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Solid film at the anode influences the process of polyvalent metal electrorefining: theoretical bifurcation analysis of the problem

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Abstract A theoretical study of polyvalent metal anodic electrorefining has been carried out, and the decisive influence of surface film on the long-term process has been shown. A mathematical model of the long-term continuous electrorefining process in the form of non-linear differential equations is proposed. The developed model was investigated by the methods of the bifurcation theory. The model predicts the following types of electrolytic system: 1. The low-valence compound of the anodic film does not form. 2. A steady-state process with a stationary thickness of the anodic deposit. 3. An unlimited accumulation of low-valence compounds at the anode. 4. An unstable steady state: a bifurcation with a transition to case 3 or to the regime of undamped oscillations. The model provides satisfactory explanations of the experimental results related to long-term continuous electrorefining processes in molten salts.

Key words Polyvalent metal · Anodic film · Electrorefining · Ionic melt · Non-linear model · Bifurcation

Notation a dimensionless parameter of Eq. 20 · b ratio of the cathodic to total electroodic surface · C concentration, $\text{mol} \cdot \text{cm}^{-3}$ · D diffusion coefficient, $\text{cm}^2 \cdot \text{s}^{-1}$ · E activation energy of the ionic conductivity of the anodic film, $\text{J} \cdot \text{mol}^{-1}$ · F Faraday's number, $\text{A} \cdot \text{s} \cdot \text{mol}^{-1}$ · f a function · g ratio of the electronic to stationary-state ionic conductivity of the anodic film · I current, A · i oxidation number of the low-valence intermediate · J flux $\text{mol} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ (without subscript is a dimensionless parameter which depends on the ionic conductivity part of the film) · k heterogeneous constant of the intervalent equilibrium, $\text{mol}^{1-i/N} \cdot \text{cm}^{-3(1-i/m)}$ · N maximum oxidation number of the polyvalent compound in the electrolyte · p dimensionless parameter · q

heat evolution or heat transfer rate, $\text{J} \cdot \text{s}^{-1}$ · R gas constant, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ · S surface area (without subscript corresponds to the total surface of the anode and cathode) · T temperature, K · ΔT temperature difference between the anode surface and the bulk, K · t time, s · \tanh hyperbolic tangent · V volume of the electrolyte, cm^3 · v molar volume of the film substance, $\text{cm}^3 \cdot \text{mol}^{-1}$ · X dimensionless concentration of the intermediate in the bulk of the electrolyte · x variable X normalised relative to a steady-state point · Y dimensionless quantity of the deposited anodic film · y normalised variable Y · α ionic part of the total conductivity of the anodic film, dimensionless · β heat transfer coefficient, $\text{J} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{K}^{-1}$ · γ dimensionless parameter of the non-linear model · δ thickness of the diffusion layer, cm · θ dimensionless temperature difference, $\theta = \Delta T/T$ · μ amount of the deposited anodic film, mol · σ specific conductivity of the film, $\Omega^{-1} \cdot \text{cm}^{-1}$ · τ dimensionless time

Subscripts a anode · c cathode · e evolution (heat); electronic · i for intermediate species (concentration); ionic · L for linearized solution of the differential equation · O referring to the bulk of the electrolyte · s steady-state point

Introduction

It is widely recognised that charge/discharge of polyvalent element compounds, being a many-electron electrochemical process, proceeds through a sequence of single-electron steps which result in the formation of a set of intermediates [1, 2]. These species, when relatively stable and sparingly soluble in the electrolyte, can be deposited at the electrode surface to form a non-metallic intermediate layer. Thus, the processes of electrochemical deposition or dissolution of a polyvalent element should actually take place not at a bare electrode, but at a three-phase system consisting of metal electrode/in-

intermediate film/liquid electrolyte. It is evident that the film in such a system is not a simple passivating layer but an active participant in the electrolytic process. This has proved to be true for a variety of cases ranging from aqueous systems [3, 4] to molten salt electrolysis [5, 6]. A review and some qualitative considerations of the mechanism of the processes in electrochemical film systems can be found in [7], which mainly concerns the electrochemistry of molten fluorides.

