

Anodization of hafnium in phosphoric acid solutions

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The kinetics of formation of anodic oxide films on hafnium electrodes either under open circuit conditions or constant current density were investigated using polarization and impedance measurements. Under open circuit conditions the oxide film was found to thicken with time following a direct logarithmic law, whereas it thickens linearly with time under galvanostatic polarization and obeys the exponential law due to Güntherschulze and Betz. An increase in phosphoric acid concentration was found to increase the rate of oxide formation and the field strength owing to incorporation of electrolyte species into the oxide during the anodization process. The break-down voltage was found to increase linearly with the logarithm of phosphoric acid resistivity and was independent of the anodizing current density. The impedance behaviour of the hafnium oxide film/solution interface was found to be purely capacitive and the impedance increases with increase in the film thickness. The film thickness was found to decrease linearly with the logarithm of time probably owing to partial dissolution of the oxide film.

1. Introduction

The ability of hafnium to form thick insulating oxide films by anodic polarization was recognized by Misch and Fisher [1] and Battist [2]. Many investigations relating to the formation of anodic oxide films on hafnium have been published [3–6]. As with other valve metals the kinetics of oxide formation under galvanostatic control was found to obey the familiar exponential law due to Güntherschulze and Betz [7, 8]. Hefny *et al.* [9] found that the anodic oxide film on hafnium was subject to chemical dissolution in HCl solutions. The rate of dissolution increases with increase in the initial film thickness and is almost independent of the acid concentration. The electronic and ionic conductivities of these films were found to be very low [10]. Recently, the role of anion incorporation on the anodization kinetics of valve metals in phosphoric acid solutions was studied [11–17]. The anodization of hafnium in phosphoric acid, however, seems to have received no attention. The aim of the present paper is to investigate the kinetics of formation of anodic oxide films on hafnium in phosphoric acid solutions either by anodic polarization or under open circuit conditions.

2. Experimental

The disc electrode was cut from hafnium rod 99.9% purity (Koch Light, UK). Details of the electrode preparation and polishing, the electrolytic cell and the electric circuit have been given elsewhere [15, 16]. All potentials were measured against a saturated calomel electrode (SCE). The solutions used were prepared from AnalaR grade phosphoric acid and triply distilled water. The experiments were carried out at $25 \pm$

0.2°C . To verify the stability of the oxide films, the electrode was anodized at a constant current density of $857 \mu\text{A cm}^{-2}$ to 20 V in 2 M H_3PO_4 solution; then the open circuit capacitance at a frequency of 1 kHz was traced with time.

3. Results and discussion

3.1. Open circuit film thickening

The variation of open circuit potential, E_{oc} , and reciprocal capacitance, C_m^{-1} , of mechanically polished hafnium electrode with logarithm of time in 0.33 M H_3PO_4 solution is shown in Fig. 1a. As can be seen, both E_{oc} and C_m^{-1} obey the following relations

$$E_{oc} = \alpha + \beta \log(t + t^0) \quad (1)$$

$$C_m^{-1} = \alpha' + \beta' \log(t + t^0) \quad (2)$$

where α , α' , β , β' and t^0 are constants. Equations 1 and 2 were derived theoretically by Gad-Allah and Abd El-Rahman [17] and were found to be applicable for many valve metals in aqueous solutions [18–20]. The increase in both E_{oc} and C_m^{-1} with time is attributed to the oxide film thickening [9, 17–22]. C_m^{-1} can be used to calculate the film thickness, x , through the equation [8, 21, 22]

$$x = \left(\frac{D\sigma}{2\pi \times 9 \times 10^5} \right) C_m^{-1} \quad (3)$$

where D is the relative dielectric constant, σ is the roughness factor, a is the electrode area in cm^2 , x is the thickness in cm and C_m is the measured capacitance in μF . The application of Equations 1 and 2 implies the existence of a high electric field strength which causes the ionic migration [17, 23]. The field strength, H , is

