RUSSIAN JOURNAL of PHYSICAL CHEMISTRY

February 1962

DIFFUSION-CONTROLLED OPERATION OF POROUS ELECTRODES

O. S. Ksenzhek

In view of the increasing use of porous electrodes, it is of interest to examine their operating characteristics when supply of the reactant is controlled by diffusion.

The steady-state operation of a porous electrode can in general be described by the following set of equations:

$$j_i = -D_i' \operatorname{grad} c_i - u_i' \frac{|z_i|}{z_i} c_i \operatorname{grad} \varphi + v c_i, \quad (1)$$

$$\operatorname{div} j_i = -Sf(\varphi, c_i) \text{ — for species undergoing discharge,} \quad (2)$$

$$\operatorname{div} j_i = 0 \text{ — for species which are not discharged,} \quad (3)$$

$$\sum c_i z_i = 0 \text{ — condition of electrical neutrality.} \quad (4)$$

Here D_i' and u_i' are the effective diffusion coefficients and mobilities of the ions in the porous electrode, and j_i is the flux of the i-th species. The latter is made up of three fluxes, due to diffusion, migration, and convection, represented in Eqn. (1) by appropriate terms.

The consumption of material in the bulk of the porous electrode is governed by Eqn. (2), where S is the specific surface of the electrode, and $f(\varphi, c_i)$ is a function expressing the kinetics of the electrode reaction in terms of the reactant concentration and the electrode polarisation.

Two types of operating conditions for a porous electrode have been considered in some detail in the literature: (1) conditions under which the convective supply of material within the porous electrode is quite high, ensuring a practically constant electrolyte concentration in it, when the intensity distribution of the process throughout the electrode is determined by the potential distribution[1-4]; and (2) conditions under which the supply of material within the electrode is achieved by a directional flow of electrolyte[5,6], the distribution of the process inside the electrode being governed by concentration and chemical polarisation.

The present paper deals with the working of a porous electrode when the supply of reactant is provided by diffusion. These conditions occur in many applications of porous electrodes which are of practical importance, in particular when the solution contains an excess of a foreign electrolyte in addition to the substances taking part in the electrode process. Under such conditions (presence of a "supporting electrolyte" and absence of convection or of a directional flow of electrolyte in the pores of the electrode) only the diffusion term remains in Eqn. (1), and Eqn. (2) can then be written as follows:

$$\operatorname{div} \operatorname{grad} c = \frac{S}{D'} f(\varphi, c). \quad (5)$$

No considerable change in polarisation can occur at different depths inside the porous electrode in this case. In the presence of a foreign electrolyte, the flow of material due to diffusion will actually be considerably greater than that due to migration[7]:

$$D' \operatorname{grad} c \gg u' c \operatorname{grad} \varphi \quad (6)$$

(where the numerical values of the flows are compared).

Since $D/u = RT/nF$, we have

$$\operatorname{grad} \varphi \ll \frac{RT}{nF} \operatorname{grad} \ln c. \quad (7)$$

Integration of inequality (7) gives

$$\Delta\varphi \ll \frac{RT}{nF} \Delta \ln c, \quad (8)$$

where Δ denotes the difference between the values at the outer surface of the electrode and in the depth of the pores.

The rate of discharge is negligible deep inside a porous electrode, and therefore the reactant concentration inside the pores can be calculated as the equilibrium value given by the Nernst equation. This concentration will be a minimum if the polarisation inside the electrode is equal to the polarisation at the surface, which is φ. If, however, the polarisation inside the electrode is less than this, the concentration will be correspondingly higher than the calculated value:

$$c_{(x=\infty)} \geqslant c_0 \exp\left(-\frac{nF}{RT}\varphi\right), \quad (9)$$

where c_0 is the concentration in the bulk of the solution. It follows from inequalities (8) and (9) that

$$\Delta\varphi \ll \frac{RT}{nF}\Delta \ln c \leqslant \varphi. \qquad (10)$$

Thus the difference in polarisation at different depths in the electrode is small, and the electrode can be approximately regarded as equipotential.

