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CONDUCTION MECHANISMS IN THE (+) VALVE METAL/OXIDE FILM/ELECTROLYTE SYSTEM

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ABSTRACT

In the present overview, the main types of conduction through barrier type oxides on valve metals are briefly discussed. The main theoretical approaches towards ionic and electronic conduction in such systems are described and the ways of comparing them to experimental data are oultined. In addition, the coupling between film growth and metal dissolution through the film during anodic oxidation of valve metals in aggressive electrolytes is emphasised. A theoretical model for this phenomenon is described and expressions for both steady-state and small amplitude ac response of the system are derived and compared to experimental data for W in sulphate-fluoride solutions.

Keywords: *valve metal, anodic oxide film, ionic conduction, electronic conduction, metal dissolution, kinetic model.*

INTRODUCTION

The anodic oxidation of valve metals is usually carried out galvanostatically (J=const) and isothermically (T = const). In such conditions, the growth rate of the anodic oxide can be considered to be in a steady state and its properties can be regarded as stationary. The potential drop through the oxide, frequently labeled as formation voltage (U_f) increases linearly with time (t), or the quantity of charge passed (Q). During film formation, the field strength ($\vec{E}$) is essentially constant. The increase of U_f and the film thickness (D) of the oxide film is limited by the occurrence of breakdown phenomena.

On the other hand, the tensiostatic formation of anodic films is carried out by applying a constant voltage through the system (U_V = const). Tensiostatic anodisation is a non-steady state process since the current causes a continuous increase of the film thickness and simultaneoysly a decrease of . As a result, a decrease of the current density with time is observed, i.e. the growth rate of the film decreases with time.

Generally speaking, the current measured in a (+) metal / anodic film / electrolyte system consists of three components: $J = J_i + J_e + J_{dis}$ (Fig. 1). The ionic current (J_i), which results from the migration of ions (metal and oxygen) under the influence of the applied electric field, initiates the growth of the anodic film. The electronic current (J_e) through the oxide film does not influence its thickness. The dissolution current (J_{dis}) can have significant values when the films are polarized in electrolytes which are aggressive to the oxide film. (Fig. 1). These three current components depend on the field strength ($\vec{E}$) and the temperature (T).

It is worth mentioning that two types of anodic oxide films can grow on valve metals: barrier and porous [1]. The barrier films are formed in electrolytes which do not dissolve the oxide film appreciably, i.e.

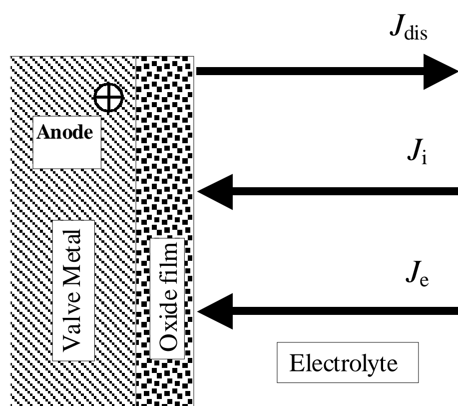


Fig. 1. Ionic (J_i), electronic (J_e) and dissolution (J_{dis}) currents in (+)valve metal/barrier oxide/electrolyte systems.

$J_{dis} \cong 0$. They have a dense structure and follow the metal surface profile (Fig. 2a). The porous films are formed in electrolytes dissolving the oxide film (J_{dis} has a significant value) and they have a double-layered structure [2]. The so-called "barrier sub-layer" grows at the metal/oxide interface. Above it a significantly thicker porous layer grows, whose pores are placed normally to the electrode surface (Fig. 2b).

IONIC CONDUCTION

The ionic current (J_i), which results from the migration of ions (metal and oxygen) under the influence of the electric field e.g. via a vacancy mechanism, initiates the growth of the anodic film. Usually the ionic conductivity is studied at high current densities (or equivalently, high field strengths). Different equations have been proposed for the $J_i(\vec{E},T)$- dependence. The applicability of three of them (the equations of *Gunterschultze-Betz* [3], *Tafel-Frenkel* and *Young* [4,5]) holds good in anodization of various valve metals. These three equations have been theoretically interpreted.

The dependency $J_i(\vec{E})_T$, to a first approximation, obeys the *Gunterschultze* and *Betz* equation:

$$J_i = A_G \exp(B_G \vec{E})_T \quad (1)$$

where A_G and B_G are constants depending on the metal (oxide) nature and the temperature.

