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Abstract

Full Text

PHYSICAL CHEMISTRY

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OSCILLOPOLAROGRAPHY WITH A PRESCRIBED SINUSOIDAL VOLTAGE FOR THE STUDY OF MOLTEN ELECTROLYTES

Polarography is one of the most important methods for studying molten electrolytes (^{1,2}). The shortcomings of this method are partly associated with the use of solid electrodes under conditions of slow polarization. The latter usually has values from 10 to 200 mV/min. During polarization the surface of the electrode may change considerably, which affects the reproducibility of the results. In some cases the products of the electrochemical reaction deposited on the electrode surface undergo irreversible changes; therefore the polarization curves shift in potential during the reverse scan (^{3,4}). In these cases comparison of cathodic and anodic polarograms does not make it possible to judge the degree of reversibility of the electrode process, as is done, for example, in amalgam polarography of aqueous solutions (^{5}).

The indicated shortcomings can be eliminated by using oscillopolarographic methods, in which polarization is carried out over a short interval of time. Several works are already known ($^{6-12}$) in which oscillopolarographic schemes were used to study molten electrolytes. Judging by the polarization rate, which was achieved in the scheme with a prescribed current,

$$\frac{dE}{dt} = 1.0\ \text{V/sec} \quad (^{6-8}),$$

and, in schemes with a prescribed voltage,

$$\frac{dE}{dt} = 1.0\text{–}5.0\ \text{V/sec} \quad (^{9-11}),$$

the methods used may be characterized as low-frequency ones, which make it possible to carry out polarization and to study the process only in one direction. They have a number of undoubted advantages over the usual polarographic method, but they do not exhaust all the possibilities of oscillopolarography with respect to molten electrolytes.

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

In order to assess directly the character of the electrode process itself, it is necessary to carry out such a polarization that both the cathodic and anodic processes can be observed, while the interval of time between them must be very small so that the products of electrolysis do not undergo any changes. From this point of view, a method of polarization by pulses in the form of an isosceles triangle is of interest; it was first applied in oscillopolarography of aqueous solutions by Ševčík (^{13}). The method makes it possible, from the difference between the potentials of the cathodic and anodic peaks, to estimate the degree of reversibility of the electrode process. For conditions in which the products of electrolysis are removed from the electrode surface (or when the change in activity of the electrolysis products is proportional to the current), the criteria of reversibility may be as follows: on the basis of the Randles relations (^{14})

$$\Delta E_{\mathrm{ob}} = E_{\mathrm{k}} - E_{\mathrm{a}} = 2.2\frac{RT}{nF}, \tag{1}$$

proceeding from Shevchik' s relations (^{13})

$$\Delta E_{\mathrm{ob}} = E_{k} - E_{a} = 3.2\,\frac{RT}{nF}. \tag{2}$$

A precise experimental check showed (^{15}) that dependence (2) is more accurate. Nigmatullin (^{16}, ^{17}) pointed out that the method can be simplified, while relation (3) remains valid, if polarization is carried out with a prescribed sinusoidal voltage. It is especially convenient to use a voltage with a frequency of 50 Hz. However, such a method had been developed only for the dropping mercury electrode.

Fig. 1. Circuit for polarization with a prescribed sinusoidal voltage. T—transformer, B—diode, C—200 μF, —cell, R_1 = 200-500 Ω, R_2 = 1-10 Ω, R_3 = 20-200 Ω; R_4 = 2-20 Ω

Fig. 2. E-t oscillograms of the prescribed voltage, recorded on an ENO-1 oscillograph. 1—contact K open, 2—contact closed

For solid electrodes this problem had still not been solved, evidently because it is difficult to polarize an electrode with a developed surface through the relatively small resistance of the electrode capacitance at a frequency of 50 Hz. Taking into account the possibilities of the method with a prescribed sinusoidal voltage,

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which at a frequency of 50 Hz makes it possible to attain a considerable rate of polarization, we decided to try to apply it to the study of molten electrolytes using solid electrodes.

