

IMPEDANCE OF ELEMENTARY ELECTROCHEMICAL ACT

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(Received 16 November 1981)

The deposition of metals from salt melts proceeds without apparent overpotential and is determined by the laws of thermodynamics. Consideration of the general regularities of electrode processes in aqueous and molten electrolytes show that it is possible to govern them by means of complex formation reactions. The overpotential is here a nonmonotonic function of composition and can shift to both sides from the initial value. For molten media, these regularities are perceptible in the case of the cathodic reduction of anionic species. Attempts to theoretically calculate the activation energy should be made considering the medium as a high temperature plasma.

The molten electrolytes permit one to carry out the electrolysis of individual systems without any concentration polarization. The experimental data on electrode admittance in melts lead to the creation of a new model of the near-electrode layer, where transport depends not on the concentration gradient but on the energy gradient.

Keywords : Impedance; Elementary Electrochemical Act; Laws of Thermodynamics; Molten Electrolyte; Concentration & Energy Gradient; Drössbach Diffusion Impedance

ACCORDING to "classical" conceptions (Sluyters, 1960), the impedance of elementary electrochemical act is modelled in the form of pure active resistance:

$$\theta = \frac{RT}{zFi_0} = \eta'_i(0) \quad \dots(1)$$

This resistance is calculated as the derivative $\eta'_i(0)$ of Tafel equation

$$i = i_0 \left[\exp \frac{\alpha z F \eta}{RT} - \exp \frac{-\beta z F \eta}{RT} \right] \quad \dots(2)$$

where η -overvoltage, i -current, i_0 -exchange current and α and β -transfer coefficients. The other faradaic impedances (impedance of homogeneous chemical reaction, diffusion impedance, impedance of heterogeneous chemical stage) have active and capacitive components. Taking Drössbach diffusion impedance as given by (Drössbach & Shulz, 1964) equation (3) and (4)

$$\frac{1}{Z_D} = \frac{z^2 F^2 C_\infty D}{RT \delta} \cdot \frac{u}{2} \cdot \frac{2 \sin u + (1+j)(\operatorname{sh} u - \sin u)}{\operatorname{ch} u - \cos u} \quad \dots(3)$$

$$u = \delta \sqrt{\frac{2\omega}{D}} \quad \dots(4)$$

we can see that at zero frequency this impedance coincides with the derivative of the stationary voltamperic curve of the diffusion polarization:

$$\epsilon = \frac{RT}{ZF} \ln \frac{i_a}{i_a - i} \quad \dots(5)$$

ω -frequency of alternating current, δ -diffusion layer thickness, C_∞ -concentration in the bulk of electrolyte, D -diffusion coefficient, ϵ -diffusion overvoltage, i_a -diffusion current, $j = \sqrt{-1}$. In fact,

$$\lim_{\omega \rightarrow 0} Z_D = \frac{RT\delta}{z^2 F^2 C_\infty D} \quad \dots(6)$$

$$\epsilon'_i(0) = \frac{RT}{zFi_a} \quad \dots(7)$$

$$i_a = zFD \frac{C_\infty}{\delta} \quad \dots(8)$$

$$\epsilon'_i(0) = \lim_{\omega \rightarrow 0} \cdot Z_D \quad \dots(9)$$

Thus, the derivative of stationary voltamperic curve is only an exceptional case of impedance, it equals the impedance at the zero frequency. Obviously, it is to be expected that

$$\eta'_i(0) = \theta = \lim_{\omega \rightarrow 0} Z \quad \dots(10)$$

but not

$$\eta'_i(0) = \theta = Z \quad \dots(11)$$

(Z -elementary act impedance).

When the pure activation polarization takes place, the total concentrations a and b of reactants do not change. However, only the active "hot" particles react on the electrode. These particles (Butler, 1923; and Delimarsky & Gorodysky, 1959) have energy which is more than some activation energies W_A^0 and W_B^0 . Their concentrations are equal to A and B . In equilibrium state, the concentration of "hot" particles is determined by Boltzmann distribution :

$$A = a \cdot \exp - \frac{W_A^0}{RT}; B = b \cdot \exp - \frac{W_B^0}{RT} \quad \dots(12, 13)$$