In turn, the *Tafel-Frenkel* equation, that has been derived starting from basic kinetic considerations, has the form:

$$J_i = A_i \exp\left(-\frac{B_i - \alpha_i \vec{E}}{k_B T}\right) \quad (2)$$

In this equation, A_i, B_i and α_i are material-specific constants, k_B being the *Boltzmann* constant. The pre-exponential factor (A_i) has a different physical meaning depending on the theoretical model employed: bulk, interface or mixed (bulk-interfacial) control of ionic conduction.

Using more sophisticated experiments e.g. during tantalum anodization it has been found [62] that the so-called *"Tafel slope"*, i.e. the derivative $(\partial \ln J_i / \partial E)_T \neq$ const. The obtained $\ln J_i(\vec{E})$-dependence is not strictly linear, but appears to be slightly convex, which has lead *Young* [5] to propose another $J_i(E,T)$- dependence:

$$J_i = A_y \exp\left(-\frac{B_Y}{k_B T}\right) \exp\left(\frac{\alpha_Y \vec{E} - \beta_Y \vec{E}^2}{k_B T}\right) \quad (3)$$

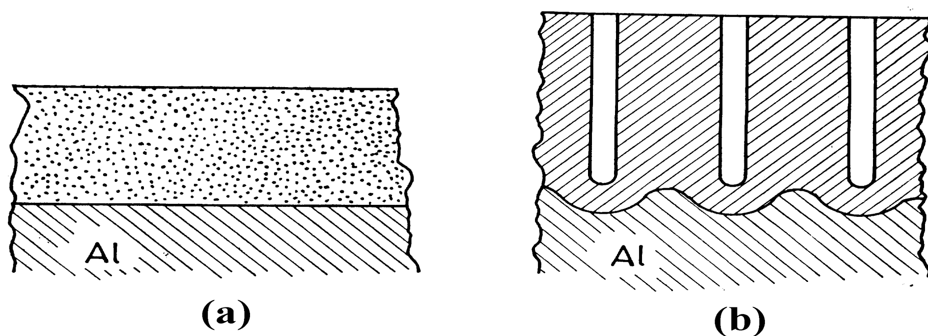


Fig. 2. Schematic picture of anodic alumina films: (a) barrier type anodic oxide film; (b) porous type anodic oxide film.

Here A_Y, B_Y, α_Y and β_Y are positive constants, the values of which depend only on the nature of the metal that is anodically oxidised. This dependence has been confirmed using experimental data for Al and Nb as well. Equation (3) has been theoretically interpreted by a range of investigators, such as *Young* [5], *Dignam* [6], *Christov* and *Ikonopisov* [7], etc. Recently *Li* and *Young* [8] have argued that since both the curvature of the steady-state $\ln J_i(\vec{E})$-dependence and the dependence of the slope of the stepped $\ln J_i(\vec{E})$ on initial steady state field strength disappear during anodic oxidation of Ta in chloride electrolyte (which has been demonstrated not to incorporate anions into the oxide), then both effects are due to anion incorporation into the outer part of the barrier film that supposedly grows via metal ion transport.

In galvanostatic regime (J=const) the kinetics of anodic oxidation is usually followed by tracing the kinetic curves $[U_f(t)]_{J,T}$ and/or $[U_f(Q)]_{J,T}$. Correspondingly, the electric field strength can be determined from kinetic data using *Faraday*'s law:

$$\vec{E} = \frac{zF\rho\sigma}{\lambda MJ}\left(\frac{\partial U_f}{\partial t}\right)_{J,T} \tag{4}$$

where z is the charge of the mobile ion/vacancy, F is *Faraday*'s number, σ is the roughness factor (the ratio between real and geometrical surface area of the sample), ρ is the density of the oxide, λ is the current efficiency (J_i/J), M is the molar weight of the anodic oxide and $(\partial U_f/\partial t)_{J,T}$ is the slope of the kinetic curve $U_f(t)$.

