Monatshefte für Chemie 129, 799–810 (1998)

Monatshefte für Chemie
Chemical Monthly

On the Role of Iodine in the Oxidation of Zr in KI Medium

A. A. Ghoneim*, **H. M. Saleh,** and **F. E. El-Taib Heakal**

Department of Chemistry, Faculty of Science, Cairo University, Giza, Egypt

Summary. The influence of I_2 on the kinetics of spontaneous as well as galvanostatically induced growth of insulating oxide films on Zr metal was studied in KI solutions as a function of concentration. The stability of the anodic oxide films on Zr surfaces was investigated by measuring the potential and the two impedance components of the electrode-solution interface under currentless conditions. In all cases, the passivating oxide films were found to grow with time. The anodic polarization carried out at different current densities produced charging curves whose potentials increases with current density. The presence of increasing amounts of I_2 in the KI medium always shifts the potential of ZrO_2 films towards more positive values, most probably because the formed triiodide ion (I_3^-) in the electrolyte enhances the formation of zirconium-iodine species at the electrode surface. A dissolution-precipitation mechanism was proposed which is consistent with the above results as well as with the results of the effect of temperature on the currentless film growth process.

Keywords. Electrochemistry; Oxide films; Zr; Surfaces; Alkali halide metals.

Zur Rolle des Iod bei der Oxidation von Zr in KI-hältigem Medium

Zusammenfassung. Der Einfluß von I_2 auf die Kinetik von sowohl spontanem als auch von galvanostatisch induziertem Oxidfilmwachstum auf metallischem Zr wurde in kaliumjodidhaltigen Lösungsmitteln als Funktion der Konzentration untersucht. Die Stabilität der anodischen Oxidfilme auf der Zirkonoberfläche wurde durch Messung des Potentials und der beiden Impedanzkomponenten der Elektroden-Lösungs-Grenzflächen bestimmt. In allen Fällen nahm die Dicke der passivierenden Oxidfilme als Funktion der Zeit zu. Die anodische Polarisation wurde bei verschiedenen Stromdichten ausgeführt; man erhielt Ladungskurven, deren Potentiale mit der Stromdichte ansteigen. Die Gegenwart von I_2 im kaliumjodidhaltigen Medium verschiebt das Potential des ZrO_2-Films zu positiven Werten, wahrscheinlich durch vermehrte Bildung von Zirkon-Iod-Species an der Elektrodenoberfläche, die durch I_3^- begünstig wird. Es wird ein Lösungs-Kristallisations-Mechanismus vorgeschlagen, der sowohl mit den obigen Resultaten als auch mit Ergebnissen bezüglich der Temperaturabhängigkeit des stromlosen Filmwachstumsvorgangs in Einklang steht.

Introduction

The electrochemical behaviour of Zr finds growing interest, mainly because of the stability of its passive film towards corrosion and its small cross-section for neutron

---

* Corresponding author

absorption, which make it a suitable material for nuclear fuels [1], but also for its wide application in chemical industries.

It is well established that Zr has great resistance to corrosion in alkaline or acidic solutions [2, 3] because of the formation of a thin protective oxide film which acts as a barrier layer [4]. ZrO_2 was found to be the main constituent of this protective film. It has a special structure which is crystalline, unlike other valve metal oxides [5].

The present study presents an attempt to investigate the role of iodine in the reactivity of the oxide growth process on Zr metal in potassium iodide either in absence or in presence of an electric field, *i.e.* spontaneously or anodically. The stability of the anodic oxide films on Zr surfaces was studied by measuring the potential and the two impedance components of the electrode-solution interface under currentless conditions.

Results and Discussions

Effect of I_2 in absence of an electric field

The open circuit behaviour of the mechanically polished Zr electrode was studied in 0.1 *M* KI solution and in solutions containing an increasing amount of iodine. As shown in Fig. 1, the variation of the reciprocal capacitance which is proportional to the oxide thickness [6] increases linearly with time indicating film thickening [7]. In each solution, the plots consist of two linear regions whose intersection point is associated with two different rates of growth, representing the inner and the outer layer [9]. Similar behaviour has been reported previously for many metals and can

