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The electrochemical behaviour of naturally passivated hafnium in aqueous solutions of different pH

W. A. BADAWY*, F. M. AL-KHARAFI
Department of Chemistry, Faculty of Science, University of Kuwait, P.O. Box 5969 Safat, 13060 Kuwait

Naturally passivated hafnium was investigated in solutions of different pH. The effect of prevailing gas on the electrochemical behaviour of the metal was studied. The steady state potential of the metal was found to be a linear function of the solution pH in the range 4–10. The slope of E_{SS} vs. pH relation is equal to 18 mV/pH indicating the exchange of three electrons in the electrochemical equilibrium. In oxygen saturated solutions, the potential gets more positive which reflects the increased passivity of the metal surface in naturally aerated and oxygen saturated aqueous solutions. The passive film is highly stable in neutral solutions due to the presence of the stable $HfO(OH)_2$. The activation energy of the passive film dissolution is relatively lower in acid solution due to the formation of the hafnyl ions HfO^{2+}. EIS and polarization experiments are consistent and the naturally occurring passive film can be fitted to a simple electronic equivalent circuit. Naturally passivated hafnium deviate slightly from ideal capacitor behaviour. Anodic oxide films on hafnium deviate greatly from the ideal capacitor behaviour and complicated electronic circuits should be proposed to fit their impedance characteristics.

1. Introduction

Many investigations have been devoted to the production of corrosion resistant materials that can be used in the growing industrial applications [1, 2]. The electrochemical behaviour of valve metals is of high technical and scientific importance because of their use in the manufacture of electrolytic capacitors, in the preparation of passive layers in thin film technology and in the growth of protective and decorative films [3]. The great demand of stable materials used in chemical process units and the application of valve metals into the purex process for waste minimization [4] make the behaviour of these metals important subject for investigation. Hafnium, as a member of the valve metals family, is scarcely investigated. Most investigations were concerned with the formation of anodic oxide films and the kinetics of dissolution of these films [5, 6]. Passive film formation and the effect of the formation medium on the electrical properties of the anodic oxide film were also subjected to some attention [7, 8]. The anodic oxides on hafnium (HfO_2) and on zirconium (ZrO_2) are more crystalline than the other valve metal oxides [9]. The a.c. response of anodically passivated hafnium electrode was investigated and interpreted in terms of different models [8]. The anodization of valve metals is always accompanied by the development of internal stresses in the formed oxide film. These stresses are related to the volume ratio of the surface oxide film to metal substrate, the surface roughness, the phase transformation, kinetic changes during oxide film formation, hydration/dehydration mechanisms and ion incorporation in the oxide film matrix [10]. In a recent work, electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) were used for the characterization of anodic oxide films on Hf [11]. The authors concluded that the anodic oxide film characteristics depend strongly on the forming electrolyte. The oxide films incorporate impurity ions and comprise a multilayer structure, the outer part of which is the most affected by the formation medium. The decrease of anodic film resistance and increase of dielectric constant with increasing film thickness were attributed to anodic breakdown because of structure changes from amorphous to a more crystalline form. From the above survey, it is clear that the metal itself and its electrochemical and surface characteristics have received little attention. Therefore, it was found to be important to investigate the behaviour of naturally passivated hafnium in aqueous solutions of different pH, in order to specify the regions where the passive film on the metal is highly stable and to explain the effect of the ambient electrolyte on the film stability which helps greatly in the application of these materials without anodization. In this respect the conventional electrochemical techniques including open-circuit measurements, potentiostatic and galvanostatic polarization methods beside the EIS technique were employed.

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* *Permanent address*: Department of Chemistry, Faculty of Science, University of Cairo, Giza-Egypt

2. Experimental procedure

Spectroscopically pure hafnium rods (Alderich, Chemie) were mounted in glass tubes of appropriate internal diameter by epoxy resin leaving a front surface area of 0.20 cm^2 to contact the test solution. The electrolytic cell is an all glass, three electrode cell with a large surface area Pt counter electrode and a Ag/AgCl/Cl^- (3M KCl) reference electrode. All solutions were prepared from analytical grade reagents and triply distilled water. The buffer solutions covering the pH range 1–13 were prepared according to the Clark and Lub's series [12]. Before each experiment, the electrodes were mechanically polished with successive grades emery papers down to 1200 grit, then with fine polishing cloth until they acquire reproducibly bright surface and washed with triply distilled water then immersed quickly in the test electrolyte. The pH of the electrolyte was always controlled before electrode immersion using a sensitive pH-meter (Metrohm 713). The electrode potential was traced as a function of time and controlled separately using a high impedance valve voltmeter (Keithley type 197A autoranging multiplier, England). Polarization measurements were carried out using an EG&G (Princeton Applied Research) model 273A Potentiostat/Galvanostat interfaced to an IBM PS/3 computer. The potentiostatic measurements were performed with programs that enable ohmic drop compensation. The EIS investigations were carried out using the IM5d-AMOS system (Zahner Elektrik GmbH & Co., Kronach, Germany). The input signal was usually 10 mV peak to peak in the frequency domain 0.1 to 10^5 Hz. Measurements to frequencies down to 10^{-4} Hz were also performed, in order to investigate the presence of another time constant at lower frequencies. No reproducible results could be obtained at lower frequencies, which can be attributed to the fact that the interactions occurring at the electrode/electrolyte interface in this case are faster than the measurement and hence no reproducibility can be achieved. The potentials were measured against the Ag/AgCl/Cl^- reference, and then refered to the normal hydrogen electrode (nhe). The gases used for solution saturation were purified and dried before bubbling in the electrolyte. The gas was bubbled at least 20 min in the test solution prior to electrode immersion. All measurements were performed at constant room temperature of ≈25 °C. Details of the experimental procedures were as described elsewhere [13, 14].

