

Physicochemical interpretation of the inflection point on chronopotentiometric and polarographic curves*

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Mathematical analysis of the equations for calculation of the potential of the measured electrode in chronopotentiometry showed that this potential has a constant value if the activity of the reduced form is different from 1. This enables us to determine whether the electrodeposited metal and the material of the measured electrode react together forming an alloy, or whether they are inactive under the given conditions. Galvanic electro-deposition from molten salts allows to conclude on the adherence stability of the deposited metal to the basic material.

Theoretical

A. An alloy is formed on the measured electrode

1. In the case of a polarographic electrolysis the dependence $E = f(i)$ is described by the Heyrovský–Ilkovič equation [1]

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d - i}{i} \quad (1)$$

Applying the condition of the existence of an inflection point [2] it may be easily found that

$$i_{\text{inflex}} = \frac{i_d}{2}, \quad (2)$$

$$E_{\text{inflex}} = E_{1/2} = \text{const.} \quad (3)$$

2. For the case of an electrolysis by chronopotentiometry the dependence $E = f(t)$ (t = time of the electrolysis) has the form of the Sand's equation

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{\sqrt{\tau} - \sqrt{t}}{\sqrt{t}} \quad (4)$$

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$E_{1/2}$ has the same meaning as in eqn (1), τ being the transition time.

From the mentioned mathematical condition of the existence of an inflection point [2] applied to the curve $E = f(t)$ we obtain

$$\frac{\partial^2 E}{\partial t^2} = \frac{RT}{nF} \left[\frac{\sqrt{\tau}(\sqrt{\tau} - 3/2 \sqrt{t})}{t^2(\sqrt{\tau} - \sqrt{t})^2} \right] = 0.$$

While $\sqrt{\tau} \neq \sqrt{t}$, and if both these values are different from zero, the expression $(\sqrt{\tau} - 3/2 \sqrt{t})$ has to be zero

$$\sqrt{\tau} - 3/2 \sqrt{t} = 0$$

thus

$$\sqrt{\tau} = 3/2 \sqrt{t}$$

and

$$t_{\text{inflex}} = 2/3 \sqrt{\tau}.$$

Introduction of this relation into eqn (4) leads to the equation for the potential of the measured electrode in the inflection point

$$E_{\text{inflex}} = E_{1/2} + \frac{RT}{nF} \ln 1/2;$$

$$E_{\text{inflex}} = \text{const.} \quad (5)$$

The developed equation according to which the potential in the inflection point on the measured curve has a constant value, when the activity of the reduced form of the electroactive species differs from 1, is valid consequently not only in polarography, but also in chronopotentiometry. For chronopotentiometric electrolysis this result seems to be not yet known.

B. The deposited metal forms a separate solid phase on the measured electrode

1. Let us consider an electrolytical process under polarographic conditions. Then the potential of the measured electrode under the above conditions follows the equation of Kolthoff and Lingane [3]

$$E = E^0 + \frac{RT}{nF} \ln \frac{\gamma_{\text{ox}}}{k_s} + \frac{RT}{nF} \ln (i_d - i). \quad (6)$$

The second derivative of this equation is

$$\frac{\partial^2 E}{\partial i^2} = - \frac{RT}{nF(i_d - i)^2} = 0;$$

$$(i_d - i) \geq 0$$

and this expression cannot be zero. The mathematical conditions for the existence of the inflection point are not fulfilled. Indeed, the polarographic curve shows a monotonous course without any inflection point [4].

The half-wave potential of such a curve is dependent on the concentration of the depolarizer

$$E_{1,2} = E_{\text{const}} + \frac{RT}{nF} \ln \frac{aC_{\text{ox}}^0}{2}, \quad (7)$$

where a is the constant sum from the Ilkovič equation.

In such a case ($a_{\text{red}} = 1$) the chronopotentiometric curve follows the equation

$$E = E^0 + \frac{RT}{nF} \ln \gamma_{\text{ox}} \frac{2i}{nF \sqrt{D_{\text{ox}} \cdot \pi}} + \frac{RT}{nF} \ln (\sqrt{\tau} - \sqrt{t}), \quad (8)$$

where i represents the constant current density pulse, the first two terms in eqn (8) being constants.

