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Nature and corrodability of thin oxide films formed on niobium in NaOH solutions

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The corrodability of thin oxide films formed on niobium either naturally or anodically was investigated in NaOH solutions of different concentrations (0.05–3.0 M) using impedance and potential measurements. Naturally formed films were found to thicken in NaOH solutions of concentrations $\leqslant 0.1$ M, while they were subjected to dissolution in NaOH solutions of concentrations $\geqslant 1.0$ M. The dissolution behaviour of anodically formed oxide films on niobium was found to depend on the thickness and alkali concentration. Anodically formed thin films ($\simeq 4$ nm resist dissolution in NaOH solutions of concentrations $\leqslant 0.1$ M, partially dissolve at [NaOH] $\simeq$ 0.5 and 1.0 M and are subject to aggressive dissolution at higher concentrations. Thick films ($\simeq 50$ nm) resist dissolution at [NaOH] $\leqslant$ 1.0 M, while they dissolve at higher alkali concentrations. The corrosion potential was found to depend on the alkali concentration and the oxide film thickness. The impedance of the oxide film was found to be purely capacitive and to increase with increasing film thickness.

1. Introduction

Valve metals are known to form stable oxides [1]. The chemical stability and electrochemical activity of these oxides are important for determining their stability as good anodic materials. Niobium is known as one of these valve metals [2]. Previous studies on the electrochemical behaviour of niobium have been concerned mainly with kinetics of metal oxidation [3–7]. The stability of the oxide films formed on niobium in various aqueous media was investigated [8–11]. However, the corrodability of thin oxide films on niobium in alkaline solutions seems to have had little attention.

The aim of the present work is to study the corrodability of thin oxide films formed either naturally or anodically on niobium in NaOH solutions using impedance and potential measurements.

2. Experimental details

Niobium disc electrodes (areas, $\sim 0.196\,\mathrm{cm}^2$) were cut from specpure niobium rod (Johnson and Matthey, London). The electrode preparation and polishing, the electrolytic cell, the electric circuit and other experimental details were essentially the same as described elsewhere [12, 13]. All solutions were prepared from carbonate free AnalaR grade sodium hydroxide stock solution by appropriate dilution using triply distilled water.

Before each experiment, the electrode surface was mechanically polished using successively finer grades of emery paper down to 4/0, until a mirror-bright surface was attained. All potentials were measured versus a saturated calomel electrode (SCE) and referred to the normal hydrogen electrode (NHE). The electrode capacitance, C_m, and resistance, R_m, were traced with time at a working frequency of 1 kHz. Complex plane analysis was studied over a frequency range of 100 to 10 000 Hz.

Anodically formed oxide films were formed by anodizing niobium electrode at constant current density of $0.5\,\mathrm{mA\,cm^{-2}}$ in 0.5 M H_2SO_4 solution up to the desired formation voltage, F_v. Then, the electrode was washed carefully with triply distilled water and transferred rapidly to the test solution where the open-circuit potential, E_h, and electrode impedance, C_m and R_m, were traced with time until steady state values attained. All measurements were carried out in naturally aerated solutions at constant temperatures of 30 ± 0.1° C.

3. Results and discussion

3.1. *Corrodability of naturally formed oxide films on niobium*

Figure 1 shows the variation of the open-circuit potential, E_h, of mechanically polished niobium electrodes with time in NaOH solutions of different concentrations (0.05–3.0 M). As can be seen, the direction of potential change depends on the alkali concentration. At [NaOH] $\leqslant$ 0.1 M, the potential drifts to more noble values and reaches a quasi-steady state after about 3 h at which the rate of film formation is nearly equal to the rate of film destruction. At higher alkali concentrations, [NaOH] $\geqslant$ 1.0 M, E_h increases initially with time to a maximum then decreases to steady state values. Generally, the quasi-steady state potential shifts to less noble values with increasing alkali concentration, *cf.* Fig. 1b. The shift of potential