3. Results and discussions

3.1. Effect of pH on the electrode potential of the hafnium electrode

The potential of naturally passivated hafnium electrode was traced over a period of 3 h in buffer solutions covering the range from 1 to 13. In all solutions the potential gets more positive with increasing immersion time in the aqueous solution. This indicates that the electrode surface becomes more passive after longer immersion time in the test solution. The results presented in Fig. 1A represent a typical example of these measurements. The figure shows the variation of the electrode potential

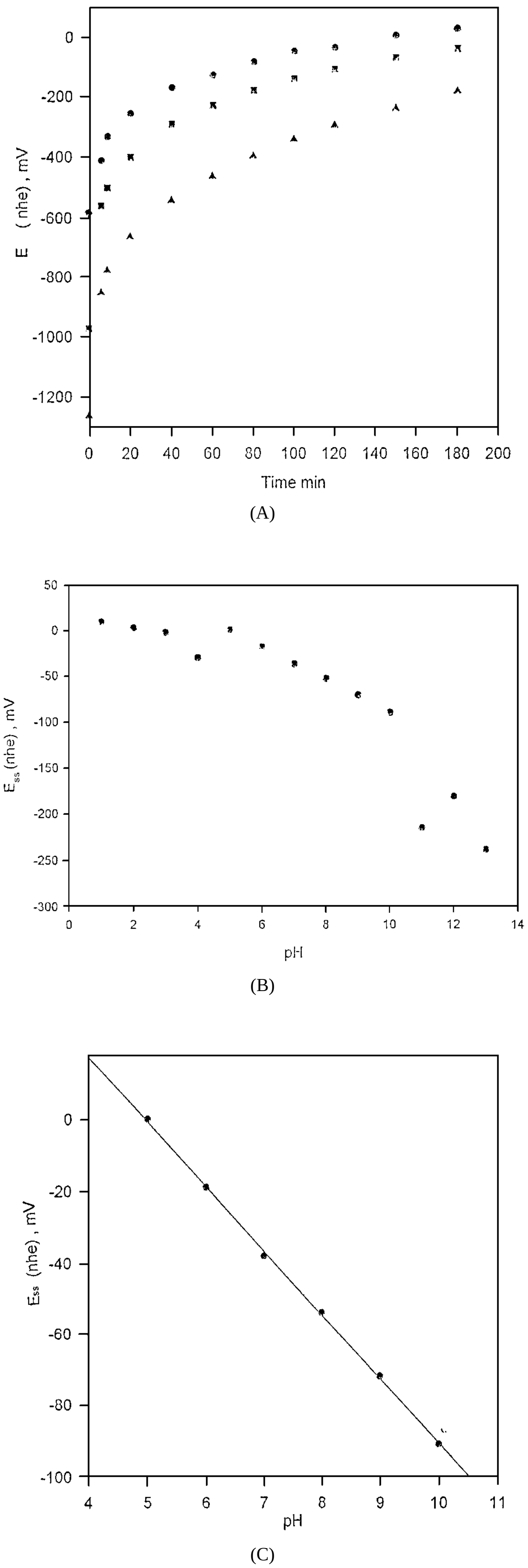


Figure 1 (A) Variation of the electrode potential of hafnium electrodes in naturally aerated solutions of different pH. (●) pH = 2, (■) pH = 7, (▼) pH = 12. (B) Steady state potential of naturally passivated Hf electrodes, E_{SS}, as a function of the solution pH in the pH range 1–13. (C) Steady state potential of Hf electrodes, E_{SS}, as a function of the solution pH in the pH range 4–10.

of hafnium in naturally aerated acid (pH = 2), neutral (pH = 7) and basic (pH = 12) solutions with the time of electrode immersion in each solution. Similar behaviour was obtained in hydrogen, nitrogen or oxygen saturated solutions. The measured potential is dependent on both the pH of the solution and the prevailing gas.

The steady state potential of the hafnium electrode was measured in naturally aerated solutions of different pH. The data are presented in Fig. 1B. As can be seen from this figure, the steady state potential of the naturally passivated electrode is a linear function of the solution pH in the range 4–10. In acid solutions pH < 4 or basic solutions pH > 10, deviation from linearity occurs. The behaviour of the electrode surface in the pH range 4–9 can be represented by:

$$E_{\mathrm{SS}} = \alpha - \beta \ \mathrm{pH} \qquad (1)$$

where α is the pH independent steady potential extrapolated from the linear relation of Fig. 1C i.e. at pH = 0, and β is the slope of this line. The values of α and β were found to be equal to 0.09 V and −0.018 V/pH, respectively. The results of Fig. 1C are similar to the Nernstian plots of the pH indicator electrodes for which:

$$E = E^\circ - \frac{0.059}{n} \ \mathrm{pH} \qquad (2)$$

where E is the steady state potential at 25 °C and E° is the pH independent standard potential of the electrode reaction. The value of n corresponds to the number of electrons involved in the electrode process.

