JOURNAL OF APPLIED ELECTROCHEMISTRY **18** (1988) 86–91

A kinetic study on the corrodability of anodic oxide films formed on molybdenum in NaOH solutions

A. G. GAD-ALLAH, H. A. ABD EL-RAHMAN, M. M. ABOU-ROMIA

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

Received 2 April 1987; revised 8 July 1987

The corrodability of anodic oxide films formed on molybdenum in NaOH solutions was studied using impedance and potential measurements. The corrosion rate was found to increase with increase of alkali concentration, film thickness and temperature and was nearly independent of the rate of oxide formation. The dissolution process was found to involve a valency change from Mo(IV) to Mo(VI) where it seemed, from cathodic polarization, that no electron transfer through the oxide film to/from the metal surface was involved during the dissolution process. In concentrated NaOH solutions ($[OH^-] \geqslant 9\,M$), the dissolution process appeared to follow zero-order kinetics.

1. Introduction

Most of the previous electrochemical studies on molybdenum showed that the metal is passivated by an insulating film composed mainly of MoO_2 [1–6] and the end product of the metal and the metal oxide dissolution is Mo(VI) [1–11]. True insulating and capacitive films were produced on the metal surface in aqueous solutions by galvanostatic anodization [12, 13]. A recent preliminary study on the stability of anodic oxide films on molybdenum highlighted the stability of the films in aqueous solutions [14]. A series of publications on the kinetics of the dissolution of anodic oxide films on W [15], Ti [16], Hf [17], Zr [18], Al [19], Sb [20] and Nb [21] has been made from our laboratory. Information about the corrodability and the dissolution kinetics of molybdenum oxide films in alkali solutions has not been reported so far.

2. Experimental details

Molybdenum disc electrodes of apparent surface area, *ca* $0.125\,cm^2$, were cut from spec. pure molybdenum rod (Johnson-Matthey, London). The electrode preparation, the electrolytic cell, the electrical circuit and details of the experimental procedure have been described previously [22, 23]. All solutions were prepared from AnalaR grade chemicals and triply distilled water. The electrode potential was measured against saturated calomel electrode (SCE) and both capacitance, C_m, and resistance, R_m, were measured at 1 kHz. The normal working temperature was 30° C.

After anodization of molybdenum at constant current density in 0.005 M H_2SO_4 acid solution to the specified formation voltage, the electrode was rinsed with triply distilled water and immersed immediately in the test solution where the corrosion potential, E_{corr}, C_m and R_m were traced with time at suitable intervals. Taking into consideration the insulating and dielectric properties of the oxide film; the increase of C_m, decrease of R_m and shift of E_{corr} with time were correlated to the oxide film thinning [15–22, 24].

3. Results and discussion

3.1. *Effect of NaOH concentration on the dissolution behaviour*

The dissolution behaviour of anodic oxide films on molybdenum in NaOH solutions of various concentrations (0.05–12 M) at 30° C is shown in Fig. 1. As can be seen, C_m^{-1} decreases with time in all cases and generally, the rate of decrease in C_m^{-1} increases with increase of alkali concentration. The corresponding variation of E_{corr} is shown in Fig. 2. As can be seen, there is no remarkable variation in E_{corr} for $[OH^-] < 8$, but for higher concentrations the variation is clear. Such variation in E_{corr} is attributed to the direct attack of the films at higher alkali concentrations. The variations of both C_m^{-1} and E_{corr} with time are consistent. The decrease of C_m^{-1} and the shift of E_{corr} towards more negative values are attributed to oxide film thinning [15–21, 24]. At the steady state (a) the recorded values of C_m^{-1}, R_m and E_{corr} are almost the same as those of the abraded electrode in the corresponding alkali solution; (b) the electrode surface acquired a mirror-bright surface like that before the anodization process. Both Figs 1 and 2 confirm the dissolution of the film formed by anodization. The resistance measurements were consistent with those of C_m^{-1} and E_{corr}, i.e. R_m was found to decrease with time.