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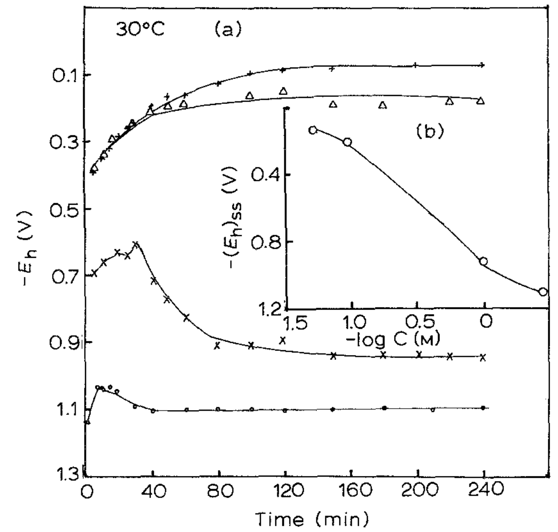

Fig. 1. (a) Variation of open-circuit potential, E_h, of mechanically polished niobium electrodes with time in NaOH solutions of concentrations: (●) 3.0, (x) 1.0, (△) 0.1 and (+) 0.05 M. (b) Steady state E_h against logarithm of NaOH concentration.

with time to more noble values is connected to the oxide film thickening [14–16], while that in the less noble direction is attributed to the dissolution and thinning of the oxide film [17–19].

The oxide film thickening and thinning is more clearly inferred from the capacitance measurements. As can be seen in Fig. 2, the reciprocal capacitance of the niobium electrode, C_m^{-1}, increases at the beginning to a maximum then decreases to reach the steady state value. It should be mentioned that the final (quasi-steady state) C_m^{-1} value is higher than the initial value for solution concentrations [NaOH] $\leqslant$ 0.1 M. In higher concentrations, [NaOH] $\geqslant$ 1.0 M, the final C_m^{-1} is lower than the initial value. The increase in C_m^{-1} is connected to the oxide film thickening while the decrease in C_m^{-1} is attributed to film thinning [15–19]. Although the initial C_m^{-1} values correspond to the air formed film and all should be the same, they are different. This behaviour is usually observed and reflects the dependence of the measured capacitance on the solution composition [10, 11, 15, 17, 24]. Under this condition, the absolute film thickness cannot be determined but a relative change in the thickness can be traced.

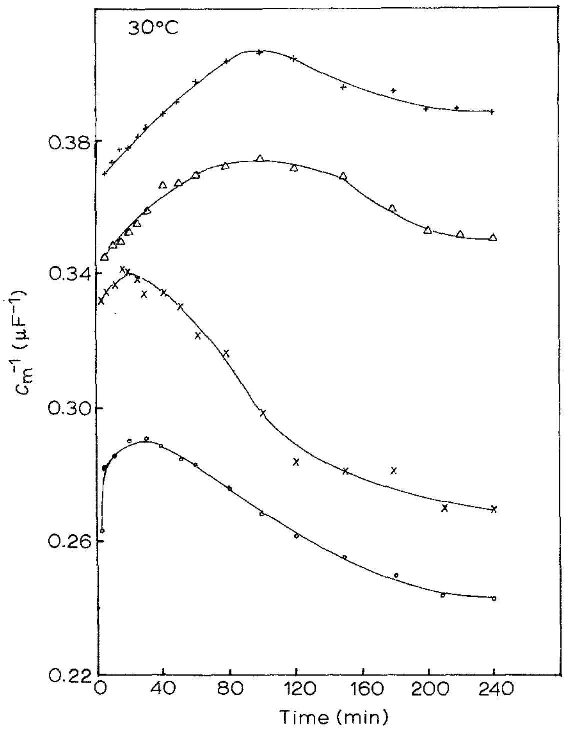

Fig. 2. Variation of reciprocal capacitance, C_m^{-1}, of mechanically polished niobium electrodes with time in NaOH solutions of concentrations: (●) 3.0, (x) 1.0, (△) 0.1 and (+) 0.05 M.