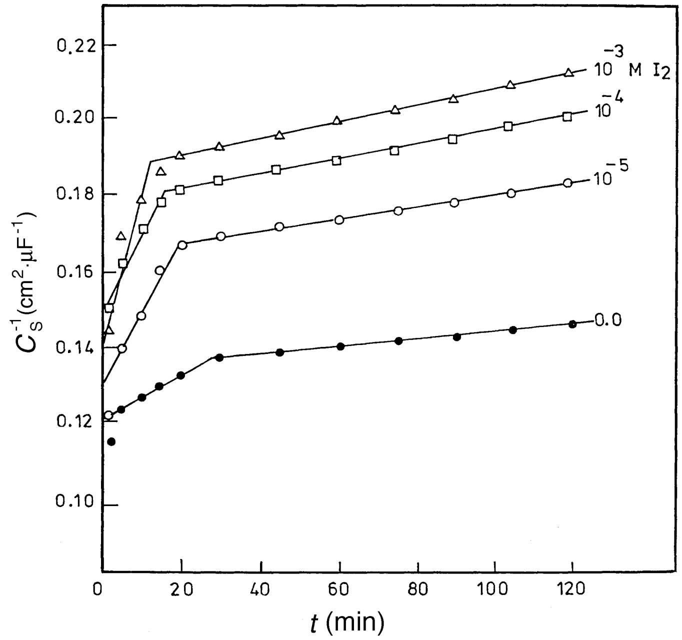

Fig. 1. Variation of C_s^{-1} with time for a Zr electrode in 0.1 *M* KI + *x M* I_2 solution ($x = 0.0$, 10^{-5}, 10^{-4}, and 10^{-3} *M*)

Table 1. Comparison of the thickening coefficients and angle θ characterizing the film growth on a Zr electrode in 0.1 M KI + x M I_2 solutions

Concentration (M)	$\beta_1 \times 10^3$	$\beta_2 \times 10^4$ ($cm^2 \cdot \mu F^{-1} \cdot min^{-1}$)	$\beta' \times 10^4$	θ (°)
0.0	0.75	1.00	2.74	29.89
10^{-5}	2.13	1.76	7.77	32.73
10^{-4}	2.20	2.94	7.87	34.28
10^{-3}	4.33	1.25	15.1	35.54

be attributed to the duplex nature of the formed film [9, 10]. The variation of oxide thickness (C_s^{-1}) with time may be expressed in the form

$$C_s^{-1} = \alpha + \beta t \tag{1}$$

where α and β are constants, (β: rate coefficient for oxide thickening ($dC_s^{-1}/dt; cm^2 \cdot \mu F^{-1} \cdot min^{-1}$); α: experimental factor). Such behaviour can be explained by assuming that the air-formed oxide film, the nature of a barrier layer; its thickening in the solution proceeds until it attains a definite thickness, and a less dense layer.

The values of the rate coefficients of film thickening for the inner layer (β_1) and the outer layer (β_2) increase regularly with increasing amount of the iodine added to the solution (Table 1). The inner layer of the film always grows at a notably higher rate than the outer layer. This behaviour may be rationalized in terms of oxide layer formation by a dissolution-precipitation mechanism [11].

The results of potential measurements (Fig. 2) indicate a continuous drift of E towards more noble values from the moment of immersion in the electrolyte. This feature may indicate that the pre-immersion oxide film on the metal surface was too thin to impart complete passivity [12]; therefore, thickening of the surface film would continue until attaining a steady state [13]. The final steady state potentials are shifted to more positive values as the iodine concentration is increased. In general, the results reveal that the presence of iodine in KI solution favours the formation of a thicker film at the electrode surface. Furthermore, this thicker film has more passivating properties than the thin one which is formed in the I_2 free iodide solution. It is generally accepted that under open circuit conditions, a strong electric field is assumed to originate from the adsorption of the anions on the oxide covered electrode [14]. This causes the creation of image charges of the same magnitude but of opposite sign at the metal/oxide interface sufficient to increase the thickness of the oxide. Consequently, the I_3^- ion will be more effective in this respect as it has a larger volume and hence more adsorbability than the I^- ion. The above behaviour may be also interpreted by assuming that iodine participates in enhancing the formation of zirconium-iodine species at the electrode surface [11] which shift the potential of the Zr electrode towards positive values and thus sustain the process of formation and growth of the oxide film.

