Stability of anodic tantalum oxide films in NaOH solutions

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The dissolution behaviour of the anodic oxide films formed on tantalum was investigated in NaOH solutions of different concentrations. In solutions of $[OH^-]$ < 3.0 M, no pronounced dissolution could be detected. However, in concentrated alkali solutions, $[OH]$ > 3 M, the dissolution occurred to different extents depending on the alkali concentration. As observed from capacitance and potential measurements, the barrier film on Ta was found to be defective owing to the incorporation of OH^- ions in the film. The nature of the barrier film and its dependence on formation rate, alkali concentration and solution temperature were investigated. Complex plane analysis illustrates the behaviour of the barrier film of different thickness, i.e. formation voltages, in NaOH solutions. The barrier film cannot be considered accurately as a perfect dielectric.

1. Introduction

Many investigations have been directed towards the production of corrosion-resistant materials to be used as efficient anodes in the manufacture of chlorine gas and caustic soda [1]. Valve metals, in general, are known to form stable oxide films in aqueous media [2]. Tantalum is a typical valve metal and many investigations have been concerned with the growth of thin oxide films on its surface [3–12]. Other studies have been concerned with the effect of surface pretreatment on the thickness of the formed oxide [13, 14]. Also, the conductivity of Ta_2O_5, the only oxide formed on Ta in various aqueous media [15], except HF [16], was studied by Vermilyea [14] and Llewelyn-Leach [17]. The present work is a systematic study of the stability of the oxide films in NaOH solutions and the factors affecting such stability, e.g. film thickness, formation rate, alkali concentration and temperature.

2. Experimental detials

The electrical circuit, electrolytic cell and details of the experimental procedure are essentially the same as those described elsewhere [18–20]. The electrodes were cut from spectroscopically pure Ta rod (Johnson-Matthey, London). The electrode was fitted into glass tubing of appropriate internal diameter by an epoxy resin (Araldite, Ciba-Geigy, Switzerland) leaving an exposed surface area of $0.196\,cm^2$. The electrolytic solutions were prepared using AnalaR grade reagents and triply distilled water. Sodium hydroxide solutions were prepared from carbonate-free NaOH solution by appropriate dilution.

Before each experiment, the electrode surface was mechanically polished with emery papers of different grades, then rubbed with soft cloth until a silvery bright surface was obtained. The electrode potentials reported were referred to the normal hydrogen electrode (NHE). The measured capacitance, C_m, and resistance, R_m, of the impedance of the anodized tantalum electrode were measured at a frequency of 1000 Hz. All measurements were carried out in an electrically controlled air thermostat at the desired temperature of 30 ± 0.1° C.

3. Results and discussion

3.1. *Effect of NaOH concentration*

An anodic oxide film was formed on tantalum at a current density of $0.51\,mA\,cm^{-2}$ up to a formation voltage of 25 V vs SCE in naturally aerated 0.5 M H_2SO_2 solution. After the formation of the oxide film, the electrode was washed with triply distilled water and transferred quickly to the NaOH solution taking the immersion moment as zero time. The open-circuit potential, E_h, and impedance components of the oxide film, C_m and R_m, were traced with time for about 4 h.

The variation of the reciprocal capacitance, C_m^{-1}, with time is illustrated in Fig. 1. Generally, C_m^{-1} decreases with time in all concentrations except in 0.05 M solution. In the case of 0.05 M NaOH solution, a slight increase in C_m^{-1} during the first 40 min is observed before the steady state is reached. In concentrations ⩾ 5.0 M solutions, a continuous decrease of C_m^{-1} is observed. Such a decrease is attributed to film dissolution whereas the decrease in C_m^{-1} for other concentrations, < 5.0 M, may be due to a change in the film properties, probably via incorporation of OH^- ions.