3.2. *Effect of film thickness*

Fig. 3A shows the variation in C_m^{-1} of anodized Mo electrodes to 50, 100, 150 and 200 V against SCE with time in 12 M NaOH solution. As can be seen, the dissolution rate increases with increase of film thickness (formation voltage increase). After complete dissolution of the film, C_m^{-1} values for all formation

0021-891X/88 $03.00 + .12

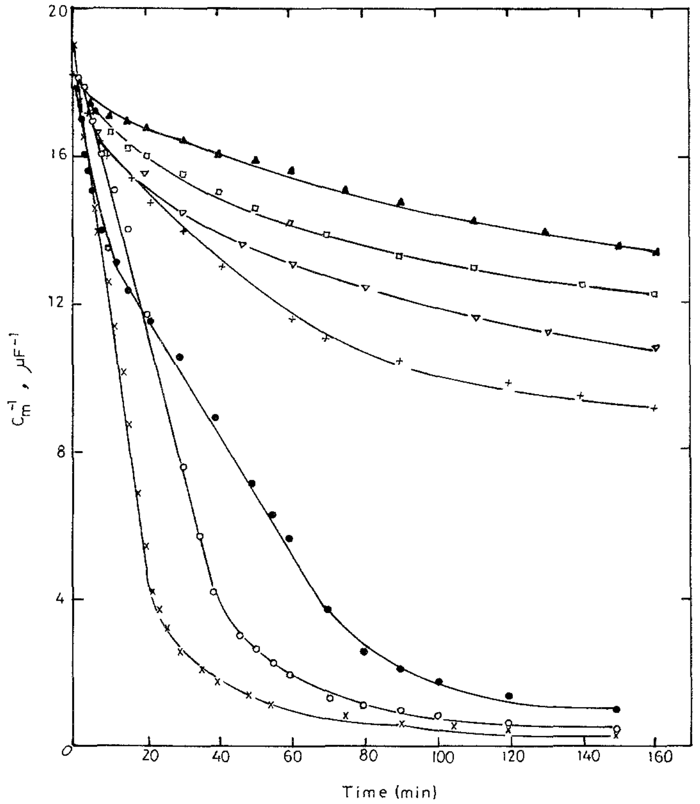

Fig. 1. Variation of open-circuit C_m^{-1} of anodized molybdenum electrodes with time in NaOH solutions of concentrations of: (▲) 0.05; (□) 1; (▽) 4; (+) 7; (●) 8; (○) 9 and (x) 10 M; formation voltage = 50 V; anodizing *cd* = 8 mA cm^{-2} and temperature = 30° C.

voltages are the same. The increase of the dissolution rate of many anodic oxide films with increase of formation voltage was reported previously [17–19, 25] and attributed most probably to the increase of the surface area exposed to the dissolving solution. Furthermore, increase of the film thickness is usually accompanied by an increase of defect concentration [17–19] which in turn increases the rate of attack and dissolution. Fig. 3B shows the linear variation of the initial film thickness, in terms of $1/C_m^0$, with the formation voltage increase.

3.3. *Effect of formation rate*

The variation of both C_m^{-1} and E_{corr} with time for anodized Mo electrodes at two different current densities during dissolution in 9 M NaOH solution are shown in Figs 4A and 4B. The rate of dissolution seems to be unaffected by variation of the formation rate. Under similar conditions, the rate of dissolution of anodic oxide films on zirconium in 1.0 M NaOH solution was found to increase with increase in formation current density [15]. Usually, the films formed