The conductivity of the film decisively influences the behaviour of the whole system both qualitatively as well as quantitatively. Trivially, when the film is a pure electronic conductor, it will be the only solid product of the electrochemical process and will grow steadily as the current flows. On the other hand, if the conductivity is purely ionic, then the behaviour will be more complicated, depending on the nature of the ion which controls the transport through the film. If it is electroactive, then a stable solid protective film may be formed, as, for example, in the case of a lithium electrode in aprotic solvents [8]. Otherwise a stable state of the system is impossible; certain critical phenomena will be observed in this situation [6, 7].

Unlike the above-mentioned extremes, the general case, when the charge transport through the film involves both ions and electrons (and/or holes), is far from clear. The main feature is that the overall Faradaic process is split into two: the outer process, at the electrolyte/film interface, caused by the electronic part of the conductivity, and the inner process, at the film/electrode interface, caused by the ionic part. Some qualitative understanding based on the treatment of the film in term of Velikanov's polyfunctional conductor (PFP) [9] has already been gained [7]. As to the quantitative description, this faces great difficulties stemming from the essential non-linearity of the relevant mathematical models. Only a few such attempts have been made to date, all of them being based on the Poincaré bifurcation analysis [10], which was subsequently developed by Hopf [11] and others [12, 13], mainly for the purpose of investigating non-linear oscillations in electronics as well as in nature. This approach could be useful for the study of the above-mentioned highly non-equilibrium electrode film systems; the work on polyvalent metal electrodeposition from aqueous electrolytes [14], anode effect in fluoride melts [15], and instability of the protective film on a lithium electrode [16] support this opinion. An essentially similar approach has been followed in the present paper in order to investigate how the surface anode film with mixed conductivity influences the macrokinetics of long-term electrorefining (i.e. purification through continuous anodic dissolution and subsequent cathodic deposition) of a polyvalent metal. In particular, electrorefining in fluoride-containing molten electrolytes is considered.

Theory

Basic physical considerations

To begin with, an adequate physical pattern of the phenomena must be considered. Figure 1 represents a simplified model when an anodic film of low-solubility intermediates is available. The film conductivity is regarded to be both ionic and metallic (see [7] for the qualitative properties of such ion-metallic systems). The Faraday process at the inner junction is bound up with the ionic current component giving rise to the film growth. The metallic part of the conductivity causes oxidation of low-valence intermediates at the outer junction (both transported from the bulk by the flux J_a and the film's constituents).

The volume concentration of the intermediate (C_x) and the film thickness (or total amount) μ are independent variables in the present model. Increasing C_x leads to increased consumption rate of the intermediate and increased rate of accumulation of the deposited film. These are, accordingly, the negative and the positive feedback in a dynamic system under consideration.

The quantity of deposit affects the rate of transport of the intermediate into the bulk of the electrolyte with cathodic flux J_c . The more film deposited, the less is the total bulk concentration of polyvalent compound, the less is the cathodic surface concentration of the intermediate, the lower is the flux J_c , and hence, the lower is the rate of volume accumulation of the intermediate. This influence, therefore, is a negative feedback.

The effect of the amount of the deposit upon its accumulation rate occurs because of the change in the ratio of the components of conductivity of the film. The most obvious reason for such an effect is an additional heat generation due to Joule heating. This would cause the anode temperature to rise as the deposit is accumulated. Since the temperature dependence of metallic electronic conductivity is slight and ionic conductivity (the F^- ion migration in our case) is of an active nature, the temperature increase should give rise to an increase in the ionic conductivity part and to an increase in the rate of

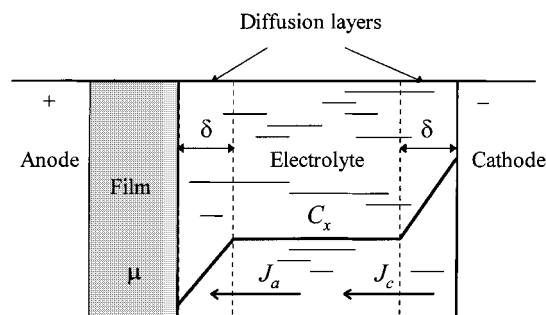


Fig. 1 Simplified scheme of electrorefining system. Distribution of the low-valence compound concentration C_x and the flows J_c and J_a are shown

accumulation of the anodic deposit. Thus, the effect of the amount of deposit μ on its accumulation rate is a positive feedback.