The results of potential measurements confirm the previous explanation obtained by the capacitance data as shown in Fig. 2. It is clear that in NaOH concentrations less than 5.0 M, there is an independency of potential on the alkali concentration indicating the higher insulating properties of the film. On the
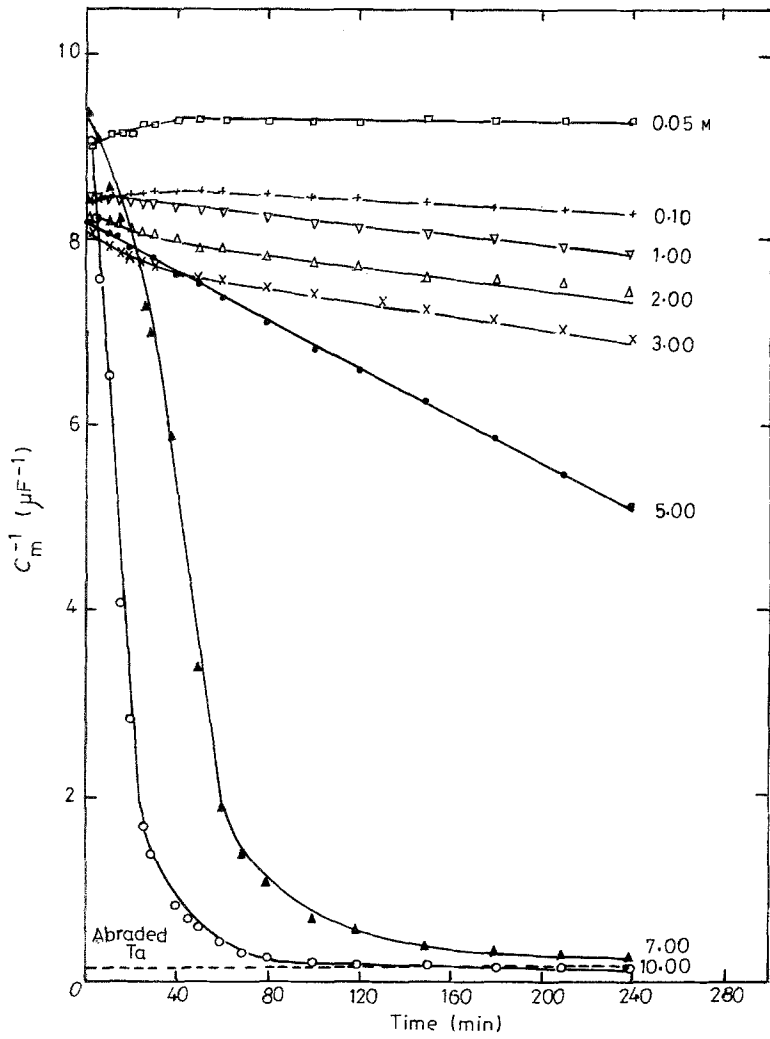
Fig. 1. Variation of reciprocal capacitance of anodized Ta electrode, 25 V, C_m^{-1}, with time in NaOH solutions of concentrations: (□) 0.05; (+) 0.10; (∇) 1.00; (△) 2.00; (×) 3.00; (●) 5.00; (▲) 7.00; (○) 10.00 M.
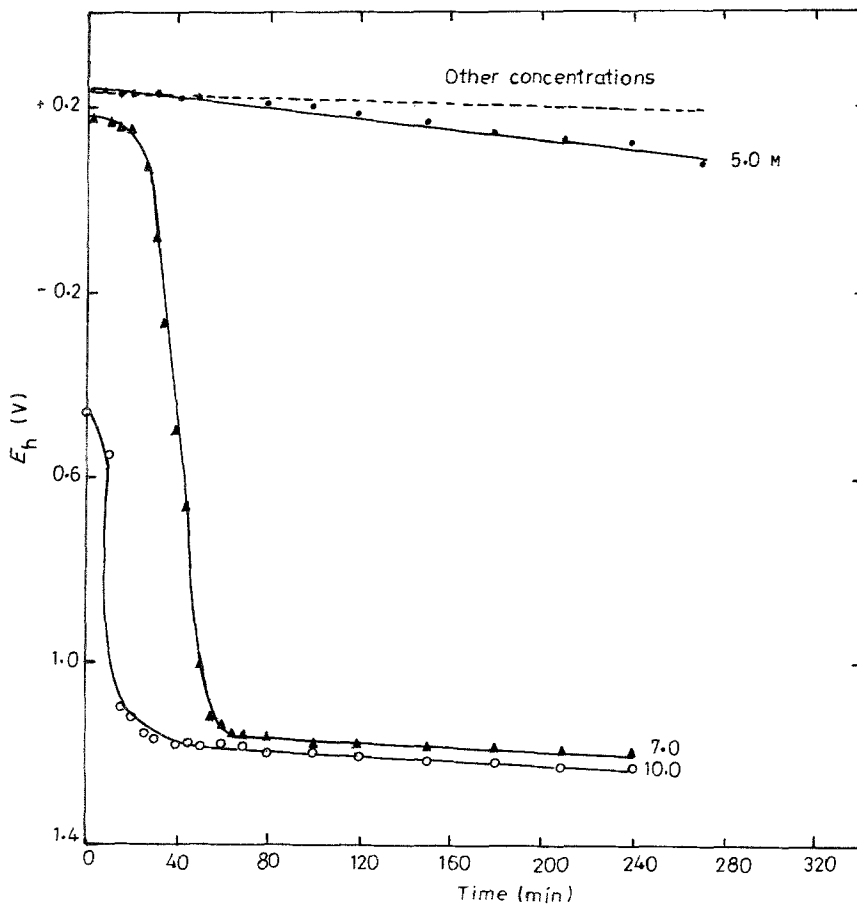