Assuming that the oxide film is a perfect dielectric, its thickness may be calculated using the familiar relation for a parallel plate condenser [20], *viz.*

$$C_m = \frac{\varepsilon}{4\pi X} \tag{1}$$

where C_m is the measured capacitance in μF cm^{-2}, X is the film thickness in cm and the permittivity of oxide as $\varepsilon \times 1.11 \times 10^{-12}$ C V^{-1} cm^{-1}, ε being the dimensionless dielectric constant. Assuming that $\varepsilon = 41.4$ [1], the change in the oxide film thickness, ΔX in nanometres, is given by

$$\Delta X = \frac{41.4 \times 1.11 \times 10^{-6} \times 10^{7}}{4\pi \Delta C_m} = 36.569 \Delta C_m^{-1} \tag{2}$$

where $\Delta C_m^{-1} = (C_m^{-1})_{\text{final}} - (C_m^{-1})_{\text{initial}}$. The values of ΔX are given in Table 1. Naturally, the ΔX values represent average results of oxide thickening and thinning. Higher ΔX values may be obtained by assuming a reasonable roughness factor [2–3], for mechanically polished niobium electrodes. The negative ΔX values at concentrations [NaOH] $\geqslant$ 1.0 M, indicate a dissolution process. The oxide film thickening is assumed to occur under high electric field strength via solid state mechanism. The electric field is created across the oxide film by adsorption of OH$^-$ ions onto the oxide film and hence, an image of opposite charge is created at the metal/oxide interface. The electric field strength was estimated in a previous work and was found to be in the order of MV cm^{-1} which is fairly enough to cause the ionic migration [10, 11, 21].

According to the Wagner–Traud representation of open-circuit corrosion, the measured potential gives

Table 1. The change in the thickness, ΔX, for mechanically polished niobium electrodes in NaOH solutions of different concentrations at 30° C

[NaOH] (*M*)	$(C_m^{-1})^{*}_{initial}$ (*cm*^{2} *μF*$^{-1}$)	$(C_m^{-1})^{**}_{final}$ (*cm*^{2} *μF*$^{-1}$)	ΔX (*nm*)
0.05	0.0625	0.0659	0.124
0.10	0.0575	0.0591	0.060
1.00	0.0558	0.0456	−0.373
3.00	0.0439	0.0412	−0.097

* The values were taken after 2 min.
** The values were taken after 4 h.

the mixed corrosion potential where the anodic and cathodic partial currents are equal [22]. Therefore, the anodic and cathodic reaction rates, R_a and R_c, may be written as follows [22]:

$$R_a = K_1 \exp (E_h/b_a) \tag{3}$$

$$R_c = K_2[H^+] \exp (E_h/b_c) \tag{4}$$

where K_1 and K_2 are constants, E_h is the mixed potential and b is the Tafel slope. The cathodic reaction is assumed to be the hydrogen evolution and the reaction order is also assumed to be unity. Thus, to a first approximation, Equations 3 and 4 give

$$E_h = b_a \ln (K_2/K_1) - b_c \ln [H^+] \tag{5}$$

The latter equation accounts for the observed dependence of E_h on the alkali concentration. However, it is known that the steady potential of passive metals covered with insulating films does not represent a simple equilibrium potential but that it depends to a great extent on the nature and thickness of the barrier film [10, 11, 17, 23].

