



Corrosion behavior of hafnium in anhydrous isopropanol and acetonitrile solutions containing bromide ions

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Abstract: The corrosion behaviors of hafnium in Et_4NBr isopropanol and acetonitrile (ACN) solutions were investigated using electrochemical measurements, ICP-AES and SEM techniques. Results revealed that the open circuit potential gets more positive due to the increased passivity of the surface oxide film with increasing immersion time until it reaches a steady state value. The potentiodynamic anodic polarization curves did not exhibit an active dissolution region near corrosion potential due to the presence of an oxide film on the electrode surface, which was followed by pitting corrosion. SEM images confirmed the existence of pits on the electrode surface. Cyclic voltammetry and galvanostatic measurements allowed the pitting potential (φ_{pit}) and the repassivation potential (φ_{p}) to be determined. φ_{pit} increased with increasing potential scanning rate but decreased with increasing temperature, Br^- concentration and ACN concentration. The impedance spectra showed that the resistances of the solution and charge transfer decreased with the increase of ACN concentration.

Key words: corrosion behavior; hafnium; acetonitrile; Et_4NBr ; electrochemical method; pitting corrosion; passive film

1 Introduction

Ongoing development of the microelectronics, starting from the early 1960s of the 20th century, involves an increase in the integration degree of emerging semiconductor devices, as well as the increase of speed and functionality of integrated circuits (ICs) [1]. But as the semiconductor industry ushered in nanometer era [2], a gate dielectric thickness in the field effect transistor (FET) reached its physical limits because of an increase in leakage currents due to tunneling effects [3]. In order to reduce the leakage current and capacitance of devices, significant attention has been paid to the high- k dielectric layers including HfO_2 , Al_2O_3 , TiO_2 , ZrO and CeO_2 as a substitution of ultra-thin silicon dioxide films [4], among which HfO_2 is considered the most promising [5]. Hafnium alkoxide is mainly used for the deposition of HfO_2 layers by atomic layer deposition (ALD), and deposited in this manner, the hafnium-based high- k dielectrics show much more stable electrical characteristics compared with the ones formed by sputtering or chemical vapors [6].

At present, the most common method of preparing hafnium alkoxides is based on the halide synthesis [7]. This method has multistep processes, and the starting materials are difficult to access. In addition, it involves various by-processes which contaminate the products and decrease their yields [8]. On the other hand, the electrochemical method has great promise for the direct conversion of the less electropositive metals to their alkoxides owing to its simplicity and high productivity as well as its continuous and non-polluting character (with hydrogen as the major by-product). In our earlier works, we prepared several tantalum and niobium alkoxides by electrochemical method [9–11]. In 1995, hafnium isopropanol was obtained for the first time by TUREVSKAYA et al [12] with the electrochemical method involving electrolysis of an isopropanol solution containing tetraethylammonium bromide with a platinum cathode and a hafnium anode. However, the electrochemical behaviors of this process have not been investigated so far.

Hafnium is a valve metal and some literatures have reported its electrochemistry in aqueous solutions [13–18]. BARTELS et al [13] investigated the

potentiodynamic oxide growth of hafnium in acidic, neutral and alkaline electrolytes and showed that its electrochemistry in acidic electrolytes is characterized by anodic breakdown of the oxides due to localized corrosion. Most investigations were related with the formation of anodic oxide films and the kinetics of dissolution of these films [13,17,18]. Titanium and tantalum, which are close to hafnium in its properties, were investigated in anhydrous alcohols, and the results indicated that they could suffer from severe corrosion [19–22].

Despite some studies on the electrochemistry of Hf in aqueous solutions, only one literature reported the electrochemical behaviors of hafnium in anhydrous ethanol [23]. In the present study, the electrochemical behavior of hafnium was investigated in anhydrous isopropanol and ACN solutions containing supporting electrolytes, by using open circuit potential measurements, cyclic voltammetry, galvanostatic, potentiodynamic anodic polarization, potentiostatic and impedance techniques. ICP-AES method of chemical analysis was also applied to confirming results obtained from electrochemical measurements. SEM examinations of the electrode surface were also performed. The effect of the ACN on the stability of the passive film was discussed.

2 Experimental

Anhydrous isopropanol was supplied by Tianjing Damao Chemical Reagent Corporation, China. Anhydrous acetonitrile (ACN) and Et_4NBr were provided from Sinopharm Chemical Reagent Corporation Limited. The working electrode employed was made from a very pure hafnium rod (99.9%), which was supplied by the Northwest Institute for Non-ferrous Metal Research, China. The electrode used was cut as cylindrical rods and mounted into glass tubes using Araldite to offer an active flat disc shaped surface of 4.28 mm^2 geometric area to contact the test solution. Prior to each experiment, the electrode was successively polished with a series of emery papers from a coarse grade of 1200 to fine grade of 3500. The electrode was then successively rinsed with ethanol and isopropanol and finally dipped in the electrolytic cell.

The experiments were performed in a 250 mL volume glass electrolytic cell utilizing Pt foils of $1 \text{ cm} \times 1 \text{ cm}$ and $2 \text{ cm} \times 2 \text{ cm}$ as auxiliary and reference electrodes, respectively. All potentials given in this work were referred to this reference electrode. The experiments were carried out in anhydrous isopropanol and ACN (30%–70%) solution containing Et_4NBr of various concentrations (0.02–0.10 mol/L). Each run was carried out in aerated stagnant solutions at the required

temperature ($\pm 1^\circ\text{C}$), using water thermostat. The gases used for studying its effects on the electrode potential of naturally passivated Hf in anhydrous isopropanol and ACN solutions 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. The sample was immersed in the solution until the potential reached a stable value (about 3 h), and then each measurement was performed.