Fig. 2. Variation of potential of anodized Ta electrode, 25 V, with time in NaOH solutions of concentrations: (– – –) 0.05, 0.1, 1.0, 2.0 and 3.0; (●) 5.0; (▲) 7.0; (○) 10.0 M.
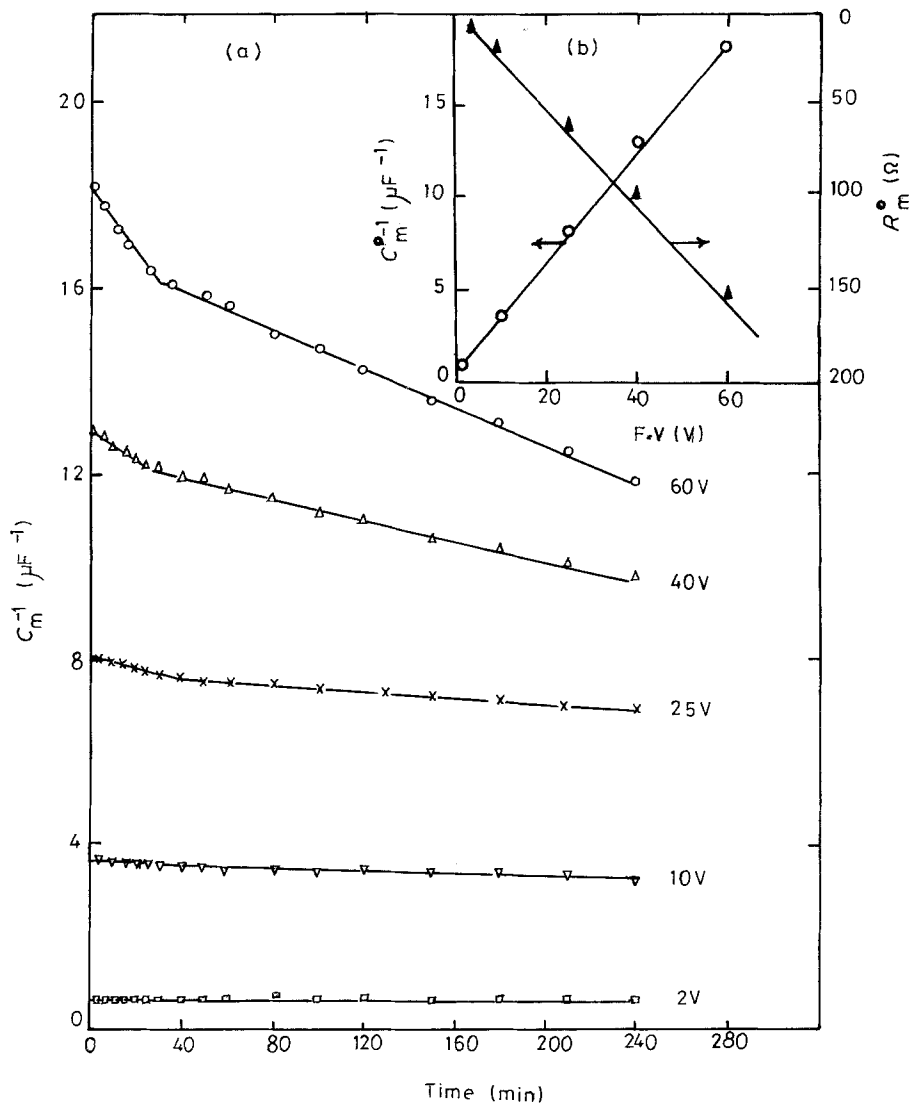
Fig. 3. (a) Variation of reciprocal capacitance of anodized Ta electrode, C_m^{-1}, of different formation voltages, with time in 3.0 M NaOH solutions. (b) Variation of both initial reciprocal capacitance, C_m^{0-1}, and resistance, R_m^0, of anodized Ta electrode with formation voltages, FV.
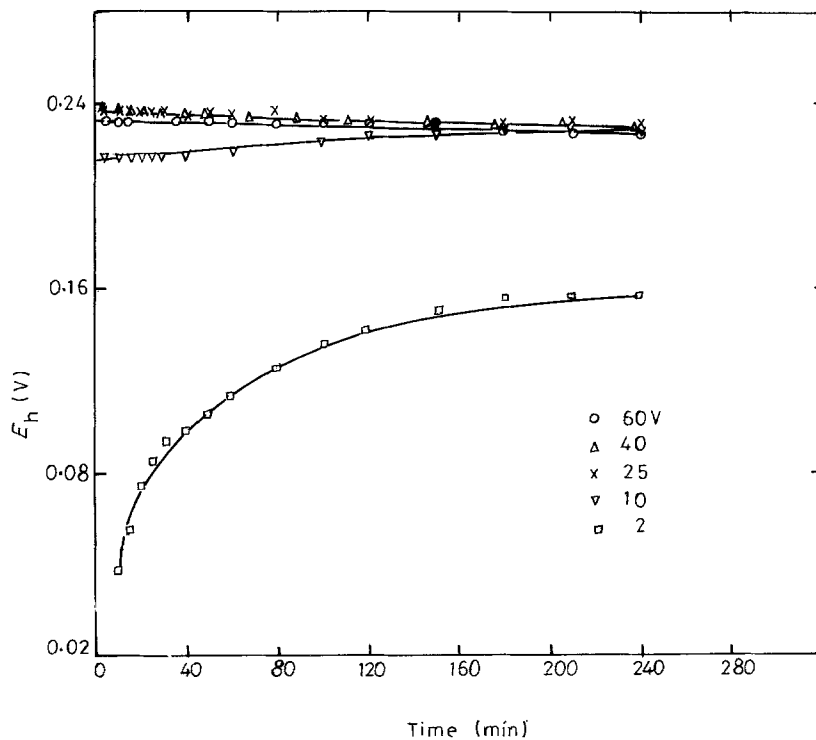