Substituting the values obtained from the linear relation of Fig. 1C, then

$$E = 0.090 - 0.018 \ \mathrm{pH} \qquad (3)$$

which means that n is equal to $\approx$3. This equation is not identical with any of the equations given in the literature for the Hf/aqueous solutions equilibria [15]. It means that the steady state potential of hafnium cannot be represented by any of the following equations:

$$\mathrm{Hf} \rightarrow \mathrm{Hf}^{4+} + 4\mathrm{e}^-$$

$$E = -1.7 + 0.015 \log[\mathrm{Hf}^{4+}] \qquad (4)$$

$$\mathrm{Hf} + \mathrm{H_2O} \rightarrow \mathrm{HfO}^{2+} + 2\mathrm{H}^+ + 4\mathrm{e}^-$$

$$E = -1.724 - 0.029\mathrm{pH} + 0.015 \log[\mathrm{HfO}^{2+}] \qquad (5)$$

$$\mathrm{Hf} + 2\mathrm{H_2O} \rightarrow \mathrm{HfO_2} + 4\mathrm{H}^+ + 4\mathrm{e}^-$$

$$E = -1.685 - 0.059 \ \mathrm{pH} \qquad (6)$$

Most likely it represents a mixed potential involving the hydrated oxide, $\mathrm{HfO_2{\cdot}H_2O}$, which is more stable than the anhydrous oxide, $\mathrm{HfO_2}$. In acid solutions the oxide dissolves according to:

$$\mathrm{HfO_2{\cdot}H_2O} + 2\mathrm{H}^+ \rightarrow \mathrm{HfO}^{2+} + 2\mathrm{H_2O} \qquad (7)$$

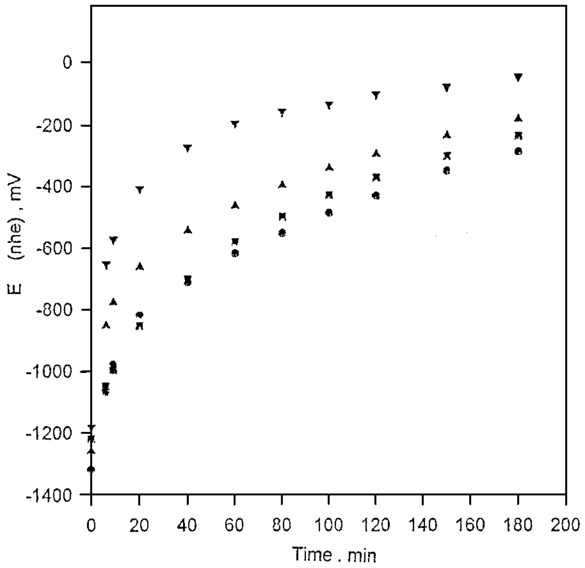


Figure 2 Effect of the prevailing gas on the electrode potential of naturally passivated Hf in solutions of pH = 7. (●) Hydrogen saturated solution, (■) Nitrogen saturated solution, (▲) Naturally aerated solution, (▼) Oxygen saturated solution.