In applying the conditions for the inflection point to eqn (8) we find:

$$\frac{\partial^2 \Delta E}{\partial t^2} = - \frac{RT}{2nF} \left[\frac{1}{2t(\sqrt{\tau} - \sqrt{t})^2} - \frac{1}{2t\sqrt{\tau}(\sqrt{\tau} - \sqrt{t})} \right] = 0$$

and

$$\frac{1}{2t(\sqrt{\tau} - \sqrt{t})^2} = \frac{1}{2t\sqrt{\tau}(\sqrt{\tau} - \sqrt{t})},$$

and consequently

$$t_{\text{inflex}} = \frac{1}{2};$$

$$\frac{\partial^3 \Delta E}{\partial t^3} = \frac{RT}{2nF t^2(\sqrt{\tau} - \sqrt{t})^2} \left[\frac{\sqrt{\tau} - 2\sqrt{t}}{\sqrt{\tau} - \sqrt{t}} + \frac{\sqrt{\tau} - 3/2\sqrt{t}}{\sqrt{\tau}} \right]. \quad (9)$$

As it may be seen, the third derivative is different from zero, because $\tau > 0$; $t > 0$; $\tau < t$; $\tau \neq t$.

Now, introducing the expression for $\sqrt{t_{\text{inflex}}}$ into eqn (8) we obtain

$$E_{\text{inflex}} = E'_{\text{const}} + \frac{RT}{nF} \ln \frac{\sqrt{\tau}}{2}. \quad (10)$$

Then from the Sand's equation

$$\sqrt{\tau} = \frac{nF \sqrt{D_{\text{ox}} \cdot \pi}}{2i} C_{\text{ox}}^0,$$

we obtain

$$E_{\text{inflex}} = E'_{\text{const}} + \frac{RT}{nF} \ln \frac{bC_{\text{ox}}^0}{2}, \quad (11)$$

where b is the constant ($i = \text{constant current pulse}$). The analogy between the results of eqn (7) and (11) is evident.

Experimental

The validity of relation (5) was verified by the following study of the potential of Pt microelectrode in chronopotentiometric electrolysis. Pt was the basic metal on which the electrodeposition of the reduced Pb(II) ions in the system of molten chlorides NaCl—KCl—PbCl₂ was performed.

The chemicals and equipment used in this electrolysis were the same as in the study of the diffusivity of Pb(II) ions made by the same authors [5]. The composition of the system was also the same: 1×10^{-4} mole PbCl_2 per gram of the molten equimolar mixture NaCl—KCl.

From the curves recorded at the constant temperature of 880°C and at various constant current pulses, we evaluated the potential of the inflection point using the tangent method according to *Delahay* [6].

Results and discussion

The evaluation of the results was performed on a MINSK 22 computer by the least-squares method. It can be seen from Table 1 that, considering the mentioned parameters, the potential of the inflection point E_{inflex} is within the range of experimental

Table 1

Potential of the inflection point of chronopotentiometric curves in the system of molten chlorides NaCl—KCl— PbCl_2 at 880°C and the PbCl_2 concentration 1×10^{-4} mole per gram of equimolar mixture NaCl—KCl

i [A cm^{-2}]	$(i \sqrt{\tau}/C_{\text{ox}}^0) \cdot 10^{-3}$ [A cm^{-2} $\text{s}^{1/2}$ mol^{-1} g^{-1}]	$\sqrt{\tau}$ [$\text{s}^{1/2}$]	E_{inflex} [V]
0.200	3.46	1.732	0.653
0.200	3.74	1.871	0.653
0.200	3.84	1.924	0.651
0.204	2.77	1.378	0.650
0.204	3.28	1.612	0.652
0.232	3.28	1.414	0.653
0.232	2.64	1.140	0.654
0.280	3.43	1.225	0.653
0.280	3.31	1.183	0.654
0.280	3.19	1.140	0.650
0.280	2.93	1.049	0.651

errors constant. This confirms that eqns (4) and (5) are fulfilled; that means that in the given case the deposited metal (lead) reacts with the material of the electrode (platinum) forming an alloy. The lead atoms evidently diffuse into the platinum lattice. Should this diffusion not occur, the potential of the inflection point would be dependent on the transition time according to eqn (10). On the other hand the existence of a Pt—Pb alloy is confirmed by [7].

Similar considerations may be found in paper [8] in connection with the potential of the solid electrode used in the polarography of molten salts. The potential of the inflection point on the curve $E = f(t)$, similarly as the half-wave potential in polarography, makes possible a relatively simple determination, whether the deposited metal reacts with the basic material (the metal of the electrode) and whether good adhesive properties of the deposited metal may be expected to result from electroplating with molten salts.

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