In a tensiostatic regime (U_f = const), the anodic oxidation kinetics is studied by tracing the $[J(t)]_{Uv,T}$ curves. As at U_f = const the ionic current density (J_i) leads to a continuous increase of the thickness (D) of the oxide and a simultaneous decrease of the electric field strength ($\vec{E} = U_f/D$):

$$\vec{E} = \frac{U_V}{D_0 + \dfrac{\lambda Mz}{zF\rho\sigma}\displaystyle\int_0^t (J_i.t)\,dt} \tag{5}$$

where D_0 is the film thickness at the start of tensiostatic oxidation, i.e. at $t = 0$.

An analytical expression of the decrease of the current density (J) with time (t) can be sought by solving simultaneously some of the equations for the ionic current density (1)-(3) with equation (5). As a result, complex integral and integro-differential equations are obtained. Such equations are usually employed for numerical calculation of the $J(t)$-dependence subject to certain assumptions. This is why different forms [9-12] of the equations for the kinetics of tensiostatic anodisation have been proposed in the literature.

ELECTRONIC CONDUCTION

The electronic conduction is usually studied during anodic polarization of already formed oxide films at potentials lower than the formation voltage, i.e. at comparatively low field strengths. In these cases an empirical equation for the $J_e(E)_T$ –dependence has been found:

$$J_e = \alpha_e \exp(\beta_e \vec{E}^{1/2})_T \tag{6}$$

where α_e and β_e are constants depending on the nature of the metal, the contact electrolyte and the temperature. Such a dependence has been experimentally found for deferent metals: Al [13], Ta [14.15], Nb [16], Bi [16]. Different models [18,19] have been proposed explaining the mechanisms of the electronic currents (*Schottky* emission, *Poole- Frenkel* effect). Only the *Christov* model [20] explained dependence of J_e on the nature and concentration of the contact electrolyte. In this model the electrolyte was considered as a semiconductor and the redox couples in it were assumed to play the role of electron donors. Based on this treatment an equation for the electronic current density is derived:

$$J_e = kAT^2\sqrt{N_d}\exp(-\chi_0/k_BT)\exp\left[\left(\frac{\varepsilon_s - 1}{\varepsilon_s + 1}\right)^{1/2}\frac{e_0^{3/2}}{\varepsilon_i^{1/2}k_BT}\vec{E}^{1/2}\right] \tag{7}$$

in which $A = 4\pi m_i e_0 k_B^2/h^3$ is the *Richardson* constant (m_i is the effective mass of the electron in the dielectric oxide), N_d is the donor concentration in the semiconductor (the electrolyte), χ_0 is the work function at the film/electrolyte interface at N_d=1, k is a quantum cor-

rection that is related to the tunneling probability of the electron at the dielectric/semiconductor interface, T is the absolute temperature, k_B is the *Boltzmann* constant, h is the *Planck* constant, e_0 is the charge of the electron, and ε_i and ε_s are the dielectric constants of the anodic oxide and the semiconductor (the contact electrolyte).

On comparing equations (6) and (7) the empirical constants α_e and β_e are assigned the following theoretical expressions:

$$\alpha_e = kAT^2\sqrt{N_d}\exp(\chi_0/k_B T) \quad (8)$$

$$b_e = \left(\frac{\varepsilon_s - 1}{\varepsilon_s + 1}\right)^{1/2} \frac{e_0^{3/2}}{\varepsilon_i^{1/2} k_B T} \quad (9)$$

Equations (8) and (9) demonstrate that the electronic current depends not only on the nature of the dielectric, but also on the nature and concentration of the contact electrolyte (via the N_d and ε_s values). It is worth mentioning that the model of *Christov* is so far the only model that includes the field, temperature and electrolyte concentration dependence of the electronic conduction. It is possible to calculate the theoretical values of the constant β_e which can then be compared to the experimental estimates. As it has already been pointed out [21] it is not completely clear which values of the two dielectric constants (ε_i and ε_s) have to be used. It has been proposed that both the optical (high-frequency) and the static (zero-frequnecy) dielectric constant are employed/ By representing the data in Arrhenius coordinates $\ln\frac{J_e}{T^2}\left(\frac{1}{T}\right)$ is is possible to determine the work function (χ_0) of the electron. It is worth noting that electronic conduction can be experimentally investigated also during prolonged tensiostatic anodization, and also by photoelectrochemical measurements.