In carrying out the experiments, the circuit shown in Fig. 1 was used. The circuit T, R_1, B, R_2 may be regarded as a generator of unipolar pulses, whose output resistance is determined by the value of R_2. With a high-power alternating-current source, the resistance R_2 can be very small. For normal operation of the circuit and for obtaining oscillograms correctly reflecting the change in capacitive and Faradaic currents as a function of potential, it is necessary to satisfy the condition

$$R_2 < \underbrace{R_4 + R}_{R} \ll R_c, \tag{3}$$

where R_c is the resistance of the electrode capacitance, and R is the resistance of the electrolyte. To satisfy condition (3), electrodes with a very small surface were used in the experiments. It was established experimentally that, as the microelectrode, it is best to use the end of a platinum wire, $d = 0.1$ mm. The surface of the unpolarized platinum macroelectrode was more than a thousand times larger. In this case the pulses of the prescribed voltage have a strictly symmetrical, undistorted form (Fig. 2) with a duty ratio equal to two. The presence of a duty ratio promotes additional electrochemical depolarization, since R_2 and R are small.

The circuit makes it possible to carry out polarization in various potential intervals. When contact K is open, the potential of the microelectrode changes from zero to a prescribed value, for example, E_2 (Fig. 2). With the contact closed, the potential of the microelectrode can change from E_1 to E_2, the magnitude $E_2 - E_1$ being determined by the resistance R_3, and the initial polarization potential E_1 by the resistance R_2.

The experiments carried out showed that the described circuit makes it possible to observe reproducible i—E oscillopolarograms, by means of which one can simultaneously study the cathodic and anodic processes at a platinum ultramicroelectrode in molten electrolytes.

The method was also tested in aqueous solutions with platinum and amalgamated silver electrodes.

Figure 3 presents an i—E oscillopolarogram of Cd^{2+} against the background of an equimolar KCl—NaCl mixture at a temperature of 720°C. Oscillogram b was recorded 20 min after oscillogram a. The measured potentials of the cathodic and anodic peaks, with an accuracy of up to 0.02 V, have the following values: $E_\mathrm{k} = -0.85$ V, $E_\mathrm{a} = -0.70$ V. These values are retained at Cd^{2+} concentrations lower than 0.00063 g-ion/mole; at higher concentrations the potential of the anodic peak shifted in the positive direction. If it is assumed that at low concentrations the change in the activity of the reduced metal is proportional

Fig. 3. i—E oscillopolarograms of Cd^{2+}, 0.00063 g-ion/mole, against the background of an equimolar KCl—NaCl mixture

Figure 3: Fig. 3. i—E oscillopolarograms of Cd^{2+}, 0.00063 g-ion/mole, against the background of an equimolar KCl—NaCl mixture

to the current, then from the Ševčík relation (2) one can theoretically determine the value ΔE for a reversible process and compare it with that found experimentally.

Fig. 3. i—E oscillopolarograms of Cd^{2+}, 0.00063 g-ion/mole, against the background of an equimolar KCl—NaCl mixture

For $R = 8.315$ W · sec/g, $T = 993$°K, $n = 2$, $F = 96450$ C, $\Delta E_{\text{rev}} = 0.14$ V. Experimentally, $\Delta E = E_{\text{k}} - E_{\text{a}} = 0.15$ V. The agreement of the theoretical and experimental values indicates that the reduced metal, during the short interval of time between the onset of the cathodic and anodic processes, which is less than 0.005 sec, undergoes no changes. Therefore the difference between the potentials of the cathodic and anodic peaks, determined by means of the proposed method, can serve as an important factor in the study of electrode reactions in melts. It is especially valuable that the magnitude of ΔE does not depend on the potential of the macroelectrode or of the reference electrode. This provides a simple possibility for experimentally determining the number of electrons and estimating the degree of reversibility of the electrode process.

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