Simplest linear model

The above considerations may be represented mathematically by the following set of differential equations obtained from the material balances (see Appendix):

$$\frac{d\mu}{dt} = \mu' = \frac{(\alpha \cdot N - i) \cdot I}{i \cdot (N - i) \cdot F} + S_a \cdot \frac{D}{\delta} \cdot C_i, \quad (1)$$

$$\begin{aligned} V \frac{dC_i}{dt} &= V \cdot C_i' \\ &= S_c \frac{D}{\delta} k \cdot C_0^{i/N} \cdot \left(1 - \mu \frac{i^2}{N^2 \cdot C_0 \cdot V}\right) - S \frac{D}{\delta} C_i, \end{aligned} \quad (2)$$

The dimensionless forms of Eqs. 1 and 2 are

$$\frac{dY}{d\tau} = Y' = J + a \cdot X, \quad (3)$$

$$\frac{dX}{d\tau} = X' = b - Y - X, \quad (4)$$

where

$$\tau = t \cdot \frac{D \cdot S}{\delta \cdot V}, \quad (5)$$

$$X = \frac{C_i}{k \cdot C_0^{i/N}}, \quad (6)$$

$$Y = \mu \cdot \frac{i^2 \cdot S_c}{N^2 \cdot C_0 \cdot V \cdot S}, \quad (7)$$

are the dimensionless variables: time, concentration and quantity of deposit respectively, and

$$J = \frac{(\alpha - \frac{i}{N}) \cdot i \cdot \delta \cdot S_c \cdot I}{N \cdot (N - i) \cdot C_0 \cdot S^2 \cdot D \cdot F}, \quad (8)$$

$$a = \frac{S_c S_a}{S^2} \cdot \left(\frac{i}{N}\right)^2 \cdot k \cdot C_0^{(i-N)/N}, \quad (9)$$

$$b = \frac{S_c}{S}, \quad (10)$$

are the dimensionless parameters.

Equations 3 and 4 represent the simplest linear model of electrorefining. This model, which does not take into account the above-mentioned positive feedback ($\mu - \mu'$) predicts three types of system behaviour in a long-term process:

1. Unlimited accumulation of the anodic deposit when $J > 0$ (or $\alpha > i/N$)
2. Absence of the anodic film when $|J|/a > b$
3. Stable steady-state conditions with a limited film thickness when $|J|/a < b$. The transient process may be smooth when $a < 1/4$ or periodic when $a > 1/4$.

Non-linear mathematical model

The actual behaviour of the electrorefining system can be more complicated owing to non-linear effects which may manifest themselves in the dependencies of the parameters on the variables of Eqs. 3 and 4. The influence of the positive feedback between the amount of deposit and its accumulation rate is considered below.

Let us suppose that the parameter J depends on the variable Y because of the temperature dependence of the part of the ionic conductivity of the film, which can be expressed in the form

$$\alpha = \frac{\sigma_i(\theta)}{\sigma_e + \sigma_i(\theta)}. \quad (11)$$

The temperature dependence of the electronic conductivity σ_e is neglected, and the dependence of the ionic conductivity is assumed to be exponential:

$$\sigma_i = \sigma_0 \cdot e^{\frac{E}{R \cdot T}} = \sigma_{T_0} \cdot e^{\frac{E}{R \cdot T_0} \theta}. \quad (12)$$

The dimensionless temperature $\theta = \frac{\Delta T}{T}$, can be expressed as a function of the variable Y from the heat balance with respect to the heat exchange taking place under stationary conditions:

$$q_e = q_t. \quad (13)$$

The heat evolution (Joule heating) is

$$q_e = \frac{I^2 \cdot v \cdot \mu}{\sigma \cdot S_a^2}, \quad (14)$$

where μ can be expressed in terms of Y from Eq. 7

The heat transfer into the bulk is proportional to the temperature difference

$$q_t = S_a \cdot \beta \cdot \Delta T = S_a \cdot \beta \cdot T \cdot \theta \approx S_a \cdot \beta \cdot T_0 \cdot \theta. \quad (15)$$