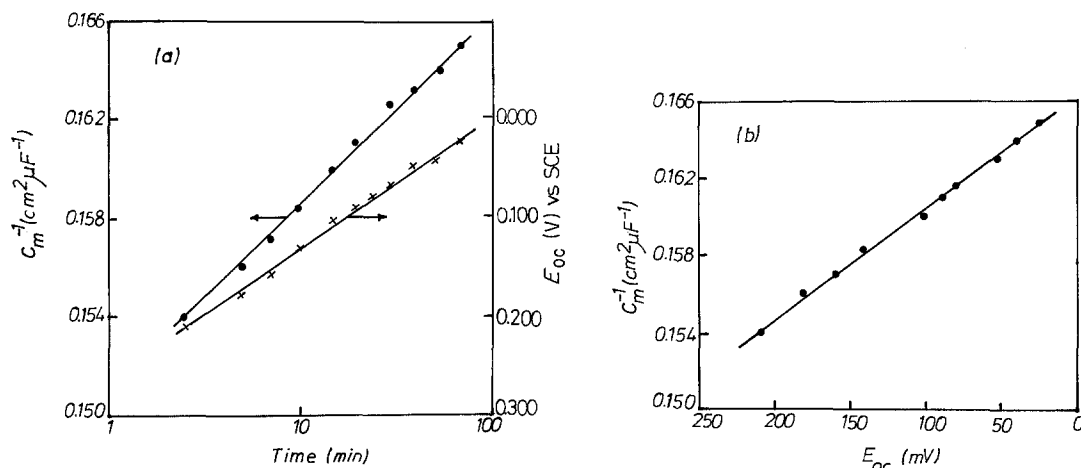


Fig. 1. (a) Variation of open circuit potential, E_{oc} , and reciprocal capacitance (1 kHz), C_m^{-1} , of mechanically polished hafnium electrode with the logarithm of time in 0.33 M H_3PO_4 acid solution at 25°C. (b) Plot of E_{oc} against C_m^{-1} .

given by [16]

$$H = dE/dx \quad (4)$$

From Equations 3 and 4 one obtains

$$H = (4\pi \times 9 \times 10^5 / Da\sigma) (dE/dC_m^{-1}) \quad (5)$$

The validity of Equation 5 is shown in Fig. 1b. Assuming that $D = 23$ [24], the estimated field strength in terms of σH is $8.16 \times 10^6 \text{ V cm}^{-1}$.

3.2. Galvanostatic anodic oxide formation

Figure 2 shows some galvanostatic anodization curves for hafnium in 0.33 M H_3PO_4 solutions (only the initial linear parts are shown). Being a valve metal, hafnium is expected to anodize according to the familiar Güntherschulze and Betz relationship between the ionic current, i , and the field strength, H [26]

$$i = A \exp(BH) \quad (6)$$

where A and B are constants called 'the electrolytic parameters'. Assuming that the oxide formation is the

only anodic process through the initial linear parts of the $E-t$ curves, i will be equal to the anodizing current used. The validity of Equation 6 can be tested by either coulometry or capacitance measurements for the thickness determination at the corresponding formation voltage, F_v . From Fig. 2 the thickness can be calculated as follows [16]

$$dx = (M/\sigma nF)(i dt) \quad (7)$$

where M and S are, respectively, the molecular weight and density of the oxide, n is the number of Faradays (F) required for the formation of one mole of the oxide and dt is the polarization time. Taking M (HfO_2) = 210.49, $S = 9.69 \text{ g cm}^{-3}$ [27], $n = 4$, the field determined by this method, H_1 , is given by

$$H_1/\sigma = (5.69 \times 10^{-5})^{-1} (dE/i dt)_i \quad (8)$$

where the field is expressed as H_1/σ to eliminate the uncertainty in σ .

The reciprocal capacitance of the hafnium electrode was found, during polarization, to increase linearly with the formation voltage as can be seen in Fig. 3.

