THEORY OF POROUS ELECTRODES. X.*

CONCENTRATION OF KOH IN PORES OF OXYGEN ELECTRODE AND MORE EXACT TRANSPORT EQUATIONS

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The characteristics of a porous nickel electrode with a silver catalyst for oxygen in alkaline electrolyte were calculated numerically from exact transport equations for the model of porous electrodes of second order. The deviations of the exact solution from the approximate one derived in the preceding work are discussed. The course of the polarization curves is similar to the approximate solution, however the concentration of KOH in the pores is obtained considerably smaller resulting in a lower gradient of concentration.

In the preceding communication[1] it has been shown that the theory based on the new model of porous electrodes of second order leads to a good agreement between calculated and measured characteristics of an oxygen electrode in alkaline electrolyte. The concentration of potassium hydroxide in the pores, however, is according to this theory rather high attaining saturation, *e.g.*, at a current of 0.3 A/cm^2 at 93°C or 0.07 A/cm^2 at 22°C, which does not seem to be in agreement with the course of the polarization curves. The calculations were based on approximate transport equations valid for diluted electrolytes. To estimate to what extent this approximation is justified, we made analogous calculations based on the more exact theory of transport in concentrated electrolytes[2].

FORMULATION OF THE PROBLEM

A sintered porous nickel electrode has the shape of a plate with a catalytic layer of thickness d 0.13 cm and contains a silver catalyst for the decomposition of hydrogen peroxide. It is dipped in 7M-KOH and loaded with a constant current density I (the current is cathodic, hence $I < 0$). One side of the plate is in contact with oxygen at an overpressure sufficient to expel the electrolyte from the pores (1 atm) of an effective diameter more than 1 µm. The conductivity of the electrode is very good and the pressure of oxygen in the pores is constant. The electrode process

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proceeds in the drowned pores of the catalyst-electrolyte system in accord with the model described previously[1] and the equation of the local polarization curve is also the same:

$$J = d_c i'_{0c} S_c \exp\left[-F(E - E_0)/2RT\right];$$ (1)

$J(\text{A/cm}^2)$ denotes local faradaic current referred to 1 cm^2 of the inner catalytic surface area of pores filled with oxygen, $d_c(\text{cm})$ thickness of the catalytic layer on the walls of these pores, $S_c(\text{cm}^2/\text{cm}^3)$ internal surface area of the catalyst, $i'_{0c} = i^0_0 c^*_{3c}$, c^*_{3c} concentration of oxygen in the electrolyte (mol/cm^3).

Electrode without Cover Layer

The transport equations are the same as in ref.[3]:

$$di_2/dx = J S_p, \qquad i_2 = \varkappa \, dE/dx + (\varkappa/2F)(1 - 2t^0_1) \, d\mu_e/dx,$$ (2), (3)

$$\tfrac{1}{2} i_2 + c_0(\varkappa/c_1) \, t^0_1 \, dE/dx = \tfrac{1}{2}(c^0 t^0_1 \varkappa/c_1 F) \left[1 + 1.578(c_1 c_T)^{1/2}/c_0\right] d\mu_e/dx$$ (4)

$$x = 0, \quad dc_1/dx = 0; \quad x = d, \ i_2 = I, \ c_1 = c_{1a}.$$ (5)

Here $i_2 \ (\text{A/cm}^2)$ denotes ionic current, $x(\text{cm})$ distance from the gas-electrode interface toward electrolyte, $S_p(\text{cm}^2/\text{cm}^3)$ internal surface area of gas pores, $\varkappa(\Omega^{-1} \text{ cm}^{-1})$ conductivity of the pore electrolyte, t^0 transference number of K^+ ions $(= 0.23)$, μ_e chemical potential of KOH, c_0 and c_1 concentrations of water and KOH $(\text{mol/cm}^3$ of electrode$)$, $c_T = c_0 + 2c_1$ and $I \ (\text{A/cm}^2)$ external current.