Electrochemical measurements were performed using a potentiostat/galvanostat (CHI660C Electrochemical Workstation provided by Shanghai CH Instrument Company, China) connected to a personal computer. Cyclic voltammetric measurements were carried out by sweeping the potential linearly from -1 V (vs Pt) more negative than the open circuit potential (ϕ_{ocp}) up to 3 V (vs Pt) in the positive direction at scanning rate of 5 mV/s , reversing with the same scan rate to the lowest potential, and finally returning to the starting potential to form one complete cycle. The potentiodynamic anodic current/potential curves were recorded from -1.0 V (vs Pt) more negative than the open circuit potential (ϕ_{ocp}) up to 3 V (vs Pt) with the required scanning rate. In galvanostatic potential/time transients, a constant anodic current density was applied on the Hf electrode and the variation in potential was recorded as a function of time. The potentiostatic measurements were carried out at a given step anodic potential ($\phi_{\text{s,a}}$) at which the current transient was recorded. EIS measurement was carried out using AC signals of amplitude 5 mV in the frequency range from 1 Hz up to 0.1 MHz . All impedance data were fit to appropriate equivalent circuits using computer program ZSimDemo 3.30d.

In order to gain more insight on the composition and the morphology of the passive oxide films grown on the surface of the tested Hf samples, the Hf samples were subjected to a JEOL JSM-6360LV scanning electron microscopy (SEM) analysis. Before performing SEM, the Hf samples were submitted to the same surface treatment, immersed in $0.06 \text{ mol/L Et}_4\text{NBr}$ isopropanol and ACN (50%) solution after anodic polarization from -1 up to 0.7 V (more negative than the pitting potential) and 2.2 V (more positive than the pitting potential) at 30°C and a scanning rate of 5 mV/s , and finally preserved in anhydrous ethanol which was deaerated with N_2 for 20 min to remove O_2 dissolved in the solution. The acceleration influence of the applied anodic potential towards pitting corrosion of Hf was evaluated in 0.06 mol/L Br^- solutions at 30°C , using an independent chemical method of analysis, namely inductively coupled plasma-atomic emission spectrometry (ICP-AES). The Hf^{4+} ions concentration was determined in the aggressive solution as a function

of the applied anodic potential after holding the sample for 5.0 min at the given potential. Measurements were carried out using Perkin–Elmer Optima 5300 Dual View inductively coupled plasma-atomic emission spectrometry (ICP-AES) instrument connected with AS 93 Plus autosampler.

3 Results and discussion

3.1 Open circuit potential measurements

Figure 1 illustrates the effect of the prevailing gas on the electrode potential of naturally passivated hafnium in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C. It is clearly observed that in both solutions the potential increases with an increase in immersion time until a steady state value in the anhydrous solution (containing less than 1% water) is obtained. This steady state value was considered as the stable open circuit potential. The increase in potential indicated that water, even if in traces, plays an important role in the electrochemical behaviour of hafnium in anhydrous solution, and the Hf surface becomes more passive after longer immersion time in the test solution. The passivation is enhanced in the presence of air, which can be seen from the positive shift in the steady state potential of hafnium in naturally aerated solution compared to the values in nitrogen saturated solutions. As a result, a shift of about 100 mV in a noble direction is observed. These phenomena may be attributed to an increased passive film thickness or increased stoichiometry of the surface oxide film [18].

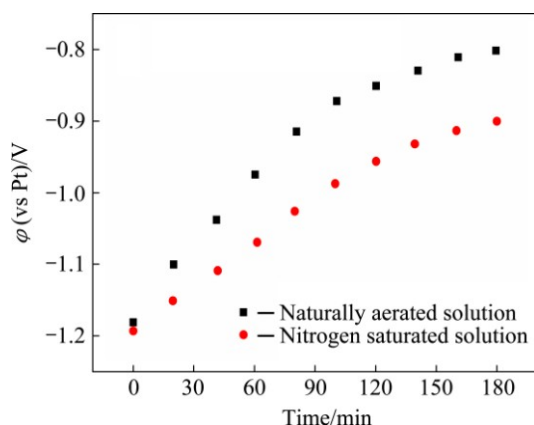


Fig. 1 Effect of prevailing gas on electrode potential of naturally passivated Hf in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C

3.2 Cyclic voltammetry measurements

Figure 2 illustrates the cyclic voltammogram of Hf starting from –1 V (vs Pt) and reversed at 3 V (vs Pt) in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C and a scanning rate of 5 mV/s. On the positive-going scan, the cathodic

current density decreases gradually and reaches a zero value near the corrosion potential (ϕ_{corr}). Subsequently, the anodic excursion scan does not exhibit an active dissolution region near ϕ_{corr} . The lack of active dissolution can be ascribed to the spontaneous passivation of Hf due to the presence of HfO_2 film on the electrode surface. It is worth noting that the passive current density increases (J_{pass} , see the inset of Fig. 2) with the applied potential. J_{pass} increase may be attributed to the replacement of chemically dissolved HfO_2 by the aggressive attack of Br^- anion following its adsorption [24]. This adsorption probably is enhanced as the applied potential is more positive. Moreover, it seems that there is a distribution of nucleation sites of different energies that nucleate at distinct potentials [25]. In other words, the more positive the applied potential is, the more the active sites will be available for pit nucleation.

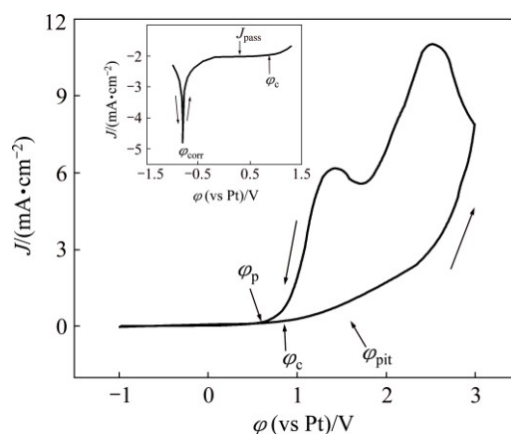


Fig. 2 Cyclic voltammogram of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C and scanning rate of 5 mV/s (Inset: Tafel curve recorded for Hf from –1 to 1.3 V (vs Pt) in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C and scanning rate of 5 mV/s)

The passive region extends up to a certain potential, denoted as the critical potential (ϕ_c). As the electrode potential exceeds ϕ_c , a slight increase in current is observed until a pitting potential (ϕ_{pit} , roughly estimated as shown in Fig. 2) is reached. When the anodic potential exceeds ϕ_{pit} , the current density goes up rapidly, without any sign of gas evolution, which suggests the breakdown of the passive oxide film, initiation and propagation of pitting corrosion.

