

GAS DIFFUSION ELECTRODE PRODUCING PERHYDROXYL IONS: CALCULATION OF CONCENTRATION DISTRIBUTION OF OXYGEN AND HO_2^- IONS IN POROUS ELECTRODE PARTICLES

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Received November 4th, 1976

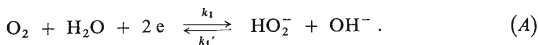
The calculation of the characteristics of a semihydrophobic porous electrode was done on the basis of a model assuming fully drowned catalyst particles around which gaseous oxygen flows. From transport equations for oxygen and for HO_2^- ions their concentration distribution in porous particles of the electrode was calculated. In addition, the approximate polarization curve and the dependence of the current efficiency with respect to HO_2^- ions on the electrode potential were calculated and compared with measured dependences.

Gas diffusion electrodes have been studied for many years mainly from the point of view of their exploiting in electrochemical current sources. Besides that, however, also the use of these electrodes in the manufacture of peroxo compounds (H_2O_2 , perborates, *etc.*¹⁻⁵) by partial cathodic reduction of oxygen has been proposed and studied. In this respect, a pronounced dependence of the yield of HO_2^- ions on the electrode material, its porous structure, concentration of HO_2^- ions, and other parameters was stated^{2,4,5}. If sodium hydroxide is used as electrolyte, a deposit of solid $\text{Na}_2\text{O}_2 \cdot 8 \text{H}_2\text{O}$ can develop in the pores of the electrode and thus prevent its correct functioning^{6,7}.

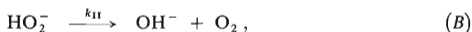
The present work deals with the calculation of characteristics of the porous electrode based on kinetic data of the studied reactions and on the structural parameters of the electrode. A similar calculation was done by Baucke and Winsel⁸ who assumed that the peroxide is formed on the three-phase boundary at the pore mouth and calculated the course of its concentration along the pore and in the radial direction. The mentioned assumption, however, is at variance with the later found circumstance that the oxygen does not react only at the three-phase boundary but mainly on the surface of drowned micropores⁹⁻¹¹.

THEORETICAL

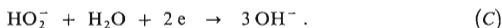
Hydrogen peroxide, or more precisely its ions are formed in alkaline medium by a two-electron reduction of oxygen:



Perhydroxyl ions can decompose chemically:



or can be reduced further:



From the preceding work it follows that HO_2^- ions are formed with a high current yield in the potential range 0.5–0.8 V (against hydrogen electrode in the same solution), where the rate of reaction (C) is according to the work of Tarasevich and co-workers¹² negligible. Therefore, in further calculations only reactions (A) and (B) will be considered.

The calculations for a semihydrophobic porous electrode will be based on the modified model of the porous electrode of the second order proposed by Micka⁹ for hydrophilic porous gas electrodes. The electrode according to this model consists of porous particles of a catalytic material containing a large number of micropores drowned with the electrolyte. Around the particles are gas pores through which the reacting gas diffuses and pores filled with the electrolyte serving for the transport of ions generated in the porous particles toward the electrolyte side of the porous electrode.

We shall consider the following sequence of processes: 1) Oxygen dissolves in the electrolyte on the surface of the porous particles and diffuses into their interior. 2) Oxygen is reduced on the inner surface of the particles to form OH^- and HO_2^- ions (Eq. (A)). 3) These ions diffuse back to the surface of the particles with a simultaneous partial decomposition of the HO_2^- ions (Eq. (B)). 4) OH^- and HO_2^- ions diffuse and migrate through the drowned intergranular pores to the electrolyte side of the electrode.

In contrast to some authors¹³, we neglect the concentration gradient in the gas pores. This is justified with electrodes where the current density is proportional to their thickness¹³. Further we shall neglect the diffusion resistance of the electrolyte film on the surface of the porous particles, which was shown in an analogous case by Micka⁹ as plausible.