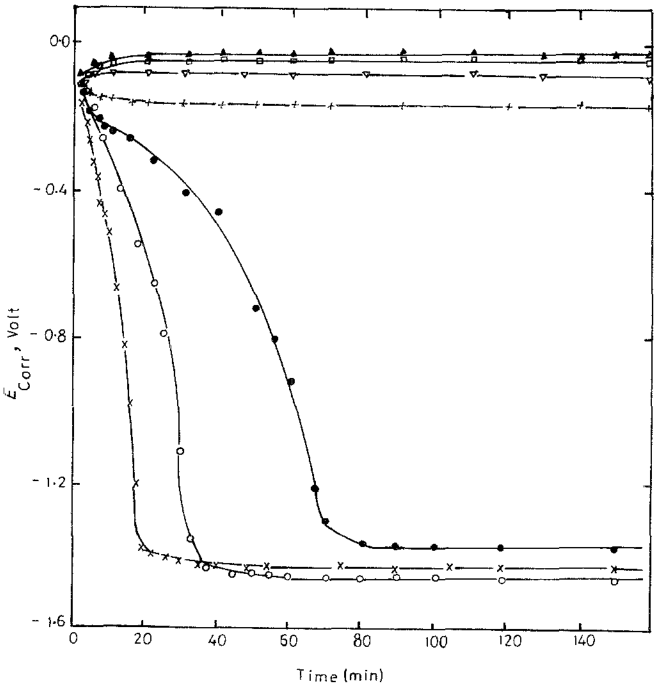

Fig. 2. Variation of E_{corr} of anodized Mo electrodes with time in NaOH solutions of various concentrations, details as in Fig. 1.

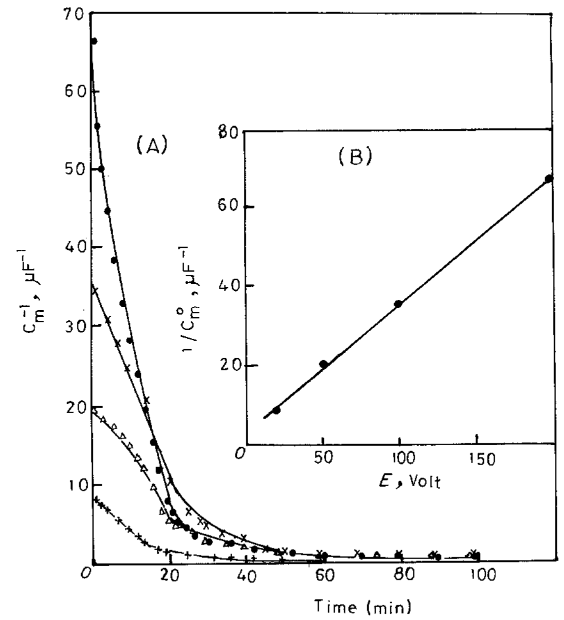

Fig. 3. (A) Variation of open-circuit C_m^{-1} of anodized Mo electrodes in 12 M NaOH solution; formation voltages were (+) 20; (△) 50; (x) 100 and (●) 200 V; anodizing $cd = 8\,\mathrm{mA\,cm^{-2}}$ and temperature = 30° C. (B) Zero-time reciprocal capacitance, $1/C_m^0$, versus formation voltage.

at high current densities are of more defective structure than those formed at lower ones [26] and it seems that the dissolution kinetics of Mo oxide films do not show this effect.

3.4. *Effect of stirring*

Figs 5A and 5B show the variations of both C_m^{-1} and R_m of anodized Mo electrodes in stirred and stagnant solutions of 9 M NaOH. As can be seen, the dissolution rate in the stirred solution is higher than that in the stagnant one, indicating the significance of species transport from/to the film surface in the dissolution process.

3.5. *Effect of temperature*

As expected for a chemical process such as the dissolution of anodic oxide films, the rate of dissolution, in terms of dC_m^{-1}/dt, increases with temperature as can be seen in Fig. 6A. The activation energy of dissolution of Mo oxide films in 9 M NaOH solution, E_a, was estimated from the Arrhenius plot shown in Fig. 6B where [19, 27]:

$$\frac{\partial \ln (\partial C_m^{-1}/\partial t)}{\partial (1/T)} = \Delta E_a/R \qquad (1)$$

The value of ΔE_a was found to be 83.1 kJ mol^{-1}.

3.6. *Impedance behaviour*

Assuming that the electrical model representing the impedance behaviour of the anodized electrode consists of a parallel connection of a condenser and a resistor in series with the solution resistance; the series equivalent impedance, Z_m, and the phase shift, θ, were calculated from the equations:

$$Z_m = (R_m^2 + (2\pi F C_m)^{-2})^{1/2} \qquad (2)$$

$$\theta = \tan^{-1}(2\pi F C_m R_m)^{-1} \qquad (3)$$

The impedance diagram of anodized Mo electrodes to different formation voltages after 1 h immersion in 5 M NaOH solution is shown in Fig. 7. The dashed lines in Fig. 7 refer to the behaviour after complete dissolution where the recorded values in Fig. 7 were the mean values obtained at the steady state dissolution of anodized Mo electrodes to 1, 5, 10, 15 and 20 V. Even after complete dissolution it seems, within the frequency range used, that the impedance behaviour of the electrode confirms the assumed model [28, 29].