Figure 3 presents SEM images of the Hf surface in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C and various anodic potentials. It is clear that at 0.7 V (vs Pt) which is more negative than ϕ_{pit} , the result gives no evidence of pitting, as shown in Fig. 3(a). On the other hand, at 2.2 V (vs Pt) more positive than ϕ_{pit} , the data reveal the

occurrence of intense pitting corrosion on the specimen exposed to the test solution, as shown in Fig. 3(b).

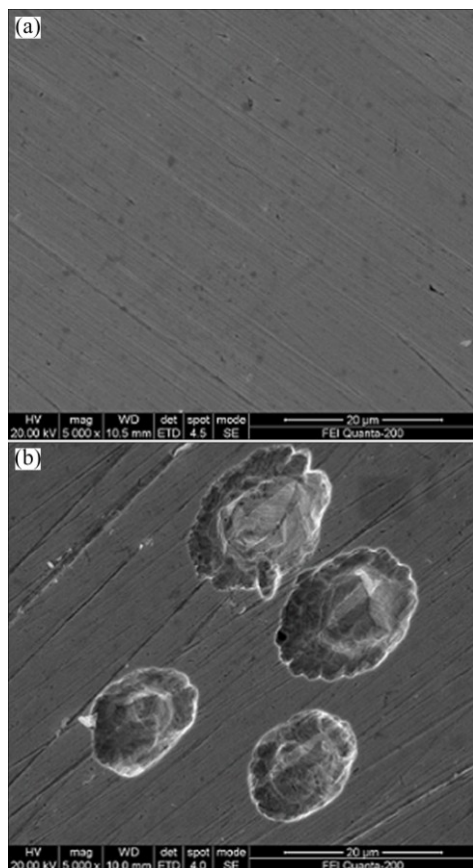
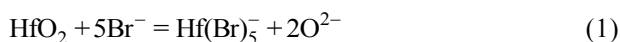
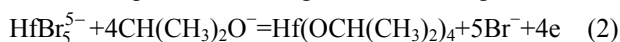


Fig. 3 SEM images of Hf surface after anodic polarization from -1 to 0.7 V (vs Pt) (more negative than pitting potential (a)) and 2.2 V (more positive than pitting potential (b)) at 30 °C and scanning rate of 5 mV/s

Pitting corrosion may be ascribed to the adsorption and incorporation of Br^- ions with the assistance of a high electric field into the oxide film on Hf [24]. The adsorption process may be followed by the removal of the oxide film particularly at flaws and defective sites as complex ions through



This reaction comprises the initial weakening of the passive film leading to passivity breakdown. At flaws and defect sites, the oxide films can be totally removed and the base metal exposed to the electrolyte. The process of oxidation of Hf may occur by the formation of soluble complexes according to the following reaction:



ICP-AES method of chemical analysis was involved to determine the concentration of Hf^{4+} ions dissolved at different applied anodic potentials ($>\phi_{\text{pit}}$). The obtained data are shown in Table 1. It is clear that the concentration of Hf^{4+} in solution, due to pitting corrosion, increases as the potential is made more

positively. This confirms polarization results that the pitting corrosion rate of Hf increases with the increase of applied anodic potential.

Table 1 Concentrations of Hf^{4+} ions due to pitting in 0.06 mol/L Br^- solutions, recorded by ICP-AES, as function of applied anodic potential ($>\phi_{\text{pit}}$) at 30 °C (Each sample was held at given potential for 5.0 min)

$\phi_{\text{s,a}}$ (vs Pt)/V	Mass fraction of $\text{Hf}^{4+}/10^{-6}$
2.00	0.039
2.05	0.049
2.10	0.14
2.15	0.22
2.20	0.58

Referring again to Fig. 2, after the potential sweep reversal from 3 V (vs Pt), the current density rises still due to the autocatalytic character of pitting [26]. Afterwards, the current density begins to decline until an anodic peak appears, which may be attributed to the oxidization of the intermediates produced and absorbed on the Hf surface. Following this, the current density decreases rapidly and linearly. This linear current–potential relationship indicates that an ohmic controlled process is taking place [27]. As a result, the flyback curve intersects the forward scanning curve at approximately 0.55 V (vs Pt), which defines the protection (repassivation) potential ϕ_{p} for the Hf electrode under the test conditions. This suggests that the surface of the Hf returns again to the passivated state. Accordingly, a hysteresis loop is clearly formed, a crucial characteristic of the pitting corrosion phenomenon. The existence of a hysteresis loop in a cyclic voltammogram suggests a delay in repassivation of an existing pit when the potential is scanned toward negative direction. The larger the hysteresis loop is, the more difficult it becomes to repassivate the pit [28].

Figure 4 illustrates the effect of the number of successively repeated cycles (5 cycles) on the general features of the voltammogram of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C and 5 mV/s. Table 2 lists the values of ϕ_{pit} and ϕ_{p} of successive cyclic voltammograms (5 cycles) of Hf in 0.06 mol/L Et_4NBr isopropanol (50%) and ACN (50%) solutions between -1 and 3 V (vs Pt) at a scanning rate of 5 mV/s and at 30 °C. It is observed that upon repetitive cycling ϕ_{pit} shifts to more positive values, while ϕ_{p} shifts in a negative direction, corresponding to a decreased susceptibility to pitting. This fact may be related to the formation of increasing amounts of corrosion product in the oxide defective sites where pitting was initiated, making further metal dissolution difficult [27].