To formulate the transport equations in the porous particles, their form must be specified. Aris¹⁴, Rester¹⁵ and Cutlip¹³ showed, however, using the ratio of the specific surface area to the volume of the particles in a dimensionless solution of a similar problem, that the results are for a cylindrical, spherical and plate-like shape of the particles very similar. For simplicity, we shall assume that the particles have the shape of plates. Micka⁹ assumes in his model that one side of the plate-like particle is in contact with the gas, the other with the electrolyte. According to our calculations it seems more likely that in the peroxide porous electrode both sides of the plate-like particles

are in contact partially with the gas, partially with the electrolyte. This seems to be indeed the case in a real electrode. If the points of contact with the electrolyte are closer together than would correspond to the dimension of the particle then the problem can be simplified by assuming one-dimensional diffusion in the plate-like particle whose surface is in contact both with the gas and with the electrolyte in the drowned intergranular pores.

The calculations will be done with respect to the symmetry of the particle under consideration only for its one half (of thickness d_c) delimited by its plane of symmetry and its surface (Fig. 1).

The diffusion equations for oxygen and HO_2^- ions in the elementary particle can be for this case written as

$$D_1 \frac{d^2 c_1}{dy^2} + \delta_1 = 0, \quad (1a)$$

$$D_2 \frac{d^2 c_2}{dy^2} + \delta_2 = 0, \quad (1b)$$

where D_1 and D_2 are diffusion coefficients of O_2 and HO_2^- ions in the porous particle, c_1 and c_2 their concentrations per unit of volume of the porous particle, δ_1 and δ_2 rates of formation of O_2 and HO_2^- ions per unit volume of the porous particle, and y is coordinate perpendicular to its surface. The potential gradient in the porous particle is neglected in view of the rather high electrolyte concentration, small dimension of the particle and low current density on its external surface.

The rate of oxygen reduction referred to a unit internal surface area of the porous particle is expressed as

$$r_1 = k_1 \bar{c}_1 \exp \left[- \frac{(1 - \alpha) F}{RT} (E - E_r) \right] - k_1' \bar{c}_2 \exp \left[\frac{\alpha F}{RT} (E - E_r) \right], \quad (2)$$

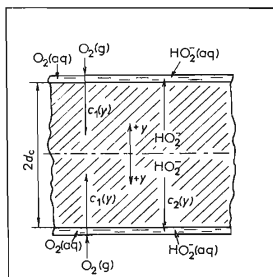


FIG. 1

Scheme of Mass Transport in a Porous Particle of the Electrode

where \bar{c}_1 and \bar{c}_2 denote concentrations of O_2 and HO_2^- ions in a given point in the porous particle. The form of this equation follows from the work of Yeager and co-workers¹⁶ according to whom the rate-controlling step of the oxygen reduction on various sorts of carbon is a one-electron process of the first order with respect to oxygen with an almost symmetrical energetic barrier (Tafel slope $b = 0.12$ to 0.15 V). The back reaction is of first order with respect to HO_2^- and independent of the concentration of OH^- ions¹⁶; the corresponding Tafel slope is 0.12 V. Accordingly, the exponents in Eq. (2) can be replaced by $\pm a(E - E_r)$, where $a = = 0.5R/RT$.

The concentrations c_i and \bar{c}_i are related as follows:

$$c_i = \bar{c}_i v_c, \quad (3)$$

where v_c denotes porosity of the particle. The decomposition of HO_2^- ions on active carbon is a first-order reaction¹⁷:

$$r_{II} = k_{II} \bar{c}_2. \quad (4)$$

The rates of formation of oxygen and HO_2^- ions in a unit volume of the porous particle can be expressed by $\delta_1 = S_c(0.5r_{II} - r_I)$ and $\delta_2 = S_c(r_1 - r_{II})$, where S_c denotes the internal surface of drowned pores per unit volume of the porous particle.