3.7. *Mechanism of the dissolution*

Although the general behaviour of dissolution of Mo oxide films is somewhat similar to that of many valve metals [15–21, 24], the mechanism of its currentless dissolution is still not fully understood. The dissolution of MoO_2 in alkaline solutions may be as

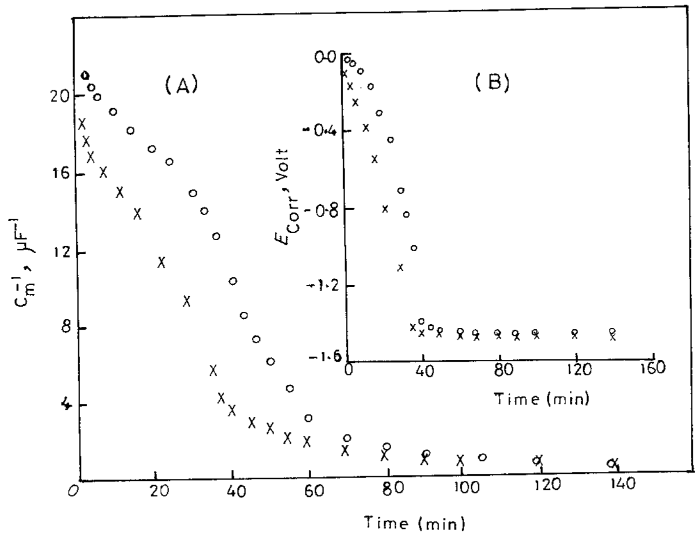

Fig. 4. Variation of open-circuit C_m^{-1} (A) and E_{corr} (B) of anodized Mo electrodes with time in 9 M NaOH solution; formation voltage = 50 V; anodizing *cds* were (O) 0.8 and (x) 8 mA cm^{-2} and temperature = 30° C.

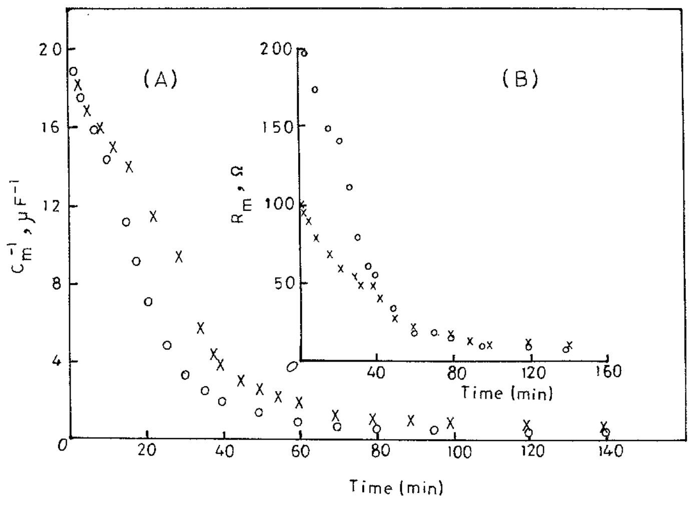

Fig. 5. Variation of open-circuit C_m^{-1} (A) and R_m (B) of anodized Mo electrodes with time in 9 M NaOH solution: (x) stagnant; (O) stirred; formation voltage = 50 V; anodized *cd* = 8 mA cm^{-2} and temperature = 30° C.

follows [4, 30]

$$3MoO_2 + 4OH^- = 2MoO_4^{2-} + Mo + 2H_2O \quad (a)$$

$$Mo + 2OH^- + 2H_2O = MoO_4^{2-} + 3H_2 \quad (b)$$

or [1, 3, 6]

$$MoO_2 + 4OH^- = MoO_4^{2-} + 2H_2O + 2e \quad (c)$$

All views indicate the oxidation of MoO_2 to soluble molybdate together with the occurrence of cathodic processes such as hydrogen evolution. The interesting question arising is whether the oxidation of MoO_2 involves electron transfer through the oxide film to/from the metal. To answer this question, an anodized Mo electrode was cathodically polarized in 0.05 M NaOH solution and the exchange current density, i_0, was determined from the Tafel plot shown in Fig. 8; $i_0 = 1.2 \times 10^{-11}$ A cm^{-2}. From Fig. 1, the dissolution rate in 0.05 M NaOH solution was determined in terms of current density as