The kinetic function $f(\varphi, c)$ in Eqn. (5) can in many cases (with sufficiently high polarisation) be satisfactorily represented by the equation

$$f(\varphi, c) = kc^r \exp\left(\frac{\varphi}{b}\right), \qquad (11)$$

where r is the order of the electrode reaction, k the velocity constant, and b a constant. On substituting (11) in Eqn. (5), we obtain

$$\operatorname{div}\operatorname{grad} c = \frac{Sk}{D'} c^r \exp\left(\frac{\varphi}{b}\right); \qquad (12)$$

which is identical with the equation describing an ordinary heterogeneous chemical reaction occurring on a porous surface with a rate constant $k' = Sk \exp(\varphi/b)$.

Henceforward we shall use the well known solution of this equation[8,9], regarding φ as a parameter. Confining ourselves to a first-order reaction ($r = 1$), we have

$$I = -nFD'\left(\frac{\partial c}{\partial x}\right)_{x=0} = nF\sqrt{SD'k}\, c_0 \exp\left(\frac{\varphi}{2b}\right), \qquad (13)$$

$$c_x = c_0 \exp\left(-\frac{x}{L_\varphi}\right), \qquad (14)$$

where $L_\varphi = (D'/Sk)^{1/2}\exp(-\varphi/2b)$ is the effective depth of penetration of the process inside the electrode, and I is the current passing through the electrode.

The maximum current is limited, of course, by diffusion of material from the bulk of the electrolyte in the electrode surface, and cannot exceed the limiting value.

$$I_{max} \leqslant I_{lim} = \frac{DnF}{\delta} c_0, \qquad (15)$$

where δ is the thickness of the diffusion layer at the electrode surface, and D the diffusion coefficient in the free electrolyte in contrast to D', which is the effective diffusion coefficient in the pores of the electrode.

Let us now compare the polarisation characteristics of porous and smooth electrodes. On the latter the dependence of polarisation on current density can be expressed by the equation

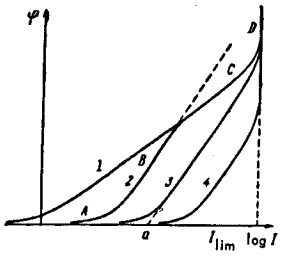
$$\varphi_{sm} = b \ln \frac{I}{nFkc_0}.$$

The corresponding expression for a porous electrode is obtained from Eqn. (13):

$$\varphi_{por} = 2b \ln \frac{I}{nFc_0\sqrt{SD'k}}. \qquad (16)$$

The diagram shows semilogarithmic polarisation curves for smooth and porous electrodes, the latter (curves 2–4) lying below the curve (1) for a smooth electrode and having double the slope of the latter along the linear portions. As the specific surface of porous electrodes increases, the polarisation curves are displaced to the right. The difference in polarisation between a porous and a smooth electrode at the same current density is

$$\Delta\varphi = \varphi_{sm} - \varphi_{por} = b \ln \frac{nFSD'c_0}{I}, \qquad (17)$$



and reaches a maximum at

$$I_0 = nF\sqrt{SD'k}\, c_0, \qquad (18)$$

which corresponds roughly with the point at which the linear portion of the polarisation curve for the porous electrode cuts the abscissa axis (point a on the diagram). when produced. The quantity I_0 given by Eqn. (18) can be regarded to some extent as the effective exchange current per unit apparent surface of the porous electrode, and the quantity $k = (SD'k)^{\frac{1}{2}}$ as the corresponding velocity constant.

The maximum decrease in polarisation on a porous electrode compared with a smooth electrode is found from Eqn. (17) by substituting the value of I_0 from Eqn. (18):

$$\Delta\varphi_{max} = b \ln \sqrt{\frac{SD'}{k}}. \qquad (19)$$

The effectiveness of a porous electrode can be assessed also by comparing the actual exchange current at a smooth electrode ($i_0 = nFkc_0$) with the effective "exchange current" at a porous electrode [as given by Eqn. (18)]. The ratio of these quantities is $(SD'/k)^{\frac{1}{2}}$. Thus the effectiveness of a porous electrode increases with increase in its specific surface and decrease in the rate of the electrode process (k).