Fig. 4. Variation of potential of anodized Ta electrode, E_h, to different formation voltages, with time in 3.0 M NaOH solutions.
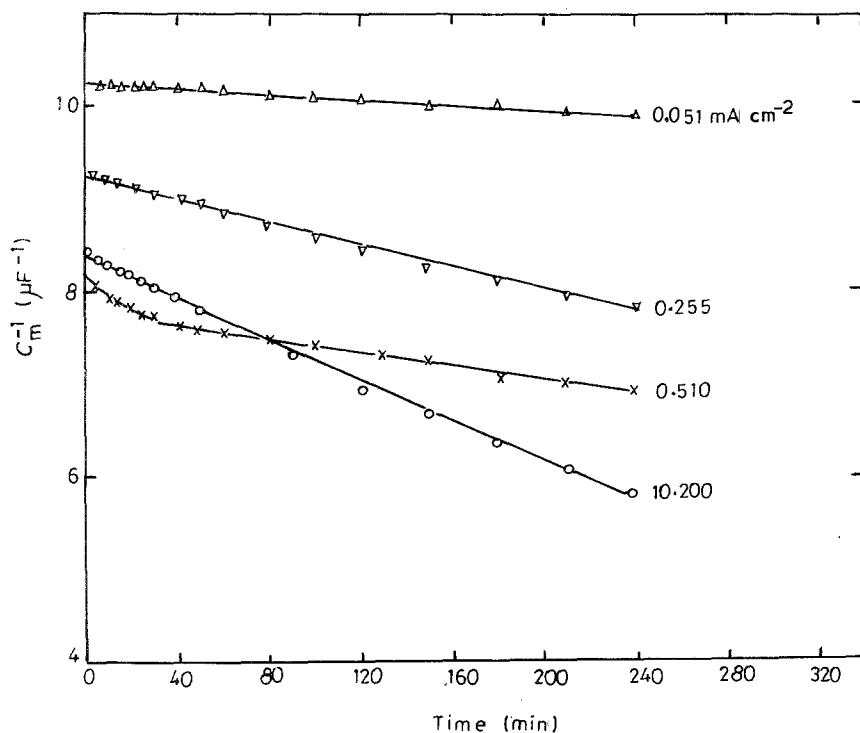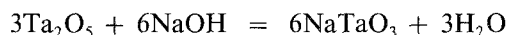
Fig. 5. Variation of reciprocal capacitance of anodized Ta electrode (FV = 25 V) with time at formation current densities of: (△) 0.051; (▽) 0.255; (×) 0.510; (○) 10.200 mA cm^{-2}, in 3.0 M NaOH solutions.

other hand, for 5.0 M NaOH solution, the potential becomes less positive with time indicating film thinning [21]. But for higher concentrations, > 5 M, there is a sharp drop to more negative potential before attaining steady state. The time required for attaining steady state is concentration dependent. The drift of electrode potential to more negative values with time indicates that the oxide film is subject to a process of dissolution and, at higher alkali concentration, e.g. 7.0

and 10.0 M, the potential obtained is nearly equal to that of the abraded electrode. This indicates that the nature of the remaining surface at the steady state is more or less the same as that of the abraded surface. The dissolution reaction is as follows

$$3Ta_2O_5 + 6NaOH = 6NaTaO_3 + 3H_2O$$

The attainment of the steady state after dissolution of the oxide film indicates that a dissolution–precipitation
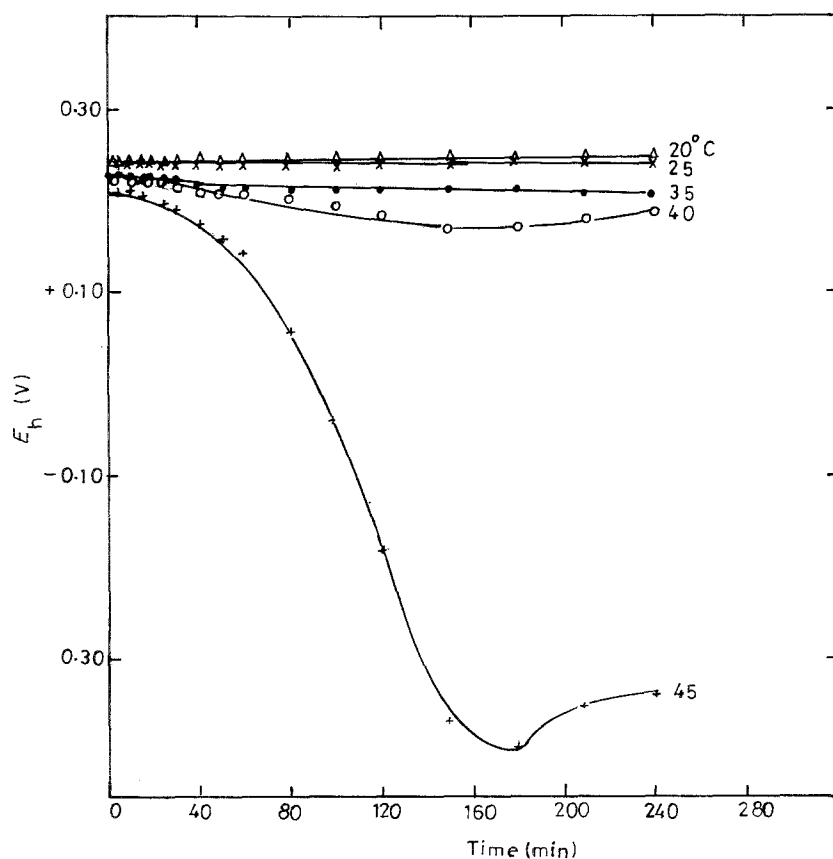

