APPLICATION OF RADIOACTIVE TRACERS TO THE STUDY OF IONIZATION AND DISCHARGE OF METAL IONS ON AMALGAM ELECTRODES

V. V. Losev and A. M. Khopin

Institute of Electrochemistry, Academy of Sciences USSR, Moscow

The study of the mechanism of electrodeposition and anode solution of metals is complicated by the fact that in the case of solid metals, together with the two usual stages of any electrochemical reaction (transfer of reacting particles and discharge or ionization of these particles) there is the extra stage of the inclusion of the discharged atom in the crystal lattice of the metal. The study of the kinetics of the ionization and discharge of metal ions on amalgam electrodes makes it possible to eliminate one of these stages (crystallization); the use of an amalgam guarantees homogeneity of the surface and easy purification of it; in addition, in work with amalgam it is possible to study the relation between the rate of the anode process and the concentration of metal in the amalgam, i.e. to obtain more complete characteristics of the anode process than in the case of a solid metal. The main difficulty in the study of the mechanism of the discharge-ionization process arises from the fact that for many metals its rate is so great that under normal conditions the rate of the whole process is limited by the transfer of the substance. Nonetheless, at the present time we can consider it proved that for a considerable number of metals the exchange current has a finite value. For a series of systems the magnitude of the exchange current has been measured by the application of new experimental methods to the study of electrochemical kinetics, namely the ac current method [1-3], nonstationary methods with oscillographic recording of the change in electrode potential after switching on a current of constant density [4-7] or measuring the current density at constant electrode potential [8] in the initial stage of the process and also by means of radioactive tracers [9, 10]. The results of studying the relation between the exchange current and the concentration of amalgams and solutions [1, 3, 9, 10] agree well with the theory of slow discharge.

Since the exchange current for the system metal – solution has a finite value, consequently, the ionization of the metal and discharge of its ions also proceeds at a finite rate. To elucidate the kinetics rules of these processes it is necessary to find experimentally the dependence of their rates on potential, concentration of reacting particles and the structure of the double layer. Meanwhile, the external polarizing current _i_, measured in electrochemical experiments, always equals the difference in the true rates of the cathode (i_c) and anode (i_a) processes (expressed in electrical units). Clearly, with cathode polarization, _i_ expresses the true rate of the cathode process i_c with a sufficient degree of accuracy only at potentials sufficiently removed from the equilibrium potential, [11]. However, the nature of the curves of the anode and cathode processes in the region of the equilibrium potential and also where the corresponding reverse process predominates are very important for elucidating the mechanism of the discharge – ionization process, especially under conditions where not one but several electrons are involved in the over-all electrochemical reaction. Only when the slope of these curves at the same potential is known is it possible to find the transfer coefficients α and β, referring to precisely this potential. In addition, the curve of the true anode process does not always retain a constant slope in the region of the equilibrium potential. In these cases it is particularly important to be able to separate the individual process and follow its kinetics in the whole region close to the equilibrium potential. For this it is necessary to label the reacting particles in one of the phases, for example, the amalgam, with a radioactive tracer; by measuring the increase in concentration of labeled particles with time in the second phase it is possible to determine the true rate of the process measured, in this case the ionization of the metal atoms, at different electrode potentials. For example, this method may be used to study the kinetics of metal ionization during cathode polarization.*

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* A short communication on some results of studying the ionization of the zinc at an amalgam electrode by this method was published previously [12]. A similar method was used by Audubert [13] for determining the true rate of the anode process during cathode polarization of a metallic copper electrode labeled with the radioactive isotope Cu^{64}, in $CuSO_4$ solution.