With respect to Eqs (2)–(4), the diffusion equations (1a,b) can be rewritten as

$$D_1 \frac{d^2 c_1}{dy^2} - S_c k_1 (c_1/v_c) \exp[-a(E - E_r)] + S_c k_1' (c_2/v_c) \exp[a(E - E_r)] + S_c k_{II} c_2 / 2v_c = 0, \quad (5a)$$

$$D_2 \frac{d^2 c_2}{dy^2} + S_c k_1 (c_1/v_c) \exp[-a(E - E_r)] - S_c k_1' (c_2/v_c) \exp[a(E - E_r)] - S_c k_{II} (c_2/v_c) = 0. \quad (5b)$$

The diffusion coefficient of HO_2^- ions is not known; we shall assume that it is equal to that of oxygen in view of the fact that both these particles have an almost equal size. The boundary conditions for the above differential equations are as follows:

$$y = 0: \quad dc_1/dy = 0, \quad dc_2/dy = 0, \quad (6a)$$

$$y = d_c: \quad c_1 = c_{1c}, \quad c_2 = c_{2c}. \quad (6b)$$

The conditions (6a) apply for the plane of symmetry of the plate-shaped particle, (6b) for its surface; c_{1c} and c_{2c} are the concentrations of O_2 and HO_2^- ions at the surface of the particle referred to its unit volume.

We introduce the following dimensionless parameters:

$$u_1 = c_1/c_{1c}, \quad u_2 = c_2/c_{2c}, \quad Y = y/d_c, \quad (7a,b,c)$$

$$A = (S_c d_c^2 k_1 / D_1 v_c) \exp[-a(E - E_r)], \quad (8a)$$

$$B = (S_c d_c^2 k'_1 / D_2 v_c) \exp[a(E - E_r)], \quad (8b)$$

$$C = c_{1c}/c_{2c}, \quad D = S_c d_c^2 k_{1l} / 2D_1 v_c, \quad (8c,d)$$

whereby the diffusion equations take the form

$$d^2 u_1 / dY^2 - Au_1 + (B + D)u_2 / C = 0, \quad (9a)$$

$$d^2 u_2 / dY^2 + ACu_1 - (B + 2D)u_2 = 0. \quad (9b)$$

The boundary conditions are now

$$Y = 0: \quad du_1/dY = 0, \quad du_2/dY = 0, \quad (10a)$$

$$Y = 1: \quad u_1 = 1, \quad u_2 = 1. \quad (10b)$$

This problem can be solved by the Laplace-Carson transformation to obtain the relative concentrations of O₂ and peroxide in the porous particles of the electrode:

$$u_1 = u_1(0) \frac{(P_1^2 - B - 2D) \cosh(P_1 Y) - (P_2^2 - B - 2D) \cosh(P_2 Y)}{K} - u_2(0) \frac{B + D}{C} \frac{\cosh(P_1 Y) - \cosh(P_2 Y)}{K}, \quad (11a)$$

$$u_2 = u_2(0) \frac{(P_1^2 - A) \cosh(P_1 Y) - (P_2^2 - A) \cosh(P_2 Y)}{K} - u_1(0) \frac{AC(\cosh(P_1 Y) - \cosh(P_2 Y))}{K}. \quad (11b)$$

Here we have introduced $P_1^2 = 0.5(A + B + 2D + K)$, $P_2^2 = 0.5(A + B + 2D - K)$, $K = [(A + B + 2D)^2 - 4AD]^{1/2}$. The relative concentrations of oxygen and peroxide in the center of the particles, $u_1(0)$ and $u_2(0)$, are obtained from Eqs (11a,b) after introducing the boundary conditions (10b). By differentiating Eqs (11a,b)

with respect to Y we obtain the gradients of the relative concentrations which serve for the calculation of the current density per unit surface area of the porous particle:

$$I_1 = \frac{2FD_1v_c}{d_c} \left[2\bar{c}_{1c} \left(\frac{du_1}{dY} \right)_{Y=1} + \bar{c}_{2c} \left(\frac{du_2}{dY} \right)_{Y=1} \right] \quad (12)$$

and the flux of peroxide ions per unit surface area of the particle:

$$N_1 = -(D_2\bar{c}_{2c}v_c/d_c) \left(\frac{du_2}{dY} \right)_{Y=1} \quad (13)$$

The value of \bar{c}_{1c} is set equal to the equilibrium concentration of oxygen in the electrolyte corresponding to the external pressure of oxygen, which seems justified in view of the negligible loss of the pressure in the electrode.