Let us determine under what conditions a porous electrode will retain its advantages over the whole practicable range of current densities, right up to the limiting external-diffusion current. This case corresponds to the conditions $I_0 = I_{lim}$ and $\varphi_{sm} - \varphi_{por} \geqslant 0$. On substituting these relations in Eqn. (17), we obtain

$$S \geqslant \frac{\xi}{\delta}, \qquad (20)$$

where ξ is the ratio of the diffusion coefficient in the free electrolyte and the effective diffusion coefficient in the porous electrode: $\xi = D/D'$. This ratio can be estimated from the structural characteristics of the porous electrode, *e.g.* from the formula[10]

$$\xi = \frac{4\beta}{N\pi d^2}, \qquad (21)$$

where β is a tortuosity factor of the pores, N the number of pores per square centimetre of electrode surface, and d the pore diameter. With many porous electrodes ξ is of the order 10–100.

The thickness δ of the diffusion layer is usually $1-5 \times \times 10^{-2}$ cm. Thus when $S \geqslant 10^2-10^4$ cm^2 cm^{-3} the polarisation of a porous electrode is less than that of a smooth electrode over the whole range up to I_{lim}. In this case three regions can be observed on the polarisation curve (curves *3* and *4*) — the internal kinetic range from 0 to about I_0, the internal-diffusion range between I_0 and I_{lim}, and the external-diffusion range near I_{lim}.

If the internal surface of the porous electrode is less than the above value of 10^2-10^4 cm^2 cm^{-3}, its polarisation curve may include an external kinetic range (curve *2*) lying between the internal- and the external-diffusion ranges. The portion of the polarisation curve of a porous electrode lying above that of the smooth electrode is not realised, since under these conditions the part played by the internal surface becomes very small compared with that of the external surface of the electrode.

In the case of rapid electrode reactions the chemical polarisation remains insignificant over the whole practicable range of current densities, and the use of porous electrodes cannot then yield substantial advantages in diminishing the polarisation. The maximum reaction velocity at which a difference in the behaviour of a porous electrode can still be observed should be less than the rate of diffusion in the layer adjacent to the electrode, which is determined by the ratio D/δ. Since D is of the order of 10^{-5} cm^2 sec^{-1}, and $\delta(1-5) \times 10^{-2}$ cm, the "rate" of diffusion is $10^{-3}-2 \times \times 10^{-4}$ cm sec^{-1}. Consequently the condition $k < 10^{-3}-2 \times \times 10^{-4}$ cm sec^{-1} specifies the upper limit to the rate of the electrode process at which the employment of porous electrodes can be of use. The advantages of employing porous electrodes increase as the rate of the electrode process decreases.

The quantity $L_e = (D'/Sk)^{\frac{1}{2}} \exp(-\varphi/2b)$ in Eqn. (14) determines the depth of penetration of the process inside the porous electrode. Substituting for φ from Eqn. (16), we obtain $L_e = nFD'c_0/I$: *i.e.* the depth of penetration is directly proportional to the reactant concentration and inversely proportional to the current density. Substituting this expression in Eqn. (17), we obtain

$$\varphi_{sm} - \varphi_{por} = b \ln SL_e. \qquad (22)$$

In all the calculations in the present work an electrode of infinite thickness has been assumed. This condition is satisfied in practice if the thickness of the electrode exceeds L_e by a factor of about 2–3:

$$L_{min} \geqslant 3L_e. \qquad (23)$$

Another condition governing the applicability of the above conclusions is that the dimensions of structural units (grains, pores) should be considerably less than L_e. The size of a structural unit in a porous solid is of the order of S^{-1}. Hence this condition can be written in the form $L_e > S^{-1}$ or $SL_e > 1$. It can be seen from Eqn. (22) that this condition is always observed if $\varphi_{sm} > \varphi_{por}$, *i.e.* in all cases in which replacement of a smooth by a porous electrode does result in a decrease in polarisation.

The present paper has considered the steady-state operation of a porous electrode, characterised by time-invariant values of the concentration and potential at different points on the electrode. We must now determine, even if only roughly, the time required for such a state to be established after the current has been switched on.