Further support for the above conclusion may be gained considering the Zr electrode impedance in a complex plane. For this purpose, the effect of frequency on the two impedance components C_s and R_s was measured when their values were

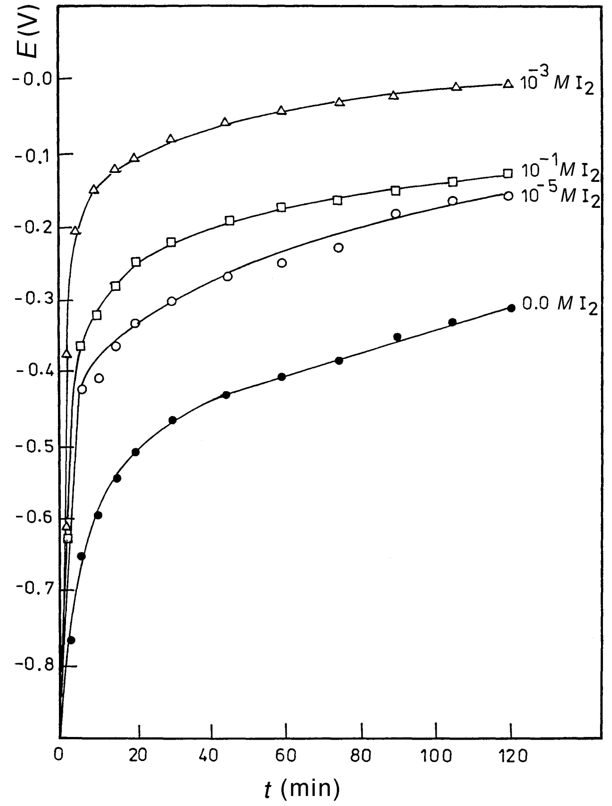

Fig. 2. Variation of open circuit potential E, with time for a Zr electrode in 0.1 M KI + x M I_2 solution ($x = 0.0$, 10^{-5}, 10^{-4}, and 10^{-3} M)

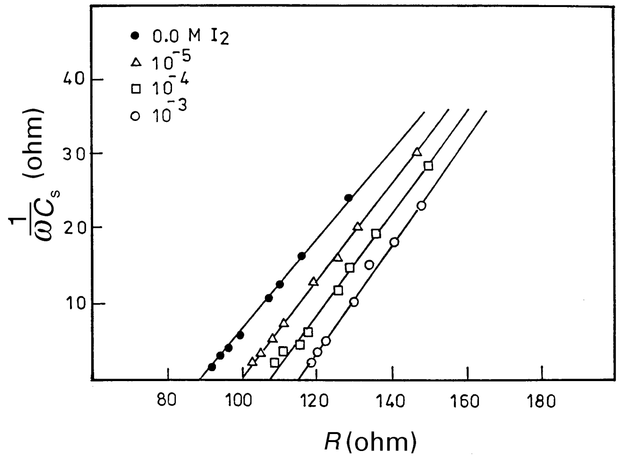

Fig. 3. *Nyquist* diagram for a Zr electrode in 0.1 M KI + x M I_2 solution ($x = 0.0$, 10^{-5}, 10^{-4}, and 10^{-3} M)

more or less constant. The corresponding *Nyquist* diagram in the frequency range between 0.2 and 15 kHz is shown in Fig. 3.

In this diagram, the real part of the impedance, R_s, is plotted against the imaginary part $1/\omega C_s$ ($\omega = 2\pi f$, f being the frequency in Hz). The slope of the straight lines, $d(1/\omega C_s)/dR_s$, gives an indication about the relative insulating properties of the passive layer on the zirconium surface [15].

The angle of this slope corresponds to the phase shift θ which depends upon the surface state. This angle varies between a maximum limit of 90° for an ideal dielectric surface oxide with excellent insulating properties and a minimum limit of 0° for very reactive systems. As shown in Table 1, the value of θ which is equal to $\tan^{-1}(d\omega C_s^{-1}/dR_s)$ was found to increase gradually parallel to the β values, *i.e.* with increasing of iodine concentration. These results reveal in general that the surface reactivity towards oxide thickening and passivity increases with increasing iodine concentration.

Effect of I_2 in presence of an electric field

Effect of current density

The growth of the anodic oxide film on mechanically polished Zr was performed galvanostatically at different current densities (cd) ranging between 2 and 7 mA per electrode area in $0.02\,M$ KI solution to which a fixed amount of $10^{-4}\,M$ I_2 was added. The variation of potential with time was followed at very short intervals. The shapes of the charging curves are shown in Fig. 4. In all cases, an almost linear increase of the potential with time was observed. At low cd, the potential rises slowly with time and increases continuously with increasing cd. However, the rate of voltage rise decreases after some time during anodization leading to breaks in the plots.