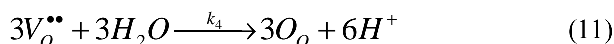
COUPLING BETWEEN OXIDE GROWTH AND METAL DISSOLUTION

To account for both the film growth and underlying valve metal dissolution under potentiostatic conditions in aggressive electrolytes, such as sulphuric or oxalic acid for Al [22-24] and fluoride-containing electrolytes for W, Nb, Ta, Ti, Zr, etc. [25-41], a quantitative model approach has been recently proposed by one of us [41,42]. It has been found to reproduce successfully both the steady-state current vs. potential curves and impedance spectra in a range of potentials [41,42]. This approach, which treats the processes of film growth and metal dissolution through the film as sequences of generation, transport and annihilation of point defects (cation and anion vacancies) and features a defect recombination reaction at the film/electrolyte interface, is briefly described below using anodisation of W in fluoride-containing electrolyte as a representative example.

The oxide of tungsten that forms at open circuit in an aqueous solution can be regarded as mixed–valency oxide in which W(V) and W(VI) position coexist the cation sublattice, together with a certain concentration of W(VI) cation vacancies [44]. A significant concentration of oxygen vacancies is assumed to exist in the anion sublattice as. W(V) cation vacancies are neglected for simplicity. The growth of the passive film proceeds at the metal / film interface with oxidation of the metal

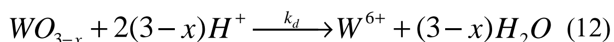
$$\mathrm{m} \rightarrow W_W^{VI} + 3V_O^{\bullet\bullet} + 6e_m \quad (10)$$

The oxygen vacancy is transported through the barrier film by high-field assisted migration and reacts with absorbed water at the film / solution interface achieving film growth



$$3V_O^{\bullet\bullet} + 3H_2O \xrightarrow{k_4} 3O_O + 6H^+ \quad (11)$$

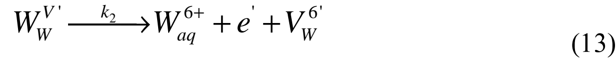
In order the film thickness to be invariant with time in the steady state, the film dissolution reaction must be included



$$WO_{3-x} + 2(3-x)H^+ \xrightarrow{k_d} W^{6+} + (3-x)H_2O \quad (12)$$

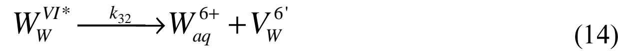
In fluoride containing electrolytes, oxyfluorocomplexes of W(VI) are probably formed, which is expected to increase the solubility of the film and thus the steady-state current density governed by chemical dissolution of

the oxide. On the other hand, W(V) at the F/S interface undergoes either oxidative dissolution as W_{aq}^{6+} or transforms into a passivating W(VI)* species that dissolves isovalently:



$$W_W^{V'} \xrightarrow{k_2} W_{aq}^{6+} + e' + V_W^{6'}$$

$$W_W^{V'} \xrightarrow{k_{31}} W_W^{VI*} + e' \quad (13)$$



$$W_W^{VI*} \xrightarrow{k_{32}} W_{aq}^{6+} + V_W^{6'} \quad (14)$$

Cation vacancies, generated by the above processes, are transported through the film via high–field assisted migration or recombine with oxygen vacancies according to the reaction

$$V_O^{\bullet\bullet} + V_W^{6'} \rightarrow null \quad (15)$$

The high-field migration equations for the transport of cation and anion vacancies are

$$J_o = -\frac{D_0}{2a} c_O(L) e^{\frac{2Fa\vec{E}_0}{RT}}, J_M = c_M(0)\frac{D_M}{2a} e^{\frac{\chi Fa\vec{\mathbf{E}}_0}{RT}} \quad (16)$$

The total defect transport current density is $I = -2FJ_o + 6FJ_m$.

The electric field strength in the metal /oxide/ electrolyte system $\vec{E}_0$ is given by the sum of all the potential drops in the system divided by the oxide film thickness [41]

$$\vec{E}_0 = \left(\phi_{M/F} + \vec{E}L + \phi_{F/S}\right)/L \quad (17)$$

where $\phi_{M/F} = (1\text{-}\alpha)E - \vec{E}L$, $\phi_{F/S} = q_n L_{F/S}/\varepsilon\varepsilon_o$, α is the polarisability of the film/solution interface, q_n is the negative surface charge due to accumulation of cation vacancies at the film/solution interface, $\vec{E}$ the field strength in the film bulk and $L_{F/S}$ is the width of the cation vacancy accumulation zone [41]. Further, according to the Mixed-Conduction Model for oxide films [43], the potential drop at the metal/film interface does not depend on the applied potential. In other words, the reactions at this interface are not considered to be rate limiting, rather, their rate is adjusted by the transport processes of point defects in the passive film. The expressions of the instantaneous partial currents due to the transport of oxygen and cation vacancies acquire the form:

$$I_0 = \frac{FD_0}{a} c_o(L) \ \exp\left\{\frac{2Fa}{RTL}\left[(1-\alpha)E + \frac{q_n L_{F/S}}{\varepsilon\varepsilon_0}\right]\right\},$$
$$I_M = \frac{6FD_0}{2a} c_M(0) \ \exp\left\{\frac{6Fa}{RTL}\left[(1-\alpha)E + \frac{q_n L_{F/S}}{\varepsilon\varepsilon_0}\right]\right\} \quad (18)$$

At the film/solution interface, cation vacancies are (i) generated with a current density $I_{M,F/S}$, (ii) transproted via high-field migration with a current density I_M and (iii) react with the oxygen vacancies according to the recombination reaction at a rate of $I_O S q_n$, where S is the cross-section of recombination. Then,

$$\frac{dq_n}{dt} = I_{M,F/S} - I_M - I_O S q_n = I_O S\left(\frac{I_{M,F/S} - I_M}{I_O S} - q_n\right) \quad (19)$$
.

According to the dissolution scheme described by reactions and , the current density due to cation vacancies at the film/solution interface is given by:

$$\frac{I_M}{6F} = J^{5'}{}_M = k_2\gamma_5 + k_{32}\gamma^*{}_6 \quad (20)$$

γ_5 and γ_6* being the fractions of the F/S interface occupied by W(V) and W(VI)*, referred to the cation sublattice only. It is assumed that the surface concentration of W(V) cation vacancies is considered as negligible with respect to γ_5 and γ_6*. The material balances in the outermost cation layer are correspondingly:

$$\frac{\beta d\gamma_5}{dt} = \frac{I_M}{6F} - k_2\gamma_5 - k_{31}\gamma_5 \quad (21)$$

$$\frac{\beta d\gamma_6*}{dt} = k_{31}\gamma_5 - k_{32}\gamma_6* \quad (22)$$

Steady state solution and total current density

In the steady state, equations and become

$$\frac{\bar{I}_{M,F/S}}{6F} - \bar{k}_2\bar{\gamma}_5 - \bar{k}_{31}\bar{\gamma}_5 = 0 \quad (23)$$

$$k_{32}\bar{\gamma}_5 - \bar{k}_{31}\bar{\gamma}_6^* = 0 \quad (24)$$

and obviously

$$\bar{\gamma}_5 + \bar{\gamma}_6^* + \bar{\gamma}_6 = 1 \quad (25)$$

$\bar{\gamma}_6$ being the surface fraction occupied by WO_3, i.e. regular W(VI) sites, at which the isovalent dissolution of the oxide (reaction) proceeds. Eqns. (20), (24), and (25) can be used to calculate $\bar{I}_{M,F/S}$:

$$\bar{I}_{M,F/S} = \frac{6Fk_{32}\left(\bar{k}_2 + \bar{k}_{31}\right)}{\bar{k}_{31} + \bar{k}_{32}}\left(1-\bar{\gamma}_6\right) = \bar{k}_M\left(1-\bar{\gamma}_6\right) \qquad (26)$$

$\bar{I}_M$ is proposed to be proportional to the surface $\left(1-\bar{\gamma}_6\right)$ not occupied by regular W(VI), whereas $\bar{I}_O$ is assumed to flow only on the fraction $\bar{\gamma}_6$.

$$\bar{I}_O = 2Fk_d c^n_{H^+}\bar{\gamma}_6 = 2Fk_d^{'}\bar{\gamma}_6 = k_{WO_3}\bar{\gamma}_6 \qquad (27)$$

where n is the reaction order of the chemical dissolution reaction, Eq. (12) with respect to H^+.

