples used were cut with the aid of a punch into flag shaped specimens of 1cm^2 working area on both side & 2cm long tag. The chemical polishing mixture for niobium is 5:5:1.5 by volume 53% HNO_3 , 49% HF, 98% H_2SO_4 .

For anodizing, a closed shell of 200 mL capacity was used. The cathode used was a platinum foil of 20cm^2 superficial area to make double layer capacitance as large as possible. Electrolytes used were 0.1M L-Ascorbic acid in 20, 40, 60 and 80% aquo-glycolic mixtures, the solvent being Ethylene glycol.

The temperatures used in the current study were ranging from 273K to 333K.

All the experiments were carried out at a constant current density of 8 mA.Cm^{-2} . The experimental procedure for the anodization is given elsewhere [6]. The kinetic results calculated are formation rate in Vs^{-1} , current efficiency (η) % and differential fields of formation (FD) in MV cm^{-1} from the conventional plots V vs. t, $1/C$ vs. t and $1/C$ vs V.

The surface morphology of the anodic film was examined using Scanning Electron microscope (SEM). The SEM's were taken at IICT, CSIR, Hyderabad.

The surface was thoroughly rinsed with distilled water and dried under infrared lamp and cleaned gently with fine tissue paper. The surface was coated with gold, Palladium conducting material using evaporation technique and signal processed secondary electron images were taken from scanning electron microscope model SEM Hitachi- S520 at 10 KV, Hitachi instruments made in Japan (Oxford link ISIS- 300 UK)

RESULTS AND DISCUSSIONS

Solvent Effect & SEM Studies

Anodization of Niobium in 0.1M L-ascorbic acid was performed by mixing various proportions of ethylene glycol to the aqueous solution (20, 40, 60 & 80%). There was an Improvement in the kinetics as given in Table-1. The relevant plots are shown in Figs-1 & 2. Aquo-organic solutions aid in the formation of good oxide films and act as better electrolytic capacitors [7]. These facts support the current results obtained in aquo-organic mixtures of 0.1M L-Ascorbic acid. It can be explained on the basis of decrease in the dielectric constant of the medium as shown in 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 20, 40, 60 & 80% aquo-glycolic media, the dielectric constant values are low leading to a marked improvement in the kinetics.

Scanning Electron micrographs

Fig-3 and Fig-4 are the scanning electron micrographs of anodic films formed on Niobium in aqueous and aquo-glycolic solutions of 0.1M L-ascorbic acid upto 200V.

Table-1: Anodic films formed on Niobium in 0.1M L-Ascorbic Acid both aqueous and aquo-glycolic-media.

Percentage of Glycol	Formation Rate, dV/dt ($V.s^{-1}$)	Current efficiency, η (%)	Differential field, F_D ($MV.cm^{-1}$)
0	1.74	61.0	5.648
20	2.17	77.1	5.591
40	2.34	83.6	5.543
60	2.46	88.5	5.504
80	2.58	92.5	5.477

Table-2: Variation of Dielectric constant as a function of time in aquo-glycolic solution