3.2. *Corrodability of anodically formed oxide films on niobium*

3.2.1. Effect of alkali concentration. Figure 3 shows the variation of E_h of anodized niobium electrodes to 2 V with time in NaOH solutions of different concentrations. The film thickness according to Equation 2 is about 3.0 nm. As can be seen in Fig. 3, the E_h variation indicates that the oxide film thickness in solutions of concentration [NaOH] $\leqslant$ 0.1 M, while it dissolves in alkali solutions of concentrations [NaOH] $\geqslant$ 2.0 M. At [NaOH] = 0.5 and 1.0 M, a state of dissolution followed by formation to thicker films rather than the initial films can be seen. The capacitance measurements, Fig. 4, show a rather similar trend. The quantity C_m^{-1} in the case of [NaOH] = 3.0 M, shows a decrease in C_m^{-1} followed by an increase until the attainment of steady state values. Such a trend may be explained by covering of the dissolved surface by a dissolution product and/or adsorbed OH^- ions.

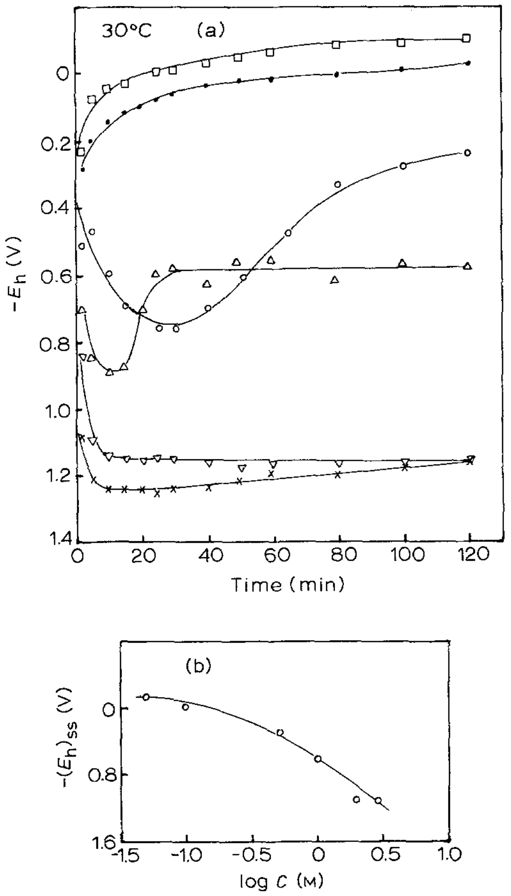

Fig. 3. (a) Variation of open-circuit potential, E_h, of anodized niobium electrodes (F_v = 2 V) with time in NaOH solutions of concentrations: (x) 3.0, (▽) 2.0, (△) 1.0, (○) 0.5, (●) 0.1 and (□) 0.05 M. (b) Steady state potential, E_h, against logarithm of NaOH concentration.

The variation of capacitance and potential for thicker films on niobium in NaOH solutions has also been studied. Figure 5 shows the variation of E_h and C_m^{-1} for anodized niobium electrodes to 40 V ($\simeq$ 50 nm oxide film thickness) with time in 0.05–3.0 M NaOH solutions. The capacitance and potential measurements show a consistency. The oxide films are stable in NaOH of concentrations up to 1.0 M while they are subject to dissolution at higher concentrations. The dissolution rate depends on the alkali concentration. As can be seen in Fig. 5, the potential at [NaOH] = 0.05–1.0 M depends on the alkali concentration but to relatively less degree as compared with that observed for thin films, *cf.* Fig. 4.

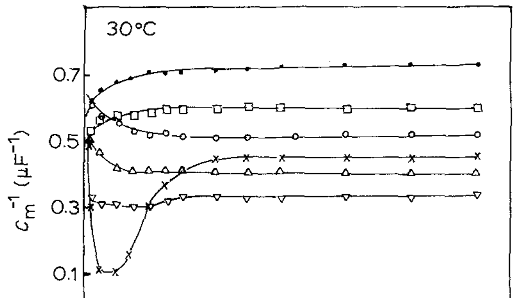

Fig. 4. Variation of reciprocal capacitance, C_m^{-1}, of anodized niobium electrodes (F_v = 2 V) with time in NaOH solutions of concentration: (x) 3.0, (▽) 2.0, (△) 1.0, (○) 0.5, (●) 0.1 and (□) 0.05 M.