The values of the true rates of the anode and cathode processes (i_a and i_c) interesting us appear in the differential equation (1), expressing the relation between the activity of the solution I and time t with cathode polarization of the amalgam at constant potential:

$$dI = \frac{(I_0 - I)\, i_a S dt}{m_a nF + (i_c - i_a) St} - \frac{I i_c S dt}{m_s nF - (i_c - i_a) St}, \tag{1}$$

where m_a and m_s are the amounts of metal in the amalgam and solution (in gram-equivalents);
I_0 is the starting activity of the amalgam;
n is the number of electrons participating in the over-all electrochemical reaction;
S is the surface of the amalgam (in cm^2).

The solution of this equation is simplified if we can neglect the change in m_a and m_s during the experiment and if the activity of the solution I is several orders less than the starting activity of the amalgam. The following expression is then obtained [14]:

$$I = \frac{i_a I_0 St}{m_a nF}. \tag{2}$$

Thus i_a at a given potential may be found if the slope of the line expressing the relation between I and t is known.

For the work we used a cell (Fig. 1) in which together with the normal electrochemical measurements, the activity of the solution was periodically measured by removal of a sample into a cylindrical glass cell with double walls, put onto a counting tube inside a lead shield. The relation between I and t found was expressed graphically and i_a at the given potential was calculated from the slope of the (I, t) line. In the same way, i_a was determined at another constant potential, and so on. Fig. 2 shows the relation between I (number of counts per minute) and t for the system zinc amalgam – 0.1 N $ZnSO_4$ at various cathode polarization values and at the equilibrium potential ($\varphi = -0.723$ v relative to a normal hydrogen electrode). There was a linear relation between I and t, indicating that the approximate equation (2) was applicable for calculation of i_a under the given conditions. Fig. 3 shows the relation between the values of i_a found in this way and the potential of the amalgam together with the normal polarization curves plotted during the same experiment relative to current. As can be seen, even with strong cathode polarization the ionization of zinc continues at a noticeable rate. At a sufficient distance from the equilibrium potential in a positive direction, the points of the true anode curve, plotted radiochemically, coincide with the anode-polarization curve, plotted from the current, which confirms the accuracy of the results obtained by the radiochemical method.*

The procedure described was used for studying the mechanism of the ionization of zinc from zinc amalgam (0.005-0.6 at. %) in 0.02 to 1 N $ZnSO_4$ solutions at 25°. The rate of exchange of zinc ions between amalgam and $ZnSO_4$ solution was very great [1, 3, 9]. Therefore, for a noticeable displacement of the potential of the amalgam electrode from the equilibrium potential, it was necessary to polarize the electrode with large currents at which concentration polarization could occur and disrupt the smooth distribution of radioactive particles within the two phases; the results of the radiochemical measurements could thus be distorted. In all experiments with zinc amalgam, we added to the solution a small amount of $[(C_4H_9)_4N]_2SO_4$ ($5 \cdot 10^{-5}$M), which produced a sharp fall in the exchange current [9, 15-17]; concentration polarization was practically absent in this case.** From an analysis of literature data [15, 19-21] it can be assumed that $[(C_4H_9)_4N]^+$ ions produce only a slowing of the ionization and discharge of zinc ions, without changing the mechanism [12].

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* A more detailed description of this method was published previously [12, 14]; at the same time, the possibilities of applying it to the measurement of the exchange current on amalgam and solid electrodes and also for analytical purposes were examined.

** On plotting the first point of the anode curve with strong cathode polarization, for some time we observed a change in the current strength at constant potential, which was apparently connected with the slow formation of an adsorbed layer of tetrabutylammonium ions [18]. Only those activity values which were measured after a stationary state had been reached were used for the calculation of i_a.

Control experiments showed that with prolonged contact of labeled zinc amalgam with 0.01 N $ZnSO_4$ {with the addition of $[(C_4H_9)_4N]_2SO_4$ }, the activity of the solution hardly changed, i.e. the amount of zinc passing into solution lay within the limits of experimental error. Consequently, the rate of spontaneous solution of amalgam is insignificantly small in comparison with the rates of ionization and discharge of zinc ions and the stationary potential of the amalgam practically coincides with its equilibrium potential.