$$\text{Dissolution rate (A cm}^{-2}) = \frac{zF}{aA}(d(\text{wt})/dt) \quad (4a)$$

$$= \frac{zF}{aA}\varrho a(dx/dt) \quad (4b)$$

and [21, 24, 31]

$$dx/dt = \frac{Da}{4\pi} \times 1.11 \times 10^{-6}(dC_m^{-1}/dt) \quad (5)$$

where *a* is the electrode area; *d*(wt)/*dt* is the rate of

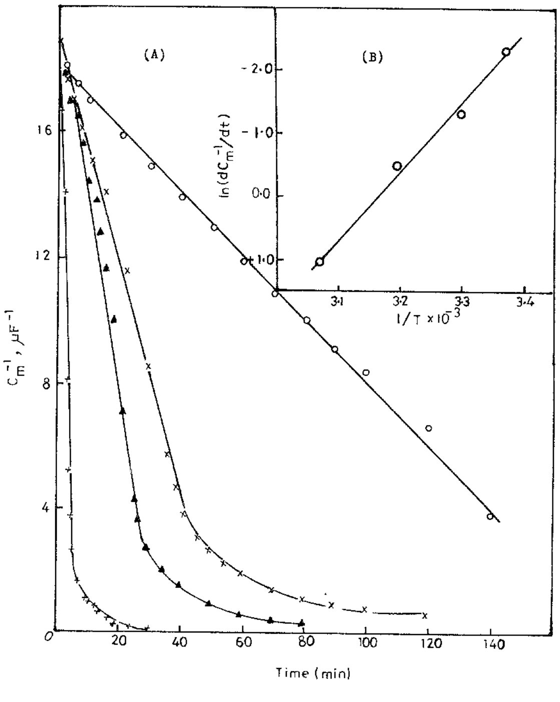

Fig. 6. (A) Variation of open-circuit C_m^{-1} of anodized Mo electrodes with time in 9 M NaOH solution at temperatures of: (O) 24; (x) 30; (▲) 40 and (+) 53° C; formation voltage = 50 V and anodizing *cd* was 8 mA cm^{-2}. (B) Natural logarithm of the dissolution rate versus the reciprocal of the absolute temperature.

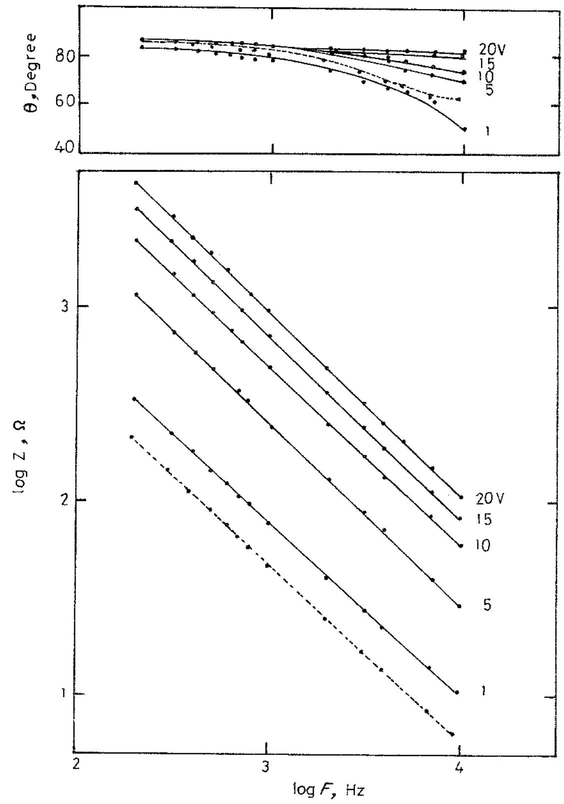

Fig. 7. Impedance diagram of anodized Mo electrode under open-circuit conditions after one hour immersion in 5 M NaOH solution; anodizing *cd* = 0.4 mA cm^{-2}; temperature = 30° C and the dashed lines referred to the electrode behaviour after complete dissolution.

