GALVANOSTATIC ELECTROLYSIS WITH CURRENT REVERSAL. CASE OF FOLLOW-UP CHEMICAL REACTION LEADING TO ELECTROACTIVE SUBSTANCE AFTER CURRENT REVERSAL*

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For the galvanostatic method with current reversal, two cases are solved, in which an electro-inactive substance M is formed by an irreversible electrode reaction and from this a substance P is formed by a chemical reaction. After the current reversal, P is consumed at the electrode. In one case, the substance P is moreover irreversibly converted to an electroinactive product Z. The corresponding schemes are $M \rightarrow P \rightarrow Z$ and $M \rightleftarrows P$. The solution is derived both for homogeneous chemical reactions and for reactions of substances accumulated on the electrode. The possibilities of distinguishing these cases from others and determination of the kinetic parameters are discussed.

During an electrode process, it can happen that the product formed by an irreversible electrode reaction is changed by a chemical reaction to a substance that can undergo further electrode processes. A typical example is the familiar ECE mechanism, which was solved also for the galvanostatic method with current reversal[1,2]. During application of this method, however, it can happen that the chemical reaction takes place between such two electrode processes, one of which proceeds only before and the other only after the current reversal. Such a case is solved in the present paper with respect to the possibility of distinguishing different electrode mechanisms by this method[3].

THEORETICAL

We shall assume that during the galvanostatic electrolysis with current reversal, a substance M is formed by an irreversible electrode reaction with n_f electrons from a depolarizer A. This substance is transformed by a chemical reaction of the first order to a substance P. After the current reversal at a time t_1, the substance P is consumed at the electrode by an electrode process with n_b electrons, while the substance M is electroinactive. Thus, we have the following scheme:

$$0 < t < t_1: \quad A \pm n_f\, e \to M\,,$$

$$t > t_1: \quad P \pm n_b\, e \to \text{products}\,, \tag{I}$$
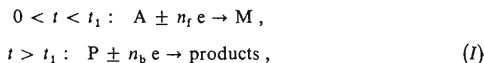
where either the upper or the lower signs apply simultaneously.

We shall further limit ourselves to the case of no more than two chemical steps. We shall assume either that the chemical reaction forming the substance P is irreversible and that P is transformed by an irreversibele first-order chemical reaction to electroinactive products Z, or that the chemical reaction forming P is reversible. The chemical reactions conjugated with the electrode processes (I) can hence be symbolized as

$$M \xrightarrow{\;k_1\;} P \xrightarrow{\;k_2\;} Z\,, \quad M \underset{k_a}{\overset{k_b}{\rightleftarrows}} P\,. \tag{A}, (B)$$
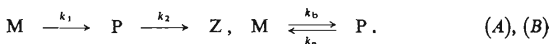
These reactions will be solved for the case where the substances M and P are only in the solution and are not adsorbed on the electrode and for the case where these substances are completely adsorbed (accumulated) on the electrode so that their concentration in the solution is negligible. As in previous communications[2-8], we shall denote the ratio of the currents after and before the reversion as $u = i/j$, the ratio of the exchanged electrons as $v = n_f/n_b$ and the transition time after the reversion τ'.

Case of Homogeneous Reaction (A)

In the case of a homogeneous reaction (A), we can use the method of calculation for a two-step follow-up reaction[4] with boundary conditions corresponding to the scheme (I). The concentration of P at the electrode surface after the current reversal is then given as

$$t > t_1, x = 0: \quad C_P = \left[j \sqrt{k_1}/n_f F(k_1 - k_2) \sqrt{D} \right] . \left\{ (k_1/k_2)^{1/2} \left\{ \mathrm{erf}\,(k_2 t)^{1/2} - \right. \right.$$
$$- \left[(1 - k_2/k_1)\, vu + 1 \right] . \, \mathrm{erf}\,\left[k_2(t - t_1) \right]^{1/2} -$$
$$- \mathrm{erf}\,(k_1 t)^{1/2} + \mathrm{erf}\,\left[k_1(t - t_1) \right]^{1/2} \right\}\,. \tag{1}$$

The transition time after the current reversal, τ', obeys the condition

$$t = t_1 + \tau': \quad C_p = 0\,, \tag{2}$$

which leads to the equation

$$(k_2/k_1)^{1/2} \left\{ \mathrm{erf}\,\left[k_1(t_1 + \tau') \right]^{1/2} - \mathrm{erf}\,(k_1 \tau')^{1/2} \right\} =$$
$$= \mathrm{erf}\,\left[k_2(t_1 + \tau') \right]^{1/2} - \left[(1 - k_2/k_1)\, vu + 1 \right] \mathrm{erf}\,(k_2 \tau')^{1/2}\,. \tag{3}$$