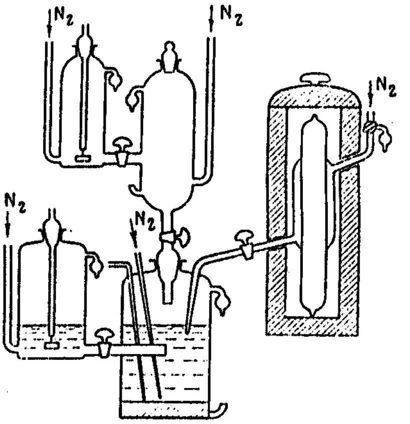

Fig. 1. Cell for measuring true anode curves.

In all the region of amalgam and solution concentration studied there was a linear relation between the logarithm of i_a and the potential of the amalgam φ (Fig. 3). This rule was also obeyed with strong cathode polarization of the amalgam, for example, with a shift in potential of 60-70 mv to the negative side of the equilibrium potential. The average value of the slope of the (φ, lg i_a) curve was $b_a = 0.051 \pm 0.003$ v, which corresponds to the value $\beta = 2.3\ RT/b_aF = 1.16 \pm 0.06$.

As Fig. 4 shows, at constant solution composition (0.3 N $ZnSO_4$), with a decrease in amalgam concentration the anode curves are displaced in a positive direction while their slopes remain unchanged. To determine the relation of i_a to zinc amalgam concentration at a given potential it is necessary to take points on the anode curves corresponding to the constant potential.

This relation, which is shown in Fig. 5 for $\varphi = -0.750$ v on a logarithmic scale,* is expressed by a straight line with a slope equal to unity; consequently, the true rate of the anode process is in direct proportion to the amalgam concentration. A change in the $ZnSO_4$ concentration over the range from 0.02 to 0.3 N at constant amalgam concentration had hardly any effect on the position of the anode curve,** which indicates that the rate of the anode process is independent of the concentration of zinc ions in the solution.

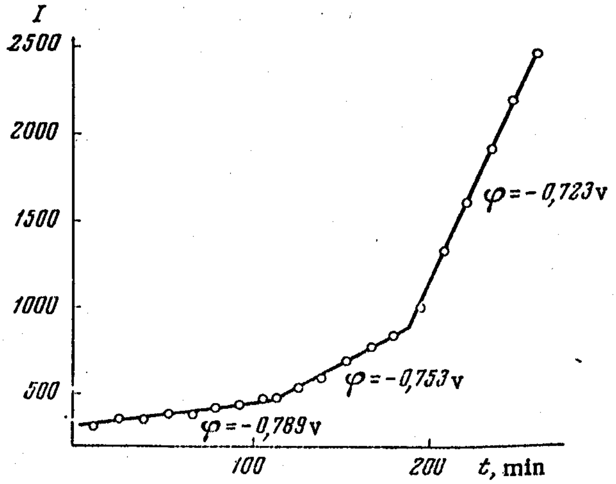

Fig. 2. Relation between solution activity and time at different potentials of the zinc amalgam (0.6 at. %).

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*It was impossible to plot a complete anode curve at low amalgam concentrations as with the cathode polarization the amalgam concentration changed appreciably with time; in this case we measured only the value of i_a at the equilibrium potential, i.e. the exchange current, and to determine the value of i_a at $\varphi = -0.750$ v, a straight line was drawn through the corresponding point with $b_a = 0.051$ v (Curves 5 and 6, Fig. 4).