EG (%)	0	20	40	60	80	100
Dielectric constant	80.0	72.8	69.2	57.8	43.2	37.7

Fig-1: Plot of formation voltage as a function of time in aquo-glycolic solution

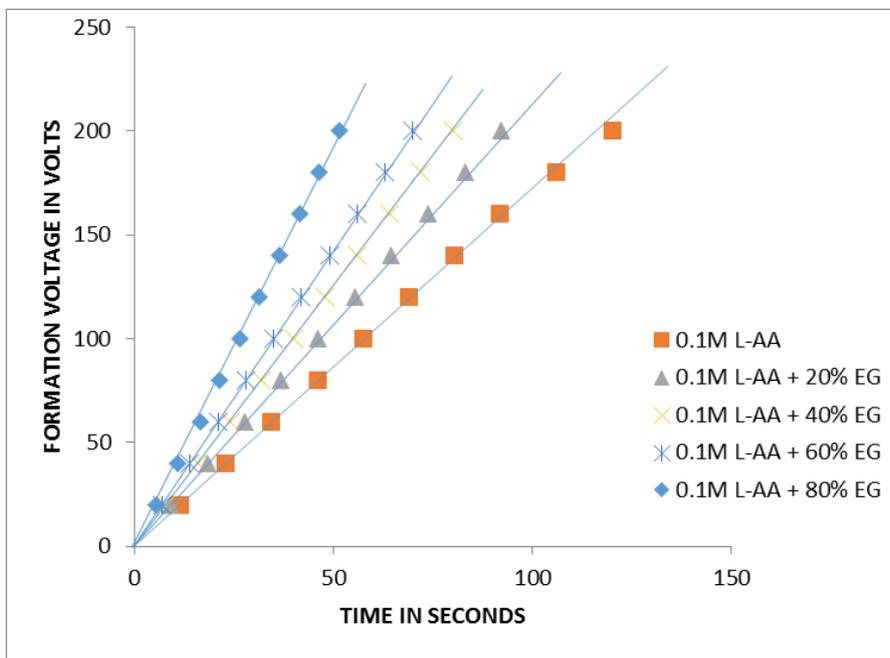


Fig-2: Plot of reciprocal capacitance as a function of time in aquo-glycolic solution

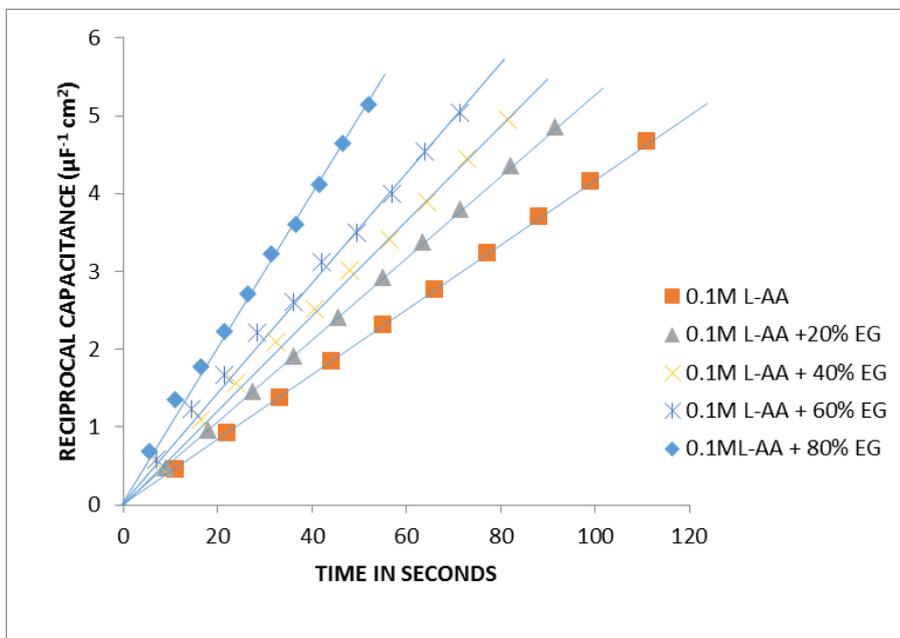


Fig-3: SEM of the film formed upto 220V in 0.1M L-ascorbic acid (aqueous medium) at room temperature (Magnification of the micrograph is X 5000)