This equation gives the following dependence in an implicit form:

$$k_2 \tau' = \chi(vu, k_2/k_1, k_2 t_1) . \qquad (4)$$

To simplify this dependence, we shall consider the case of sufficiently rapid chemical reactions. If we assume that

$$k_1 t_1 > 6 \ \wedge \ k_2 t_1 > 6 , \qquad (5)$$

Eq. (3) simplifies to the form

$$(k_2/k_1)^{1/2} \left[1 - \text{erf} (k_1 \tau')^{1/2} \right] = 1 - \left[(1 - k_2/k_1) vu + 1 \right] \text{erf} (k_2 \tau')^{1/2} . \qquad (6)$$

This equation gives the following dependence in the implicit form:

$$k_2 \tau' = \chi(vu, k_2/k_1) . \qquad (7)$$

The dependence of $k_2 \tau'$ on vu for different values of the ratio of k_2/k_1 obtained by solving Eq. (6) is shown in Fig. 1 in bilogarithmic coordinates.

For $k_2 = k_1$, Eq. (6) takes the form of an identity. By performing the limit, we obtain for this point from (6):

$$k_2 = k_1 : \quad (2vu + 1) \, \text{erf} (k_2 \tau')^{1/2} = 1 + 2 \exp (-k_2 \tau') (k_2 \tau'/\pi)^{1/2} . \qquad (8)$$

Further it is possible to derive from Eq. (6) limiting expressions for very small and very large ratios of k_2/k_1:

$$k_2/k_1 \to 0 : \quad \chi(vu, k_2/k_1) \to \text{argerf}^2 \left[1/(1 + vu) \right] , \qquad (9)$$

$$k_2/k_1 \to \infty : \quad \chi(vu, k_2/k_1) \to \pi k_1/4 k_2 v^2 n^2 . \qquad (10)$$

The limiting equation (9) represents a transition for the case of a single-step follow-up irreversible chemical first-order reaction and it can be interpreted as negligibility of the process $P \to Z$. Further it is seen from Fig. 1 that the dependence of $\log \tau'$ on $\log u$ approaches with increasing k_2/k_1 a straight line with a slope of -2 in accord with the limiting relationship (10).

Case of Reaction (A) *with Completely Adsorbed Substances*

In the case where reaction (A) takes place and all participating substances remain on the electrode surface, we can apply the method of solution for a two-step follow-up reaction in a completely adsorbed state[5] with a modification corresponding to the

scheme (*I*). We obtain for the concentration of P on the electrode surface after the current reversal the expression:

$$t > t_1 : \quad \Gamma_p = [j/n_t F k_2 (1 - k_2/k_1)] \{1 - \exp(-k_2 t) - [(1 - k_2/k_1) vu + 1] \cdot$$

$$\cdot [1 - \exp[-k_2(t - t_1)]] + (k_2/k_1) [\exp(-k_1 t) - \exp[-k_1(t - t_1)]]\} . \quad (11)$$

The transition time after the current reversal obeys the condition

$$t = t_1 + \tau' : \quad \Gamma_p = 0 , \quad (12)$$

which leads to the equation

$$(k_2/k_1) \{\exp(-k_1 \tau') - \exp[-k_1(t_1 + \tau')]\} = \exp(-k_2 \tau') -$$

$$- \exp[-k_2(t_1 + \tau')] - vu(1 - k_2/k_1) [1 - \exp(-k_2 \tau')] . \quad (13)$$
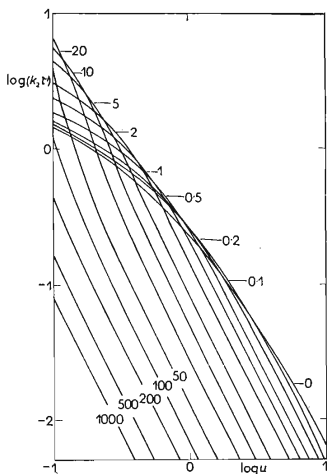

FIG. 1

Dependence of $k_2\tau'$ on the Ratio of Currents u for Various Ratios of Rate Constants k_2/k_1

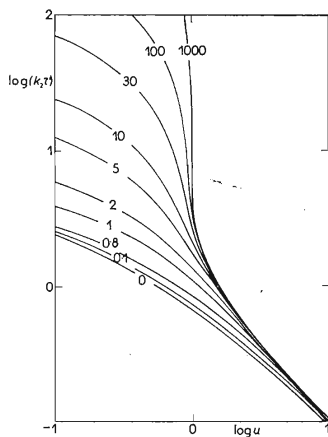Reaction (*A*), all reactants diffuse freely, numbers in figure gives the corresponding values of k_1/k_2.