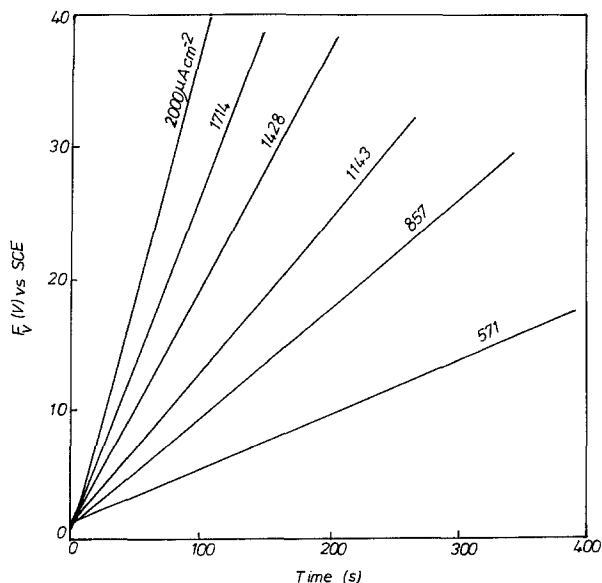


Fig. 2. Galvanostatic anodization curves for hafnium electrodes at different current densities in 0.33 M H_3PO_4 acid solutions at 25°C.

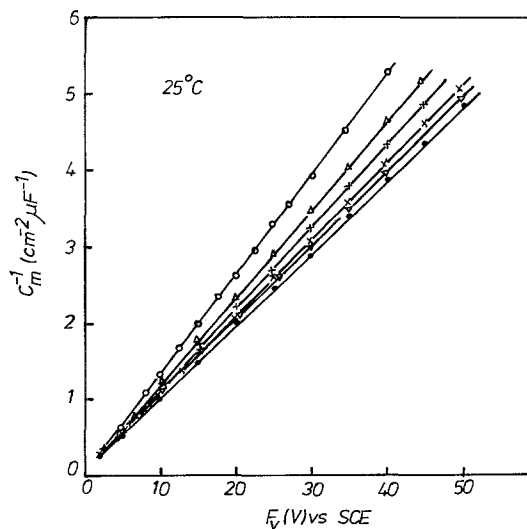


Fig. 3. Plots of reciprocal capacitance, C_m^{-1} , against formation voltage, F_v , during anodization of hafnium electrodes at different current densities in 0.33 M H_2PO_4 acid solutions at 25°C; \circ 571, Δ 857, $+$ 1143, \times 1428, ∇ 1714 and \bullet 2000 $\mu\text{A cm}^{-2}$.

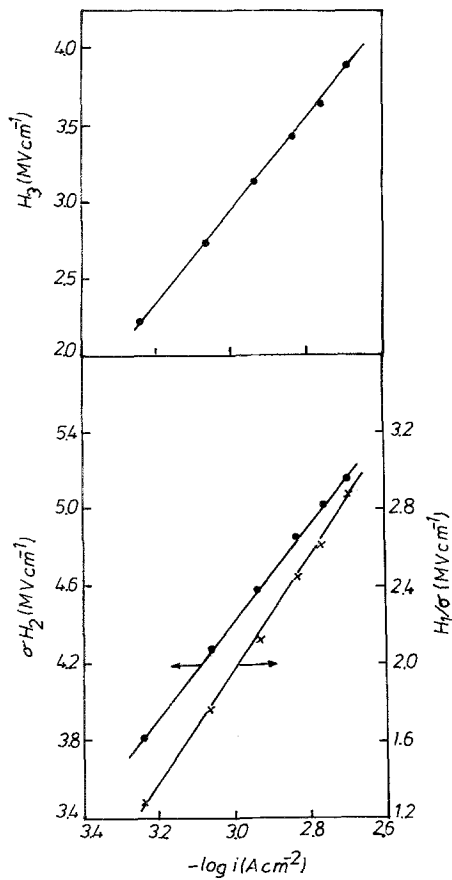


Fig. 4. Variation of the field strength with logarithm of the anodizing current density in 0.33 M H_3PO_4 acid solutions at 25°C.