If supposing that the concentrations A and B of "hot" particles do not change along the electrode normal X (the equilibrium Boltzmann distribution is established rapidly), we come to the equation (11). If assuming that $A = A(x, t)$ and $B = B(x, t)$, i.e., the concentrations of "hot" particles at near electrode layer do change (the equilibrium Boltzmann distribution is not established rapidly), we come to the equation (10). From the last point of view, the basic formulae of slow discharge theory are following :

$$i = zF [k_1 A(0, t) - k_2 B(0, t)] \quad \dots(14)$$

$$A(0, t) = a_\infty \exp - \frac{W_A - \alpha z F \varphi(t)}{RT} \quad \dots(15)$$

$$B(0, t) = b_\infty \exp - \frac{W_B + \beta z F \varphi(t)}{RT} \quad \dots(16)$$

$$A_\infty = a_\infty \exp - \frac{W_A - \alpha z F \varphi_e}{RT} \quad \dots(17)$$

$$B_\infty = b_\infty \exp - \frac{W_B + \beta z F \varphi_e}{RT} \quad \dots(18)$$

$$\eta = \varphi_e - \varphi \quad \dots(19)$$

$$A(0, t) = A_\infty \exp \frac{\alpha z F \eta(t)}{RT} \quad \dots(20)$$

$$B(0, t) = B_\infty \exp - \frac{\beta z F \eta(t)}{RT} \quad \dots(21)$$

$$k_1 A_\infty = k_s a_\infty^\beta I_\infty^* = k_2 B_\infty \quad \dots(22)$$

$$k_s = k_1^\beta k_2^\alpha \exp - \frac{\alpha W_B - \beta W_A}{RT} \quad \dots(23)$$

where t is time, a_∞ and b_∞ are total concentrations, A_∞ and B_∞ are bulk concentrations of "hot" particles, φ the potential, φ_e the equilibrium potential, k_1 , k_2 , k_s the electrochemical velocity constants).

Regeneration (Gorodysky *et al.*, 1978) of the "hot" particles concentration at near electrode layer can occur at least by two ways :

(1) due to the diffusion of "hot" particles from the bulk of electrolyte with the velocity $D_A \left(\frac{\partial^2 A}{\partial x^2} \right)$ and $D_B \left(\frac{\partial^2 B}{\partial x^2} \right)$;

(2) due to the redistribution of energy, when "cold" particles a and b are running against the solvent S , with the velocity $x_1 S a_\infty - x_A \cdot S A$ and $x_2 \cdot S b_\infty - x_B \cdot S B$. Thus,

$$\frac{\partial A(x, t)}{\partial t} = D_A \frac{\partial^2 A(x, t)}{\partial x^2} + x_1 S a_\infty - x_A \cdot S A(x, t) \quad \dots(24)$$

$$\frac{\partial B(x, t)}{\partial t} = D_B \frac{\partial^2 B(x, t)}{\partial x^2} + x_2 S b_\infty - x_B S B(x, t) \quad \dots(25)$$

where D_A and D_B are diffusion coefficients, S —solvent concentration, x_1 and x_2 are velocity constants of energy transfer from the solvent and x_A and x_B are velocity constants of energy transfer to the solvent. In the bulk of electrolyte

$$X_1 S a_\infty = X_A S A_\infty \quad \dots(26)$$

$$X_2 S b_\infty = x_B S B_\infty \quad \dots(27)$$

When alternating current is superposed, the oscillations of concentrations ΔA and ΔB take place (Ukshe, 1969; and Grafov, 1973) around the equilibrium values A_∞ and B_∞

$$A(x, t) = A_\infty - \Delta A(x, t) = A_\infty - \overline{\Delta A}(x) \cdot e^{j\omega t} \quad \dots(28)$$

$$B(x, t) = B_\infty - \Delta B(x, t) = B_\infty + \overline{\Delta B}(x) \cdot e^{j\omega t} \quad \dots(29)$$

($\overline{\Delta A}$ and $\overline{\Delta B}$ are amplitude values of oscillations). The equations (24) – (29) give the system

$$j\omega \cdot \overline{\Delta A}(x) = D_A \frac{d^2 \overline{\Delta A}(x)}{dx^2} - X_A S \cdot \overline{\Delta A}(x) \quad \dots(30)$$

$$j\omega \cdot \overline{\Delta B}(x) = D_B \cdot \frac{d^2 \overline{\Delta B}(x)}{dx^2} - X_B S \cdot \overline{\Delta B}(x) \quad \dots(31)$$

with general solution (Kamke, 1965)

$$\overline{\Delta A}(x) = c_1 \cdot \text{ch} \cdot x \sqrt{\frac{j\omega + X_A S}{D_A}} + c_2 \cdot \text{sh} \cdot x \sqrt{\frac{j\omega + X_A S}{D_A}} \quad \dots(32)$$

$$\overline{\Delta B}(x) = c_3 \cdot \text{ch} \cdot x \sqrt{\frac{j\omega + X_B S}{D_B}} + c_4 \cdot \text{sh} \cdot x \sqrt{\frac{j\omega + X_B S}{D_B}} \quad \dots(33)$$

(c_1, c_2, c_3, c_4 —integration constants).