Assuming that a steady-state solution of the Eqs. 3 and 4 exists (case 3 of the linear model), we can use new variables

$$y = (Y - Y_s) \cdot p; \quad x = (X - X_s) \cdot p, \quad (16)$$

where

$$X_s = \frac{-J_s}{a}; \quad Y_s = \sigma + \frac{J_s}{a} \quad (17)$$

and bring Eqs. 3 and 4 to the normalised form

$$y' = \gamma \cdot f(y) + a \cdot x, \quad (18)$$

$$x' = -y - x. \quad (19)$$

The function $f(y)$ is a non-linear function of y . Taking into account Eqs. 8 and 11–16, it may be written in the form

$$f(y) = \frac{e^{2 \cdot y} - 1}{e^{2 \cdot y} + g}. \quad (20)$$

The dimensionless parameters of the Eqs. 18 and 20 are

$$p = \frac{N^2 \cdot C_0 \cdot V \cdot v \cdot S \cdot I^2 \cdot E}{2 \cdot i^2 \cdot S_c \cdot S_a^3 \cdot \sigma_s \cdot \beta \cdot T_0^2 \cdot R}, \quad (21)$$

$$\gamma = \frac{N \cdot \delta \cdot V \cdot v \cdot E \cdot I^3}{2 \cdot i \cdot (N - i) \cdot S \cdot S_a^3 \cdot \sigma_s \cdot \beta \cdot T_0^2 \cdot R \cdot D \cdot F}, \quad (22)$$

$$g = \frac{\sigma_e}{\sigma_{i,s}}. \quad (23)$$

The value of the parameter g does not differ significantly from 1. Thus, a hyperbolic tangent can be a fair approximation for the function of Eq. 20. Further, if the system is not far from a steady-state point, the approximate formula for a hyperbolic tangent can be used:

$$f(y) = \frac{e^{2y} - 1}{e^{2y} + g} \approx \frac{e^{2y} - 1}{e^{2y} + 1} = \tanh y \approx y - \frac{y^3}{3}. \quad (24)$$

Using the simplifications in Eq. 24, the non-linear model of Eqs. 18 and 19 can be reduced to one second-order differential equation:

$$y'' - [(\gamma - 1) - \gamma \cdot y^2] \cdot y' + \frac{\gamma}{3} \cdot y^3 + (a - \gamma) \cdot y = 0$$

or approximately:

$$y'' - [(\gamma - 1) - \gamma \cdot y^2] \cdot y' + (a - \gamma) \cdot y = 0. \quad (25)$$

Equation 25 includes one additional parameter γ . The dependence of the system's behaviour on this parameter is expressed by the bifurcation diagram (Fig. 2). This includes four parts:

1. $\gamma < 1$; $a < (\gamma + 1)^2/4$ – stable steady state; a smooth transient process
2. $\gamma < 1$; $a > (\gamma + 1)^2/4$ – stable steady state; damped oscillations in a transient process
3. $\gamma > 1$; $a < (\gamma + 1)^2/4$ – unstable steady state; an unlimited accumulation of the anodic deposit
4. $\gamma > 1$; $a > (\gamma + 1)^2/4$ – unstable steady state; undamped self-oscillations (a limit cycle).

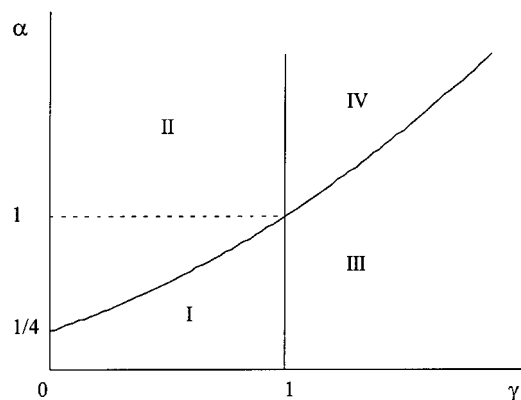


Fig. 2 Bifurcation diagram of the system (Eqs. 18 and 19). Region 4 corresponds to the oscillatory behaviour

Thus, γ is the bifurcation parameter of the non-linear model. The Hopf's bifurcation occurs at $\gamma = 1$, stability of the steady-state being lost and a limit cycle being born. The system gains the regime of the undamped oscillations, region 4 in Fig. 2. Equation 25 corresponds to Van der Pole's equation in this case [13]. Its approximate periodic solution can be obtained by Krylov-Bogoliubov's method [18] (see Appendix). This solution is represented by the ellipse on the phase plane (Fig. 3), where more precise numerical solutions of the system of Eqs. 18 and 20 are also shown. These have the shape of distorted ellipses in the vicinity of the rough harmonic solution. It confirms the validity of the simplifications of Eq. 24.