Hence Equation 5 can be used to calculate the field strength, σH_2 , from capacitance measurements. The validity of Equation 6 is shown in Fig. 4. To eliminate the uncertainty in σ , the figure shows also the variation of the geometric mean, H_3 , of both H_1/σ and σH_2 with $\log i$; where

$$H_3 = (H_1/\sigma)(\sigma H_2) \quad (9)$$

the average value of the roughness factor, σ , was found to be 1.6 ± 0.13 . The electrolytic parameters A and B and the activation distance, a^* , are given in Table 1. a^* is given by [22, 28]

$$a^* = RTB/nF \quad (10a)$$

Equation 10a is obtained by a direct comparison of the empirical Equation 6 with the exponential law derived by Yahalom and Hoar [28] on the basis of the theory of rate processes. According to Yahalom and Hoar

$$i = zF(kT/h)(\bar{n}/N) \exp(-\Delta G_0^*/RT) \exp(zFH a^*/RT) \quad (10b)$$

Table 1. Electrolytic parameters A and B and activation distance a^* for anodization of hafnium in 0.33 M H_3PO_4 acid solutions

| Method | $A(A\text{ cm}^{-2})$ | $B(\text{cm V}^{-1})$ | $a^*(\text{nm})$ |
|------------------------------------|-----------------------|-----------------------|------------------|
| Coulometry (Equations 6 and 8) | 20.1×10^{-5} | 0.82×10^{-6} | 0.053 |
| Capacitance (Equations 5 and 6) | 1.71×10^{-5} | 0.92×10^{-6} | 0.059 |
| Equations 6 and 9 | 12.4×10^{-5} | 0.71×10^{-6} | 0.046 |

where z is the valency of the mobile ion, \bar{n} is the number of charge carriers per cm^2 , ΔG_0^* is the standard free energy of activation for the ionic jump in absence of field and N , h , k , T and R have their usual meanings. A comparison between Equations 6 and (10b) shows that

$$A = zF(kT/h)(\bar{n}/N) \exp(-G_0^*/RT) \quad (10c)$$

$$B = zFa^*/RT \quad (10d)$$

For valve metals, the formation rate dE/dt , is usually related to the anodizing current density by the empirical relation [22]

$$(dE/dt)_i = at^b \quad (11)$$

where a and b are constants. Figure 5 shows the validity of Equation 11. The constants a and b were found to be $10\,000\text{ V s}^{-1}$ and 1.65.

3.3. Effect of electrolyte concentration

The anodizing behaviour of hafnium at $857\ \mu\text{A cm}^{-2}$ in phosphoric acid solutions of different concentrations was tested and the $E-t$ curves obtained were similar to those shown in Fig. 2. As can be seen in Fig. 6, the rate of formation and $dE/i\ dt$ (and, consequently, the field strength) increase with increase in electrolyte concentration, as previously reported for tantalum [12, 13]. In their model, Albella *et al.* [13] introduced the following relation

$$dE/i\ dt = \frac{1 + \gamma A}{1 + \gamma} (dE/i\ dt)_0 \quad (12)$$

where $(dE/i\ dt)_0$ is $dE/i\ dt$ for pure oxide, that is, without electrolyte incorporation, A is the ratio of equivalent weight of incorporated species to that of HfO_2 and γ is a constant. The factor $(1 + \gamma A)/(1 + \gamma)$ in Equation 12 expresses the correction due to the electrolyte incorporation (through the factors A and γ). Previous studies showed that γ is related to the electrolyte concentration through the following approximate law [13]

$$\gamma = \bar{a}(C)^b \quad (13)$$

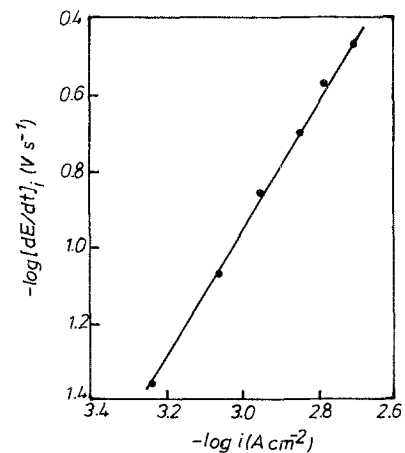


Fig. 5. Relation between the logarithm of rate of formation, dE/dt , and logarithm of the anodizing current density for hafnium in 0.33 M H_3PO_4 acid solutions at 25°C.