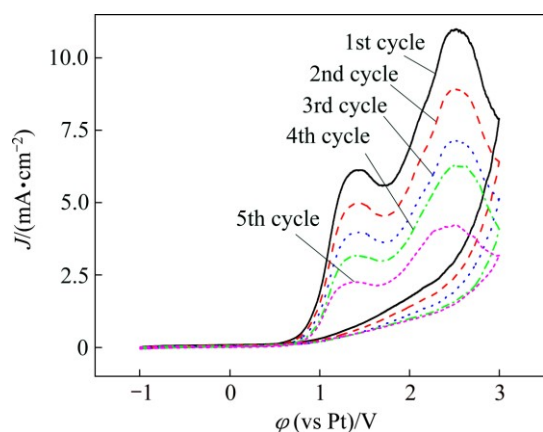


Fig. 4 Successive cyclic voltammograms (5 cycles) of Hf in 0.06 mol/L Et_4NBr isopropanol (50%) and ACN (50%) solutions between -1 and 3 V (vs Pt) at scanning rate of 5 mV/s and 30 °C

Table 2 Values of ϕ_{pit} and ϕ_{p} of successive cyclic voltammograms (5 cycles) of Hf in 0.06 mol/L Et_4NBr isopropanol (50%) and ACN (50%) solutions between -1 and 3 V (vs Pt) at scanning rate of 5 mV/s and 30 °C

Cycle No.	ϕ_{pit} (vs Pt)/V	ϕ_{p} (vs Pt)/V
1st	1.61	0.546
2nd	1.72	0.569
3rd	1.81	0.618
4th	1.89	0.701
5th	1.91	0.777

3.3 Potential/time transient measurements

To study the growth kinetics of the oxide film formed on Hf surface and its breakdown, Hf electrode was anodized galvanostatically in 0.06 mol/L Et_4NBr anhydrous isopropanol (50%) and ACN (50%) solutions at 30 °C and different current densities (5 – 100 $\mu\text{A}/\text{cm}^2$), as shown in Fig. 5. The steep linear increase in potential with time is ascribed to the initial formation and growth of the oxide film. A potential maximum occurs at a certain potential. This maximum is considered to be the pitting potential (ϕ_{pit}), which corresponds to the competition between two processes, namely further oxide film growth and its breakdown. After ϕ_{pit} , the potential decays to a steady value that corresponds to the repassivation potential (ϕ_{p}). It is clear in galvanostatic curves that ϕ_{p} is the only potential nearly constant and independent of time and current [28]. The values of ϕ_{p} obtained from cyclic voltammetry in Fig. 2 and galvanostatic measurement in Fig. 5 are in good agreement. Moreover, the values of maximum (ϕ_{pit}) are dependent upon the constant current density applied (see Fig. 5). It is observed in galvanostatic curves that the slope of the linear increase of the potential against time

increases with the increase of current density. This behaviour is attributed to the rise in the rate of ion transport across the pre-existing oxide film toward the metal/oxide interface, where the growth of the oxide film takes place [29]. A rise in the current density enhances the electric field across the oxide film, which results in the increase in the rate of ion transport. Therefore, the higher the current density is, the higher the rate of the oxide growth is. This may explain the positive shift of the pitting potential with the increase in current density.

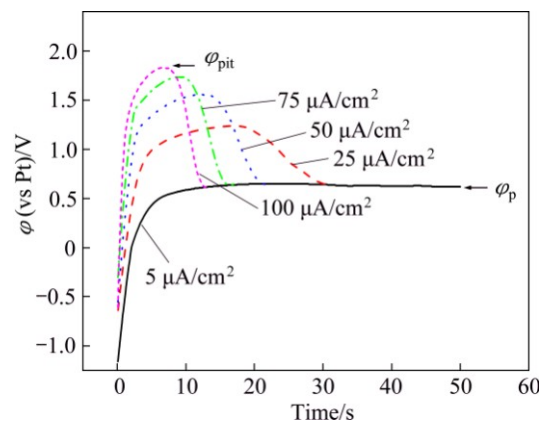


Fig. 5 Potential–time transients recorded for Hf in 0.06 mol/L Et_4NBr anhydrous isopropanol (50%) and ACN (50%) solutions at 30 °C and different current densities

3.4 Potentiodynamic measurements

Figure 6 shows the effect of the potential scanning rate (v) on the potentiodynamic polarization of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions with 0.06 mol/L Et_4NBr at 30 °C. This figure suggests the importance of the appropriate choice of v when determining the pitting potentials. It is observed that increasing sweep rate shifts ϕ_{pit} to more noble values. This suggests that the time of anodization plays an

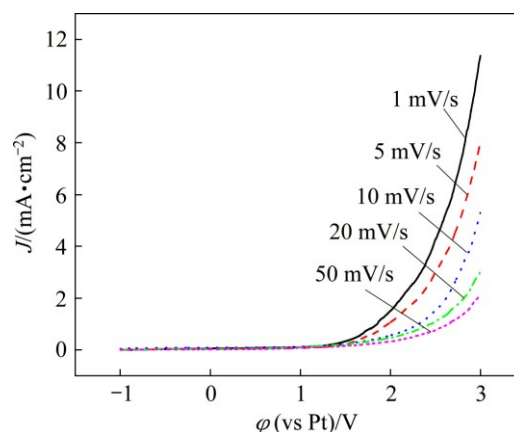


Fig. 6 Potentiodynamic polarization curves of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at 30 °C and various potential scanning rates (v)

important role in determining the pitting potential. This can be explained in terms of the incubation time [30] needed for Br^- to break down the oxide layer and reach the base metal surface. Increasing the sweep rate corresponds to less time to form a soluble complex at a certain potential. As a result, the passive film is not rapidly dissolved, resulting in the formation of a thicker passive layer. Consequently, for a higher scanning rate, pitting initiation occurs only at more positive potentials, corresponding to a sufficiently short pit incubation time.