**At higher $ZnSO_4$ concentrations there was a certain shift in the anode curve in a positive direction, apparently caused by the increased retarding action of tetrabutylammonium ions as a result of their increased adsorption with an increase in the ionic strength of the solution [22]

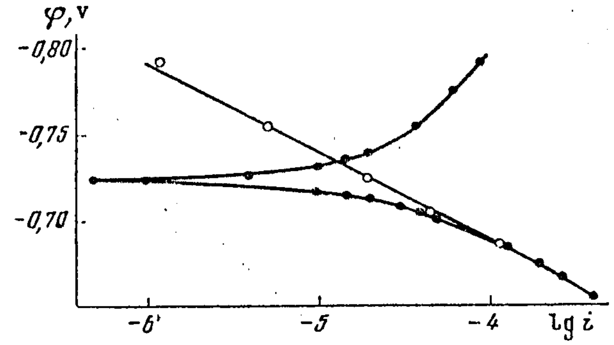

Fig. 3. Polarization curves for zinc amalgam (0.6 at. %) in 0.1 N $ZnSO_4$+ 0.01 N H_2SO_4. O – true anode curve plotted radiochemically; ◐– normal polarization curves plotted from the current.

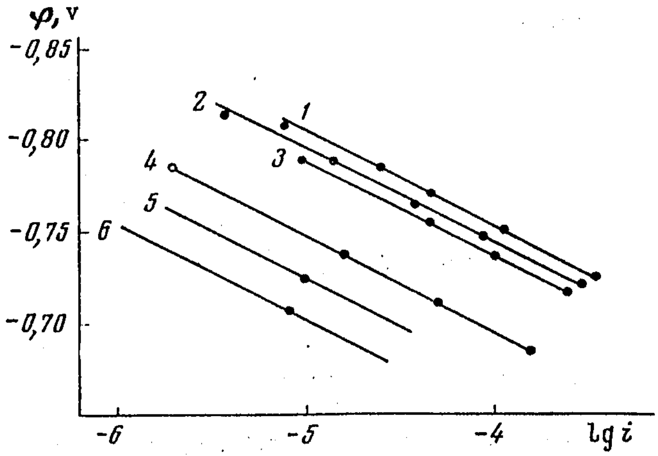

Fig. 4. True anode curves at various amalgam concentrations (in at. %). 1) 0.543; 2) 0.446; 3) 0.123; 4) 0.032; 5) 0.014; 6) 0.0046.

Thus, the experimental results of studying the anode process may be expressed by the following equation.

$$i_a = k[Zn]\, e^{\beta\varphi F/RT}, \text{ where } \beta = 1.16. \qquad (3)$$

For a direct determination of the true rate of the cathode process i_c with anode polarization of the amalgam it is necessary to place a solution of labeled $ZnSO_4$ in contact with inactive zinc amalgam and measure the rate of increase of the activity of the amalgam when the latter is under anode polarization. These measurements were made in a cell similar to that illustrated in Fig. 1 with the difference that the cell for removing a sample of solution was replaced by a capillary tube for removing a sample of amalgam, placed in the lower part of the cell [14]. Figure 6 shows the relation between the values of i_c found radiochemically and the amalgam potential together with normal polarization curves, plotted from the current.

As can be seen, the discharge of the zinc ions proceeds at an appreciable rate even with strong anode polarization of the amalgam and there is a linear relation between the logarithm of i_c and the potential.* The average

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*The decrease in slope of the cathode curve at more positive potentials is apparently connected with disruption of the uniform distribution of labeled zinc atoms in the amalgam at strong anode polarization due to the lack of mixing of the amalgam.

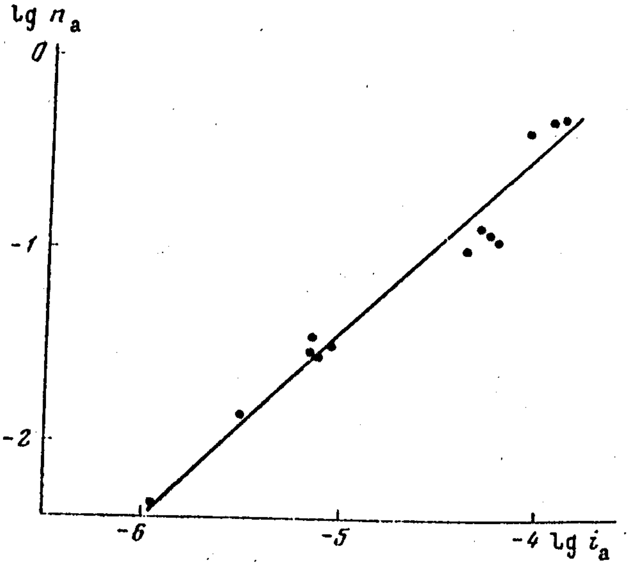

Fig. 5. Relation of i_a to amalgam concentration $\underline{n}$ at $\varphi = -0.750$ v.