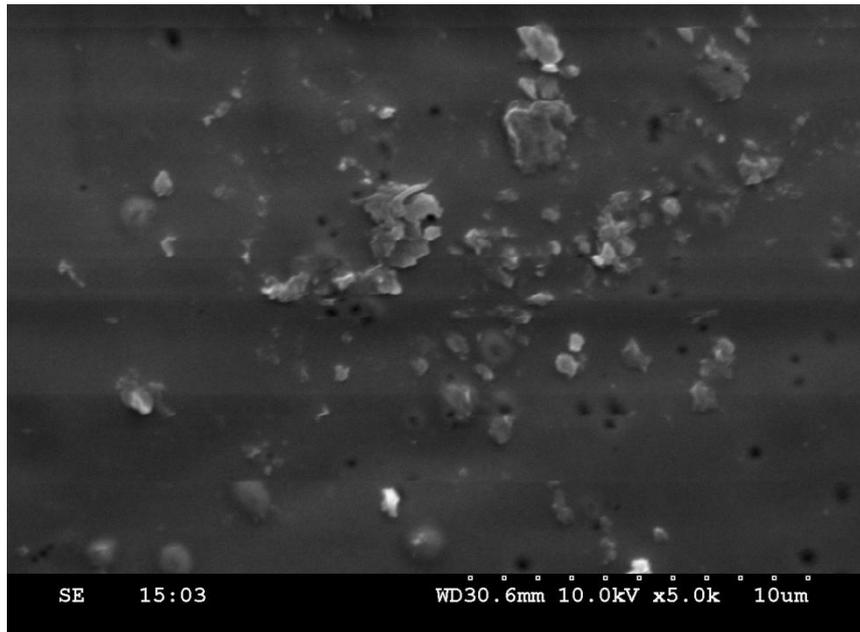
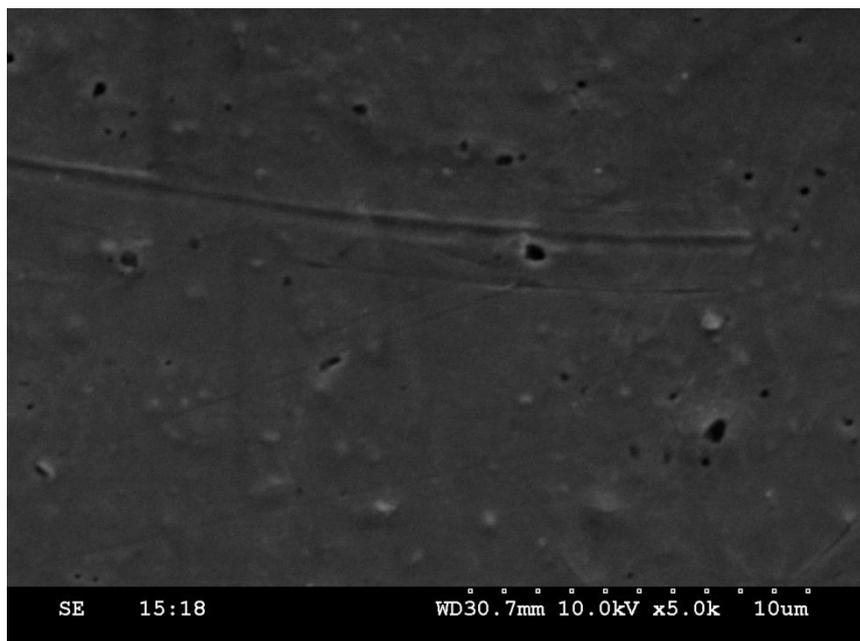


Fig-4: SEM of the film formed upto 220V in 0.1M L-ascorbic acid (glycolic medium) at room temperature (Magnification of the micrograph is X 5000)



When compared, the roughness and non-uniformity of the surface are decreased when electrolytic medium is changed from aqueous to aquo-glycolic medium (fig-4) is observed to be smoother than the film formed in aqueous medium.

Vermilyea studied the formation of anodic films on tantalum in aqueous [8] and non-aqueous [9] solutions. He suggested that the composition of film depends on the solution in which it is formed.

Nageshwar rao et al. [10] observed a change in the dielectric constant of oxide films by changing the medium from aqueous to glycolic.

Vermilyea [9] reported that the optical thickness was smaller in the non-aqueous solutions and the increase in weight for a given charge passed could be as much as twice that expected.

Moshashi Koyama [11] carried out anodization of titanium in non-aqueous media and confirmed that the oxide film consists of double layers and suitable for electrolytic capacitors.

Wei Wei et al. [12] reported the growth of layers by anodization of tantalum in a non-aqueous electrolyte consisting of an optimized glycerol/ethylene glycol mixture with the addition of NH_4F

Schmidt et al. [13] observed that the layers of TiO_2 obtained in non-aqueous electrolytes are much adherent and uniform than those realized in aqueous media.

Climent Montoliu et al. [14] studied the anodization of titanium in acid, alkali and neutral baths (aqueous and aquoglycolic) and suggested from the structure and dielectric properties, that the anodic coatings formed in non-aqueous media acts as better dielectric capacitors.

Panasa Reddy et al. [15] and Lavanya et al. [16] also studied in trisodium citrate, 0.1 M KOH (aquo-glycolic) respectively and found that the breakdown voltage was higher when anodized in ethylene glycol medium. This was also supported by other worker [17]. Shukla [18] carried out the study of effect of aquo-glycolic media on anodization of zircaloy-4 in 0.1 M sulphamic acid and found that the addition of solvent improved the kinetic results.