The appearance of a break in the charging curve indicates that the film formation is not the only reaction occurring during anodization as previously reported for Zr [16] and Sb [17]. There is a measurable dissolution action which

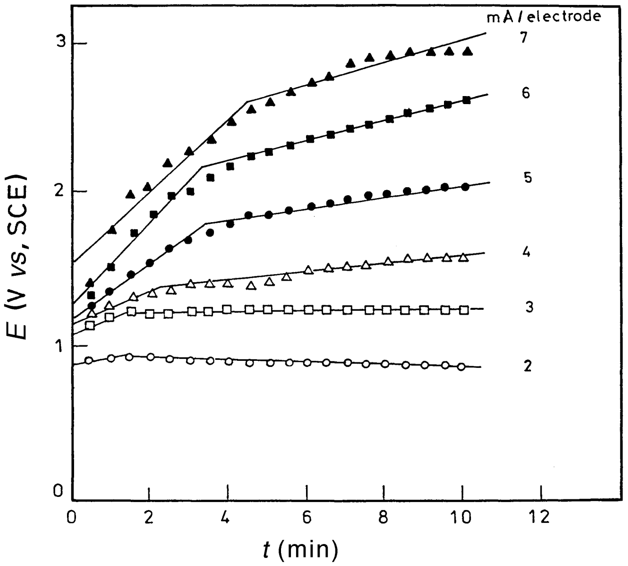

Fig. 4. Anodic charging curves for Zr electrode in 0.02 M KI + 10^{-4} M I_2 solution at different current densities

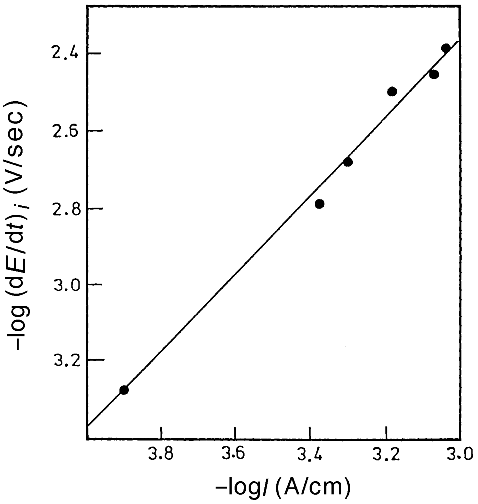

Fig. 5. Relation between logarithm of oxide formation rate and logarithm of current density in 0.02 M KI + 10^{-4} M I_2 solution

starts after ~2–5 minutes of anodization. The oxide formation rate at constant current density represented by (dE /dt)$_i$ during the steep potential rise of the anodic charging curves has been related for most valve metals to the anodizing current density (*i*) by the empirical equation [18]

$$(\mathrm{d}E/\mathrm{d}t)_\mathrm{i} = ai^b \tag{2}$$

where *a* and *b* are empirical constants characteristic of the system.

The validity of this equation is shown in Fig. 5. The applicability of equation (2) to the present results may be taken as a criteria for the behaviour of Zr metal as a valve metal in KI + I_2 solution. This conclusion is in good agreement with the previously reported results [11] where the typical behaviour of a valve metal for the potentiodynamic electroformation and growth of a ZrO_2 film on zircaloy-4-electrodes in an acid solution containing iodide and iodine has been observed.

Effect of I_3^- Concentration

Figure 6 shows the results obtained with a mechanically polished Zr electrode at a selected cd of 3 mA per electrode in 0.02 M KI + xM I_2, x varying between $10^{-5}M$ and $10^{-3}M$). The results reveal two different trends for the charging curves. Thus, at concentrations of I_3^- lower than $2.5\times10^{-4}M$ no change of potential was observed during the time limit of the experiments. However, at higher I_3^- concentration ($\geq 2.5\times10^{-4}M$), the normal shape of the *E/t* displays was obtained, and the oxide film growth takes place with two different rates which increase with the amount of I_2 present in the iodide solution. The increase of I_2 concentration shifts the whole charging curves towards more positive potential values, probably because of increasing anion adsorption on the oxide surface which in turn increases the oxide formation rate.