Fig. 6. Variation of potential of anodized Ta electrode (FV = 25 V), with time in 3.0 M NaOH solutions at different temperatures.
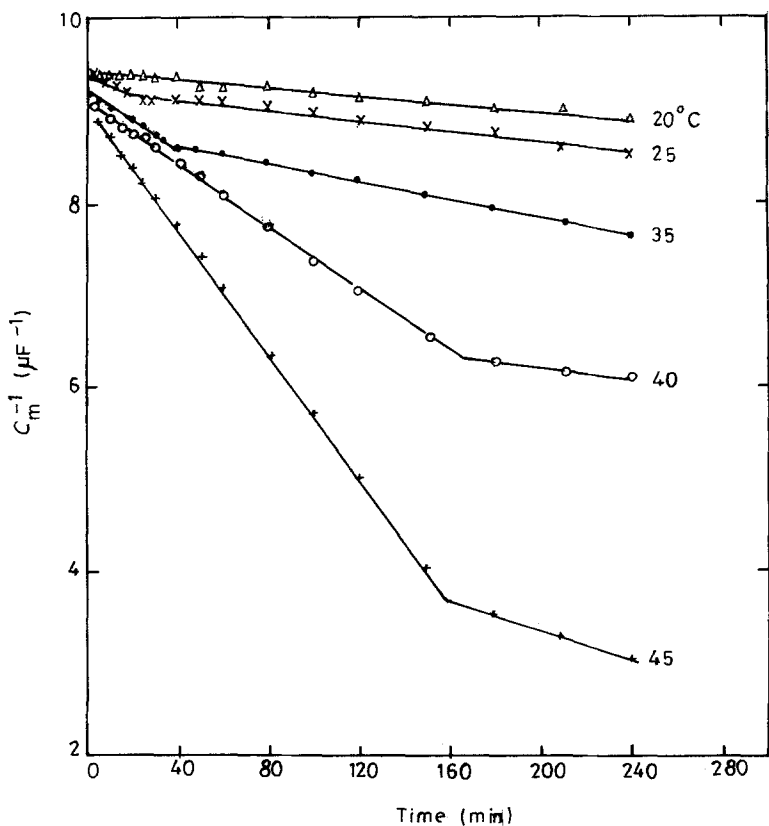
Fig. 7. Variation of reciprocal capacitance of anodized Ta electrode, FV = 25 V, with time in 3.0 M NaOH solutions at different temperatures.

mechanism is followed [15]. This implies that the dissolution process is followed by precipitation of sodium tantalate, which is insoluble, on the electrode surface.

3.2. Effect of formation voltage

The oxide films were formed as previously described up to formation voltages of 2, 10, 25, 40 and 60 V.

After each formation voltage was reached, the applied current was interrupted and the corrosion potential and impedance of the surface oxide film were followed with time in 3.0 M NaOH solutions. Figure 3a shows the variation of C_m^{-1} with time. As can be seen from this figure the decrease in C_m^{-1} becomes pronounced with increase in formation voltage. Also there is a break in the C_m^{-1}-time curve for formation voltage
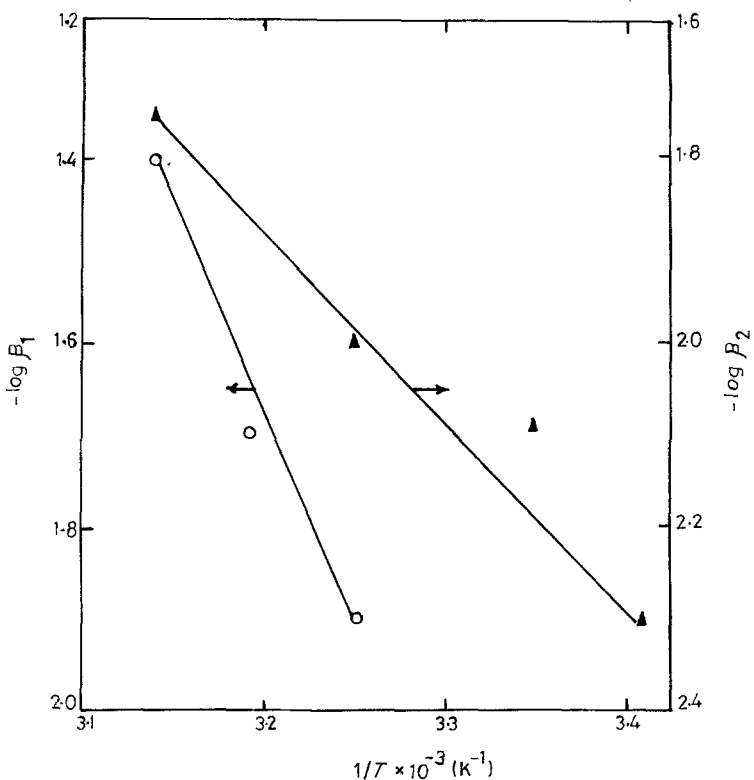

Fig. 8. Variation of logarithm of dissolution rate of anodized Ta electrode, FV = 25 V, with $1/T$, in 3.0 M NaOH solutions.
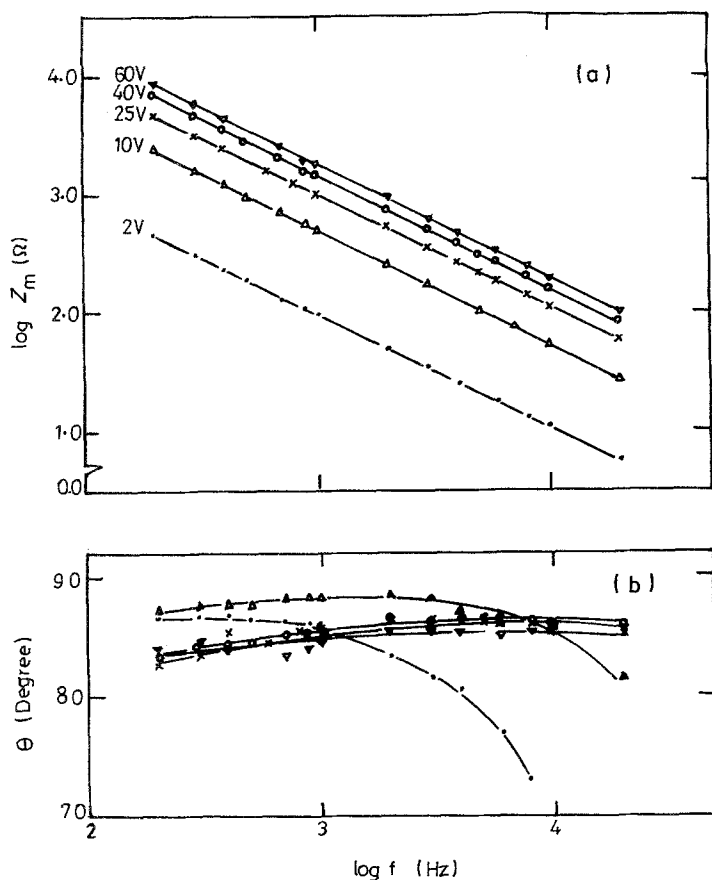
Fig. 9. Impedance diagram of the anodized Ta electrode, FV = 25 V, in 3.0 M NaOH solutions. (a) Bode plot; (b) phase shift, θ, vs log f.

