Comparison of the Kinetics of Anodization of Titanium and Niobium in Lithium Phosphate and Lithium Sulphate

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Titanium and niobium were anodized in 0.1 M lithium phosphate and 0.1 M lithium sulphate at a constant current density of 8mA.cm^{-2}. When titanium was anodized in lithium sulphate, the rate of film formation decreased suddenly at about 50 V. This behaviour, however, was not observed when the anodization was carried out in lithium phosphate. The formation rate, ionic current efficiency and differential field during anodization of niobium in lithium phosphate, were found to be more than those for the film formation in lithium sulphate.

Anodic oxidation of Ti and Nb have been reviewed by Young [1]. Day and Keil [2] studied the anodic oxidation of Nb in glacial acetic acid - sodium tetraborate solution over a potential range of 70 V. Kover and Musselin [3] have made a comparitive study of anodic oxide films on Ti, Nb and Ta. Several papers of anodic oxidation of Ti, Zr and Nb have been published [4-6]. In the present work, we have studied and compared the kinetics of film formation on Ti and Nb in lithium phosphate and lithium sulphate electrolytes.

EXPERIMENTAL

Titanium and niobium samples (0.125 mm thick and about 99.7% purity) were supplied by N.F.C., Hyderabad. Niobium samples were polished in a mixtue of HNO_3, HF and H_2SO_4 in the volume ratio of 5:5:12.5 and Ti samples were polished in a mixture of HNO_3, HF, H_2SO_4 and H_2O in the volume ratio of 2:1:2:1. Specimens were cut with the help of a punch to give a working area of 1 cm^2 and a tag 2 cm long. The tags were anodized in 0.1 M H_3PO_4 to about 270 V.

The platinum cathode had a large surface area of 30 cm^2 to make the double layer capacitance as large as possible. Specimens were suspended from the anodized tag and dipped into the electrolyte.

In the present work, the experiments were all done at constant current density using a stabilized power supply unit (supplying constant currents from 0-50 mA. cm^{-2}) - a unit built by Gargya Research Instruments, New Delhi. The current was measured accurately on a milliammeter (ITL model MC 110). A shorting switch was incorporated so that the current could be set prior to use. The potential across the cell was measured with the help of a voltmeter.

Capacitance measurements were made with the help of a L.C.R. bridge. Since the oxide film behaves as a dielectric and the system metal-metal oxide interface, oxide-oxide electrode interface-electrolyte can be considered as a parallel plate capacitor, the thickness of the film can be determined using capacitance measurements. The parallel plate capacitor can be

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schematically represented as metal/oxide/ electrolyte.

The equation for A.C. capacitance is given by

$$C = \frac{\varepsilon A}{4 \pi D \cdot 9 \times 10^{11}} \text{ in farads}$$

where ε = dielectric constant of the medium i.e. oxide
A = Area in cm^2
D = thickness of the dielectric medium in cm units.

The reciprocal capacitance can be a measure of thickness. The electrical double layer capacity (C_{edl}) at the oxide-electrolyte interface must be high in comparison to the capacity of the oxide. The resultant capacitance (C_r) of combined capacitances in series is given by

$$\frac{1}{C_r} = \frac{1}{C_{oxide}} + \frac{1}{C_{edl}}$$

Where C_{edl} is very large, the measured resultant capacitance, C_r, approximates closely to that of the oxide (C_{oxide}) to within usualy ± 1%.

In the present work, the capacitance of the electrode was measured in series with a subsidiary electrode of platinum mesh. The capacitance of the subsidiary electrode was constant and much larger than that of the valve electrode, so that the measured capacitance is considered as equal to that of the latter. The charge on the solution side of the oxide is effectively equivalent to the normal electrical double layer, which is relatively large and probably virtually constant. Hence the capacitance actually measured is effectively that of the valve electrode itself.

RESULTS AND DISCUSSION

Niobium and titanium samples were anodized in 0.1 M solutions of lithium phosphate and lithium sulphate separately at a constant current density of 8 mA. cm^{-2} and at room temperature.

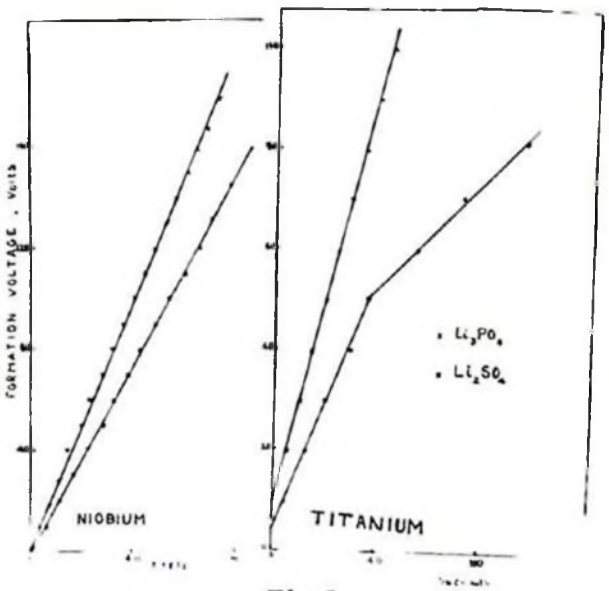


Fig.1

The variation of formation voltage vs time was measured. The plots of formation voltage vs time for the anodization of Ti and Nb in the two electrolytes are shown in Fig.1. Formation voltage plot of Ti in lithium phosphate was found to be linear upto breakdown voltage whilst the plot in lithium sulphate consisted of two linear portions intersecting at about 50 V. The values of formation rate (dV/dt) for the anodization in the two electrolytes are given in Table 1.