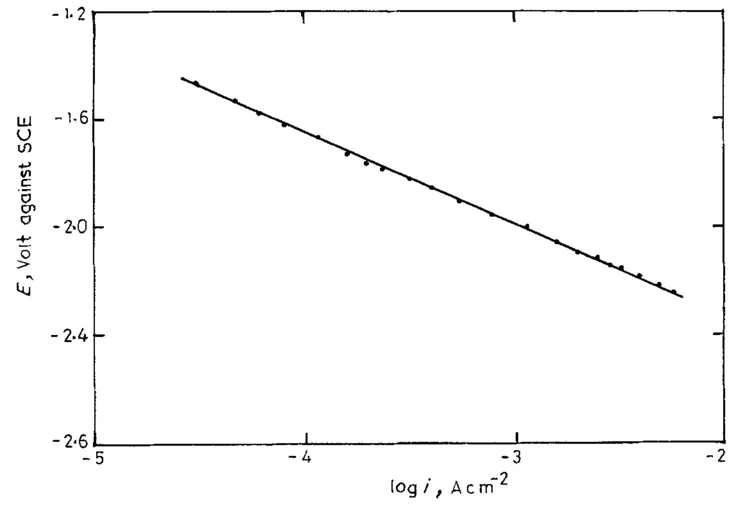

Fig. 8. Cathodic polarization of anodized Mo electrodes to 50 V in 0.05 M NaOH solution at 30° C.

dissolution in $g\,sec^{-1}$; x the film thickness; zF the number of Faradays involved and A, ϱ and D are the molecular weight, density and dimensionless dielectric constant of the oxide film, respectively. Taking $A_{MoO_2} = 127.9$, $z = 2$, $\varrho = 6.4$ [32], $D = 29.4$ [33] and $dC_m^{-1}/dt = 4.1 \times 10^{-4}\,\mu F^{-1}\,sec^{-1}$ then from equations (4) and (5) the dissolution current density is $1.6 \times 10^{-5}\,A\,cm^{-2}$. Comparing the dissolution cd with i_0 obtained from cathodic polarization shows that the dissolution cd is much higher than i_0 indicating that no electron transfer through the oxide film to/from the metal surface is involved in the dissolution process.

It should be mentioned that up to $\geqslant 90\%$ decrease in both C_m^{-1} and R_m, the interference colours and the general appearance of the film remained unchanged during the dissolution process. But after longer times the film disappeared completely. The decrease in C_m^{-1} and R_m with time cannot be attributed to the film thinning but most probably is attributed to loss of the insulating properties of the film before its dissolution. The dielectric properties of the films could not be returned by immersion of the electrode in electrolytes in which the oxide is stable, i.e. the loss of insulating properties by ion incorporation inside the films may be disregarded. The loss may be attributed to chemical interactions between MoO_2 and OH^- ions, e.g. (3):

$$MoO_2 + 2OH^- = MoO_2(OH)_2 + 2e \qquad (d)$$

or hydration of MoO_2 [4, 34]

$$\begin{aligned} MoO_2 + H_2O &= MoO(OH)_2 + H_2O \\ &= Mo(OH)_4 \qquad (e) \end{aligned}$$

In NaOH solutions of concentrated ($[OH^-] \geqslant 9\,M$), the kinetics of dissolution appeared to follow zero-order kinetics with respect to film thickness, i.e. dC_m^{-1}/dt = constant. Since the dissolution of solid inorganic materials such as oxide films is largely governed by the solid state properties [35, 36], e.g. atomic disorder and also by the medium aggressiveness [37], it seems from our results that the medium aggressiveness is the main factor determining the dissolution behaviour of Mo oxide films and not the solid state properties of the oxide film. Generally, the stable oxide films in the common reagents follow zero-order kinetics with respect to the film thickness during dissolution [14, 21, 37].