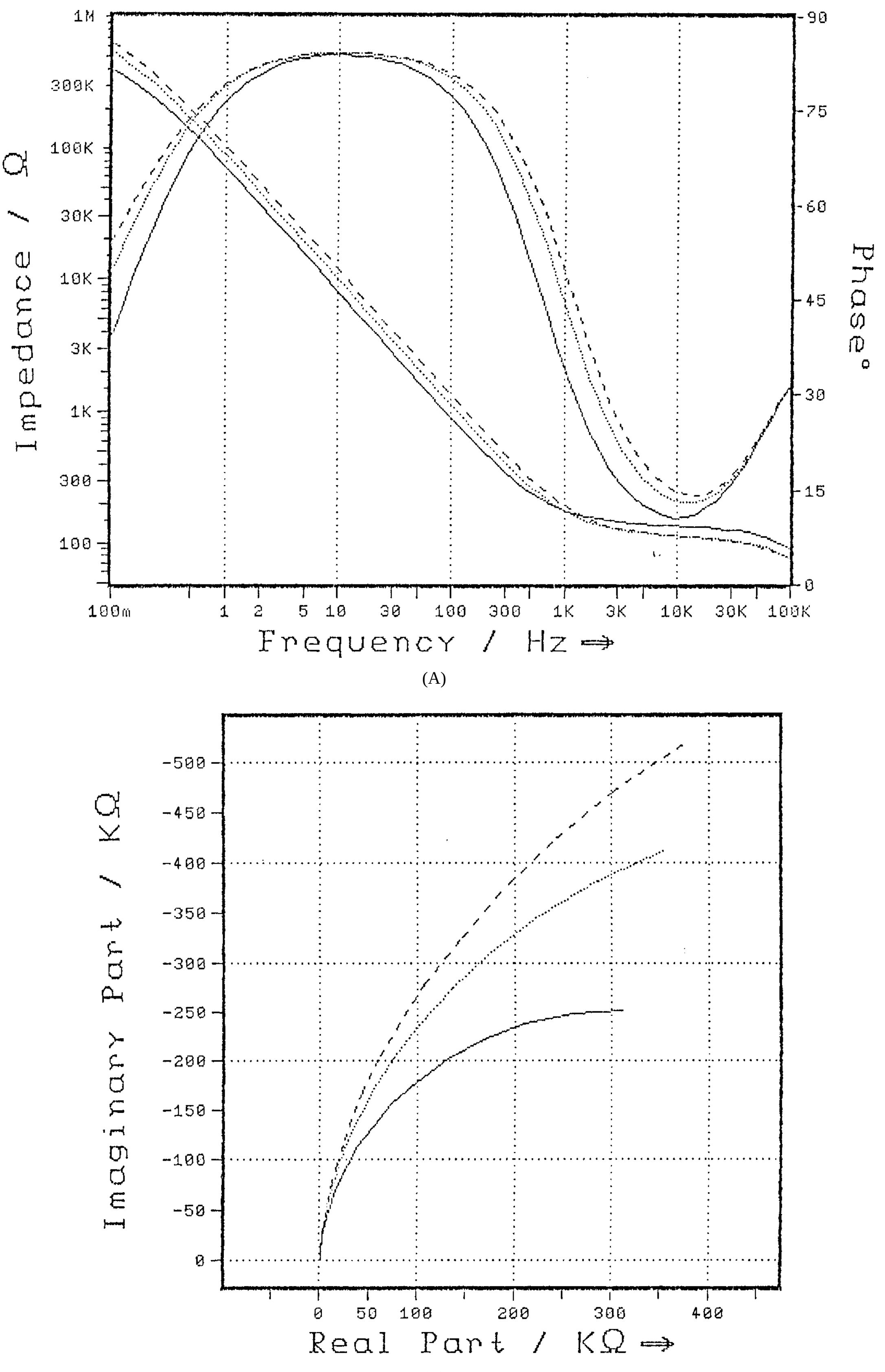
In basic solutions the reaction can be represented by:

$$\mathrm{HfO_2{\cdot}H_2O} + 2\mathrm{OH}^- \rightarrow \mathrm{HfO_3{\cdot}2H_2O} + 2\mathrm{e}^- \qquad (8)$$

In moderately acid, neutral and basic solutions the metal surface is covered by a barrier film of hydrated oxide which reflects its high corrosion resistance [15]. The passivity of this barrier layer increases in the presence of air or oxygen as can be seen from the positive shift in the steady state potential of hafnium in oxygen saturated solutions compared to the values in hydrogen or nitrogen saturated solutions. Fig. 2 presents the effect of the prevailing gas on the electrode potential of hafnium in solutions of pH 12. Similar results have been obtained in acid and neutral solutions (pH 2 and 7). In all solutions the electrode potential gets more positive with immersion time until it reaches the steady state value. The presence of oxygen shifts the electrode potential towards more positive values which reflects the increased passivity of the electrode surface in oxygen saturated solutions. A shift of about 400 mV in the positive direction is recorded. This can be attributed to an increased passive film thickness or increased stoichiometry of the surface oxide film. The general trend of the electrode potential in acid, neutral or basic solutions is the same. The difference in the stability of the barrier film in each solution can be investigated by EIS and polarization experiments.

3.2. EIS and polarization measurements

Electrochemical impedance spectroscopy (EIS) is a powerful technique in the investigation of corrosion and passivation phenomena. It is a steady state technique which is capable of accessing relaxation phenomena whose relaxation times vary over orders of magnitudes and permits single averaging within an experiment to obtain high precision levels [16]. The electrode