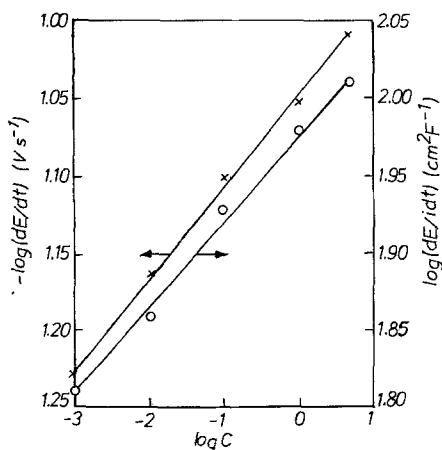


Fig. 6. Variation of $\log (dE/dt)_i$ and $\log (dE/i dt)$ with logarithm of the concentration of phosphoric acid solution for anodization of hafnium electrodes at $857 \mu\text{A cm}^{-2}$, at 25°C .

where \bar{a} and \bar{b} are constants. Knowing that $\gamma \ll 1$ [13], Equation 12 becomes

$$dE/dt = (1 + \gamma A)(dE/i dt) \quad (14)$$

From Equations 13 and 14

$$dE/dt \propto \gamma \propto (C)^{\bar{b}}$$

Figure 6 shows the validity of the above relation. Hence, the increase in dE/dt and $dE/i dt$ with increase in phosphoric acid concentration may be reasonably attributed to the incorporation of the electrolyte species (especially phosphate anions) during the anodizing process [12–14].

3.4. Potentiostatic curves

The dependence of the anodizing current density on time at constant anode potential (i.e. potentiostatic conditions) can be derived from galvanostatic charging curves at some selected constant values of potential, F_v . Examples of the potentiostatic curves are shown in Fig. 7a. The current decreases asymptotically with time, as is usually observed during passive film formation under potentiostatic control for random electrodeposition and instantaneous nucleation under diffusion control [29]. Figure 7b shows that $\log i$ is linearly related to the logarithm of time at each F_v and that the slope $(d \log t / d \log i)_{F_v}$, increases with increase in F_v . The straight lines are expressed by the relation

$$i(t)^{\bar{\theta}} = \text{constant} \quad (15a)$$

where $\bar{\theta}$ is the slope of the log/log relation. Ammar *et al.* [30] postulated Equation 15a on the basis of the theory of galvanostatic anodization under the condition of high field. Since at constant F_v both i and H decrease with time (Fig. 7), the oxide thickness must increase with time. In this case, one may write

$$dx = (M/SnF\sigma) \int_0^t i(t) dt = (M/SnF\sigma) Q(i, t) \quad (15b)$$

where Q is the charge and is a function of i and t . The

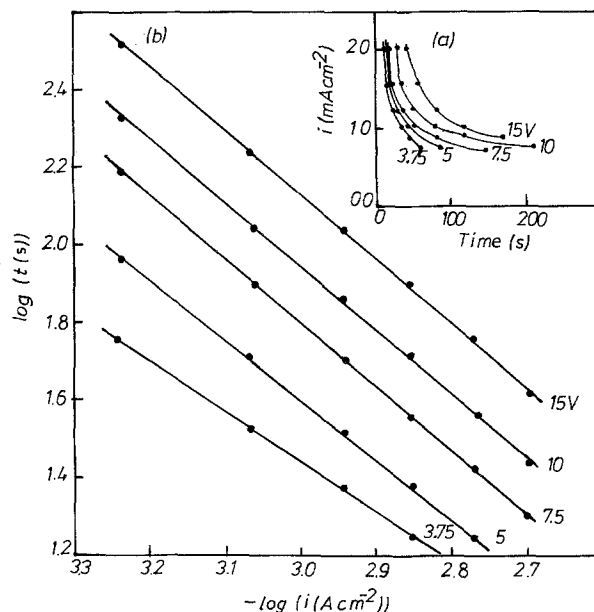


Fig. 7. (a) Current density/time relations derived from galvanostatic anodic charging curves for hafnium in $0.33\text{ M H}_3\text{PO}_4$ acid solutions at some selected constant F_v values. (b) Relation between $\log i$ and logarithm of time.