Effect of Temperature

Anodizations were carried out on Niobium at various temperatures ranging from 273K to 333K and at a constant current density of 8 mA.cm^{-2} . The conventional plots were drawn as shown in the Fig: 5 & 6 . From these plots, the kinetic results were calculated. It was observed that the formation rate, current efficiency, differential field & break down voltage were found to be increasing linearly with the decrease in temperature as shown in Table-3.

The decrease in the field, formation rate & Breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

Colton & Wood [19] reported that the BDV was decreased with increase in temperature in the case of titanium oxide films and explained the observation on the basis of dissolution of the film.

Bhaskar reddy et al [20] observed the similar trend of decreasing kinetic results with increase in temperature in 0.1M potassium tartarate.

The same results were observed by many others [21-26].

Fig-5: Plot of formation voltage as a function of time at different temperatures.

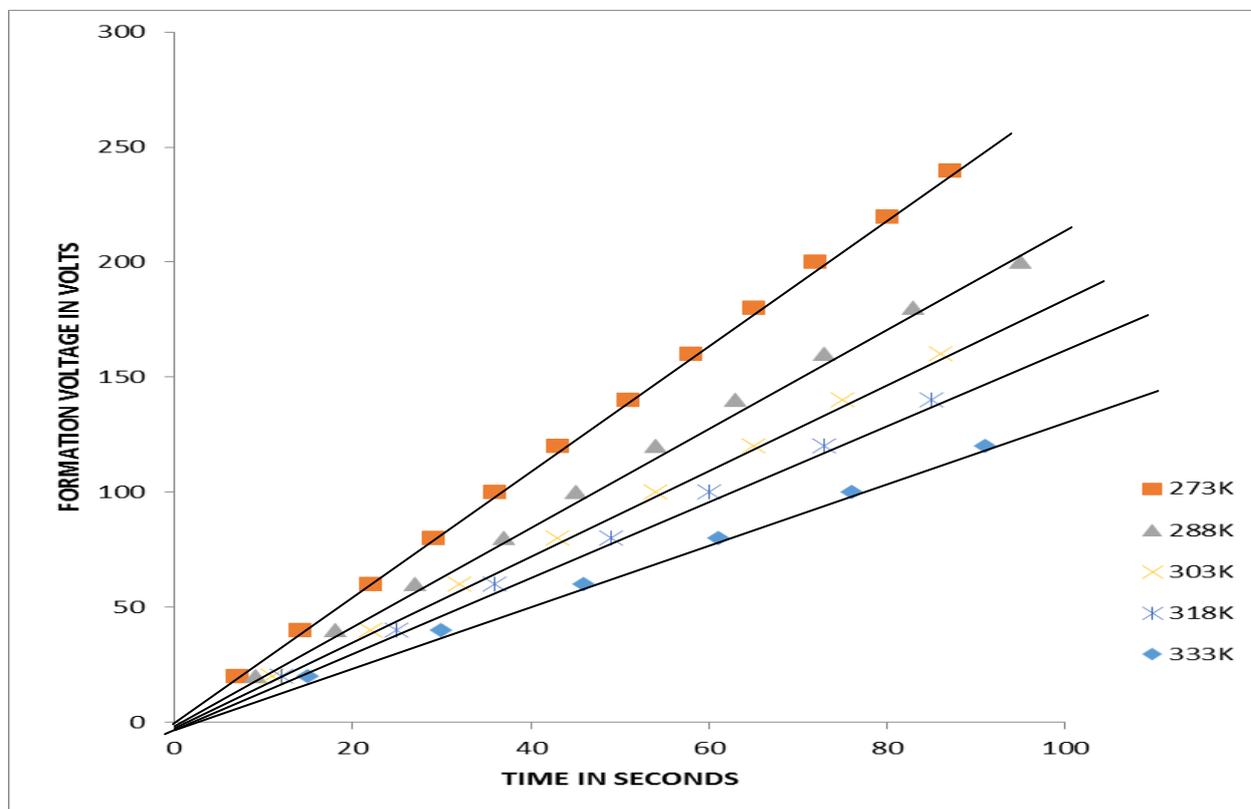


Fig-6: Plot of Reciprocal Capacitance as a function of time at different temperatures.