If we define $\bar{\gamma}_6$ as a function of the reaction rates for the formation of W(V) and W(VI) centers

$$\bar{\gamma}_6 = \frac{k_{WO_3}}{\bar{k}_M + k_{WO_3}} \qquad (28)$$

then

$$\bar{I}_M = \frac{\bar{k}^2_M}{\bar{k}_M + k_{WO_3}} \qquad (29)$$

$$\bar{I}_O = \frac{\bar{k}^2_{WO_3}}{\bar{k}_M + k_{WO_3}} \qquad (30)$$

Small amplitude ac solution

From the assumption that currents transported by oxygen and cation vacancies are additive, and taking into account the electronic properties of the oxide, the impedance of the system can be defined as the parallel combination of the impedance due to generation and transport of cation vacancies (Z_M), the impedance due to transport and consumption pf oxygen vacancies (Z_O) and the impedance due to the dielectric properties of the oxide film, i.e. its capacitance.

$$Z = R_{el} + \left[j\omega C + \frac{1}{Z_O} + \frac{1}{Z_M}\right]^{-1} \qquad (31)$$

where R_{el} is the electrolyte resistance and C is the film capacitance

$$C^{-1} = \frac{(1-\alpha)}{\varepsilon\varepsilon_0\vec{E}}\bar{E} \qquad (32)$$

Impedance due to transport and consumption of oxygen vacancies

For a small amplitude sinewave perturbation around a steady-state equation transforms into:

$$\tilde{q}_n = \frac{\bar{I}_0 S\alpha\tilde{E}\dfrac{\varepsilon\varepsilon_0}{L_{F/S}}}{j\omega + I_0 S} \qquad (33)$$

where $\tilde{x}$ indicates the complex amplitude of a variable x. The migration current of oxygen vacancies in such conditions is given by

$$\tilde{I}_o = \frac{2\bar{I}_0 B}{\bar{L}}\left[(1-\alpha)\tilde{E} + \tilde{q}_n\frac{L_{F/S}}{\varepsilon\varepsilon_0}\right], B = \frac{2Fa}{RT} \qquad (34)$$

Solving (33) and (34) simultaneously, we obtain for the impedance of transport of oxygen vacancies

$$Z_{O,f}^{-1} = \frac{\Delta I_0}{\Delta E} = \frac{2\bar{I}_0 B}{\bar{L}}\left[(1-\alpha) + \frac{\bar{I}_0 S\alpha}{j\omega + \bar{I}_0 S}\right] \qquad (35)$$

In order to account for the capacitive behaviour observed in the impedance spectra at low frequencies, the ac modulation of the film thickness has to be taken into account. The expression for the ac current density due to that phenomenon has the form

$$\tilde{I} = \frac{(1-\alpha)}{\lambda\vec{E}}\frac{V_m}{6F}j\omega\tilde{E} \qquad (36)$$

which corresponds to a pseudo-capacitance in series with te impedance due to transport of oxygen vacancies, $\lambda = \frac{\bar{I}_O}{\bar{I}_O + \bar{I}_M}$ being the current efficiency for film formation:

$$C_0 = \left(\bar{I}_O + \bar{I}_M\right)\frac{(1-\alpha)}{\bar{I}_O\vec{E}}\frac{V_m}{6F} \qquad (37)$$

The total impedance due to oxygen vacancies is then expressed as

$$Z_O = Z_{O,f} + \frac{1}{j\omega C_0} \qquad (38)$$

Impedance due to generation and transport of cation vacancies

The faradaic impedance due to the the generation of cation vacancies at the F/S interface is derived from Eqs. (20), (21) and (22).

$$Z^{-1}_{M,F/S} = 6F\left[\tilde{k}_2\bar{\gamma}_5 + \bar{k}_2\tilde{\gamma}_5 + k_{32}\tilde{\gamma}^*_6\right] \quad (39)$$

$$\begin{aligned} j\omega\beta\tilde{\gamma}_5 &= \frac{Z^{-1}_{M,F/S}}{6F} - \tilde{k}_2\tilde{\gamma}_5 - \tilde{k}_2\bar{\gamma}_5 - \tilde{k}_{31}\bar{\gamma}_5 - \bar{k}_{31}\tilde{\gamma}_5 \\ j\omega\beta\tilde{\gamma}^*_6 &= \tilde{k}_{31}\bar{\gamma}_5 - \bar{k}_{31}\tilde{\gamma}_5 - k_{32}\tilde{\gamma}^*_6 \end{aligned} \quad (40)$$