> 10 V. The data obey the equation

$$C_m^{-1} = \alpha - \beta t$$

where α is equal to C_m^{-1} at zero time, i.e. C_m^{0-1}, and β is the slope which corresponds to the rate of dissolution. Figure 3b shows the anodic oxide films on tantalum grow linearly with increasing formation voltage, i.e. C_m^{0-1} and R_m^0 with FV at zero immersion time. This anodic oxide growth occurs by high field ion migration in the film, both of metal ions outwards and oxygen ions inward [16, 22, 23]. Such ions are injected at both the metal–oxide and oxide–solution interfaces, respectively.

It is known that as the formation voltage increases, the rate of chemical attack of the oxide film increases [18]. Also, the rate of anion penetration becomes pronounced. The coefficients, β_1 and β_2, for dissolution of the barrier film increase with increasing formation voltage, cf. Table 1. The values of β_1 and β_2 are the slopes of the first (outer layer) and second segment (inner layer), respectively. The presence of two different rate coefficients for the dissolution led to the

Table 1. The dissolution coefficients, β_1 and β_2, of anodic oxide film on tantalum in 3.0 M solutions

FV (V)	β_1 ($cm^2\,\mu F^{-1}\,min^{-1}$)	β_2 ($cm^2\,\mu F^{-1}\,min^{-1}$)
60	7.00×10^{-2}	2.00×10^{-2}
40	4.00	1.00
25	2.00	0.25
10	0.13	0.13
2	0.00	0.00

assumption that the barrier film on tantalum is duplex in nature. The outer layer dissolves more quickly than the inner one. Similar results were found on Mo [24], Zr [25, 26], Ti [27], Bi [28] and Al [19].

The variation of potential with time shows that the potential is nearly invariant with time and independent of FV (except for 2 V) as can be seen in Fig. 4. According to Vijh [30], as the film thickness increases the insulating properties increase and the potential becomes independent of the medium composition and concentration. At small formation voltages, e.g. 2 V, the film thickness is insufficient and the electrode potential responds to the medium composition. The increase of potential with time is associated with film thickening probably by OH⁻ ion adsorption which is below the limit necessary to attack the oxide and, thus, oxide growth is favoured to reach the steady stage [20].