The value of dV/dt (2.5 $V.sec^{-1}$) for the anodization of Ti in Li_2SO_4 corresponds to the initial rate of formation and is independent of thickness upto a formation voltage of 50 V. The rate of film formation was found to fall beyond 50 V and is found to be 0.97 $V.sec^{-1}$.

Table 1

Formation rate dV/dt (V.sec^{-1}) in different Electrolytes

Sample	Li_3PO_4	Li_2SO_4
Niobium	2.3	1.5
Titanium	4.0	2.5 (below 50 V)
		0.97 (beyond 50 V)

The plots of reciprocal capacitance vs time for the anodization of Nb (Fig.2) are found to be linear in both the electrolytes. Thus the field strength required to maintain a constant ionic current through the film is independent of the thickness of the film. It is interesting to note that the formation rate, ionic current efficiency and differential field are high in lithium phosphate than in lithium sulphate. The values are summarized in Table 1 and Table 2.

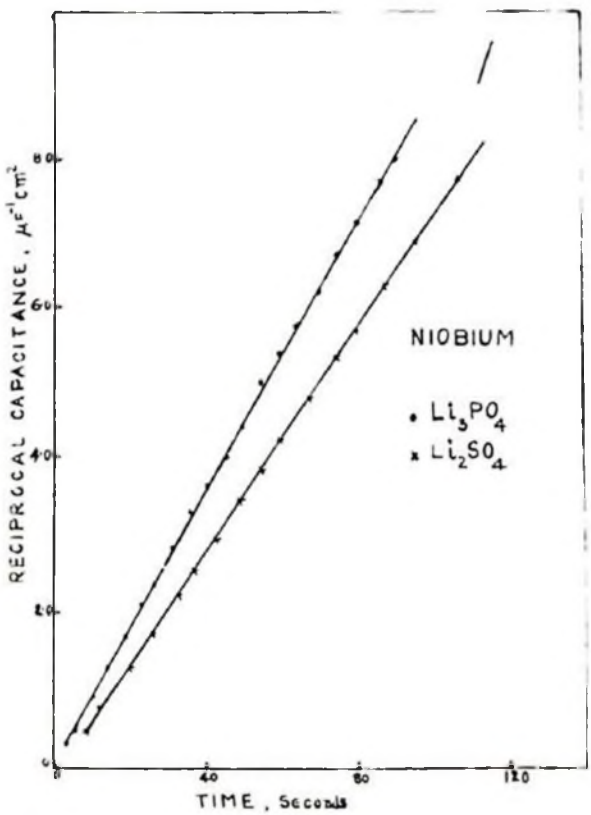


Table 2

Parameters for anodization of Niobium

Lithum salt Electrolyte	Current eff.(%)	Differential field (MV.cm^{-1})
Phosphate	90	3.3
Sulphate	75	1.7

The field strength required to maintain a constant ionic current through the film has been reported to be independent of the thickness of the film and the evidence has been examined by Young [1].

There are two methods of evaluating field strength across the oxide:

1. An integral field defined as V/D.
2. A differential field by $(dV/dD)_{W,a,q}$

where V = oxide overpotential formation voltage (for thick films)
D = thickness
W = the height of the energy barrier
a = the half jump distance associated with 'W'
q = charge on mobile ion or vacancy

If the current efficiency is not 100%, the total current passed is made up of an ionic current (which is responsible for the growth of the oxide), electronic current (which liberates oxygen) and leakage current (down the cracks and other imperfections across the film). For a chemically polished specimen, the leakage current may be considered to be negligible and the current efficiency (η) is given by

$$\eta = \frac{\Delta D \text{ (experimental)}}{\Delta D \text{ (calculated)}}$$

Current efficiency is calculated from the rate of film formation. As the rate of film formation increases, the current efficiency increases.

CONCLUSION

When niobium is anodized in 0.1 M phosphate, the current efficiency is 90% whilst it is found to be 75% in 0.1 M sulphate.

The values of the rate of film formation are found to be high when Ti and Nb are anodized in Li_3PO_4 than in Li_2SO_4. Hence it may be concluded that 0.1 M Li_3PO_4 is a better electrolyte for the anodization of Ti and Nb than 0.1 M Li_2SO_4. This may be attributed to the amount of anion incorporation (7) which might be more when anodized in Li_3PO_4 than in Li_2SO_4.

ACKNOWLEDGEMENTS

The author (Dr. P. Shobha Rani) is thankful to the C.S.I.R., New Delhi for the award of Research Associateship. The authors are also thankful to the Head, Department of Chemistry, Osmania University for providing the facilities.

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