$$\tilde{\gamma}^*_6 = \frac{\bar{k}_{31}\tilde{\gamma}_5 + \tilde{k}_{31}\bar{\gamma}_5}{\beta j\omega + k_{32}} \quad (41)$$

$$\tilde{\gamma}_5 = \frac{Z^{-1}_{M,F/S}}{6F\left(\beta j\omega + \bar{k}_2 + \bar{k}_{31}\right)} - \frac{\bar{\gamma}_5\left(\tilde{k}_2 + \tilde{k}_{31}\right)}{\left(\beta j\omega + \bar{k}_2 + \bar{k}_{31}\right)} \quad (42)$$

$$Z_{M,F/S} = 6Fb_2\bar{k}_2\bar{\gamma}_5\left[1 + \frac{b_{31}\bar{k}_{31}\left(\bar{k}_2 - \bar{k}_{31}\right)}{\left(1 + j\left(\frac{\omega\beta\bar{k}_2 b_2}{b_2 k_{32}\bar{k}_2 + b_{31}\bar{k}^2_{31}}\right)\right)\left(b_2\bar{k}_2 k_{32} + b_{31}\bar{k}^2_{31} + \bar{k}_{31}\bar{k}_2\left(b_2 - b_{31}\right)\right)}\right] \quad (43)$$

The impedance of the transport of cation vacancies is written in complete analogy to equation (35) as

$$Z_{M,f}^{-1} = \frac{\Delta I_M}{\Delta E} = \frac{6\bar{I}_M B}{\bar{L}}\left[(1-\alpha) + \frac{I_0 S\alpha}{j\omega + I_0 S}\right] \quad (44)$$

The total impedance due to generation and transport of cation vacancies, Z_M, is then given by:

$$Z_M = Z_{M,f} + Z_{M,F/S} \quad (45)$$

The total impedance is then calculated using equations (31), (32), (38) and (45). It is worth mentioning that the predictions of this model have been successfully compared to both steady-state current vs. potential curves and electrochemical impedance spectra at a range of potentials for W in sulphate-fluoride electrolytes, and the main kinetic and transport parameters have been estimated as depending on the pH and fluoride concentration [46].

CONCLUSIONS

In this brief overview of conduction mechanisms in valve metal/oxide/electrolyte systems, the main components of the current flowing through such systems have been described in some detail. The main theoretical equations that govern both electronic and ionic conduction have been given and discussed, and the methods of their comparison to experimental data in order to estimate the main kinetic, transport and structural parameters that characterise the different conduction types have been outlined.

In addition, a quantitative kinetic model involving processes at the film/solution interface and in the film bulk and also dissolution of metal through the oxide and oxide growth/dissolution as parallel reaction paths has been found to reproduce quantitatively the steady-state current vs. potential curves and the impedance spectra in a wide range of potentials and solution compositions. The pseudo-inductive feature at intermediate frequencies is explained by the interaction between two current carriers of opposite sign which accelerates the transport of the major current carrier in the transient regime. The main effect of electrolyte composition is on the cross-section of recombination of current carriers at the film/solution interface, which can be tentatively ascribed to the influence of adsorbed fluoride ions on the defect structure of the outermost layer of the anodic film.

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REFERENCES

1. L. Young, Anodic oxide films, Academic Press, New York, 1961.
2. F.Keller, M.Hunter, D.Robinson, J. Electrochem. Soc., **100**, 1953, 411.
3. A. Gunterschultze, H.Betz, Z.Phys. **92**, 1934, 367.
4. L.Young, Proc. Roy. Soc. **A 258**, 1960, 496.
5. L.Young, Proc. Roy. Soc. **A 263**, 1961, 395.
6. M.Dignam, Can. J. Chem., **42**, 1964, 1155.
7. S. Christov, S. Ikonopisov, J. Electrochem. Soc., **116**, 1969, 56.