FIG. 2

Dependence of $k_2\tau'$ on the Ratio of Currents

Meaning of symbols as in Fig. 1; reactants M, P, Z are accumulated on the electrode.

This equation gives a dependence of the type (4) in the implicit form. To simplify this dependence, we shall consider the condition (5); Eq. (13) is then simplified to

$$(k_2/k_1) \exp(-k_1\tau') = \exp(-k_2\tau') - vu(1 - k_2/k_1)[1 - \exp(-k_2\tau')] . \quad (14)$$

This equation gives a dependence of the form (7) in the implicit form. The dependence of $k_2\tau'$ on the ratio of the currents, u, obtained by solving Eq. (14) for different values of k_2/k_1 is shown in Fig. 2 in bilogarithmic coordinates. For $k_2 = k_1$ Eq. (14) takes also the form of an identity; by performing the limit we obtain for this point

$$k_2 = k_1 : \quad (1 + vu + k_2\tau') \exp(-k_2\tau') = vu . \quad (15)$$

Besides we can derive from Eq. (14) limiting relationships for very small or very large values of k_2/k_1:

$$k_2/k_1 \to 0 : \quad \chi(vu, k_2/k_1) \to \ln[(vu + 1)/vu] , \quad (16)$$

$$k_2/k_1 \to \infty ; \quad vu > 1 : \quad \chi(vu, k_2/k_1) \to \ln[vu/(vu - 1)] , \quad (17a)$$

$$k_2/k_1 \to \infty ; \quad vu < 1 : \quad \chi(vu, k_2/k_1) \to (k_2/k_1) \ln(1/vu) + 1 . \quad (17b)$$

The limit (16) corresponds to a transition to a one-step follow-up irreversible first-order reaction and expresses the negligibility of the process P → Z. The limits (17) show that in the region $vu = 1$ a profound change of the value of τ' with u at large values of k_2/k_1 must take place, as illustrated by Fig. 2.

Case of Homogeneous Reaction (B)

In the case of a homogeneous reaction (B), we can use the method of calculation for a reversible follow-up first-order reaction[6] with boundary conditions corresponding to the scheme (1). The concentration of P at the electrode surface after the current reversal is then given by the equation

$$t > t_1, x = 0 : \quad C_p = [j/n_f F(K + 1)(Dk)^{1/2}] \{2(kt/\pi)^{1/2} - 2(vu + 1) .$$
$$. [k(t - t_1)/\pi]^{1/2} - \text{erf}(kt)^{1/2} + (1 - vuK) \text{erf}[k(t - t_1)]^{1/2}\} , \quad (18)$$

where

$$k = k_a + k_b , \quad K = k_a/k_b . \quad (19)$$

By applying the condition (2) we obtain for the transition time after the current reversal, τ', from Eq. (18)

$$(1 + t_1/\tau')^{1/2} = vu + 1 + \tfrac{1}{2}(\pi/k\tau')^{1/2} \left[\text{erf} \, (kt_1 + k\tau')^{1/2} + \right.$$
$$\left. + \, (vuK - 1) \, \text{erf} \, (k\tau')^{1/2} \right] . \qquad (20)$$

This result gives a relation among $k\tau'$, K and t_1/τ' in the implicit form. If the reaction (B) is sufficiently rapid, so that

$$k\tau' > 6 , \qquad (21)$$

Eq. (20) simplifies to

$$(1 + t_1/\tau')^{1/2} = vu + 1 + \tfrac{1}{2}vuK(\pi/k\tau')^{1/2} . \qquad (22)$$

For the case of a very slow reaction, the error integrals in Eq. (20) can be expanded in series for small arguments. A calculation of the value of $(1 + t_1/\tau')^{1/2}$ with neglection of higher-order terms gives the limit

$$k\tau' \to 0 : \quad (1 + t_1/\tau')^{1/2} \to \left[3vu(K + 1)/k\tau' \right]^{1/3} . \qquad (23)$$

Case of Reaction (B) *with Completely Adsorbed Substances*

If during the reaction (B) all participating reactants are completely bound to the electrode surface, we can use the method of solution for a reversible follow-up first-order reaction in the completely adsorbed state[5] with modification of the equations corresponding to the scheme (1). The concentration of P on the electrode surface after the current reversal is then given as

$$t > t_1 : \quad \Gamma_P = \left[j/n_t Fk(K + 1) \right] \{ kt_1 - vuk(t - t_1) - 1 + \exp(-kt) -$$
$$- \, (vuK - 1) \left[1 - \exp \left[-k(t - t_1) \right] \right] \} , \qquad (24)$$

with the definitions (19). By applying the condition (12) we obtain for the transition time after the current reversal, τ', from Eq. (24) the result