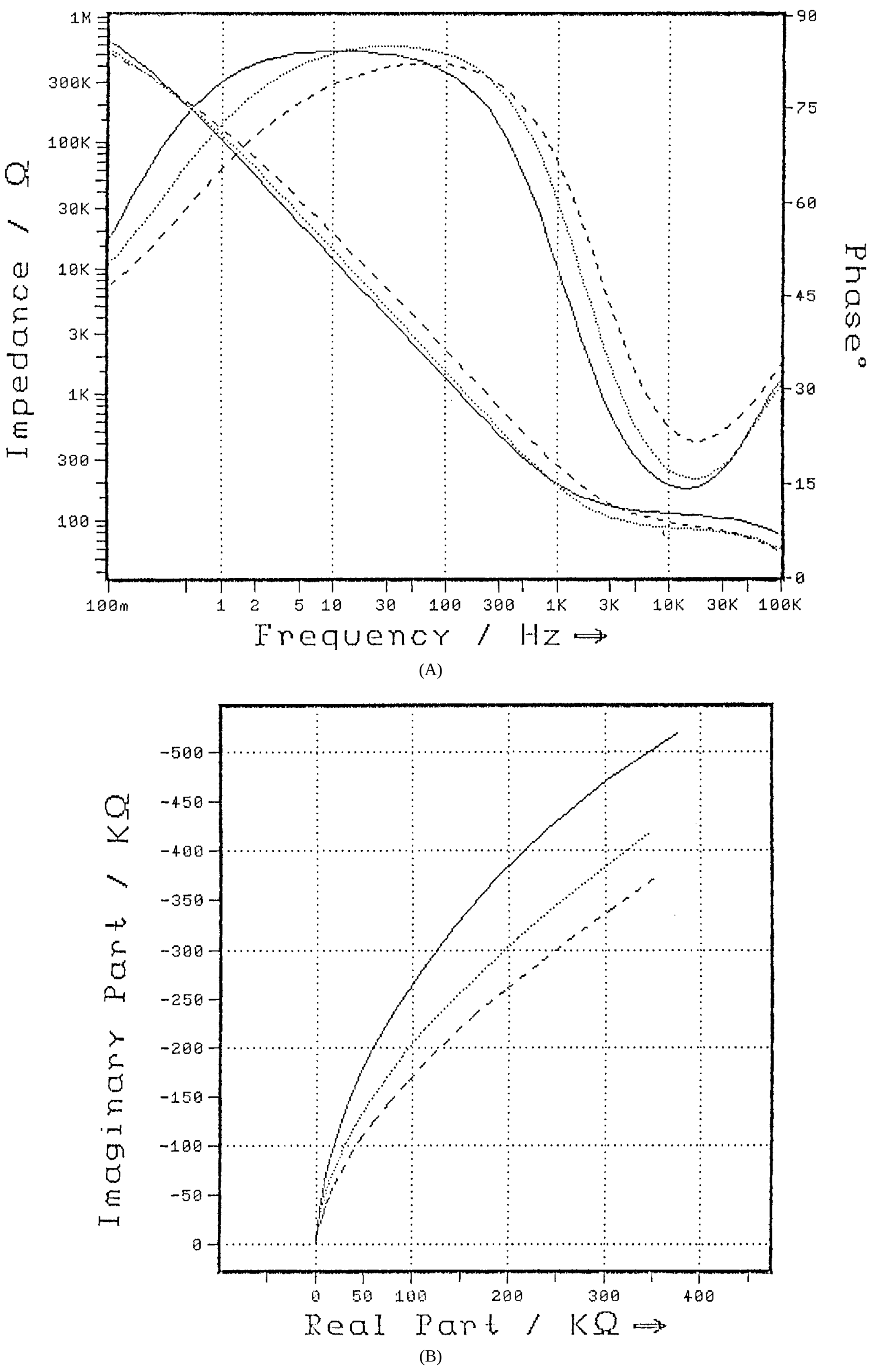


(A)

(B)

Figure 3 EIS characteristics of hafnium at different time intervals of electrode immersion in naturally aerated solutions of pH = 7. (A) Bode plots, (B) Nyquist plots. (——) 15 min, (. . . .) 60 min and (- - - - -) 180 min.

impedance of hafnium was traced over three hours of electrode immersion in aqueous solutions of different pH. The impedance behaviour of the naturally passivated electrode in solutions of pH = 7 is presented as Bode plots in Fig. 3A and Nyquist plots in Fig. 3B. The presence of the frequency as independent variable in Bode plots enables the comparison between experimental data and theoretical data according to specific electronic models [11, 17, 18]. The impedance spectra of Fig. 3 show a linear variation of log Z vs. log f which is characteristic of capacitive behaviour [16, 17]. The phase angle, θ, does not reach a value of 90°, which is an indication of a non-ideal capacitive behaviour [11, 13]. The impedance behaviour of the hafnium electrodes in acid or basic solution is similar to that obtained in neutral solutions with different values of polarization resistance, R_p, and electrode capacitance, C. The impedance spectra after 3 h of electrode immersion in naturally aerated solutions of $\mathrm{pH} = 2$, 7 and 12 are presented in Fig. 4. In all solutions, the behaviour represents an



(A)

(B)

Figure 4 Bode plots (A) and Nyquist plots (B) of naturally passivated hafnium electrodes after 3 h of immersion in acqueous solutions of different pH. (- - - - -) $\mathrm{pH} = 2$, (——) $\mathrm{pH} = 7$, (. . . .) $\mathrm{pH} = 12$.

electrode covered with a passive oxide film for which the interfacial impedance, Z, is given by:

$$Z = \frac{R_p}{1 + j2\pi f R_p C} + R_S \tag{9}$$

where f is frequency in Hz, R_S the solution resistance and $j = \sqrt{-1}$. The value of R_p represent a good parameter in determining barrier film stability. The electrode capacitance, C, can be taken as a measure of the passive film thickness [19] where

$$\delta = \frac{K}{C} \tag{10}$$

δ is the oxide film thickness in cm, C, is the electrode capacitance in μF and K is a constant which is given by:

$$K = 1.77 \times 10^{-7} DA\sigma \tag{11}$$

where D is the relative dielectric constant of the oxide film, σ is its roughness factor and A is the electrode area. The relative dielectric constant of the oxide film on Hf, which considered to be HfO_2 or hydrate oxide can be taken as 24 assuming that the oxide film is compact and has no porous structure or cracks [11, 20]. For anodically formed oxide films, the value of D was found to depend on both the formation medium and the anodization coefficient of the formed film [11]. Comparison between the impedance data of the naturally passivated hafnium electrode in solutions of pH 2, 7 and 12 at different time intervals of electrode immersion shows a continuous increase of the electrode impedance from the moment of electrode immersion in each solution which indicates the continuous passivation and barrier film thickening with time (cf. Table I). For comparison the electrode was anodized in 0.33 M phosphoric acid for 5, 10, 20, 40 and 80 V and the impedance behaviour of each anodized surface was compared to the naturally passivated surface. The results reveal that the anodic oxide film undergoes oxide film dissolution even in neutral solutions. The impedance data of the naturally passivated electrode and anodized electrodes at different time intervals are summarized in Tables I and II. The thickness of the anodic oxide film, δ, formed at different formation voltages, V_F, in 0.33 M H_3PO_4 at a current density of 1 mA cm^{-2} was calculated according to Equation 10 taking into consideration that the value of D is 24 [20] and the average value of the roughness factor, σ, is 1.17 [21, 22]. The variation of the oxide film thickness, δ, and that of the electrode capacitance, C, with the anodization potential, V_F, is presented in Fig. 5. The anodization constant was found to be equal to 0.64 nm/V. This lower value compared to that reported recently (≈1.8 nm/V [11]) can be attributed to the effect of concentration of the formation medium and the formation current density. The thickness of the naturally occurring oxide film, δ°, can be obtained by extrapolation of the linear relation to $V_F = 0$. For this series of measurements a thickness of 0.26 nm for the native oxide film was extrapolated.

TABLE I Corrosion resistance of naturally passivated hafnium electrode in different pH

	R_p (kΩ cm^2)		
Time (min)	pH 2	pH 7	pH 12
15	65.78	79.94	69.8
30	71.6	86.34	78.6
60	81.6	108.7	85.0
120	95.1	121.5	92.4
180	102.4	127.8	108.26

TABLE II Effect of the formation voltage on the corrosion resistance of the oxide film formed anodically (1.0 mA cm^{-2} in 0.33 M H_3PO_4) on hafnium in pH 7

	R_p (kΩ cm^2)				
Time (min)	5 V	10 V	20 V	40 V	80 V
15	247.2	266.4	468.0	543.2	1150.0
30	222.0	248.8	460.8	546.0	820.0
60	214.0	238.0	343.6	339.4	396.0
120	229.0	236.0	343.8	324.6	234.0
180	239.8	245.8	354.6	350.6	224.0

TABLE III Values of the polarization resistance, R_p, corrosion current, i_{corr}, and corrosion potential, E_{corr}, of the hafnium electrode in naturally aerated solutions of different pH

pH	R_p (kΩ cm^2)	i_{corr} (nA cm^{-2})	E_{corr} (mV)
2	66.50	482.0	−293
7	81.16	297.0	−282
12	66.20	494.5	−342

Polarization experiments are consistent with the EIS data. The values of the polarization resistance, R_p, corrosion current, i_{corr}, and the corrosion potential, E_{corr} as obtained from the linear polarization experiments and Tafel plots are summarized in Table III. The results of Tables I and III show that the oxide film on hafnium is more stable in neutral solutions. This can be attributed to the fact that in neutral solutions the electrode surface is covered by the hydrated oxide, $HfO(OH)_2$, which represent the most stable barrier layer on Hf [15]. The impedance behaviour of the passive film on hafnium can be fitted to that of a simple electronic model consisting of a parallel combination of resistor representing the polarization resistance, R_p, and a capacitor representing the electrode capacitance, C, both in series to a small resistor, R_S, representing the ohmic drop in the solution as presented in Fig. 6A. The results of data fitting for the naturally passivated Hf after 3 h of electrode immersion in solution of pH = 7 are presented in Fig. 6B. The solid lines represent the best complex non-linear fitting of the experimental data. The computer generated values of R_p, R_S and C are 640 kΩ, 0.11 kΩ and 1.36 μF, respectively. The percentage error in the absolute impedance, Z, is about 2.7% and the deviation in the phase angle, θ, is 1.6°. The same fitting procedure was applied to phosphoric acid anodized electrodes for different formation voltages. The results of data fitting show that the anodically formed oxide films deviate greatly from the