Figure 7 illustrates the effect of the temperature on the potentiodynamic polarization curves of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions with 0.06 mol/L Et_4NBr at a scanning rate of 5 mV/s. As the solution temperature is increased, ϕ_{pit} shifts to more negative values, indicating an increased susceptibility to pitting. The facilitating influence of increasing temperature can be explained on the basis that the solubility of oxide film is enhanced with an increase in temperature [31]. This may make the thickness of the passive film decrease and its porosity increase and hence a less protective film results. In addition, the increasing temperature can accelerate the rates of diffusion of the reactant and product species into and from the pit cavity.

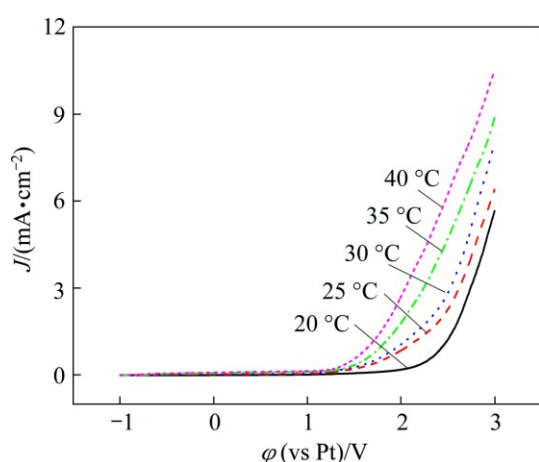


Fig. 7 Potentiodynamic polarization curves of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions containing 0.06 mol/L Et_4NBr at scanning rate of 5 mV/s and various temperatures

Figure 8 illustrates the effect of the Et_4NBr concentration on the potentiodynamic polarization of Hf in anhydrous isopropanol (50%) and ACN (50%) solutions at scanning rate of 5 mV/s and 30 °C. It is observed that the increase in Et_4NBr concentration shifts ϕ_{pit} in a negative direction, corresponding to the increased susceptibility towards pitting. These results might be due to the weakening of the passive film as a result of the competition among its formation, the formation of the soluble intermediate and the increase of the number of aggressive Br^- ions that dissolve the

passive layer [19,32]. The higher the bulk Br^- ion concentration is, the higher the local Br^- ion concentration that is responsible for initiating pit formation in defect areas and enhancing the exposed metal dissolution is.

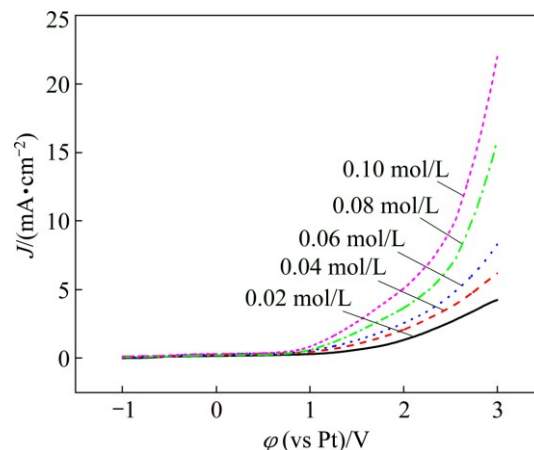


Fig. 8 Potentiodynamic polarization curves of Hf in isopropanol (50%) and ACN (50%) solutions containing various concentrations of Et_4NBr at scanning rate of 5 mV/s and 30 °C

Figure 9 presents the effect of the ACN concentration on the potentiodynamic polarization of Hf in anhydrous isopropanol and ACN solutions with 0.06 mol/L Et_4NBr at scanning rate of 5 mV/s and 30 °C. It is clear that increasing the ACN concentration shifts ϕ_{pit} towards more negative potentials, corresponding to decreased resistance towards pitting. Such promoting effect of ACN concentration on the pitting corrosion process can be explained on the basis that an increase in ACN concentration accelerates the rates of migration and diffusion of the reactant.

3.5 EIS measurements

EIS is a very convenient technique that is helpful

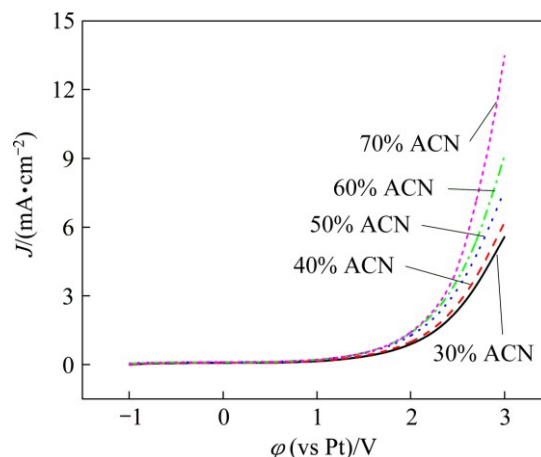


Fig. 9 Potentiodynamic polarization curves of Hf in isopropanol and ACN solutions of various concentrations with 0.06 mol/L Et_4NBr at scanning rate of 5 mV/s and 30 °C

for analyzing various steps involved in an electrochemical reaction by measuring the impedance system response to a small AC potential signal in a wide frequency range [33]. Figure 10 shows the characteristic Nyquist and Bode diagrams of Hf in isopropanol and ACN solutions of various concentrations with 0.06 mol/L Et_4NBr at 2.5 V (vs Pt) and 20 °C. Although various processes occur simultaneously, only one semi-circle (i.e., time constant) in the Nyquist diagrams is observed. This result could either denote that the time constants of the individual processes, suggested by BRETT [34],