References

[1] T. Heumann and G. Hauck, *Z. Metallk* **56** (1965) 75.
[2] L. L. Wikstrom and K. Nobe, *J. Electrochem. Soc.* **111** (1969) 525.
[3] M. N. Hull, *J. Electroanal. Chem.* **30** (1971) App. 1; **38** (1972) 143.
[4] M. Pourbaix, 'Atlas of Electrochemical Equilibria', Pergamon Press, Oxford (1966) p. 272.
[5] H. Hobuyoshi and S. Katsushisa, *Nippon Kinzoku* **44** (1980) 1312.
[6] J. N. Wanklyn, *Corr. Sci.* **21** (1981) 211.
[7] W. Muthmann and F. Fraunberger, *Ber. Bayr. Akad.* **34** (1904) 201.
[8] H. Kuessmer, *Z. Elektrochem.* **16** (1910) 756.
[9] E. Becker and H. Hilberg, *ibid.* **31** (1925) 32.
[10] J. Besson and G. Drautzburg, *Electrochim. Acta* **3** (1960) 158.
[11] M. König and H. Göhr, *Ber. Bunsenges. Phys. Chem.* **67** (1963) 837.
[12] S. Ikonopisov, *J. Electroanal. Chem.* **35** (1972) Appl. 1.
[13] A. G. Gad-Allah and H. A. Abd El-Rahman, *J. Applied Electrochem.*
[14] W. A. Badawy, A. G. Gad-Allah, H. A. Abd El-Rahman and M. M. Abou-Romia, *Surf. Technol.* **30** (1987) 365.
[15] M. A. Ameer, M.Sc. Thesis, Cairo University (1984).
[16] M. M. Hefny, A. A. Mazhar and M. S. El-Basiouny, *Br. Corros. J.* **17** (1982) 38.
[17] M. M. Hefny, M. S. El-Basiouny, A. G. Gad-Allah and S. A. Salih, *Electrochim. Acta* **28** (1983) 1811.
[18] M. S. El-Basiouny, A. A. Mazhar, F. El-Taib Heakal and M. A. Ameer, *J. Electroanal. Chem.* **147** (1983) 181.
[19] W. A. Badawy, M. S. El-Basiouny and M. M. Ibrahim, *Indian J. Tech.* **24** (1986) 1.
[20] M. M. Hefny, W. A. Badawy, A. S. Mogoda and M. S. El-Basiouny, *Electrochim. Acta* **30** (1985) 1017.
[21] W. A. Badawy, A. G. Gad-Allah and H. H. Rehan, *J. Applied Electrochem.* **17** (1987) 559.
[22] M. S. El-Basiouny, A. M. El-Kot and M. M. Hefny, *Corrosion* **36** (1980) 284.
[23] W. A. Badawy, A. G. Gad-Allah, H. A. Abd El-Rahman and M. M. Abou-Romia, *Surf. Technol.* **27** (1986) 187.
[24] J. W. Diggle, T. C. Downie and C. W. Goulding, *Electrochim. Acta* **15** (1970) 1079.
[25] R. S. Alwitt and R. G. Hills, *J. Electrochem. Soc.* **112** (1965) 974.
[26] S. Hirora, H. Chiba, T. Tanaka and H. Hooke, *Oyo Butzuri* **26** (1957) 651.
[27] J. O'M. Bokaris and E. C. Potter, *J. Chem. Phys.* **20** (1952) 614.

[28] B. D. Cahan and C. Chen, *J. Electrochem. Soc.* **129** (1982) 474.

[29] F. El-Taib Heakal and S. Haruyama, *Corr. Sci.* **24** (1984) 185.

[30] W. M. Latimer, 'Oxidation Potentials', 2nd Edn., Prentice Hall, New York (1952) p. 250.

[31] L. Young, 'Anodic Oxide Films', Academic Press, London (1961).

[32] J. W. Meller, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Vol. XI, Longmans (1948) p. 527.

[33] D. J. Desmet and J. L. Ord, *J. Electrochem. Soc.* **130** (1983) 280.

[34] C. Paal and H. Büttner, *Berichte* **48** (1915) 220.

[35] J. W. Diggle, 'Oxide and Oxide Films', Vol. I, Marcel Dekker Inc., New York (1972) p. 35.

[36] M. M. Hefny, A. S. Mogoda and M. S. El-Basiouny, *Br. Corros. J.* **21** (1986) 109.

[37] M. M. Hefny, M. S. El-Basiouny and A. S. Mogoda, *Corrosion* **39** (1983) 266.