The impedance of this system is determined as

$$Z = \frac{\alpha \cdot \Delta\eta}{\Delta i} + \frac{\beta \cdot \Delta\eta}{\Delta i} \quad \dots(34)$$

Here the peak values ' $\Delta\eta$ ' of the overvoltage

$$\eta(t) = 0 \pm \Delta\eta(t) = 0 \pm \Delta\eta \cdot e^{j\omega t} \quad \dots(35)$$

according to equations (20) and (21) equal to

$$- \alpha \cdot \Delta\eta = \frac{RT}{zf} \cdot \frac{\overline{\Delta A}(0)}{A_\infty} \quad \dots(36)$$

$$-\beta \cdot \Delta\eta = \frac{RT}{zF} \cdot \frac{\overline{\Delta B}(0)}{B_\infty} \quad \dots(37)$$

The peak values ' Δi ' of current

$$i = 0 \pm \Delta i = 0 \pm \Delta i \cdot e^{i\omega t} \quad \dots(38)$$

are determined as the concentration gradient of "hot" particles at the electrode surface :

$$\Delta i = zF D_A \cdot \overline{\Delta A}'_\alpha(0) = -zF D_B \cdot \overline{\Delta B}'_\alpha(0) \quad \dots(39)$$

The equations (32), (33) are solved at the boundary condition

$$\Delta A(\delta) = \Delta B(\delta) = 0 \quad \dots(40)$$

which denotes the constancy of "hot" particles concentration at the outer boundary of the diffusion layer.

As a result

$$Z = \frac{RT}{z^2 F^2} \left[\frac{\text{th } \delta \sqrt{\frac{j\omega + X_A S}{D_A}}}{A_\infty D_A \sqrt{\frac{j\omega + X_A S}{D_A}}} + \frac{\text{th } \delta \sqrt{\frac{j\omega + X_B S}{D_B}}}{B_\infty D_B \sqrt{\frac{j\omega + X_B S}{D_B}}} \right] \quad \dots(41)$$

At zero frequency, taking into account (22),

$$\begin{aligned} \lim_{\omega \rightarrow 0} Z &= \frac{RT}{z^2 F^2} \left[\frac{\text{th } \delta \sqrt{\frac{X_A S}{D_A}}}{A_\infty \sqrt{D_A X_A S}} + \frac{\text{th } \delta \sqrt{\frac{X_B S}{D_B}}}{B_\infty \sqrt{D_B X_B S}} \right] \\ &= \frac{RT}{z^2 F^2 a_\infty^\beta b_\infty^\alpha k_s} \left[\frac{k_1 \text{th } \delta \sqrt{\frac{X_A S}{D_A}}}{\sqrt{D_A X_A S}} + \frac{k_2 \text{th } \delta \sqrt{\frac{X_B S}{D_B}}}{\sqrt{D_B X_B S}} \right] \quad \dots(42) \end{aligned}$$

The equation (42) should be compared with the derivative of the stationary voltamperic curve. This curve can be obtained from the solution for the stationary system :

$$0 = D_A \cdot \frac{d^2 A(x)}{dx^2} + X_1 S a_\infty - X_A S A(x) \quad \dots(43)$$

$$0 = D_B \cdot \frac{d^2 B(x)}{dx^2} + X_2 S b_\infty - X_B S B(x) \quad \dots(44)$$

In the condition of stationary electrolysis (constant potential)

$$A(0) = A_0 = \text{const}; \quad B(0) = B_0 = \text{const}. \quad \dots(45, 46)$$

and in the condition of constancy of concentration at the outer boundary of diffusion layer

$$A(\delta) = A_\infty, \quad B(\delta) = B_\infty \quad \dots(47, 48)$$

this solution is

$$\begin{aligned} i &= zFD_A(A_\infty - A_0) \sqrt{\frac{X_A S}{D_A}} C \operatorname{th} \delta \sqrt{\frac{X_A S}{D_A}} \\ &= zFD_B(B_0 - B_\infty) \sqrt{\frac{X_B S}{D_B}} C \operatorname{th} \delta \sqrt{\frac{X_B S}{D_B}} \\ &= zF(k_1 A_0 - k_2 B_0) \end{aligned} \quad \dots(49)$$

Thus

$$D_A \sqrt{\frac{X_A S}{D_A}} = \frac{(k_1 A_0 - k_2 B_0) \operatorname{th} \delta \sqrt{\frac{X_A S}{D_A}}}{A_\infty - A_0} \quad \dots(50)$$

$$D_B \sqrt{\frac{X_B S}{D_B}} = \frac{(k_1 A_0 - k_2 B_0) \operatorname{th} \delta \sqrt{\frac{X_B S}{D_B}}}{B_0 - B_\infty} \quad \dots(51)$$

As the final result,

$$\lim_{\omega \rightarrow 0} Z = \frac{RT}{z^2 F^2 a_\infty^\beta b_\infty^\alpha k_3} = \frac{RT}{zF i_e} \quad \dots(52)$$

which coincides with equation (10).