A rigorous discussion of this problem presents considerable difficulty, and reduces to solving the set of equations

$$\frac{\partial \varphi}{\partial t} = \frac{1}{\rho' C} \operatorname{div} \operatorname{grad} \varphi - nF \frac{Skc}{C} \exp(\varphi/b)\dagger, \qquad (24)$$

$$\frac{\partial c}{\partial t} = D' \operatorname{div} \operatorname{grad} c - Skc \exp\left(\frac{\varphi}{b}\right)\dagger \qquad (25)$$

with the initial conditions

$$\varphi_{(x,0)} = 0 \text{ and } c_{(x,0)} = c_0$$

and the boundary condition (with $x = 0$)

$$D'nF \operatorname{grad} c + \frac{1}{\rho'} \operatorname{grad} \varphi = -I;$$

where C is the capacity of the double layer per unit volume of the porous electrode, and ρ' the effective resistance of the electrolyte in the pores. Immediately after the current has been switched on, there is insufficient time for the reactant concentration in the pores of the electrode to change appreciably, and the current is used up mainly in charging the electrical double layer on the electrode:

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} \simeq 0, \quad \left(\frac{\partial \varphi}{\partial x}\right)_{x=0} \simeq -\rho' I.$$

The time characterising the rate of propagation of the charging wave within the pores is found from Eqn. (24):

$$\tau_{el} = \rho' C x^2. \qquad (26)$$

The time characterising the spreading of the diffusion process over the same distance is

$$\tau_{dif} = \frac{x^2}{D'}. \qquad (27)$$

Comparison of these quantities shows convincingly that, in practically all possible cases, the charging wave greatly outstrips the diffusion wave:

$$\frac{\tau_{el}}{\tau_{dif}} = \rho' C D' \simeq 10^{-3}-10^{-7}; \qquad (28)$$

which allows us to regard the polarisation in Eqn. (25) as constant.

The cause of the change in concentration inside the electrode is the electrode reaction, which in turn is caused by polarisation. During the initial charging period the diffusion term in Eqn. (25) can be neglected, and the change in concentration is then determined by the rate of discharge:

$$\frac{\partial c}{\partial t} = -Skc \exp\left(\frac{\varphi}{b}\right); \qquad (29)$$

whence it follows that the time required for establishment of a steady-state is of the order of

$$\tau = \frac{1}{Sk} \exp\left(-\frac{\varphi}{b}\right). \qquad (30)$$

With slow electrode processes the time required for establishment of a steady-state can be extremely great. The operating conditions of a porous electrode during the initial period after the current has been switched on, when $t \ll \tau$, are then similar to those discussed previously[1-4], and are governed by the distribution of potential.

SUMMARY

An examination has been made of the operating conditions of porous electrodes when the supply of the reactant

† More exactly $\exp(\varphi/b)$ should be replaced by a function such that $f(\varphi) \to 0$ as $\varphi \to 0$, for example $2 \sinh(\varphi/b)$.

is controlled by diffusion. The equation to the polarisation curve has been deduced, and the limits of its applicability have been determined. Use of porous electrodes is shown to be most effective with slow electrode processes.

1. J. J. Coleman, Trans. Electrochem. Soc., 90, 545 (1946).
2. V. S. Daniel'-Bek, Zhur. Fiz. Khim., 22, 697 (1948).
3. A. N. Frumkin, Zhur. Fiz. Khim., 23, 1477 (1949).
4. O. S. Ksenzhek and V. V. Stender, Dokl. Akad. Nauk SSSR, 107, 280 (1956).
5. R. M. Perskaya and I. A. Zaidenman, Dokl. Akad. Nauk SSSR, 115, 548 (1957).
6. I. Z. Zaidenman and R. M. Perskaya, Zhur. Fiz. Khim., 33, 50 (1959) [Russ. J. Phys. Chem., Abs., 2 (1959)].
7. V. G. Levich, "Fiziko-Khimicheskaya Gidrodinamika" (Physicochemical Hydrodynamics), Fizmatgiz, Moscow, 1959.
8. Ya. B. Zel'dovich, Zhur. Fiz. Khim., 13, 756 (1939).
9. D. A. Frank-Kamenetskii, "Diffuziya i Teploperedacha v Khimicheskoi Kinetike" (Diffusion and Heat transfer in Chemical Kinetics), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1947.
10. V. V. Stender, "Diafragmy dlya Elektroliza Vodnykh Rastvorov" (Diaphragms for the Electrolysis of Aqueous Solutions), Moscow–Leningrad, 1948.