$$t_1/\tau' = vu + (1/k\tau') \{ 1 - \exp \left[-k(t_1 + \tau') \right] +$$
$$+ \, (vuK - 1) \left[1 - \exp(-k\tau') \right] \} , \qquad (25)$$

which gives an implicit relationship among $k\tau'$, vu, K and t_1/τ'. If the reaction (B) is sufficiently rapid, so that the inequality (21) holds, Eq. (25) simplifies to the form

$$t_1/\tau' = vu + vuK/k\tau' . \qquad (26)$$

If the reaction is very slow, we obtain from Eq. (25) in a similar manner as in the

case of a homogeneous reaction the limit

$$k\tau' \to 0 : \quad t_1/\tau' \to [2vu(K + 1)/k\tau']^{1/2} . \tag{27}$$

DISCUSSION

It follows from the above results that the combination of the electrode process (I) with the reaction (A) or (B) preserves the principal characteristics of linear processes[3] — the transition time after the current reversal, τ', is independent on the current, j, at a constant ratio of the currents after and before the current reversal, u. In the case of the reactions (A), which are sufficiently rapid so that the condition (5) applies, τ' is independent also on the time of current reversal, t_1 (the characteristics of rapid irreversible follow-up reactions[3]). The form of the dependence of $\log \tau'$ on $\log u$ is given by the ratio of the rate constants, k_2/k_1.

In the case of rapid homogeneous reactions (A), the slope of the dependence of $\log \tau'$ on $\log u$ increases with the value of k_2/k_1 up to a limit given by Eq. (10). Of the hitherto solved cases, a higher slope of this dependence (as compared with the case of a homogeneous follow-up first-order reaction) was found only with an irreversible follow-up reaction accelerated by the electrode surface[7]. Hence, at a higher slope of the dependence of $\log \tau'$ on $\log u$ it is possible to consider one of these two mechanisms. Their distinguishing cannot be done only on the basis of galvanostatic experiments. If the dependences correspond to the reaction (A), it is possible to determine from the form of the curve the range of the values of k_2/k_1 and from the experimental data and the working curve also the value of k_2. In such a case we obtain the values of both rate constants. We can estimate from Fig. 1 that the experimentally accessible range of k_2/k_1 is about $0.1 - 20$.

Also in the case of rapid reactions (A) and substances accumulated on the electrode the slope of the dependence of $\log \tau'$ on $\log u$ increases with the value of k_2/k_1. At higher values of k_2/k_1 inflexion point appears close to the value of $vu = 1$ (Fig. 2). The lower limit for determining this inflexion from the experimental data depends on the scatter of the values and it will be obviously close to the value of $k_2/k_1 = 5$. Since such an inflexion on the $\log \tau' - \log u$ curve was not found in any of the hitherto studied cases, its occurrence can be considered as a good indication of the mentioned case at higher values of k_2/k_1.

At lower values of k_2/k_1, the form of the $\log \tau'$–$\log u$ curves is intermediate between the case of a simple irreversible follow-up reaction of a completely adsorbed substance and that of a simple homogeneous irreversible follow-up reaction. A similar form was found in the case of an irreversible follow-up reaction with a linear adsorption[8]. With such a form of the curves it is hence possible to consider one of these two mechanisms. Their distinguishing must be done on the basis of other facts.

The values of both rate constants can be– similarly as with homogeneous reactions — obtained from the experimental curve.

If the electrode process (I) is conjugated with reaction (B) which is sufficiently rapid so that the condition (21) applies, it is possible to use the same type of dependences as with reversible follow-up reactions of the depolarization product[3]. For a homogeneous reaction, the dependence of $(1 + t_1/\tau')^{1/2}$ on $1/\sqrt{\tau'}$ is linear; for reactions of substances completely accumulated on the electrode the dependence of t_1/τ' on $1/\tau'$ is a straight line. These cases cannot be therefore distinguished on the basis of experimental results from other rapid reversible reactions.

The difference between the reaction (B) and other reversible reactions is, however, realized in the case of a small reaction rate. With a homogeneous reaction where the immediate depolarization product is consumed at the electrode after the current reversal, the dependence of $\sqrt{(1 + t_1/\tau')}$ on $1/\sqrt{\tau'}$ passes with decreasing values of $k\tau'$ through a maximum[6] and decreases back to the value of $u + 1$. With an analogous reaction of completely adsorbed substances, the dependence of t_1/τ' on $1/\tau'$ must with decreasing value of $k\tau'$ pass through a maximum and decrease to the value of u. In contrast, with reaction (B) even during decreasing the reaction rate to zero the values of $\sqrt{(1 + t_1/\tau')}$ and t_1/τ' increase steadily in the mentioned dependences, as can be seen from the limits (23) and (27).

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