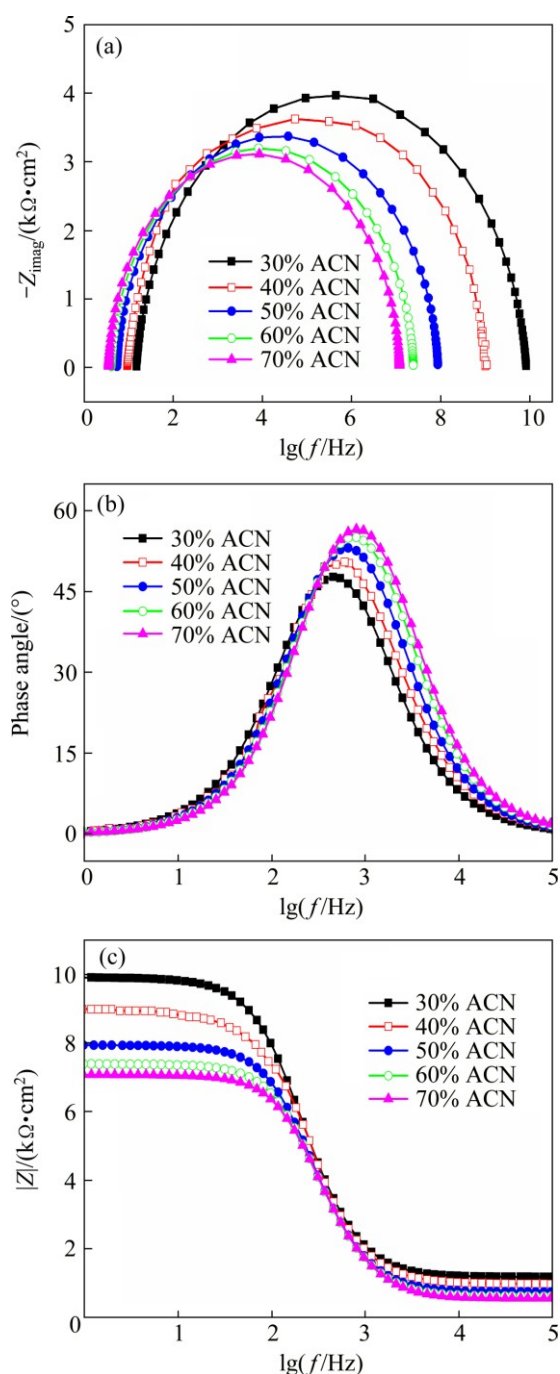


Fig. 10 Complex plane impedance plots recorded for Hf in isopropanol and ACN solutions of various concentrations with 0.06 mol/L Et_4NBr at 2.5 V (vs Pt) and 20 °C

strongly overlap, or that one process dominates and, therefore, excludes the other processes in this frequency range. The other possible explanation for this capacitive time constant is the oxide film itself. The oxide film is considered a parallel circuit of a resistor due to ionic conduction in the oxide, and a capacitance due to the dielectric properties of the oxide. It is clear that the diameter of the semicircle decreases with the increase in ACN concentration. This can be explained in terms of its promoting effect on the breakdown of the passive oxide film, initiation and propagation of pitting corrosion. Depressed semicircles are usually obtained for practical electrode/solution interface, which is considered to be related to the roughness of electrode surface. Results of the present work indicate that the corrosion of Hf in isopropanol and ACN solutions of these concentrations at 2.5 V (vs Pt) enhances the roughness of the Hf surface resulting from the formation of pits.

A more effective method, which better exhibits the frequency dependence of the impedance data, is the so-called Bode diagram, as shown in Fig. 10(b). The high frequency limit ($f > 10$ kHz) represents the solution resistance (R_s). The low frequency limit ($f < 2$ Hz) corresponds to the sum of R_s and the charge transfer resistance (R_{ct}), which is, in the first approximation, determined by both the electronic conductivity of the oxide film and the polarization resistance of the dissolution and repassivation processes. In these two borderline cases (at high and low frequencies) the phase angle (θ) between current and potential assumes a value of $\sim 0^\circ$, corresponding to the resistive behaviour of R_s and ($R_s + R_{ct}$). At medium frequencies capacitive phenomenon of the system is evident, determined by the dielectric properties of the oxide film. The phase shift between current and voltage approaches values from 45° to 60° . The capacitive time constant is attributed to the formation of the oxide layer or to the oxide layer itself, namely the oxide film is considered to be a parallel circuit of a resistor due to ionic conduction in the oxide, and a capacitance due to the dielectric properties of the oxide.

It is necessary to match an appropriate model for the impedance which can be used to fit the experimental data and extract the parameters which characterize the corrosion process. The matching one is presented in Fig. 11, in which R_s represents the electrolyte resistance, and R_{ct} corresponds to the charge transfer resistance. Q is a constant phase element (CPE) related to the oxide film capacitance and the double layer capacitance. CPE is a constant phase element used to describe the distribution of the microscopic level by an empirical impedance function of the type [35]:

$$Z_{cpe} = [Q(j\omega)^n]^{-1} \quad (3)$$

where ω is the angular frequency, $j^2 = -1$ is the imaginary number and n is the CPE exponent, which reflects the deviation of the capacitance from the ideal capacitive behavior. The value of -1 is characteristic of an inductance, the value of 1 corresponds to a capacitor, the value of 0 corresponds to a resistor and the value of 0.5 can be assigned to diffusion phenomenon. The fitting electrochemical parameters are listed in Table 3. The capacitance increases as the ACN concentration is enhanced. This trend can be explained by assuming an oxide film thickness decrease with increasing ACN concentration, because the thickness of the oxide film is inversely proportional to the calculated electrode capacitance [36]. Moreover, the resistances of the solution and charge transfer decrease evidently with increasing ACN concentration, which confirms the polarization results.