3.2.2. Effect of oxide film thickness. Oxide films of different thickness were formed on niobium electrodes in 0.5 M H_2SO_4 by anodizing the electrodes at constant current density of 0.50 mA cm^{-2}. Figure 6 shows the initial and steady parameters, E_h, C_m and R_m, for such films on the formation voltage, F_v, in 0.05 M NaOH.

As can be seen in Fig. 6a, the sensitivity of E_h to change decreases with increase of the film thickness, i.e. formation voltage and at sufficiently high thicknesses, the potential is practically independent of the medium composition. This is attributed to the high insulating properties of such films [23].

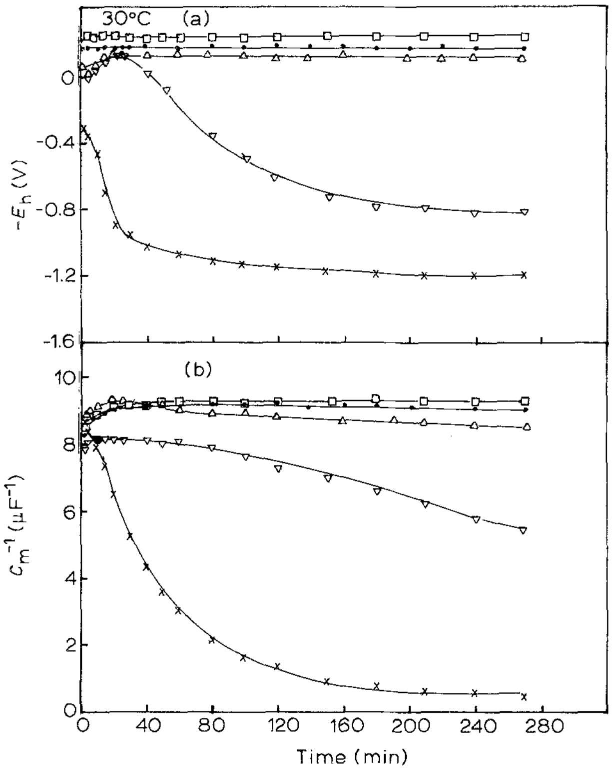

Fig. 5. Variation of open-circuit potential, E_h (a) and capacitance, C_m (b), of anodized niobium electrodes (F_v = 40 V) in NaOH solutions of concentration: (x) 3.0, (▽) 2.0, (△) 1.0, (●) 0.1 and (□) 0.05 M.

Figure 6b shows the linear dependence of the initial C_m^{-1} on the formation voltage. This indicates that the film thickness increases linearly with formation voltage, F_v. The formation ratio was estimated from Fig. 6b to be ~1.3 nm V^{-1}. The difference between the initial and final values of C_m^{-1} and R_m increase as the film thickness increases. The final C_m^{-1} values are always higher than the initial values, i.e. the oxide film may thicken, probably via adsorption and accumulation of OH$^-$ ions onto the film surface. On the other hand, the final R_m values are lower than the initial ones. The latter behaviour is connected to the increase of the oxide film conductivity most probably via incorporation of OH$^-$ ions into the film [9, 24]. Similar results were obtained in 1.0 M NaOH solutions as can be seen in Fig. 7.