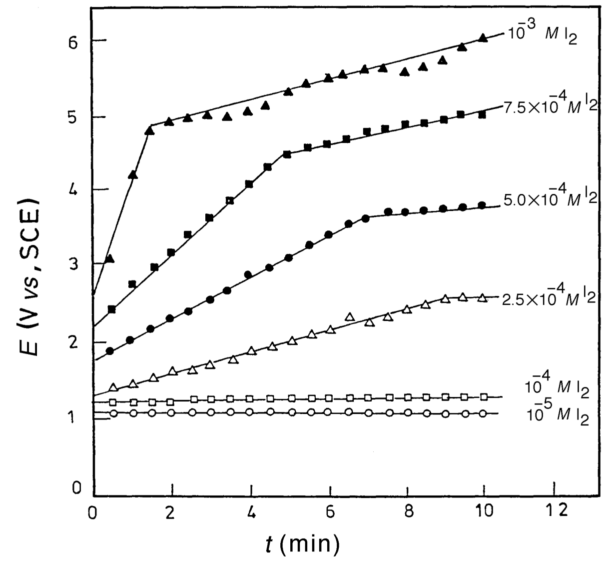

Fig. 6. Anodic charging curves for a Zr electrode at $cd = 3\,\mathrm{mA\cdot cm^{-2}}$ in 0.02 *M* KI + *x* *M* I_2 solutions ($x = 10^{-5}$, 10^{-4}, 2.5×10^{-4}, 5.0×10^{-4}, 7.5×10^{-4}, and 10^{-3} *M*)

Currentless behaviour of anodic ZrO_2

KI solution

To study the effect of KI concentration on the open circuit behaviour of anodic ZrO_2, the oxide film was first formed galvanostatically at $1.0\,\mathrm{mA\cdot cm^{-2}}$ on a mechanically polished Zr electrode until 30 V in 0.05 *M* H_2SO_4 solution. After formation of the oxide film, the electrode was washed with triply distilled water and immersed quickly into KI solutions of different concentrations (0.01–2.0 *M*). The open circuit potential E, capacitance C_s, and resistance R_s of the formed anodic ZrO_2 film were followed with time for about 2 hours.

As can be seen from Fig. 7, a linear increase of C_s^{-1} with the immersion time t was obtained for the first 10 minutes, indicating film thickening. After a short period (10 min) C_s^{-1} attained a steady value, and no further increase in the oxide film thickness occurred. The first linear relationship between C_s^{-1} and t follows Eq. (1) which indicates that the growth mechanism of the oxide film on the ZrO_2 surface in KI medium is a zero order reaction. Values of oxide thickening coefficients were calculated as a function of iodide ion concentration and are given in Table 2. The results indicate a marked decrease in the rate of oxide thickening with increasing KI concentration. This is easily rationalized as the iodide ion can be adsorbed at the oxide covered electrode with further formation of zirconium iodide species through a dissolution-precipitation mechanism [19]. When the iodide concentration is increased, the oxide production-dissolution process is shifted more towards dissolution with an ultimate decrease in the oxide thickening coefficient β. Moreover, when the two rates of the opposing processes are balanced after certain period of time, no variation of film thickness is observed, and C_s^{-1}

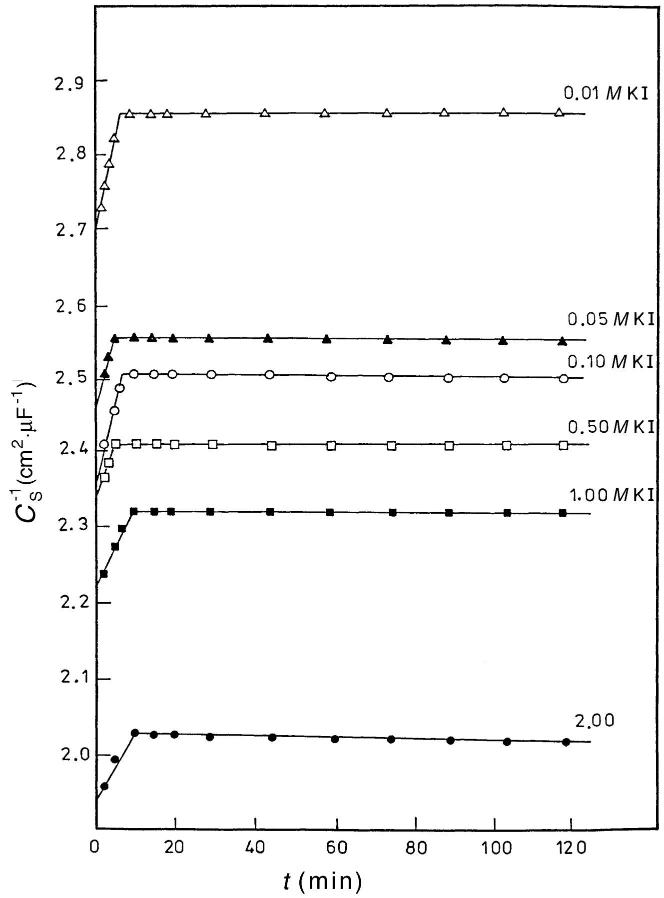

Fig. 7. Variation of C_s^{-1} with time for the preformed anodic ZrO_2 film in KI solutions of different concentrations

