

BRIEF
COMMUNICATIONS

Evaluation of the Efficiency of Electrolysis in Cells of Various Designs in Inversion-Voltammetric Determination of Lead

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Abstract—Efficiency of the stage of pre-electrolysis in inversion-voltammetric measurements was examined in relation to the hydrodynamic modes used.

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The pre-electrolysis stage is a constituent of several electrochemical methods of analysis: inversion voltammetry (IVA), controlled-potential coulometry (CPC), and zero-reference combined electrochemical technique [1–3]. It is known that the electrolyte agitation efficiency strongly affects the sensitivity of the methods mentioned above, because in all of them, the deposition current is inversely proportional to the diffusion layer thickness δ , the parameter that characterizes the intensity of mass transfer.

Traditionally, IVA measurements are carried out with a rotating disk electrode (RDE), whose theory has been developed by Levich [3]. The same hydrodynamic system was employed in [1, 5, 6] in a zero-reference electrochemical method in which the pre-electrolysis efficiency is determined by the coulometric constant:

$$K = DS/(\delta V), \quad (1)$$

where D is the diffusion coefficient; S , electrode area; δ , diffusion layer thickness; and V , volume of the solution under study in the cell.

It follows from Eq. (1) that the constant K depends not only on δ , but also on the working electrode area S . The dependence of K on the volume has been studied previously [1, 6]. In the RDE method, it is not always possible to make larger the working electrode area at a fixed solution volume, which is necessary for using the zero-reference method. Another hydrodynamic model, a rotating cylindrical electrode (RCE), is

possible, which allows use of large electrodes at small solution volumes [6].

The limiting diffusion current to the RDE is given by the equation [3]

$$i_d = 0.62nFc_0\omega^{0.50}\nu^{-0.167}D^{0.667}, \quad (2)$$

where n is the number of electrons involved in the electrode reaction; F , Faraday number; c_0 , solution concentration in the cell; ν , kinematic viscosity; ω , angular rotation rate; and D , diffusion coefficient.

The limiting diffusion current to the RCE can be found using the equation [6, 7]

$$i_d = 0.0791nFc_0\omega^{0.70}d_i^{-0.30}\nu^{-0.344}D^{0.667}, \quad (3)$$

where d_i is the electrode diameter.

Equation (2) is satisfied for the RDE in a wide range of rotation rates [3]. For the RCE (the general scheme of the electrode is shown in Fig. 1a), there exist three fluid flow modes resulting from different electrode rotation rates.

(1) Simple laminar flow with concentric current lines, observed at low cylinder rotation rates. This flow merely sets the substance in a circular motion, without any increase in the mass-transfer rate.

(2) Flow with Taylor vortices, a cellular flow with a velocity component directed from one cylinder toward the other. This flow is also regular, laminar, and stable; it requires a higher electrode rotation rate and contributes to the mass-transfer rate.

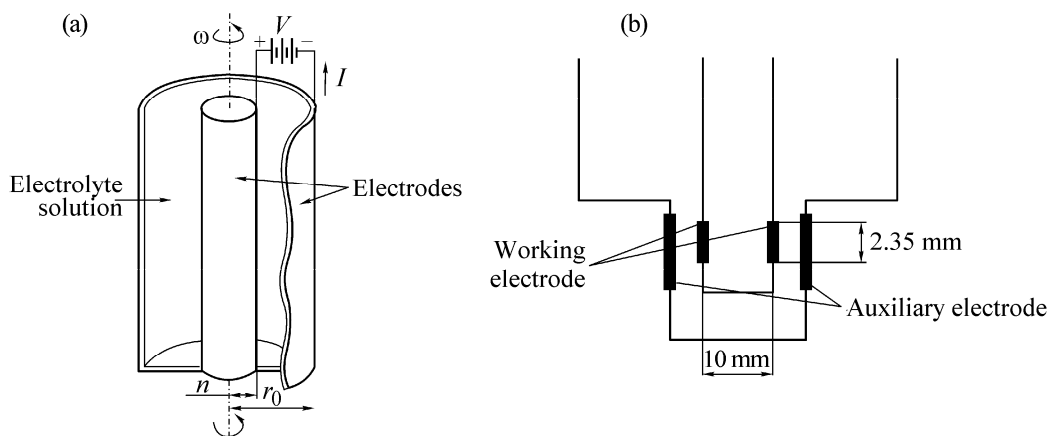


Fig. 1. (a) General scheme of a rotating cylindrical electrode and (b) schematic of the working cell: ω is the angular rotation rate of the cylindrical electrode; r , radius of the inner electrode; r_0 , radius of the outer electrode; and V , voltage applied across the electrodes.

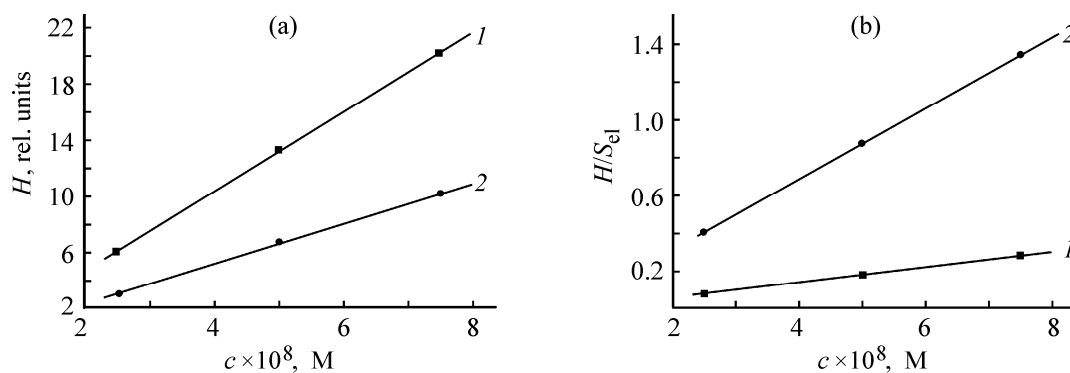


Fig. 2. (a) Height H of the ionization peak and (b) ratio between the analytical signal and the electrode area, H/S_{el} , vs. the solution concentration c in the working cell. Electrode rotation rate 1200 rpm. Electrode: (1) cylindrical and (2) disc-type; the same for Fig. 3.