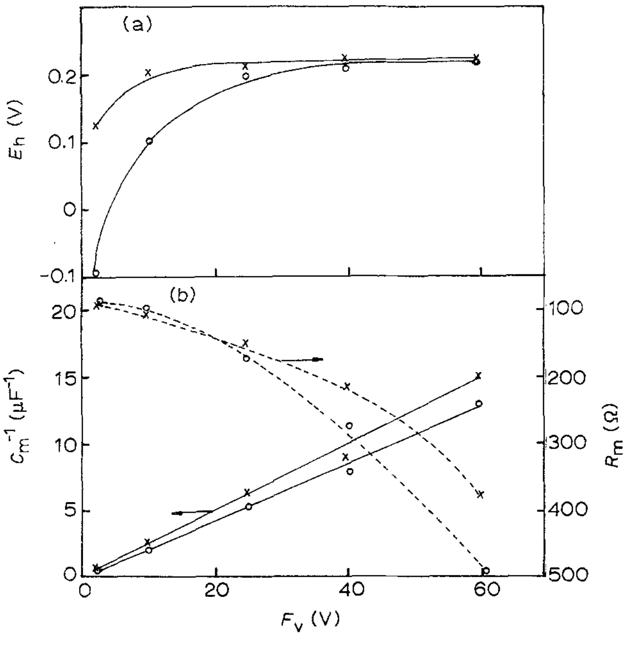

Fig. 6. Dependence of open-circuit potential, E_h (a), and reciprocal capacitance, C_m^{-1} (——) and resistance, R_m, (– – – –) (b), on formation voltage, F_v, for niobium electrodes in 0.05 M NaOH solutions at 30° C. (○) Initial values and (x) quasi-steady state value.

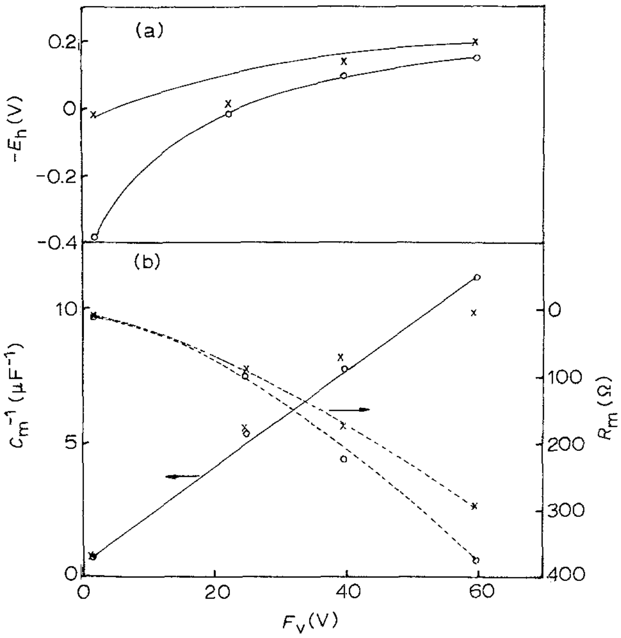

Fig. 7. Dependence of open-circuit potential, E_h (a), and reciprocal capacitance, C_m, (——) and resistance, R_m (– – – –) (b) on formation voltage, F_v, for niobium electrodes in 1.0 M NaOH at 30° C. (○) Initial values, and (x) quasi-steady state value.

3.3. *Impedance behaviour of the anodic oxide films on niobium*

The effect of frequency on the two vector components of the niobium electrode impedance, C_m and R_m, was studied. The frequency range used was 100 to 10 000 Hz. Figure 8 shows the impedance in the complex plane, i.e. $1/\omega C_m$ against R_m, for a mechanically polished niobium electrode in NaOH solutions of different concentrations. The resistance at $1/\omega C_m \rightarrow 0$, corresponds to the solution resistance, R_{sol}. As the solution concentration increases, R_{sol} decreases as expected. The phase shift, θ, corresponding to the slope, $d(1/\omega C_m)/d(R_m - R_{sol})$, is ~83°. Such a value indicates that the oxide film/solution interface is highly impeded and the impedance behaviour is purely capacitive. However, since θ deviates from 90° the treatment of the oxide film as a perfect dielectric is only an approximation.