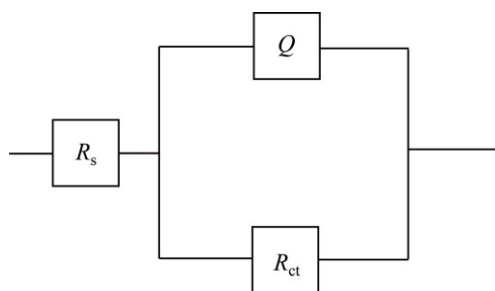


Fig. 11 Equivalent circuit used to fit experimental impedance data

Table 3 Electrochemical parameters obtained by fitting

ACN content/%	$R_s/(\Omega \cdot \text{cm}^2)$	$Q/(\text{s}^n \cdot \text{W}^{-1} \cdot \text{cm}^{-2})$	n	$R_{ct}/(\Omega \cdot \text{cm}^2)$
30	1153.45	1.4724	0.91	8806.55
40	998.57	3.2487	0.90	8037.43
50	769.66	3.5931	0.88	7190.34
60	650.68	4.6815	0.89	6690.32
70	440.90	5.1023	0.91	6582.10

3.6 Current/time transient measurements

In order to gain more information about the kinetics of passivity breakdown of the Hf electrode in isopropanol (50%) and ACN (50%) solutions, potentiostatic current density–time transients are recorded at various positive step potentials $\varphi_{s,a}$. Figure 12 represents the current transients of Hf in isopropanol (50%) and ACN (50%) solutions with 0.06 mol/L Et_4NBr at 20 °C. For $\varphi_{s,a} < \varphi_{\text{pit}}$, as shown in Fig. 12(a), the current densities gradually decrease to stable state values (J_{ss}), suggesting that the low potential is not enough to induce pitting corrosion. This tendency is ascribed to the formation of an oxide passive layer on the anode surface. It is interesting to note that in Fig. 13, a positive

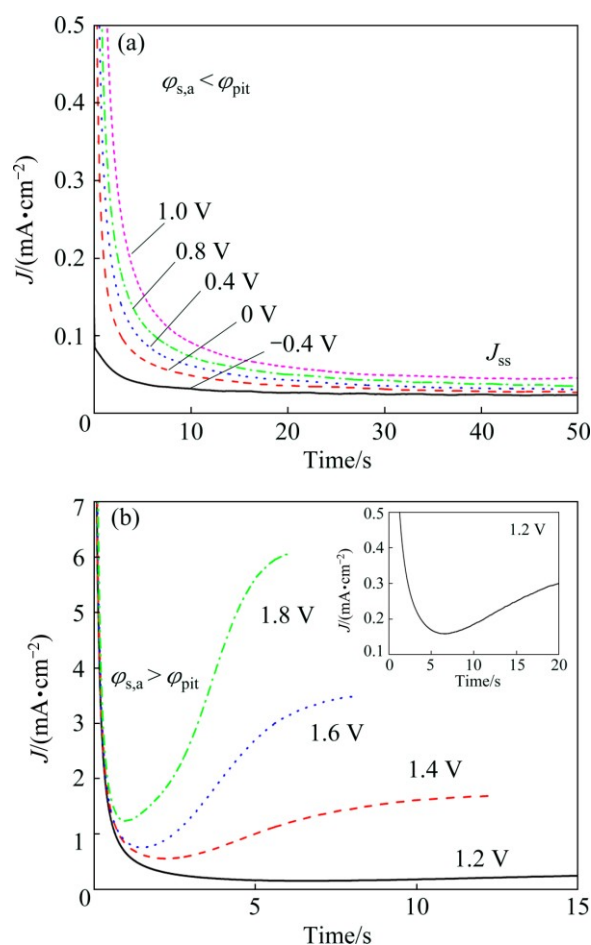


Fig. 12 Potentiostatic current density–time transients recorded for Hf in isopropanol (50%) and ACN (50%) solutions with 0.06 mol/L Et_4NBr at 20 °C and various $\varphi_{s,a}$ (Inset: Potentiostatic current density–time transient of Hf in isopropanol (50%) and ACN (50%) solutions with 0.06 mol/L Et_4NBr at 1.2 V (vs Pt): (a) $\varphi_{s,a} < \varphi_{\text{pit}}$; (b) $\varphi_{s,a} > \varphi_{\text{pit}}$)

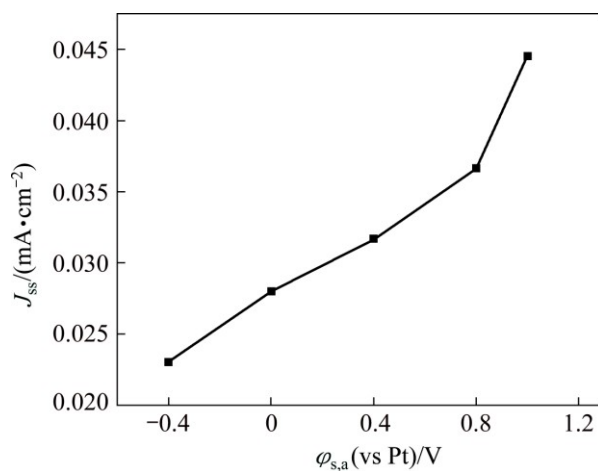


Fig. 13 Dependence of $\varphi_{s,a}$ on steady state current density (J_{ss}) for Hf in isopropanol (50%) and ACN (50%) solutions with 0.06 mol/L Et_4NBr at 20 °C (values of J_{ss} are taken from Fig. 12(a) at $t=40$ s)

correlation between J_{ss} and the potential applied is observed. This result may be related to the thinning of the passive layer, namely the more positive the potential applied, the thinner the passive layer will be.

In this case, if the contribution of the double layer charging process is neglected, the overall transient current density can be indicative of two main processes, namely the passive layer growth (J_{gr}) and Hf electrodisolution through the passive layer (J_{dis}),

$$J = J_{gr} + J_{dis} \quad (4)$$

The growth of the passive layer may be attributed to the establishment of an oxide film on the electrode surface. The dissolution of the Hf through the passive layer can be assigned to the cation diffusion from the metal/film interface to the film/solution interface. It is important to note that as time goes on, the current density is nearly a constant. This can be explained on the basis that the rates of these two processes are nearly the same at the steady state current, resulting in the nearly constant thickness of the passive film.