The approximate formula for the oscillatory solution period in a real time scale is:

$$T \approx \frac{2 \cdot \pi \cdot \delta \cdot V}{D \cdot \sqrt{S_c \cdot S_a}}. \quad (26)$$

This gives a period value of the order of about 10 h.

Some experimental results

It is clear that the developed theory is applicable to long-term processes with operating times of dozens or hundreds of hours (see Eqs. 5 and 26). As for the short-term laboratory experiments, the following conclusions can

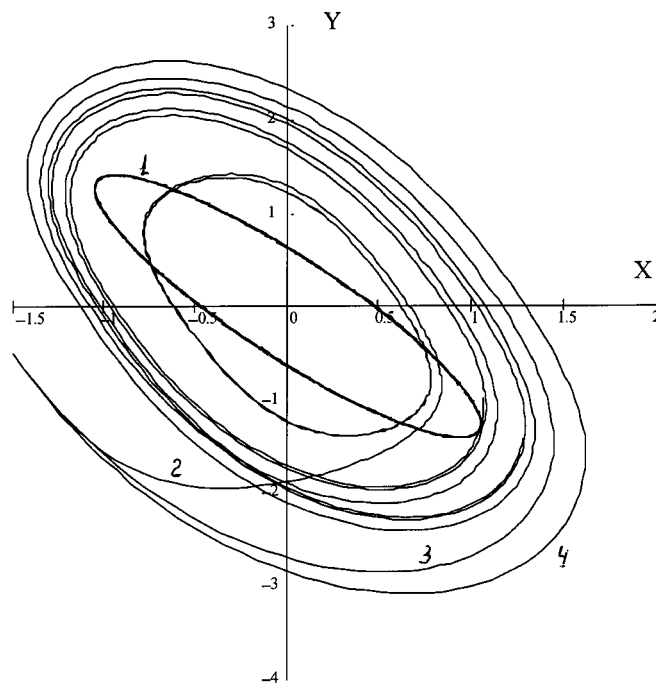


Fig. 3 Oscillatory solutions (limit cycles) of the differential equations (Eqs. 18 and 19) on the phase plane under the following approximations of the non-linear function $f(y)$: 2 $y - y^3/3$, 3 $\tanh y$, 4 $(e^{2y} - 1)/(e^{2y} + 1.25)$. The ellipse (1) corresponds to an approximate harmonic solution by the small parameter method (see Appendix); parameter values $a = 3$, $\gamma = 2$

be drawn. Their results could hardly be reproducible, especially when the system falls into type 3 or 4 of Fig. 2. It can be seen that this is the case when the numerous data on the electrorefining of Nb and Ta in chloride-fluoride melts are considered. The current efficiency, purity and other parameters differ significantly in the work of different authors [19].

We reinvestigated this process under the condition of long duration. Electrorefining was conducted continuously in the molten mixture $\text{KCl} - \text{NaCl} - \text{K}_2\text{NbF}_7$ (K_2TaF_7) at $720 \pm 10^\circ\text{C}$ in the course of 1 or 2 weeks. Two different types of electrolyzers were used, i.e. laboratory type and pilot plant cells, with operating currents up to 50 A and 300 A respectively. The techniques, other conditions and results of the experiments were described in [20].

It was found that the cathode current efficiency oscillated about a mean value. The amplitudes differed significantly, but the period (9–10 h for Nb and 12 h for Ta) remained constant with good precision. Figure 4 represents examples of such dependencies [20].

These results can be interpreted in terms of developed theory as follows. The system under consideration must be related to the type 4 bifurcation diagram (Fig. 2), with an unstable steady state and an oscillatory behaviour. The order of magnitude of the experimental period is in a good agreement with that theoretically predicted. Furthermore, the theory predicts an independence (or a very weak dependence) of the parameter $T \cdot \sqrt{S_a \cdot S_c} / V$ on the operating current and cell design and its inverse proportionality to the diffusion coefficient (see Eq. 34). This is borne out in practice, the parameter values being $(1.48 \pm 0.11) \cdot 10^3$ s/cm (laboratory cell) and $(1.51 \pm 0.18) \cdot 10^3$ s/cm (pilot plant cell) for Nb and about twice this figure $(3.24 \pm 0.25) \cdot 10^3$ s/cm for Ta, whose diffusivity is less (see [20] for more details).