Dnepropetrovsk Institute of Chemical Technology

Received 29th October 1959

PHOTOCATALYTIC PROPERTIES OF ZINC OXIDE IN THE REDUCTION OF METHYLENE BLUE. V. POISONING BY METAL IONS

I. N. Barshchevskii

Previous communications have been devoted to the poisoning of irradiated lead-ion-activated zinc oxide by sodium nitrate and nitrite, and by *m*- and *p*-nitrophenols[1] and to the action on photocatalysts of barium, calcium, lead, and copper ions, and hydrogen sulphide[2-6]. These investigations suggested that the poles of the bipolar active centre of the photocatalyst [3] are substantially displaced towards its extremities[1].

Since the theory of active centres of metallic catalysts was based, in the case of "dark" catalysis, mainly on an investigation of poisoning, in order to elucidate the nature and structure of the active centres of photocatalysts another study of poisoning has been made, using metal ions as the poisons. Some preliminary conclusions on the causes of the activity and poisoning of a heterogeneous semiconductor photocatalyst have been attempted.

EXPERIMENTAL

In order to obtain comparable results, the subject of the investigation, as before[1,6], was zinc oxide activated by lead ions ($\alpha = 3.574 \times 10^{-3}$ % Pb^{2+}), the preparation of which has been described previously[2-5,7]. The sample of zinc oxide[1-7] was calcined by means of a gas burner in a current of nitrogen in a photoreactor for 10 min. Under these conditions, the semiconductor reversibly loses oxygen and becomes yellow[8] (formation of *F*-centres). The reaction solution is added to the still hot yellow zinc oxide.

In this work formaldehyde[2-7] was used as the electron-donor and methylene blue[1-7] as the electron-acceptor.

The reaction was carried out in an atmosphere of chemically pure nitrogen[9], which was obtained and purified as described earlier[1,6] and stored in a gas holder. It is known that the process studied is extremely sensitive to the presence of traces of oxygen[10]. Therefore, in order to displace the equilibrium in the direction of the formation of leuco-(methylene blue), in later experiments the nitrogen was passed through a saturated solution of ammonium chloride in aqueous ammonia ($d = 0.95$, "analytical reagent" grade) in the presence of metallic copper[9]. The copper was previously washed free from organic impurities with dichloroethane, toluene, ether, and alcohol, etched with hydrochloric acid, and washed with twice-distilled water until there was no reaction for chloride ion in the wash waters. Finally, the nitrogen was passed through dilute sulphuric acid, water, and a suspension of $Mn(OH)_2$ in water[9].

The nitrogen purified in this way was passed for 30 min through a capillary into a photoreactor with plane-parallel walls, calibrated with the reaction mixture. The calibration of 150 vessels showed that their internal dimensions varied within the following limits: thickness 1 ± 0.1 mm, width 9 ± 0.4 mm, length 240 ± 4.8 mm. The photoreactor is sealed with the capillary inside. The whole of the system used for deoxygenation was previously "conditioned" in an atmosphere of nitrogen for a long time.

When these conditions were observed, the equilibrium concentration of oxygen, calculated from the equilibrium concentration of methylene blue in the photoreactor, was 0.4×10^{-8} mole ml^{-1}, and the average velocity of the reverse reaction was less than the average velocity of the direct reaction by a factor of 500. We assumed that it was possible to neglect the mean velocity of the oxidation of the leuco-dye.

These operations and the subsequent measurements were carried out in diffused light on an FK-51 photocolorimeter close to the upper meniscus of the reaction solution, after the reactor had stood for 5 min in the dark to allow the valves of the apparatus to warm up: measurement time 2–3 min; red filter, $\lambda_{max} = 640$ mμ; the spectral characteristics of the filter were obtained on an FM universal photometer.

Before the beginning of the reaction, the sealed photoreactor was shaken vigorously in order to ensure a distribution of the zinc oxide as uniform as possible throughout the solution. The vessel was rotated in a frame at 14 rev min^{-1} 21 cm from a 1000 W incandescent lamp. The temperature of the experiment was maintained at 29° ± 1° with the help of a small four-bladed fan.

At fixed time intervals, the reactor was removed, the system investigated colorimetrically, and the results were compared with a calibration curve; the reproducibility of the experiments did not exceed ±5.2% (Fig. 1).

The concentration of the ammonium acetate ("analytical reagent" grade) solution used[11] was found by titration in the presence of formaldehyde (hexamethylenetetramine method) with caustic soda[12-14].