Table 2. Currentless thickening coefficient β in KI solutions of different concentrations

Concentration (*M*)	β (cm^2 · μF^{-1} · min^{-1} × 10^3)
0.01	225
0.05	175
0.10	17
0.50	15
1.00	10
2.00	8

ceases to increase with time. On the other hand, the data for R_s did not show any variation with the immersion time in the KI solutions. As expected, however, R_s value decrease with increasing KI concentration, presumably because R_s is a less sensitive index for the formation/dissolution process of the oxide [10, 15] and

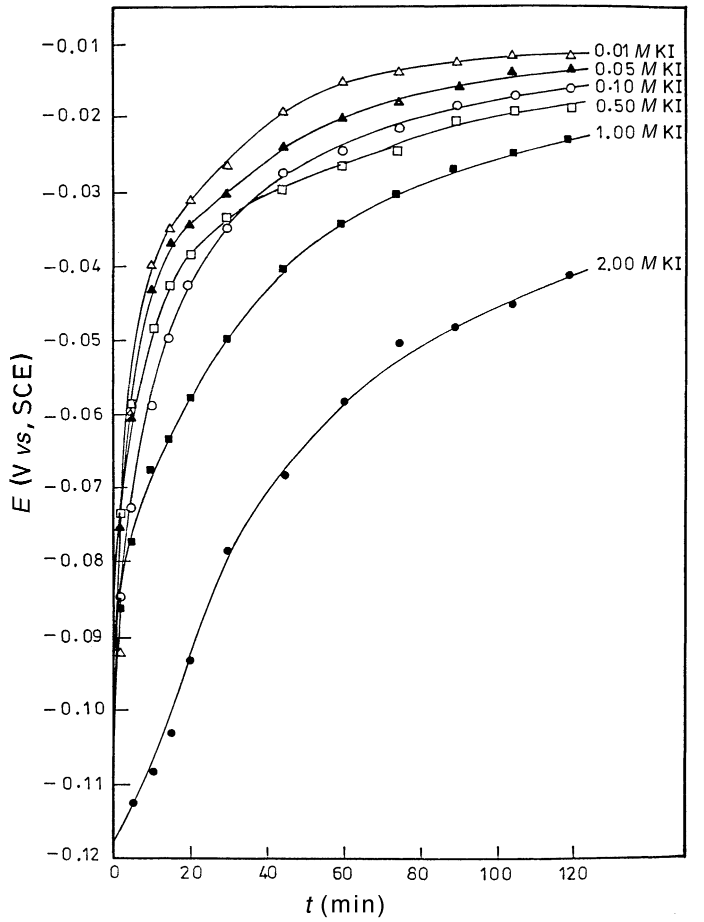

Fig. 8. Variation of the open circuit potential E with time for the preformed anodic ZrO_2 film in KI solutions of different concentrations

hence its value does not relate to the properties of the oxide but rather to those of the solution.

The tendency of the open circuit potential E to move towards more positive values in any of the iodide solutions (Fig. 8) provides additional evidence for the currentless oxide film formation and growth on the anodic ZrO_2 film in KI solution.

It has been reported that the rates of chemical dissolution (r) of anodic oxide films on some valve metals including Zr are related to the energy of defect formation, in the oxide (E_f) [20]. The value of r itself is proportional to the concentration of the intrinsic defects, (D) in a given oxide. The author has found a linear relation between $\ln r$ and E_f; the intrinsic defects in the oxide film play an asymmetrical role, and in his case, their constructive action outweighed their destructive effect. Our present results are in good agreement with this idea; they show clearly that soon after immersing the ZrO_2 film in the iodide solution for a short period of time (~10 min), the intrinsic defects in the anodic oxide film equally enhance each of the two reverse processes, *i.e.* oxide formation (constructive) and oxide dissolution (destructive).

$KI + I_2$ solution

The effect of iodine addition to the iodide solution on the currentless thickening process of the preformed anodic oxide film was examined. For this purpose, an anodic ZrO_2 film with a definite thickness was formed in 0.05 *M* H_2SO_4 until a potential of 30 V under a controlled cd of 1.0 mA · cm^{-2}, and the electrode was transferred quickly to the naturally aerated 0.5*M* KI solution containing various concentrations of iodine (0.0, 10^{-5}, 10^{-4}, and 10^{-3}*M*). The open circuit potential and capacitance of the oxide coated surface were followed for a period of 2 hours at 30°C.