However, for $\varphi_{s,a} > \varphi_{pit}$, as shown in Fig. 12(b), the current density initially decreases to a minimum value at a certain incubation time (t_i) and then rises until a steady state current is attained. The steady state current is probably achieved between the metal dissolution and oxide film formation including a blockade by pitting corrosion product. This increase in current indicates that pit growth is the dominant process and a number of well-developed pits could be observed following this active period. In this case, the overall transient current density is given by three contributions:

$$J = J_{gr} + J_{dis} + J_{pit} \quad (5)$$

where J_{pit} is the pit growth current density.

It is worth noting that both the incubation time (t_i) and the pit growth current density, J_{pit} (the rising part of the transient), depend on the values of $\varphi_{s,a}$. As $\varphi_{s,a}$ is made more positively, t_i becomes shorter and J_{pit} becomes larger.

Figure 14 presents the current transients of Hf in isopropanol (50%) and ACN (50%) solutions containing Et_4NBr of various concentrations at 20 °C and 2.5 V (vs Pt). These suggest that as the concentration of Et_4NBr is increased, t_i becomes shorter and J_{pit} becomes larger. Relevant information about the pitting growth of Hf can be derived from the analysis of the rising part of the current transients which in all cases fit J_{pit} vs $t^{1/2}$ linear relationships (not shown here). These results can be described by [37]

$$J_{pit} = At^{1/2} \quad (6)$$

and suggest that the pit growth is an instantaneous three-dimensional nucleation. The values of A are associated with $\varphi_{s,a}$, $[\text{Br}^-]$, $[\text{ACN}]$ and temperature.

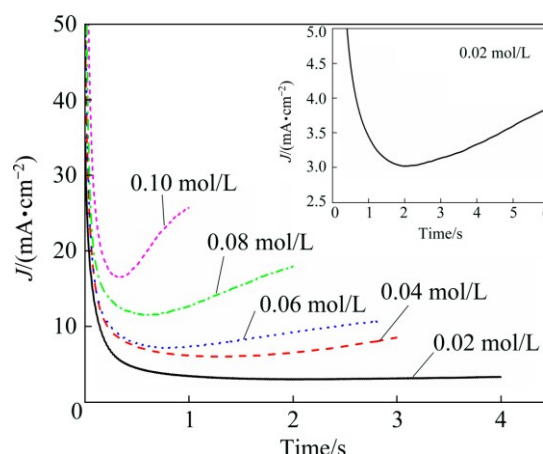


Fig. 14 Potentiostatic current density–time transients recorded for Hf in isopropanol (50%) and ACN (50%) solutions containing Et_4NBr of various concentrations at 20 °C and 2.5 V (vs Pt) positive to φ_{pit} under these conditions (Inset: Potentiostatic current density–time transients of Hf in isopropanol (50%) and ACN (50%) solutions with 0.02 mol/L Et_4NBr at 2.5V (vs Pt))

4 Conclusions

1) Open circuit potential measurements, potentiodynamic anodic polarization, cyclic voltammetry, galvanostatic, potentiostatic and impedance techniques, complemented by ICP-AES analysis and SEM examinations, were applied to investigating the electrochemical behavior of Hf in anhydrous isopropanol and ACN solutions containing Et_4NBr . Results reveal that the open circuit potential gets more positive due to the increased passivity of the surface oxide film with increasing immersion time until it reaches a steady state value. Potentiodynamic anodic polarization curves do not exhibit an active dissolution region near corrosion potential due to the presence of HfO_2 film on the electrode surface, which is followed by pitting corrosion as a result of the passivity breakdown by the aggressive attack of Br^- .

2) Cyclic voltammetry measurements reveal that repetitive cycling φ_{pit} shifts to more positive values, whereas φ_p shifts to a negative direction, corresponding to a decreased susceptibility to pitting. The analysis of the potential–time transients reveals that the applied anodic current density has a significant influence on the values of φ_{pit} . On the other hand, the φ_p values are independent of the applied current density. SEM images confirm the existence of pits on the electrode surface.

3) The potentiostatic current density–time transients show that as the concentration of ACN and the potential applied are increased the incubation time (t_i) becomes shorter and the pit growth current density (J_{pit}) becomes larger. The pit growth is an instantaneous three-

dimensional nucleation. Impedance measurements show that the resistances of the solution and charge transfer decrease with the increase of ACN concentration.

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铅在含溴离子无水异丙醇与乙腈溶液中的腐蚀行为

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摘 要: 运用电化学测量、ICP-AES 分析和 SEM 形貌观测技术研究铅在 Et_4NBr 为支持电解质的无水异丙醇与乙腈(ACN)溶液中的电化学腐蚀行为。结果表明, 开路电位随着浸入时间的增加而不断变正, 直到达到一个较稳定数值, 开路电位的上升与表面氧化膜钝化有关。在线性极化曲线中接近腐蚀电位的阳极极化段未出现活性溶解, 这是其表面自发形成钝化膜的结果, 之后, 电位继续增加, 点蚀发生。SEM 形貌图证明电极表面点蚀坑的存在。循环伏安曲线与恒电流测量可以确定点蚀电位(φ_{pit})和再钝化电位(φ_{p})。 φ_{pit} 随着扫描速率的增加而增大, 但随着温度、溴离子浓度和 ACN 浓度增加而减小, 连续重复扫描会使 φ_{pit} 正移。诱导时间对于点蚀长大必不可少。阻抗谱表明, 溶液电阻和电荷转移电阻随着 ACN 浓度升高而降低。

关键词: 腐蚀行为; 铅; 乙腈; Et_4NBr ; 电化学方法; 点蚀; 钝化膜

(Edited by Wei-ping CHEN)