(3) Turbulent flow characterized by rapid random fluctuations of velocity and pressure. Here is also included a fluctuating velocity component that is directed from one cylinder to the other and provides a substantial increase in the mass-transfer rate, which is uniform over the cylinder surface. This flow provides an effective agitation and requires the largest rotational moment.

Equation (3) is satisfied for the turbulent motion mode in a wide range of electrode rotation rates [6].

In this communication, the efficiencies of electrolysis with RDE and RCE are compared.

EXPERIMENTAL

The electrolysis efficiency was studied by the IVA method on a PLS-1 polarograph (Belarus) with an AKV-07 transducer (Akvilon NPKF, Moscow) in the ac mode. A solution of lead ions, with a concentration of 10^{-3} M, was prepared from a solution of a State standard sample (1 mg cm^{-3}) (SSS 7252-96). Solutions with concentrations of 10^{-5} and 10^{-6} M were prepared

by dilution of the 10^{-3} M solution. The solutions were prepared from reagents of chemically pure and analytically pure grades and twice-distilled water. The measurements were made on a thin-film mercury-graphite electrode, with the electrode rotation rate in the accumulation stage varied from 1200 to 1800 rpm. The choice of the range of rotation rates was determined by the agitation intensity used in the IVA. All the potentials are given relative to a saturated silver chloride reference electrode. Platinum foil rolled-up in the form of a cylinder and placed along the inner wall of the lower part of the cup served as the auxiliary electrode. A solution of the following composition (M) was used as a supporting electrolyte: $1 \times 10^{-4} \text{ Hg(NO}_3)_2 + 5 \times 10^{-2} \text{ HCl} + 1 \times 10^{-4} \text{ HNO}_3$. The pre-electrolysis was carried out at a potential of -0.9 V. To satisfy the condition of a full dissolution of the metal from the amalgam, a low potential sweep rate was used (5 mV s^{-1}) [1]. The solution volume was constant (4 ml); the areas of the disc-type and cylindrical electrodes were 7.5 and 73.8 mm^2 , respectively. The experiments were carried out in the quartz cell shown in Fig. 1b.

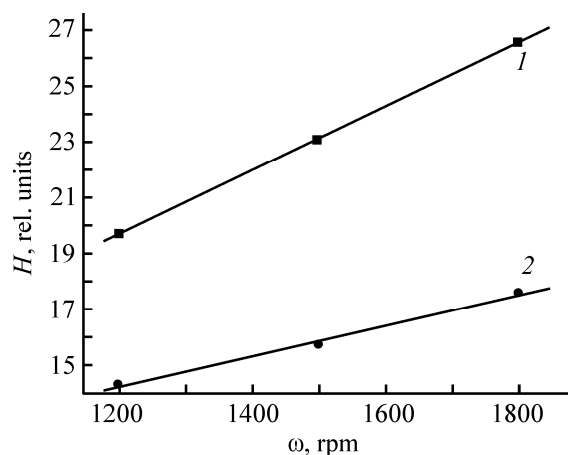


Fig. 3. Height H of the ionization peak vs. the electrode rotation rate ω .

The dependence of the current of Pb(II) dissolution from the amalgam on RDE and RCE in a solution at its different concentrations is shown in Fig. 2. The observed dependence is linear, in good agreement with Eqs. (2) and (3). The dependence of the dissolution (and, accordingly, deposition) current on the electrode rotation rate is shown in Fig. 3. At electrode rotation rates in the range 1200–1800 rpm, the dependence is almost linear in both cases and has slope rates $b_1 = 0.5$ for RDE and $b_2 = 0.7$ for RCE, also in good agreement with Eqs. (2) and (3). The value of b_2 equal to 0.7 indicates that a turbulent fluid motion occurs in the given case at the rotation rates studied.

The dependences of the currents of lead ionization from the amalgam on the rate of RDE and RCE rotation in the accumulation stage indicate that, at the electrode rotation rates within the range studied, the efficiency of electrolysis in the cell with RCE exceeds that in the cell with RDE. The efficiency of electrolysis with RCE is higher because of the larger electrode area, compared with RDE, in agreement with the data

in Fig. 2b, which shows how the ratio between the height of the peak of lead ionization from the amalgam and the electrode area depends on the Pb(II) concentration in solution. The run of the dependence points to a higher efficiency of mass transfer in a cell with RDE, compared with RCE, at the electrode rotation rates within the range under study. Thus, the RDE provides a higher mass-transfer rate, compared with RCE, but the efficiency of electrolysis is higher with RCE because of its larger area at the given cell design.

CONCLUSIONS

It was shown that the efficiency of electrolysis in an electrochemical cell with a rotating cylindrical electrode exceeds that in a cell with a rotating disc electrode because of the possibility of using a larger-area cylindrical electrode at the same volume of a solution under study.

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