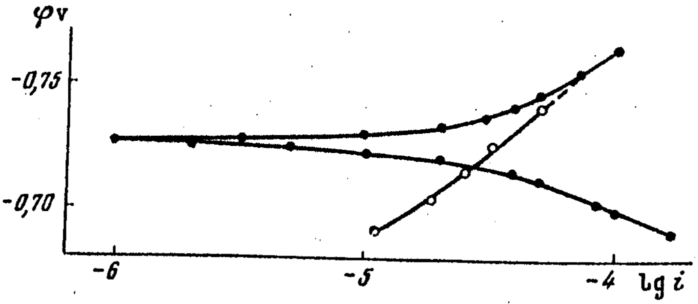

Fig. 6. Polarization curves for zinc amalgam (0.3 at. %) in 0.1 N $ZnSO_4$ + 0.01 N H_2SO_4. O – true cathode curve plotted radiochemically; ● – normal polarization curves plotted from the current.

value of the slope of the(φ, lg i_c) curve $b_c = 0.080 \pm 0.005$ v, which corresponds to the value $\alpha = 2.3\ RT/b_cF = 0.74 \pm 0.05$*. Consequently, the sum of the coefficients α and β in the region of the equilibrium potential is 1.90 ± 0.11, i.e.,close to the theoretical value of 2.

The results obtained, namely the linear relation between the logarithms of i_a and i_c and the electrode potential over a wide range around the equilibrium potential and the closeness of the sum of the coefficients α and β to two, i.e. to the total number of electrons participating in the reaction, shows that the slowest stage of the ionization and discharge of zinc ions is the electron-transfer stage. If we start from the hypothesis on single electron transfers in elementary electrochemical acts, since the simultaneous addition or removal of several electrons is less probable, then it can be assumed that the ionization of zinc consists of two successive one-electron stages**.

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* This value of α is more accurate than that found previously [12] by an indirect method (combination of the true anode curve with the polarization curves plotted from the current); the approximate value of $\alpha = 0.64$.

** The possibility of Zn^+ ions arising at a zinc anode is apparently indicated by the results of studying the anode solution of zinc in solutions of nitrates [23] and perchlorates [24].

$$Zn \rightarrow Zn^+ + e;\ Zn^+ \rightarrow Zn^{2+} + e.$$

As theoretical analysis shows [25], when the exchange currents of two successive one-electron stages are comparable in size, one of the curves (φ, lg i_a or φ, lg i_c) must have a break close to the equilibrium potential. Since in our experiments these curves retained a linear character in the region of the equilibrium potential, the difference between the exchange currents of the two successive one-electron stages must be large and, consequently, one of these stages may be regarded as the equilibrium one. Let us assume that the equilibrium stage is the removal of the first electron and, consequently, the rate of the whole process is limited by the rate of the second stage:

$$i_a = k'[Zn^+]\, e^{\beta'\varphi F/RT}.$$

By using the equilibrium conditions of the first stage we obtain

$$i_a = k''[Zn]\, e^{(1+\beta')\varphi F/RT} = k''[Zn]\, e^{\beta\varphi F/RT}$$

where $\beta = 1 + \beta'$. For the cathode process we find

$$i_c = k'''[Zn^{2+}]\, e^{-\alpha\varphi F/RT}\ *$$

Thus, with the assumption that the rate of the whole process is limited by the rate of the second stage, the condition that $\beta > \alpha$ must be observed as $\alpha + \beta = 2$, which agrees with our data and also with the results of determining the coefficients α and β by other methods.** It is not difficult to show that the assumption that the stage $Zn \rightarrow Zn^+ + e$ is slow leads to the relationship $\alpha > \beta$, which is contrary to experimental data.