3.3. Effect of formation current density

Anodic oxide films were formed, as described previously, up to 25 V at different current densities of 0.051, 0.255, 0.510 and 10.200 mA cm⁻² and the electrodes were then transferred to the dissolving medium (3.0 M NaOH solution). Figure 5 shows that the rate of decrease in C_m^{-1} increases as the current density increases, i.e. the anodic oxide film formed at low current density is less affected than that formed at higher current density. As previously observed for anodized Nb electrodes [21] and most valve metals [31], increase in formation current density increases the number of defects in the anodic oxide film.
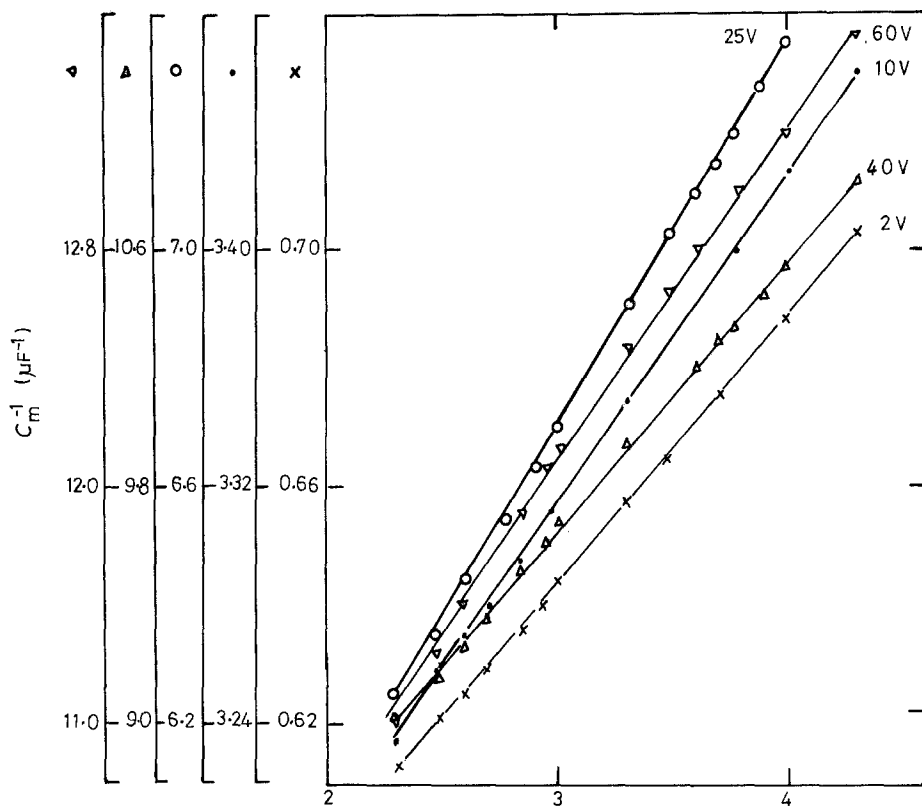
Fig. 10. Variation of series equivalent reciprocal capacitance, C_m^{-1}, of anodized Ta electrode with log f, in 3.0 M NaOH solutions.
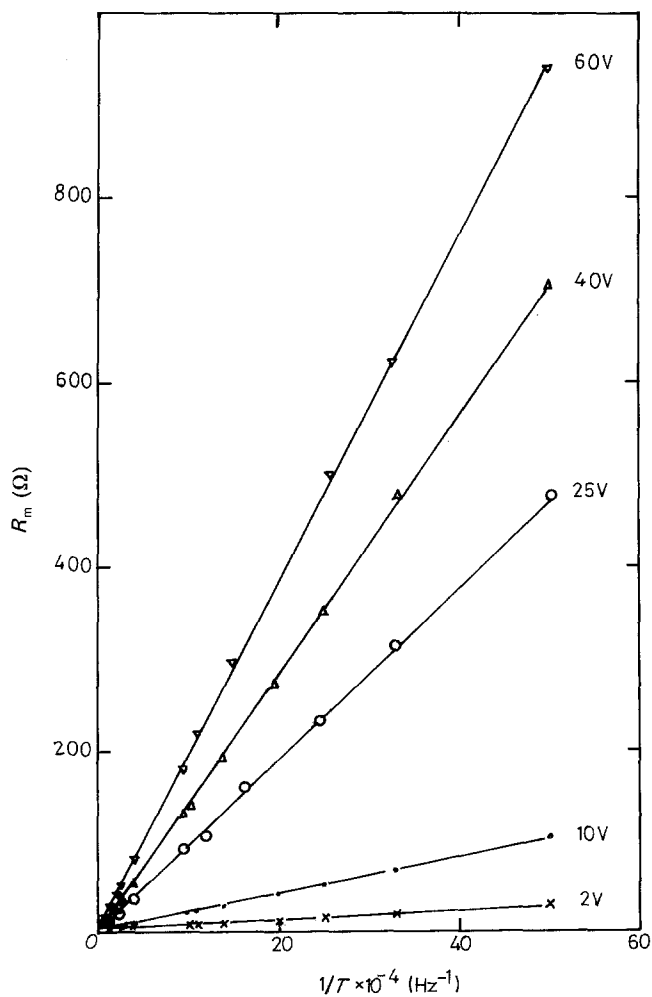

Fig. 11. Variation of series equivalent resistance, R_m, of anodized Ta electrode with f^{-1}, in 3.0 M NaOH solutions.
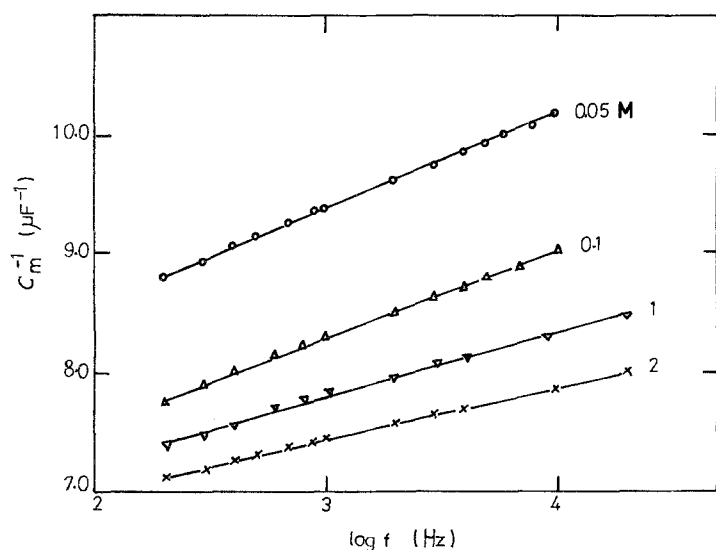
Fig. 12. Variation of series equivalent reciprocal capacitance, C_m^{-1}, of anodized Ta electrode, FV = 25 V, with log f in NaOH solutions.

3.4. Effect of temperature

A tantalum electrode was anodized as previously described up to a formation voltage of 25 V vs SCE. The effect of temperature on the stability of the anodic oxide film was followed in 3.0 M NaOH solutions using potential and capacitance measurements. It is obvious from Fig. 6 that the potential remains more or less constant with time for temperature $\leqslant 40^\circ$ C. At a temperature of 45° C the potential initially drifts to less positive values with time, then increases to more positive values and tends to a stable value. The potential results show that decrease in temperature, $\leqslant 40^\circ$ C, has no effect on the stability of the anodic oxide film in 3.0 M NaOH solution. At higher temperatures, $> 40^\circ$ C, the structure of the oxide film becomes more opened leading to increase of OH$^-$ ion incorporation and chemical attack of the oxide film.