The potential *E* was found to increase with time in the noble direction by a similar fashion to that described before. As the I_3^- ion concentration in the solution is increased the potential is shifted gradually towards less positive values. Obviously, in absence of an electric field the presence of I_3^- ion retards greatly the film thickening process on the preformed anodic ZrO_2 film in the iodide medium. This is in good agreement with the results of capacitance measurements shown in Fig. 9. Within the time of the initial part of the curve, the outer layer of the ZrO_2 film is assumed to thicken by a rate which was found to decrease as the concentration of I_3^- in the iodide solution is increased.

It has to be noted generally that in an iodide solution the role played by iodine in the reactivity of anodic oxide film on Zr metal in absence of the field is opposite to its role in presence of the field. Thus, whereas I_3^- enhances oxide formation and growth under anodization, it retards the film thickening process under currentless conditions. This behaviour may be attributed to the difference in the nature of the step controlling the process in the two cases.

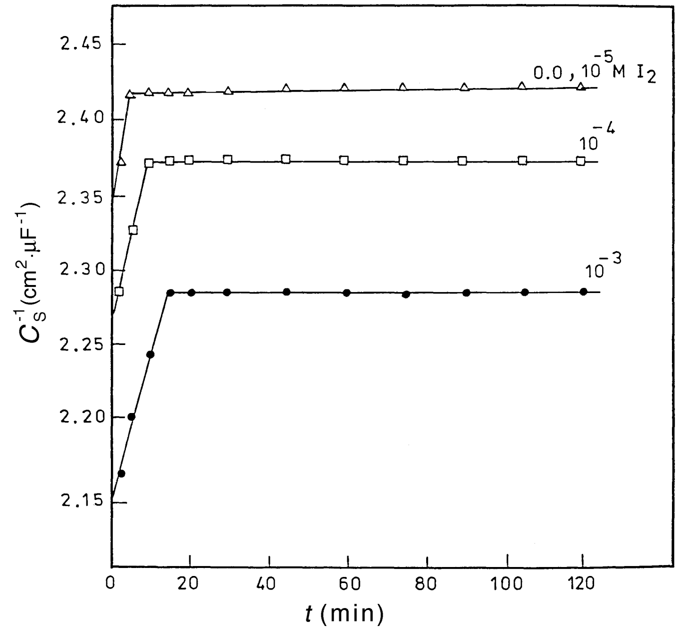

Fig. 9. Variation of C_s^{-1} with time for the preformed anodic ZrO_2 film in 0.5 *M* KI + *x M* I_2 solution ($x = 0.0$, 10^{-5}, 10^{-4}, and 10^{-3} *M*)

Following the formalism of the *Cabrera-Mott* model [21], it has been assumed by Schrebler *et al* [11] that during potentiodynamic formation of ZrO_2 films the presence of iodine mainly enhances the formation of zirconium iodine species at the electrode surface and shifts the potential at which ZrO_2 film formation usually appears towards more positive values. Our results accord generally with this observation and show a clear participation of I_3^- in the electrochemical process associated with the formation and thickening of the ZrO_2 film in presence of the field. However, under currentless conditions the formation of similar zirconium iodine species such as $ZrOI_x$ which retard greatly the oxide formation process on the anodic ZrO_2 film cannot be excluded. Increasing the I_3^- concentration would lead to further formation of this species and therefore to further inhibition of the oxide growth process in absence of the field.

Effect of temperature

To investigate the influence of temperature on the currentless thickening process of the anodically formed ZrO_2 film in KI solution, the Zr electrode was passivated in $0.05M$ H_2SO_4 solution at $1.0\,mA \cdot cm^{-2}$ till 30 V *vs* SCE. The applied current was then interrupted, and the capacitance C_s and the potential E were followed for a period of two hours in $0.1M$ KI solution at different temperatures ranging from 10 to 50°C .

For the first 15 min, the thickening rate of the oxide film was found to decrease with increasing temperature as might be expected due to the chemical nature of the process [22]. Then, C_s^{-1} attains a constant value, indicating cessation of further net oxide film formation.