The effect of film thickness on the impedance diagram is shown in Fig. 9. The impedance, Z_m, was calculated as follows [19].

$$Z_m = (R_m + 1/\omega C_m)^{1/2} \quad (6)$$

$$\theta = \tan^{-1}[d(1/\omega C_m)/d(R_m - R_{sol})] \quad (7)$$

As can be seen from Fig. 9, Z_m increases with increase

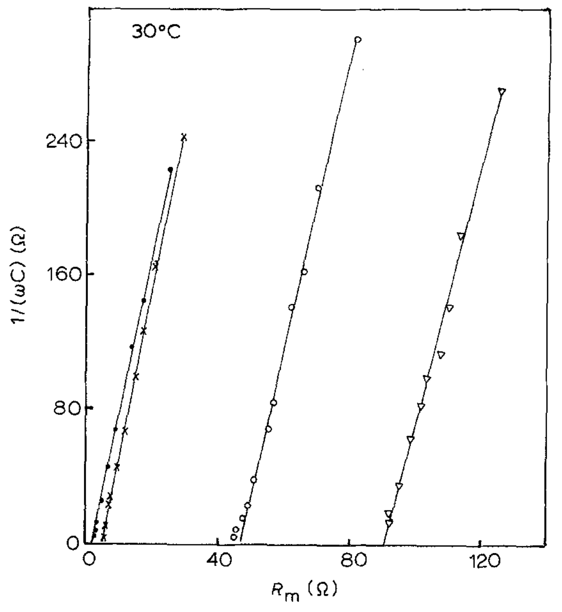

Fig. 8. Complex plane impedance plot of mechanically polished niobium electrodes after attainment of steady states in NaOH solutions of concentration: (●) 3.0 and 2.0, (x) 1.0, (○) 0.1 and (▽) 0.05 M.

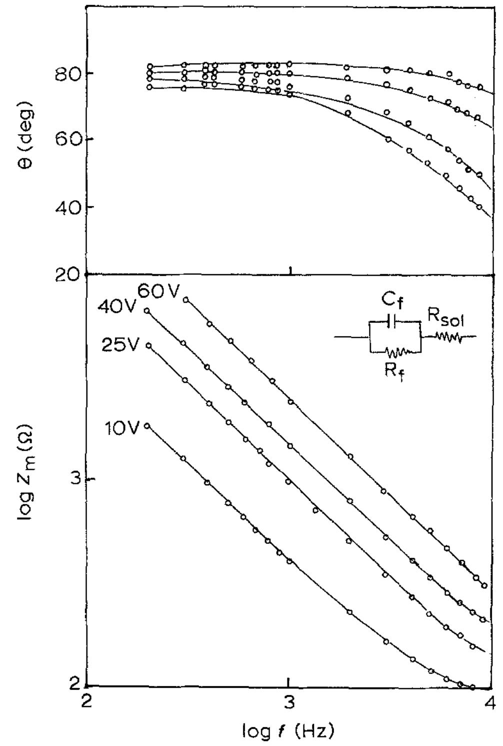

Fig. 9. Impedance diagram of anodized niobium electrode (to 10, 25, 40 and 60 V) in 0.05 M NaOH solutions at 30° C. (C_f and R_f are the film capacitance and resistance, and R_{sol} is solution resistance).

of the film thickness, i.e. the insulating properties of these films increases with increase in their thickness. The slope, d log $|Z_m|$/d log f, is nearly -1, which agrees well with the expected slope of the electrical equivalent of the film/solution interface shown in Fig. 9. The phase shift, θ, for thick films did not reach the ideal value ($\theta = 90°$). Thus, the thick oxide films on niobium are not as perfect dielectrics as naturally formed films.

4. Conclusion

The corrodability of oxide films formed on niobium either naturally or anodically (thin and thick) in alkaline solutions depends on the alkali concentration and the nature and thickness of the film. These films cannot be treated as perfect dielectric materials. The insulating properties of the films increases with increase in their thickness.

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