8. Y.-M. Li, Y. Young, Proc. R. Soc. Lond, A **454**, 1998, 239.
9. W.van Geel, H. Emmens, Z. Phys., **87**, 1934, 220.
10. K.Nagasse, Met.Inst.Sci.Ind.Res., Osaka Univ., **1** 1955, 67.
11. R.Dreiner, J.Electrochem. Soc., **111,** 1964, 350.
12. A. Ammar, S. Darwish, M.Khalil, Corrosion, **32** 1976, 173.
13. S. Ikonopisov, Electrochim. Acta, **14**, 1969, 761.
14. V. Malinenko, L. Odynets, S. Chekmasova, E. Hanina, Electrokhimiya, **7**, 1971,1846.
15. L. Odynets, S. Chekmasova, Electrokhimiya, **9**, 1973, 1177.
16. S. Ikonopisov, N. Elenkov, J.Electroanal. Chem., **86,** 1978, 417.
17. N.Elenkov, S.Ikonopisov, V.Trifonova, A.Girginov, Surf.Technol., **9**, 1979, 379.
18. A. Charlesby, Acta Met., **1**, 1953, 348.
19. A.Smith, Can.J.Chem., **35**, 1957, 1151.
20. S. Christov, J. Electroanal. Chem., **105**, 1979, 275.
21. N. Morgulis, Zh. Eksp. Teor. Fiz., **16**, 1946, 959.
22. H. Masuda, K. Fukuda, Science, **268**, 1995, 1466.
23. H. Masuda, F. Hasegawa, S. Ono, J. Electrochem. Soc., **144**, 1997, 127.
24. O. Jessensky, F. Mueller, U. Goesele, J. Electrochem. Soc., **145**, 1998, 3735.
25. D. Gong, C.A. Grimes, O.K. Varghese, Z. Chen, E.C. Dickey, J. Mater. Res., **16**, 2001, 3334.
26. G.K. Mor, O.K. Varghese, M. Paulose, N. Mukherjee, C.A. Grimes, J. Mater. Res., **18**, 2003, 2588.
27. V. Zwilling, E. Darque-Ceretti, A. Boutry-Forveille, Electrochim. Acta, **45**, 2001, 921.
28. R. Beranek, H. Hildebrand, P. Schmuki, Electrochem. Solid State Lett., **6**, 2003, B12.
29. H. Tsuchiya, P. Schmuki, Electrochem. Commun., **6**, 2004, 1131.
30. S. Shingubara, K. Morimoto, H. Sakaue, T. Takahagi, Electrochem. Solid State Lett., **7**, 2004, E15.
31. I. Sieber, B. Kannan, P. Schmuki, Electrochem. Solid State Lett., **8**, 2005, J10.
32. W.J. Lee, W. H. Smyrl, Electrochem. Solid State Lett., **8**, 2005, B7.
33. I. Sieber, H. Hildebrand, A. Friedrich, P. Schmuki, Electrochem. Commun., **7**, 2005, 97.
34. Q. Lu, T. Hashimoto, P. Skeldon, G.E. Thompson, H. Habazaki, K. Shimizu, Electrochem. Solid State Lett., **8**, 2005, B17.
35. H. Tsuchiya, J. Macak, I. Sieber, P. Schmuki, Small **7**, 2005, 722.
36. J. Macak, K. Sirotna, P. Schmuki, Electrochim. Acta, **50**, 2005, 3679.
37. J. Macak, H. Tsuchiya, P. Schmuki, Angewandte Chemie, **44**, 2005, 2100.
38. Q. Cai, M. Paulose, O.K. Varghese, C.A. Grimes, J. Mater. Res., **20**, 2005, 230.
39. L. V. Taveira, J. M. Macαk, H. Tsuchiya, L. F. P. Dick, P. Schmuki, J. Electrochem. Soc., **152**, 2005, B405.
40. I. Sieber, P. Schmuki, J. Electrochem. Soc., **152**, 2005, C639.
41. K.S. Raja, M. Misra, K. Paramguru, Electrochim. Acta, **51**, 2005, 154.
42. M. Bojinov, Electrochim. Acta, **42,** 1997, 3489.
43. M. Bojinov, S. Cattarin, M. Musiani, B. Tribollet, Electrochim. Acta, **48**, 2003, 4107.
44. Geonja Lim, Jong-Ho Lee, Ji-Won Son, Hae-Weon Lee, Joosun Kim, J. Electrochem. Soc., **153**, 2006, B169.
45. M. Bojinov, G. Fabricius, T. Laitinen, K. Mäkelä, T. Saario and G. Sundholm, Electrochim. Acta, **45**, 2000, 2029.
46. V. Karastoyanov, M. Bojinov, Bulg. Chem. Commun., 2008, in print.