The value of \bar{c}_{2c} (concentration of HO_2^- at the surface of the porous particle) changes with the distance from the gas side of the electrode. It can be calculated by solving transport equations of the ions in the intergranular pores, which will be the subject of a next communication¹⁷. If we neglect the concentration changes of the ions in the direction normal to the electrode surface, we can calculate approximately the polarization curve using the relations

$$I_2 = S_p d_c I_1, \quad N_2 = S_p d_c N_1, \quad (14), (15)$$

where I_2 denotes current and N_2 flow of HO_2^- ions referred to unit geometric surface area of the electrode, S_p surface area of porous particles in unit volume of the electrode, and d_c electrode thickness.

The current efficiency with respect to the peroxide is given as

$$\eta(\text{H}_2\text{O}_2) = 2FN_2/I_2 \quad (16)$$

The concentrations of O_2 and HO_2^- ions in the porous particles and the approximate polarization curve were calculated as follows. For every given potential value and electrolyte composition, the dimensionless parameters A through D were first calculated. The relative concentrations of O_2 and HO_2^- ions in the center of the porous particles were then obtained by solving the system (11) with the boundary conditions (10b). The dependences of the relative concentrations of O_2 and HO_2^- ions on the distance from the center of the particle were then obtained from the Eqs (11). These equations in the differentiated form gave the concentration gradients of oxygen and HO_2^- ions at the surface of the porous particle and from them the current densities I_1, I_2 and the current yield of the peroxide were obtained. All calculations were done on a Hewlett-Packard 9830 type computer.

EXPERIMENTAL

The measured electrode was prepared from active carbon bonded with teflon. To decrease the relatively high activity of this material for the decomposition of alkaline peroxide solutions, the active carbon was pretreated by heating with a sulfide⁴. Afterwards it was mixed with an aqueous dispersion of teflon (Fluon GP 1), filtered off, dried, milled, and pressed into the form of a plate (at 30 MPa). A nickel screen served as a current collector. The content of teflon in the dry mixture was 12% (by weight). The electrode had a thickness of 0.8 mm and contained 35 mg of carbon per cm².

Measurement of polarization curves. During the measurement, the electrode was fed with oxygen in a 50% excess against the theoretical feed. Its overpressure was 270–700 Pa (2–5 Torr). The electrolyte (5M-KOH) was led into the anode compartment of the electrolyser, passed through a diaphragm, and on the outlet from the cathode compartment it was subjected to a manometric determination of HO₂⁻ ions. The rate of flow was adjusted so that the catholyte contained about 0.1M-HO₂⁻. The current yield of the peroxide was calculated from the cathodic current, rate of flow and concentration of the peroxide on the outlet. The measurement was carried out at a steady state during polarization of the cathode with a constant current at 20°C.

RESULTS AND DISCUSSION

The equations derived were applied to the given active carbon electrode whose surface was during operation nearly completely wetted with the electrolyte¹⁷ in accord with the assumption involved in the present model. The data used in the calculation were obtained mostly by measurement on the electrode or on the active carbon used¹⁷, others were taken from the literature as follows.

The rate constant for the reduction of oxygen (which is practically independent of the sort of the carbon¹⁸) was taken from the work of Storchak and Sysoeva¹⁸. The rate constant of the back reaction k'_1 was calculated from the value of the exchange current density of the reaction (1) and from the equilibrium concentrations of perhydroxyl ions in the electrolyte used (0.1M-HO₂⁻). The rate constant of the decomposition of these ions on the active carbon surface, k_{II} , was obtained by volumetric measurements¹⁷. The electrochemically active surface area of the electrode, S_e , was determined by the measurement of the electrode capacity¹⁷. The porosity of the particles, v_e , was determined by the measurement of the apparent density of the wetted and dry electrode¹⁷. The value of d_e was estimated from the average size of the active carbon particles measured microscopically and their external surface area was estimated from their size. The concentration of oxygen in the electrolyte and its diffusion coefficient were taken from the work of Davies and coworkers¹⁹. Diffusion coefficients in the porous particles were calculated by dividing the value for the free solution (5M-KOH) by the tortuosity factor of pores which was set equal to 1.4. Thus, the input data were obtained as follows:

$$k_1 = 5 \cdot 10^{-5} \text{ cm/s} \quad S_e = 1.2 \cdot 10^6 \text{ cm}^2/\text{cm}^3$$

$$\begin{array}{ll}
 k'_1 = 8 \cdot 10^{-8} \text{ cm/s} & S_p = 400 \text{ cm}^2/\text{cm}^3 \\
 k_{11} = 1 \cdot 4 \cdot 10^{-9} \text{ cm/s} & D_1 = D_2 = 4 \cdot 7 \cdot 10^{-6} \text{ cm}^2/\text{s} \\
 d_c = 8 \cdot 10^{-4} \text{ cm} & \bar{c}_{1c} = 1 \cdot 6 \cdot 10^{-7} \text{ mol/cm}^3 \\
 d_e = 0 \cdot 08 \text{ cm} & \bar{c}_{2c} = 1 \cdot 10^{-4} \text{ mol/cm}^3
 \end{array}$$

The relative concentrations of oxygen and peroxide ions in the porous particles at different overvoltages calculated by the method given in the preceding section are shown in Figs 2 and 3. It was assumed that the concentration of HO_2^- ions outside the porous particles was 0.1M. It is seen from Fig. 2 that the region in which the relative concentration of oxygen varies (the reduction region of the dissolved oxygen) becomes narrower with increasing overvoltage. At an overvoltage of -0.2 V, almost all oxygen reacts in a surface layer of the particles whose relative thickness is 0.2.

The increment of the relative concentration of HO_2^- ions in the porous particles is very small. The reason for this is the rather high concentration of these ions in the external electrolyte as compared with the dissolved oxygen. The curves of the concentration of HO_2^- ions show two regions. In the proximity of the particle surface ($Y = 0.8 - 1$) there is a gradient of concentration of these ions due to their formation in the surface layer and their diffusion out from the particles. In larger depths in the

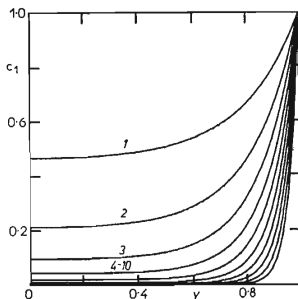


FIG. 2

Relative Oxygen Concentration in a Porous Particle as Function of Relative Distance from its Plane of Symmetry

Overvoltage values: 1 0.02 V; 2 0.04 V; 3 0.06 V; 4 0.08 V; 5 0.1 V; 6 0.12 V; 7 0.14 V; 8 0.16 V; 9 0.18 V; 10 0.2 V.

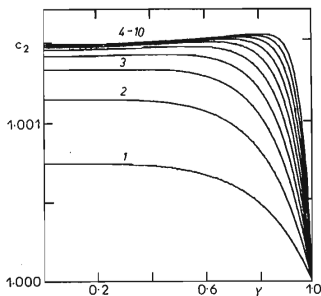


FIG. 3

Relative Concentration of HO_2^- Ions in a Porous Particle as Function of Relative Distance from its Plane of Symmetry

Overvoltage values as in Fig. 2.

porous particles there exists a gradient of an opposite direction due to the decomposition of HO_2^- ions on the internal surface of the particles and their flow from the surface layer of the particles toward the center.