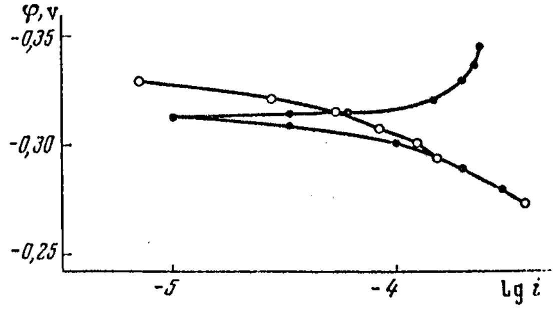

Fig. 7. Polarization curves for cadmium amalgam (0.55 at. %) in 1N $CdSO_4$. ○ – true anode curve; ● – normal polarization curves plotted from the current.

We also studied the anode process of the ionization of cadmium amalgam (0.55 at. %) in 1 N $CdSO_4$ with the aid of the radioactive tracer Cd^{115}. As in the case of zinc, $[(C_4H_9)_4N]_2SO_4$ was added to the solution. Here, together with a sharp fall in the exchange current, there appeared a limiting current with cathode polarization, connected with retardation of the penetration of Cd^{2+} ions through the dense adsorbed layer [17], but the anode polarization curves, plotted from the current, at a distance from the equilibrium potential always retained a linear form [18].

Assuming that the cathode and anode processes proceed independently, it can be supposed that the linear character of the anode curves will be retained more in the region of the equilibrium potential and with cathode polarization, i.e. at a lower anode process rate, and that the true anode curve for cadium will be analogous to the true anode curve for zinc. However, as can be seen from Fig. 7, with a small displacement of the potential in a negative direction from the equilibrium potential, the slope of the anode curve falls considerably, i.e. the rate of the anode process is considerably reduced and this reduction begins in the region of potentials in which the cathode polarization curve changes to the limiting penetration current. In addition, at values somewhat more positive that

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* As can be seen from these relationships, in this case only α of the two coefficients α and β determined experimentally actually characterizes the slow stage of the electrode process, while the transfer coefficient β', corresponding to the ionization act, may be found from experimental data only from the relation $\beta' = \beta - 1$. This difference in the physical meaning of the coefficients α and β for electrochemical reactions involving several electrons cannot be detected by using the relation $\alpha + \beta = 1$. In other words, the relation $\alpha + \beta = 1$ assumes that all the electrons are added in one elementary act. Therefore, we assumed the relation $\alpha + \beta = 2$ which does not predetermine the mechanism of the ionization process.

** The simultaneous determination of both coefficients for zinc amalgam was achieved only by Gerischer [3], who obtained the values $\beta = 1.44$ and $\alpha = 0.56$; from the slope of the polarization curves plotted on a flowing electrode, O. A. Esin [26] obtained $\alpha = 0.68$ and Koryta̧ [27], $\alpha = 0.62$; by determining the relation between the exchange current and the amalgam concentration, B. V. Ërshler and K. I. Rozental' [1] found the value $\alpha = 0.83$ and V. A. Pleskov and N. B. Miller [9], $\alpha = 0.50$ v. All the values of the coefficients presented were recalculated in accordance with our assumption that $\alpha + \beta = 2$.

the equilibrium potential, an inflexion is observed on the anode curve. The nature of these effects is still unclear; however, this example shows that the possibility of isolating one of the two coupled processes and following its kinetics in the region of the equilibrium potential and with predomination of the reverse process undoubtedly opens up new prospects of studying the mechanism of electrode processes and, in particular, may help to elucidate the mechanism of the hindering action of dense adsorbed films.

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