exponential law may be written in the general form which applies to galvanostatic and potentiostatic conditions as [22]

$$i = dQ/dt = A \exp(BF_v/(x_0 + (M/SnF\sigma)Q)) \quad (15c)$$

where x_0 is the oxide film thickness before polarization. From Equation 15c one obtains

$$\frac{d \ln i}{dt} = - \frac{BF_v (M/SnF\sigma) dQ/dt}{(x_0 + (M/SnF\sigma)Q)^2} \quad (15d)$$

From Equations 15c and d, the following relation is obtained

$$\frac{d \log i}{d \log t} = -(2.303 M/SnF\sigma BF_v) \left(\log \frac{i}{A} \right)^2 = -\bar{\theta} \quad (15e)$$

Equation 15e resembles Equation 15a, which is based on experimental data, and the dependence of $\bar{\theta}$ on i and F_v is indicated. The fact that $\bar{\theta}$ decreases with increase in F_v is evident from Equation 15a.

3.5. Electrical breakdown

The electrical breakdown during the anodizing of valve metals is a well known phenomenon and it practically terminates anodic oxide film formation [31–33]. The break-down usually occurs when F_v reaches a certain value termed the breakdown voltage, E_B , which can be detected by the appearance of series of visible sparks and a descending voltage oscillation [31]. The most important factors affecting the value of E_B are the metal type and the electrolyte type and its concentration. E_B is related to the electrolyte resistivity, ρ , by the following empirical relation [31, 34, 35]

$$E_B = a_B + b_B \log \rho \quad (16)$$

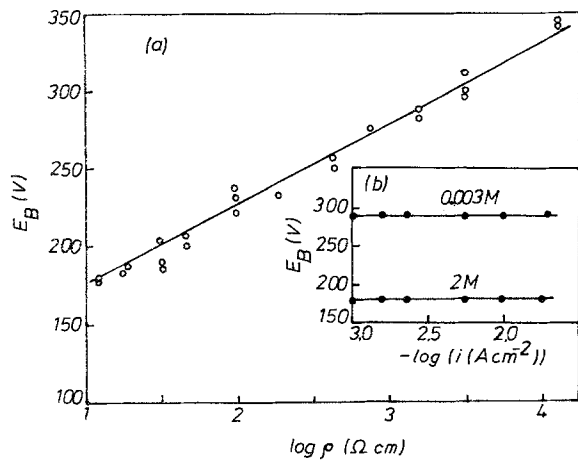


Fig. 8. (a) Breakdown voltage, E_B , during anodization of hafnium at 10 mA cm^{-2} plotted as a function of resistivity of phosphoric acid solutions at 25°C . (b) Variation of E_B with $\log i$ in two different phosphoric acid solutions.

where a_B and b_B are constants. The validity of Equation 16 is shown in Fig. 8a. Figure 8b shows that E_B is nearly independent of the anodizing current density, as is usually reported for valve metals [31, 36, 37].

3.6. Impedance behaviour

The impedance diagram of an anodized hafnium electrode for different formation voltages when immersed in $0.33 \text{ M H}_3\text{PO}_4$ solutions is shown in Fig. 9. The impedance, Z_m , and the phase shift, θ , were calculated from the series equivalent resistance and capacitance of the model shown in Fig. 9. Z_m increases as the film thickness (or F_v) increases and at higher frequencies Z_m decreases to the solution resistance, R_{sol} . The slopes, $d \log Z_m / d \log F$, are approximately equal to -1 , in agreement with the proposed electrical model. The values of θ (77 to 87°) show that the impedance behaviour is purely capacitive and indicates that the