Another kind of system is formed in the electrorefining of silicon in a $\text{KCl} - \text{KF} - \text{K}_2\text{SiF}_6$ melt. A number of short-term laboratory experiments on the process have been carried out and excellent results obtained [21].

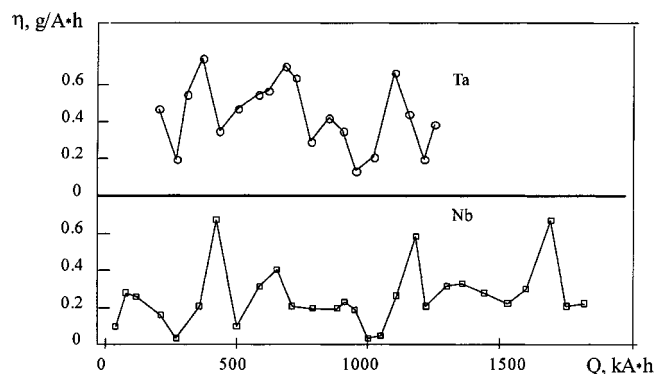


Fig. 4 Examples of the periodic changes of the current efficiency in long-term laboratory electrorefining of niobium and tantalum at the constant current 20 A (Ta) and 29 A (Nb). Similar oscillations were also observed in a pilot plant electrolyser at current 120 A [20]

Nevertheless, an attempt to reproduce these results in a large-scale process was unsuccessful: the problems arose after operation for approximately 24 h. They manifested themselves in increasing cell voltage, electrolyte temperature and decreasing current efficiency. This ultimately led to technological failure and termination of the process. The cause was established to be slag accumulation at the anode area. Hence, in terms of the developed ideas, this system is of the type in which unlimited anode deposit accumulation occurs (type 3, Fig. 2). Obviously, such systems could not be used in continuous large-scale technical processes.

Conclusions

1. As a result of the effects of a solid intermediate film at the anode, long-term continuous processes of polyvalent element electrorefining have features which cannot be predicted from data from short-term laboratory experiments.

2. Three main types of such systems are possible: (a) anodic dissolution without anodic film formation, (b) unlimited accumulation of low-valence compounds at the anode up to complete breakdown of the whole technological process, (c) the electrolytic process proceeding in the presence of an anodic film of a certain stationary thickness.

3. The presence of additional non-linear effects may cause the loss of the stability of the steady-state condition. There are two possibilities for this case: (a) a change to the conditions of the unlimited accumulation of the anodic deposit, and (b) bifurcation with the birth of a stable limit cycle, the system going over to an undamped oscillations regime.

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Appendix

The derivation of the differential equations of the process

Because of the mixed conductivity of the anodic film, the Faradaic process at the anode splits into two, i.e. at the inner junction (metal/film) and the outer one (film/electrolyte).

Let us denote the ionic current part as α . Then, at current I and in a time interval of dt the quantity of deposit

$$d\mu_{\text{int}} = \frac{\alpha \cdot I}{i \cdot F} dt \quad (1a)$$

is formed at the inner junction.

At the outer junction, $(1 - \alpha) I dt$ Coulombs of electricity are consumed at the same time to oxidise the portion of the film substance $d\mu_{\text{ext}}$, and the portion of the intermediate transferred from the bulk by the flux J_a is

$$(1 - \alpha) \cdot I \cdot dt = -(N - i) \cdot F \cdot d\mu_{\text{ext}} + S_a \cdot J_a \cdot dt. \quad (2a)$$

To determine the flux, Nernst's model of stationary diffusion with linear distribution of the concentration across the layers of the constant thickness is used, and the concentration of the intermediate is assumed to be zero, i.e. the anode discharge proceeds at limit current condition. Then

$$J_a = \frac{D}{\delta} \cdot C_i. \quad (3a)$$

The differential equation (Eq. 1) is obtained by combination of the equation for the material balance of the film substance

$$\mu' = \frac{d\mu}{dt} = \frac{d\mu_{\text{int}}}{dt} + \frac{d\mu_{\text{ext}}}{dt} \quad (4a)$$

with Eqs. 1a–3a.