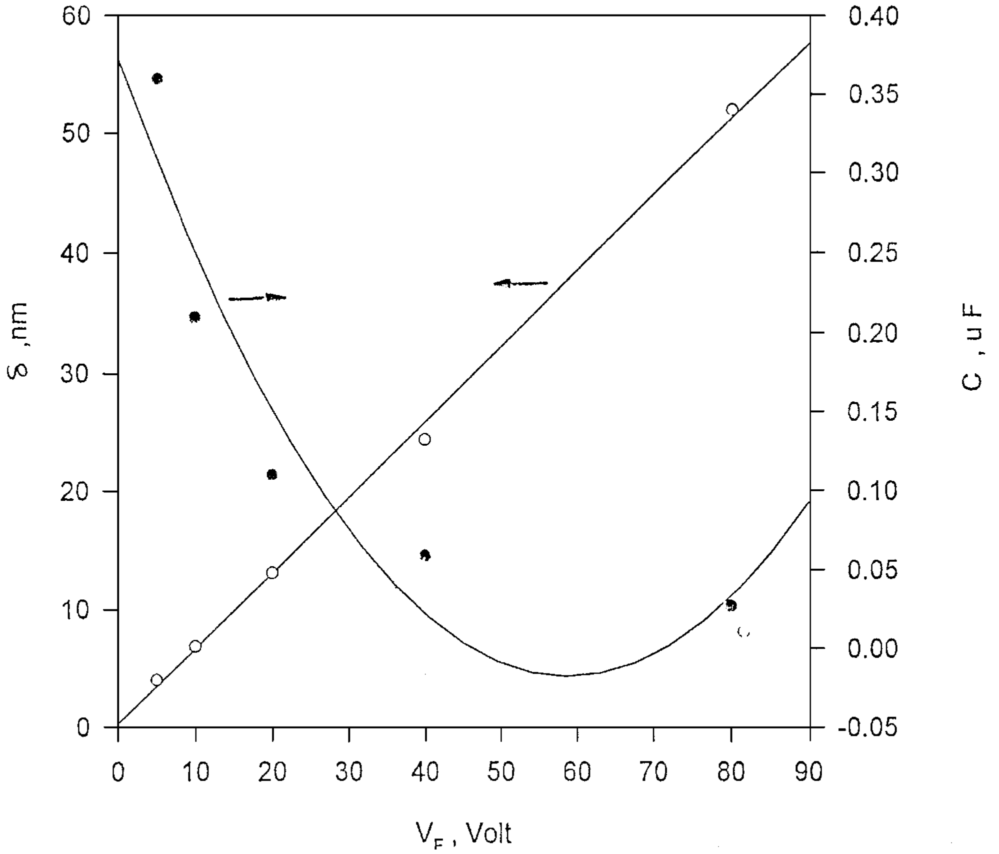


Figure 5 Variation of the electrode capacitance, C, and anodic oxide film thickness, δ, on Hf with the formation voltage V_F. (○) Oxide film thickness, δ, (●) electrode capacitance, C.

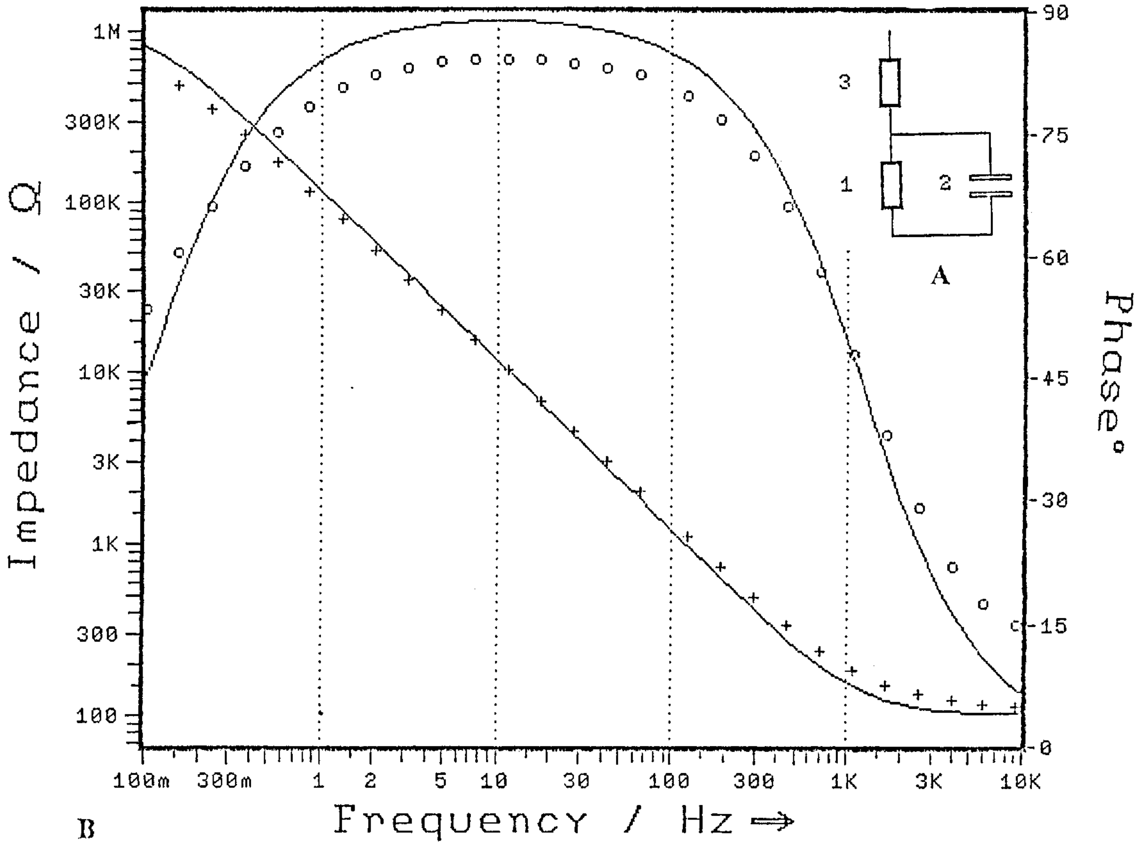


Figure 6 (A) Equivalent circuit of the electrode/electrolyte interface of naturally passivated Hf in aqueous solutions. (1) R_p = polarization resistance, (2) C = Electrode capacitance, (3) R_s = solution resistance. (B) Experimental (○○○) and theoretical (——) impedance data of Hf electrodes after 3 h immersion in naturally aerated solution of pH 7. $R_s = 0.11\ k\Omega$, $R_p = 640\ k\Omega$, $C = 1.36\ \mu F$.