On the other hand, the variation of C_m^{-1}, which is a more sensitive indicator of surface reactivity, with time at different temperatures is illustrated in Fig. 7. It can be seen that C_m^{-1} varies linearly with time and decreases, generally, for all temperatures. The rate of decrease increases with increase of temperature. Also, there is a change of gradient in the C_m^{-1}-time plots. The time to the change of gradient increases with increased temperature. For each temperature the rates of change of C_m^{-1} with time, β_1 and β_2, are presented in Fig. 8. The activation energy may be calculated from the slopes of Fig. 8 as follows

$$2.303R(\text{d} \log \beta_1/\text{d}1/T) = 88.07 \text{ kJ mole}^{-1}$$

and

$$2.303R(\text{d} \log \beta_2/\text{d}1/T) = 38.39 \text{ kJ mole}^{-1}$$

The two different values obtained from the two segments, which are comparable with those found in the case of Nb in NaOH solution [21], indicate that the effect of temperature on the dissolution of anodized tantalum is also significant and needs further investigation.

3.5. Complex plane analysis

The effect of frequency on the two vector components of the electrode impedance, C_m and R_m, for the anodized Ta electrode up to 2, 10, 25, 40 and 60 V formation voltages in 3.0 M NaOH solutions was recorded at the steady state (after $\simeq 3$ h). Figure 9a shows the impedance of anodized Ta electrodes on a Bode plot. As can be seen, the impedance increases with film thickness (i.e. formation voltages) and the relations are linear. The slopes of all lines, d log Z_m/ d log f, are similar and equal to -1 confirming the electrical model of the metal–solution interface proposed previously [22]. The phase shift, θ, of the impedance diagram, Fig. 9a, is nearly independent of frequency as previously reported by Young [16] and does not reach 90° as necessary for a perfect dielectric material. However, the deviation of θ from 90° means that the oxide film cannot be treated accurately as a perfect dielectric due to its reaction with solution [32].

The relations C_m^{-1} vs log f and R_m vs f^{-1} for anodized Ta electrodes up to different formation vol-

Table 2. Rate of variation of both C_m^{-1} and R_m of the anodized Ta electrodes, different FV, with frequency in 3.0 M NaOH solutions

FV (V)	$dC_m^{-1}/d \log f$	dR_m/df^{-1}	Ratio
2	0.044×10^6	0.05×10^5	8.8
10	0.112	0.20	5.6
25	0.68	0.90	7.6
40	1.12	1.40	8.0
60	1.08	1.90	5.7

Table 3. Rate of variation of both C_m^{-1} and R_m of the anodized Ta electrode, FV = 25 V, with frequency in NaOH solutions of different concentrations

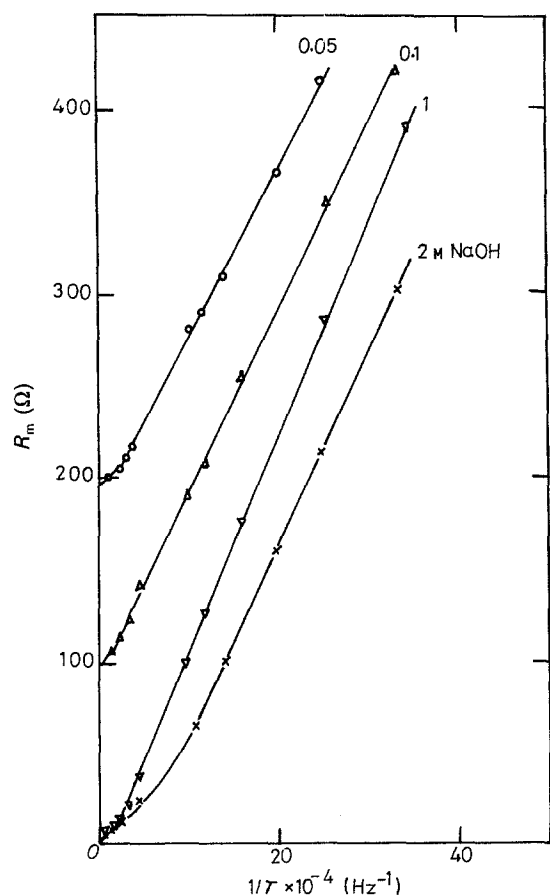| [NaOH] (M)	$dC_m^{-1}/d \log f$	dR_m/df^{-1}	Ratio
0.05	1.30×10^6	0.90×10^5	14.4
0.10	1.20	1.00	12.0
1.0	0.55	1.15	4.8
2.0	0.50	1.00	5.0

Fig. 13. Variation of series equivalent resistance, R_m, of anodized Ta electrode, FV = 25 V, with reciprocal frequency, f^{-1}, in NaOH solutions.

tages are shown in Figs 10 and 11. The variations are linear, the ratios of the slopes, $dC_m^{-1}/d \log f$ and dR_m/df^{-1} are given in Table 2. Comparisons of the slope ratios obtained for anodized Ta and Nb [21] in alkaline media reflect the high stability of both oxides in the respective solutions.

On the other hand, the effect of alkali concentration on the anodized Ta electrode (FV = 25 V) is presented in Figs 12 and 13. The variations are linear and the slopes of the lines are listed in Table 3. The susceptibility and resistivity of the oxide film toward alkali can be shown from the effect of frequency on each of C_m^{-1} and R_m. The ratios $(dC_m^{-1}/d \log f)/(dR_m/df^{-1})$ in different alkali concentrations and for different film thickness are different from those obtained previously in acid and neutral solutions [13]. The difference is probably attributable to the nature of the dissolving medium and the oxide film thickness.

Acknowledgement

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