Eq. 2 can be obtained from the balance of the intermediate in the electrolyte, which is supported by the cathodic flux J_c to the bulk and the anodic flux S_a from the bulk (see Fig. 1):

$$V \cdot C_i = S_c \cdot J_c - S_a \cdot J_a. \quad (5a)$$

Apart from the above-mentioned Nernst diffusion, the following assumptions and approximations were made in the derivation of Eq. 2.

Intervalent equilibrium between polyvalent species at the cathode surface is assumed. A convenient notation of this equilibrium, according to [17], is

$$\left(1 - \frac{i}{N}\right) \cdot E(0) + \frac{i}{N} \cdot E(N) = E(i), \quad (6a)$$

where the symbols $E(0)$, $E(i)$, $E(N)$ correspond to polyvalent metal compounds, oxidation numbers being zero, and i and N respectively.

The activity of $E(0)$ is regarded to be 1 (solid pure metal). Further, the concentration C_N of the high-valence compound $E(N)$ at the surface of the cathode and in the bulk are assumed to be equal. This is acceptable for not very dilute solutions. We can now express the cathodic surface concentration of the intermediate by

$$C_{i,\text{cath}} = k \cdot C_N^{i/N}. \quad (7a)$$

Further, the charge balance equation in the form

$$NC_0 = N \cdot C_N + i \cdot C_i + \frac{i \cdot \mu}{V} \quad (8a)$$

is used, where C_0 is the total initial concentration of the electrolyte. This means that the electrolyte at the initial time condition contains only the high-valence compound $A(N)$ with a concentration of C_0 , and no additions of salts to the melt during the process are made.

Now the cathodic concentration $C_{i,\text{cath}}$ required for the determination of the flux

$$V_c = \frac{D}{\delta} \cdot (C_{i,\text{cath}} - C_i) \quad (9a)$$

can be obtained by determining of C_N from Eq. 8a and substituting it into Eq. 7a. The power function obtained may be expanded into a series and, after neglecting the second and higher order members, may be written in the form

$$C_{i,\text{cath}} = k \cdot C_0^{i/N} \cdot \left(1 - \frac{\mu \cdot i^2}{N^2 \cdot C_0 \cdot V}\right). \quad (10a)$$

This linearising simplification is sufficiently correct under the condition

$$C_i \ll \frac{\mu}{V} \ll \frac{N}{i} C_0. \quad (11a)$$

Finally, Eq. 2 is obtained by substitution of Eqs. 3a, 9a and 10a into Eq. 5a.

2. The approximate solution of the non-linear second-order differential equation by the small-parameter (Krylov-Bogoliubov) method.

If the non-linear term of the differential equation may be thought of as a small disturbance, the above-mentioned method can then be applied to derive an approximate solution. Eq. 25 is presented as follows:

$$y'' + w^2 \cdot y + \gamma \cdot f(y, y') = 0, \quad (12a)$$

where

$$w^2 = a - \gamma \quad (13a)$$

and non-linear function

$$f(y, y') = -\gamma \cdot y' \cdot \left(\frac{\gamma - 1}{\gamma} - y^2\right). \quad (14a)$$

The solution is sought in a form

$$y = r(\tau) \cos \varphi(\tau) \quad (15a)$$

by a common technique described elsewhere [18].

Finally, the approximate periodic solution of the limit cycle type is obtained in the form:

$$y_L = 2 \cdot \sqrt{\frac{\gamma - 1}{\gamma}} \cos(w \cdot \tau + \varphi_0), \quad (16a)$$

where the dimensionless frequency w is approximately equal to $\sqrt{a - \gamma}$. The dimensionless period $T = 2\pi/w$ of the oscillation, then, is equal to $2\pi/\sqrt{a - \gamma}$. Therefore, the formula of Eq. 26 for the real time scale period is accurate to a constant coefficient. This coefficient is of the order 1 and should increase as the current I and concentration C_0 increase. This is hard to verify experimentally because of the very long duration of the tests.

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