TABLE IV The % error in the absolute impedance, Z, and the deviation in the phase angle, θ, for the naturally passivate hafnium electrodes in solutions of different pH

pH	% error in, Z	Deviation in θ
2	4.7%	2.2°
7	2.7%	1.6°
12	3.1%	1.6°

proposed electronic equivalent circuit. As an example the percentage error in the absolute impedance of 80 V anodized electrode after 3 h immersion in solutions of pH = 7 was found to be equal to 5.1% and the deviation in the phase angle was 2.7°. It means that the naturally occurring passive film on Hf deviates slightly from ideal capacitor behaviour. Its behaviour approaches that of the simple equivalent circuit of Fig. 6A. Anodization of the electrode leads to the formation of barrier layers which deviate greatly from ideal capacitive behaviour. For such anodic films multilayer structure models have been proposed [11]. They cannot be represented by simple equivalent circuits like that of Fig. 6A. For naturally passivated electrode the deviation from the proposed electronic model is increased in acid medium. The percentage error in the absolute impedance and the deviation in the phase angle in the different solutions are presented in Table IV.

3.3. Effect of temperature on the behaviour of the naturally passivated hafnium electrode

The effect of temperature on the stability of the naturally occurring passive film on hafnium was investigated in acid, neutral and basic solutions. The measurements were performed in naturally aerated buffer solutions of pH 2, 7 and 12 using an all glass three electrode double walled cell. The temperature was controlled by Haake thermostat model D8, Fisons. As the temperature increases the oxide film dissolves. The rate of oxide film dissolution is directly proportional to the measured corrosion current at each temperature. In all solutions the rate of oxide film dissolusion increases with increasing temperature. The variation of i_{corr} with temperature was plotted in the form of Arrhenius plots according to Equation 12 [21].

$$\frac{\mathrm{d}\log i_{\mathrm{corr}}}{\mathrm{d}1/T} = -\frac{E_{\mathrm{a}}}{R} \qquad (12)$$

where E_{a} is the activation energy and R is the gas constant.

The data are presented in Fig. 7. The activation energy of the oxide film dissolution processes is calculated from the slopes of the linear relations of Fig. 7 and presented in Table V. It is clear from the values shown in this Table that the activation energy of the oxide film dissolution in neutral media is relatively higher than that in acid or basic solutions. This reflects the relatively high stability of the naturally occurring passive film on Hf in neutral solutions. The lower activation energy of the dissolution process in acid solutions can be explained by the shift of equilibrium of Equation (7) to the formation of the hafnyl ions. In basic solutions the formation of the solid phase $HfO_3 \cdot 2H_2O$ according to Equation 8 increases the activation energy of the process compared to the acid solution in which an aqueous phase ($HfO^{2+}_{\mathrm{aq.}}$) is formed that enhances the dissolution process and hence lowers the activation energy.

TABLE V Activation energy of the hafnium passive film dissolution in naturally aerated solutions of pH 2, 7 and 12

pH	E_{a} (kJ mol^{-1})
2	50.00
7	59.40
12	61.50

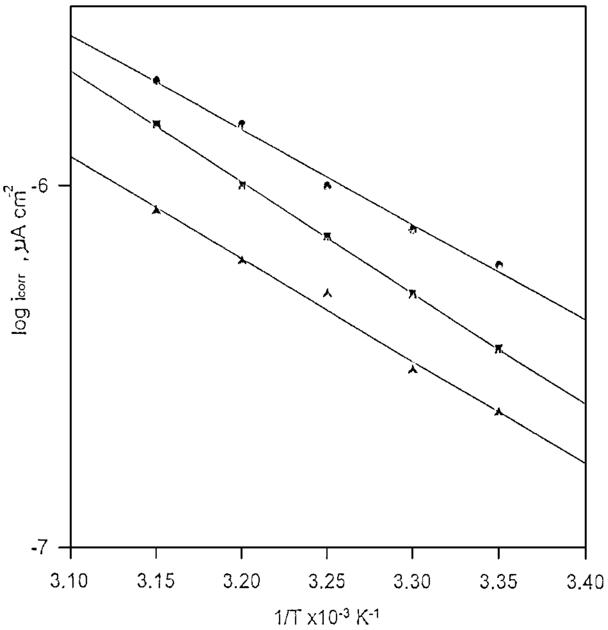


Figure 7 Arrhenius plots ($\log i_{\mathrm{corr}}$ vs. $1/T$) of the dissolution of the passive film on Hf in naturally aerated solutions of different pH. (●) pH = 2, (■) pH = 7, (▲) pH = 12.

4. Conclusion

Although hafnium appears to be a very base metal, its surface is always covered by a passive film which consists mainly of HfO_2 or the highly stable $HfO(OH)_2$. In acid solutions oxide film dissolution occurs with relatively lower activation energy ($\approx$50 kJ mol^{-1}). The naturally occurring passive film is highly stable in neutral solutions and approaches a perfect dielectric behaviour. Its steady state potential is a linear function of the solution pH in the range 4–10.

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