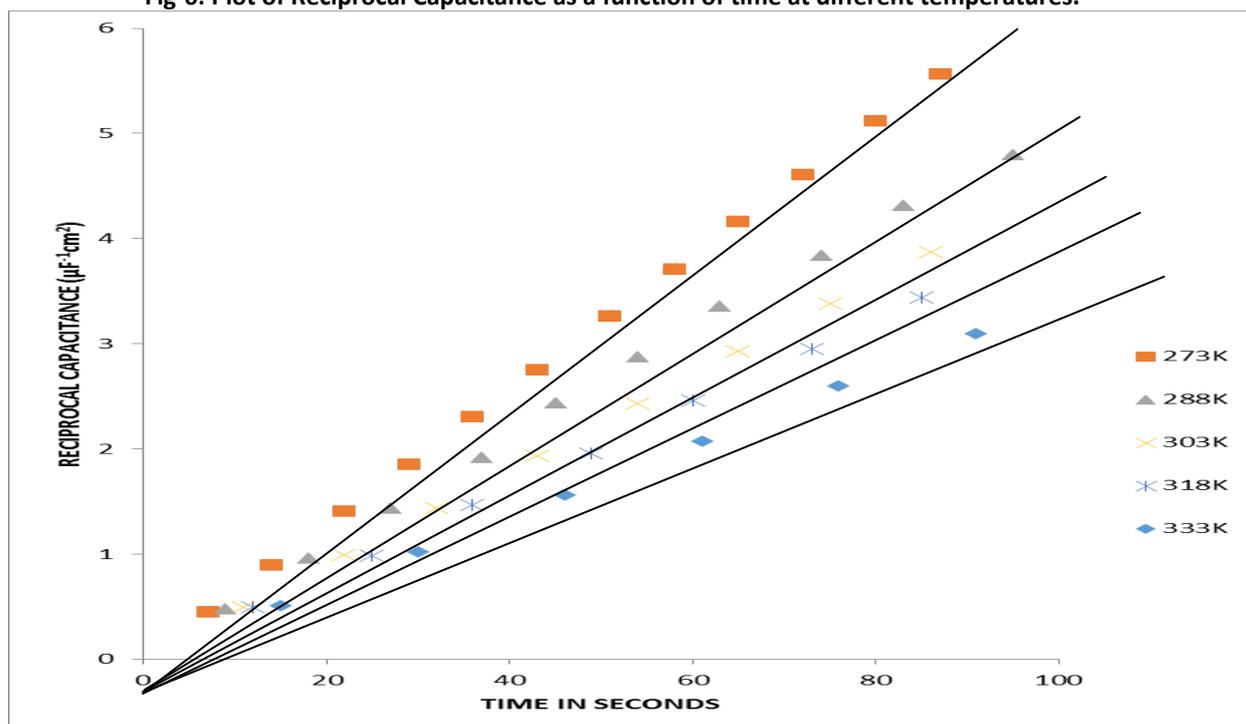


Table-3: Anodic films formed on Niobium in 0.1M L-Ascorbic Acid at different temperatures.

Temperature ,T (K)	Formation rate,dV/dt (V.s ⁻¹)	Current efficiency, η (%)	Differential field, F _D (MV.cm ⁻¹)	Break down voltage (V _B), Volts
273	2.76	92.0	5.940	240
288	2.00	69.0	5.740	215
303	1.74	61.0	5.648	202
318	1.66	59.3	5.550	175
333	1.31	49.2	5.290	150

CONCLUSIONS

By changing the solvent medium from aqueous to glycolic, the kinetics of film formation on Niobium in 0.1 M L-ascorbic acid have been studied and it is observed that the peak voltage, formation rate, current efficiency are increased but differential field of formation decreased with the glycol content of solution. This can be attributed to the decrease in the dielectric constant of the solution with the increase in glycol content of the solution.

It was also observed that the kinetics were good at low temperatures. It was observed that the formation rate, current efficiency, differential field & break down voltage were found to be increasing linearly with the decrease in temperature. The decrease in the field, formation rate & Breakdown voltage with the increase in temperature may be attributed to the decrease in the incorporation of anions into the film and may also be due to the dissolution of the film with the increase in temperature.

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