Figure 10 represents the *Arrhenius* plots for the rate of currentless thickening of the anodic ZrO_2 film at different temperatures from which the heat of activation E_a

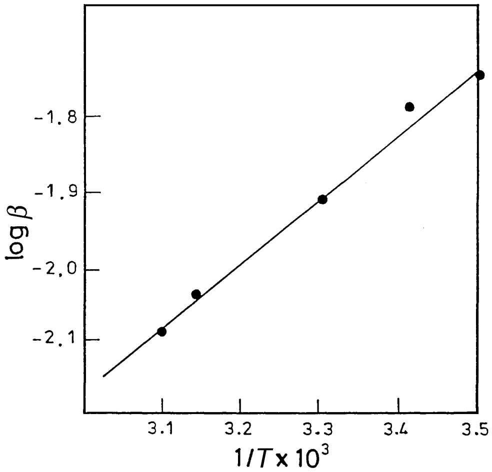

Fig. 10. *Arrhenius* plot for the preformed anodic ZrO_2 film in 0.1 M KI solution at different temperatures

is estimated to be 17.8 $KJ \cdot mol^{-1}$ using Eq. (4).

$$E_a = -2.303R\left(\frac{\delta \log (dC_s^{-1}/dt)}{d(1/T)}\right) \quad (4)$$

Experimental

Apparatus and technique have been described previously [23]. The electrode used was made from 99.9% zirconium rod (Koch – light laboratories, Ltd, England) and was fixed in a glass tube with araldite resin, leaving a surface area of 0.1256 cm^2 to contact the test solution. The electrolytic solutions were prepared from AR reagents (BDH) and triply distilled water. Unless otherwise stated, all experiments were run at $30 \pm 0.5°C$, and the solutions were used unstirred and naturally aerated. The electrode was mechanically polished using emery paper down to 8/0 grade and then rubbed with a soft cloth until a silvery bright surface was obtained.

The anodizing current was supplied from a constant current electronic instrument, and the electrode potential was measured against a saturated calomel electrode (SCE). Measurements of electrode impedance were carried out by a high precision standardized ac bridge of symmetrical Wien type. The electrode capacitance C_s, and resistance R_s, were traced with time at a frequency of 1.0 kHz; for complex plane analysis, the frequency was varied within the range of 0.5 to 15 kHz. An amplitude of 10 mV was used throughout.

References

[1] Urbanic VF (1984) In: Adamson RB (ed) Zirconium in the Nuclear Industry. Sixth International Symposium, American Society for Testing and Materials, p 554
[2] Meyer RE (1959) J Electrochem Soc **106**: 930
[3] Ortega C, Siejka JS (1967) J Electrochem Soc **129**: 495
[4] Young L (1961) Anodic Oxide Films. Academic Press, New York, p 51
[5] Whitton JL (1968) J Electrochem Soc **115**: 59
[6] Leach JSL, Pearson BR (1982) Electrochim Acta **29**: 1271
[7] Johnson AB, Smith T, Hill GR (1961) Trans Faraday Soc **57**: 2299
[8] Rogers GT, Draper PHG, Wood SS (1968) Electrochim Acta **13**: 251
[9] Cox B (1970) J Electrochem Soc **117**: 654
[10] El-Taib Heakal F, Mogoda AS, Mazhar AA, Ghoneim AA (1990) Corrosion – NACE **46**: 247
[11] Schrebler R, Gómez H, Córdova R, Gardiazabal I (1989) Corros Sci **29**: 1257
[12] Williams DE (1982) Electrochim Acta **27**: 411
[13] Masing L, Young L (1962) Can J Chem **14**: 903
[14] Abd El-Kader JM, Shams El-Din AM (1979) Br Corros J **40**: 14
[15] Bekheet AM, Hefny MM, El-Basiouny MS (1982) Ann Chim (Rome) **72**: 611 (1982)
[16] Wood GC, Pearson C (1967) Corros Sci **7**: 119
[17] El-Basiouny MS, Hefny MM, Mogoda AS (1985) Corrosion **41**: 611
[18] Adams GB, van Rysselberghe P, Maraghini M (1955) J Electrochem Soc **102**: 502
[19] Gardiazabal J, Córdova R, Gómez H, Schrebler R (1988) J Electroanal Chem **240**: 299
[20] Hefny MM (1994) Collect Czech Chem Commun **59**: 2579
[21] Cabrera N, Mott NF (1948–1949) Rep Prog Phys **12**: 163
[22] Schlain D, Kenahan CB, Steele DV (1955) J Electrochem Soc **102**: 102
[23] Mogoda AS, El-Taib Heakal F, Ghoneim AA (1992) Thin Solid Films **219**: 146

Received December 27, 1996. Accepted (revised) July 7, 1997