The first approximation of the polarization curve was calculated as indicated in the theoretical section; it is shown in Fig. 4 together with the curve measured on the active carbon electrode. It is seen that the agreement is good although the theoretical curve was calculated under the assumption of constant concentration of HO_2^- ions in the intergranular pores and zero potential gradient in the direction from the gas to the electrolyte side. A smaller curvature of the theoretical curve may be due to the fact that the transfer coefficient was set equal to 0.5; the value obtained by Storchak and Sysoeva¹⁸ for the slope of the polarization curve on active carbon was somewhat lower than $2RT/F$ corresponding to $\alpha > 0.5$.

The calculated and measured dependences of the current yield for the peroxide on the potential are shown in Fig. 5. The current yield increases with increasing negative potential in accord with the assumption that the peroxide decomposes in the pores in the given potential range only chemically (reaction (B)) and is not appreciably reduced by reaction (C). The theoretical current yield is, however, considerably higher than the measured one in the whole region. This difference is apparently due to the assumption that the concentration of HO_2^- ions in the intergranular pores is the same as in the external electrolyte. Our further calculations

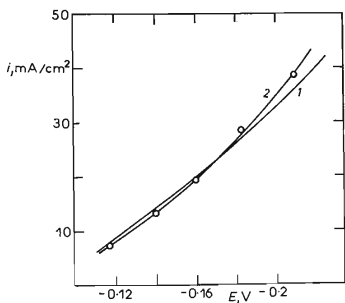


FIG. 4
Polarization Curves of Active Carbon Porous Electrode

1 Calculated; 2 measured. 5M-KOH, 0.1M- H_2O_2 ; 20°C; against Hg/HgO electrode in 5M-KOH.

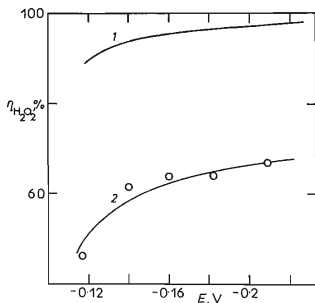


FIG. 5
Current Yield with Respect to Peroxide on Active Carbon Electrode

Data for curves same as in Fig. 4.

showed, however, that the concentration of HO_2^- ions markedly increases toward the gas side of the electrode¹⁷, which results in a higher decomposition rate of these ions in the electrode.

LIST OF SYMBOLS

a	constant equal to $F/2RT$
c_1, c_2	concentrations of oxygen and HO_2^- ions in mol/cm^3 of porous particle
u_1, u_2	relative concentration of oxygen and HO_2^- ions
\bar{c}_1, \bar{c}_2	concentrations of oxygen and HO_2^- ions in mol/cm^3 of electrolyte
c_{1c} and c_{2c}	concentrations of oxygen and HO_2^- ions in the surface layer of the porous particle, mol/cm^3
$u_1(0)$ and $u_2(0)$	relative concentrations of oxygen and HO_2^- ions in the center of the porous particle
D_1, D_2	diffusion coefficients of O_2 and HO_2^- in the porous particle, cm^2/s
d_c	half thickness of the porous particle, cm
d_e	thickness of the porous electrode, cm
E	potential of the porous particle, V
E_r	equilibrium potential, V
F	Faraday's constant, $96\,500\text{ C}$
k_1	rate constant of reduction of O_2 , cm/s
k_1'	rate constant of the back reaction, cm/s
k_{11}	rate constant of the decomposition of HO_2^- ions, cm/s
I_1	current density on the outer surface of the porous particle, A/cm^2
I_2	current density per unit of geometric surface area of electrode, A/cm^2
N_1	flow of HO_2^- ions per unit of outer surface area of the porous particle, $\text{mol/cm}^2\text{ s}$
N_2	flow of HO_2^- ions per unit of geometric surface area of electrode, $\text{mol/cm}^2\text{ s}$
S_c	electrochemically active surface area per unit volume of the porous particle, cm^2/cm^3
S_p	outer surface area of porous particles per unit volume of electrode, cm^2/cm^3
v_c	porosity of porous particles
y	coordinate from the center of the porous particle, cm
Y	relative coordinate, y/d_c
α	transfer coefficient
$\eta(\text{H}_2\text{O}_2)$	current yield of the peroxide, %

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