If we assume that the equilibrium Boltzmann distribution is established in no time, we have $X_A \gg \omega$, $X_B \gg \omega$ and

$$Z = \frac{RT}{z^2 F^2} \left[\frac{\operatorname{th} \delta \sqrt{\frac{X_A S}{D_A}}}{A_\infty D_A \sqrt{\frac{X_A S}{D_A}}} + \frac{\operatorname{th} \delta \sqrt{\frac{X_B S}{D_B}}}{B_\infty D_B \sqrt{\frac{X_B S}{D_B}}} \right] \quad \dots(53)$$

which leads to equation (11).

It is convenient to do the separation of active and capacitive components in the equation (41) for each of two series elements of impedance :

$$Z = Z_\alpha + Z_\beta = \frac{\alpha \cdot \Delta\eta}{\Delta i} + \frac{\beta \cdot \Delta\eta}{\Delta i} \quad \dots(54)$$

Then

$$\begin{aligned} \frac{1}{Z_\alpha} &= \frac{z^2 F^2 A_\infty D_A Y_A}{RT \delta (\operatorname{ch} \cdot 2f_A \cdot Y_A - \cos 2g_A Y_A)} [f_A \cdot \operatorname{sh} \cdot 2f_A \cdot Y_A \\ &\quad + g_A \cdot \sin 2g_A Y_A + j(g_A \cdot \operatorname{sh} \cdot 2f_A Y_A - f_A \cdot \sin 2g_A Y_A)] \\ &= \frac{1}{y_{A1}} + \frac{1}{y_{A2}} + \frac{1}{X_A} \end{aligned} \quad \dots(55)$$

$$\begin{aligned} \frac{1}{Z_B} &= \frac{z^2 F^2 B_\infty D_B Y_B}{RT\delta (\operatorname{ch} 2f_B Y_B - \cos 2g_B \cdot Y_B)} [f_B \cdot \operatorname{sh} \cdot 2f_B \cdot Y_B \\ &\quad + g_B \cdot \sin 2g_B Y_B + j(g_B \cdot \operatorname{sh} 2f_B Y_B - f_B \sin 2g_B Y_B)] \\ &= \frac{1}{y_{B1}} + \frac{1}{y_{B2}} + \frac{1}{X_B} \end{aligned} \quad \dots(56)$$

Here

$$f_A = \sqrt{\sqrt{X_A^2 + \omega^2} + X_A} \quad \dots(57)$$

$$f_B = \sqrt{\sqrt{X_B^2 + \omega^2} + X_B} \quad \dots(58)$$

$$g_A = \sqrt{\sqrt{X_A^2 + \omega^2} - X_A} \quad \dots(59)$$

$$g_B = \sqrt{\sqrt{X_B^2 + \omega^2} - X_B} \quad \dots(60)$$

$$Y_A = \frac{\delta}{\sqrt{2D_A}}, \quad Y_B = \frac{\delta}{\sqrt{2D_B}} \quad \dots(61, 62)$$

The series elements Z_α and Z_β of the total impedance consist of the parallel components y_1 , y_2 and X .

REFERENCES

- Butler, J. A. V. (1923) *Trans. Faraday Soc.*, **19**, 659, 729.
 Delimarsky, Yu. K., and Gorodysky, A. V. (1959) *Zh. fiz. Khim.*, **33**, 137.
 Drössbach, P., and Schulz, J. (1964) *Electrochim. acta*, **9**, 1391.
 Gorodysky, A. V., Kublanovsky, V. S., and Pototskaya, V. V. (1978) *Extend. Abstr.*, 29 *Meet. int. Soc. Electrochem., Budapest*, Part I, 485.
 Grafov, B. M., and Ukshe, E. A. (1973) Electrochemical circuits of alternating current. In: "Science", Moscow.
 Kamke, E. (1965) Reference book of common differential equations. In: "Science", Moscow.
 Sluyters, J. H. (1960) *Rec. trav. chim.*, **79**, 1092.
 Ukshe, E. A. (1969) *Synthesis of Alternating Current Electrochemical Circuits*. Institute of Scientific and Technical Information, Moscow.

Discussion

H. C. GAUR (*University of Delhi, Delhi*): In your treatment only mononuclear complexes are considered. How will it be affected by considering the presence of dinuclear complexes, e.g., M_2X_2 ?

A. V. GORODYSKY: I suppose the general dependences will be valid.