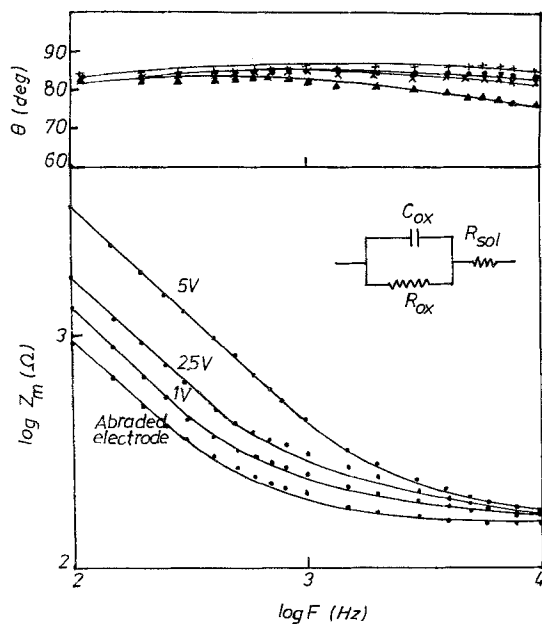


Fig. 9. Impedance diagram for anodized hafnium electrode immersed in $0.33 \text{ M H}_3\text{PO}_4$ acid solutions at 25°C . Formation voltages were \bullet 5, \times 2.5, \blacktriangle 1 V and $+$ abraded electrode.

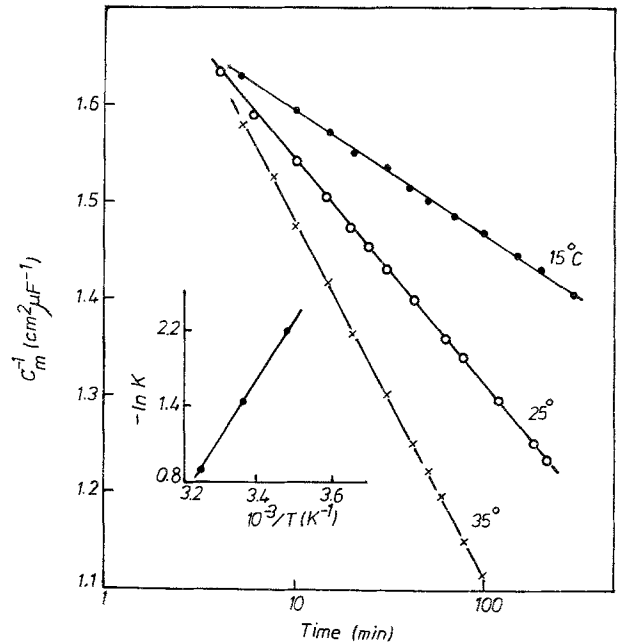


Fig. 10. Variation of reciprocal capacitance, C_m^{-1} , of anodized hafnium electrodes ($F_v = 20 \text{ V}$) with logarithm of time in $2 \text{ M H}_3\text{PO}_4$ acid solutions at different temperatures. Inset: relation between the dissolution rate constant, K , and the reciprocal of the absolute temperature.

oxide film/solution interface can be treated, approximately, as a perfect capacitor [15].

3.7. Stability of anodic oxide film on hafnium

The stability of an anodically formed oxide film on hafnium was tested in $2 \text{ M H}_3\text{PO}_4$ acid solutions at different temperatures. Figure 10 shows that C_m^{-1} decreases linearly with logarithm of time. Such a decrease may be attributed to the partial chemical dissolution of the oxide film. The results are in agreement with the previously reported data in HCl [9] and in NaOH [38]. The oxide film thinning process can be expressed by the following relation

$$C_m^{-1} = K' - K \log(t + t^0) \quad (17)$$

where K , K' and t^0 are constants. Equation 17 was theoretically derived by assuming that the rate of dissolution depends on the concentration of atomic defects and that the concentration of defects decreases exponentially with the film thickness [38]. The activation energy of dissolution was estimated from Fig. 10 by the relation [38, 39]

$$\frac{d \ln K}{d 1/T} = -E_a/R \quad (18)$$

E_a was found to be 50.3 kJ mol^{-1} , which is comparable with that reported in NaOH solutions; $E_a = 50.0 \text{ kJ mol}^{-1}$ [38].

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