On introducing dimensionless parameters and solving with respect to the derivatives we obtain from Eqs (1)–(5):

$$\frac{dp}{d\xi} = K e^{-\eta}, \quad \frac{du}{d\xi} = p \frac{dI}{\varkappa \lambda_2} \frac{c_1/c_0 + 0.46}{1.578(c_1 c_T)^{1/2}/c_0 + 1.54} \left(\frac{d \ln a_\pm}{du}\right)^{-1},$$ (6), (7)

$$\frac{d\eta}{d\xi} = p \frac{dI}{\varkappa \lambda_1} - 0.27p \frac{dI}{\varkappa \lambda_2} \frac{c_1/c_0 + 0.46}{1.578(c_1 c_T)^{1/2}/c_0 + 1.54},$$ (8)

$$\xi = 0, \quad du/d\xi = 0; \quad \xi = 1, \ p = 1, \ u = 1,$$ (9)

where $p = i_2/I$, $\xi = x/d$, $K = dd_c i'_{0c} S_c S_p/I$, $\eta = F(E - E_0)/2RT$, $u = c^*_1/c^*_{1a}$, c^*_1 and c^*_{1a} are analytical concentrations of KOH in the pores and in the external electrolyte, $\lambda_1 = 2RT/F$, $\lambda_2 = 0.46RT/F$ and $a_\pm$ denotes mean molal activity of KOH.

Electrode with Cover Layer

The transport of electrolyte in the cover layer of thickness $\bar{d} = 0.07 \text{ cm}$ is described by Eqs (3) and (4), where $i_2 = I$, hence also by Eq. (7), where $p = 1$. The x variable is in the range from d to $d + \bar{d}$ and the boundary condition is

$$\xi = 1 + d/\bar{d}, \quad u = 1.$$ (10)

Eq. (8) for $p = 1$ gives the „ohmic potential drop" in the cover layer. The value of u for $\xi = 1$,

which serves as a boundary condition for the operating layer, is obtained from the solution of Eq. (7). Eqs (6)—(8) apply for the operating layer together with the boundary conditions

$$\xi = 0, \quad du/d\xi = 0; \quad \xi = 1, \quad p = 1. \qquad (11)$$

The equations for both cases were solved on a NE 4130 type digital computer analogously as in ref.[3], from which the numerical values of the necessary parameters were taken. The coefficient K was set equal to $1/|I|$ since the factor $dd_c|i'_{0c}|\, S_c S_p$ can be included in the constant E_0 in Eq. (1) and thus also in the definition of η in Eq. (6). The polarization of the operating layer is denoted as $\eta_d = F(E_d - E_0)/2RT$; its comparison with the approximate solution is based on Eq. (30) in ref.[1], which can be now written in the form $-F(E_d - E_0)/2RT = 2\ln|I| - \ln(\sqrt{u_0} - 1) + C$, where $C = \ln(t_2/4d_c c_{1a} D_{12} F |i'_0|\, S_c S_p)$ can be expressed as $C = \ln(d/4KI^2\lambda)$. Since $K|I| = 1$, $d/\lambda = 6\cdot71|I|$ at 93°C and $22\cdot36\,|I|$ at 22°C (ref.[1]), we obtain $C = 0\cdot517$ (93°C) and $1\cdot721$ (22°C).

RESULTS AND DISCUSSION

The calculated dependences of the dimensionless concentration on the inner end of the pores (for $x = 0$), u_0, on the current density given by the oxygen electrode at 22°C are shown in Fig. 1. Since a saturated solution of KOH would be $14\cdot5$M
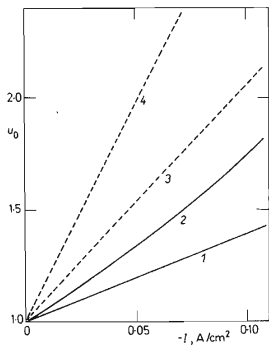

FIG. 1

Dependence of Dimensionless Concentration of KOH in the Pores on Current Density

1, 2 Exact theory; *3, 4* approximate theory; *1, 3* electrode without cover layer; *2, 4* with cover layer. Critical value of $u_0 = 2\cdot07$; 22°C.
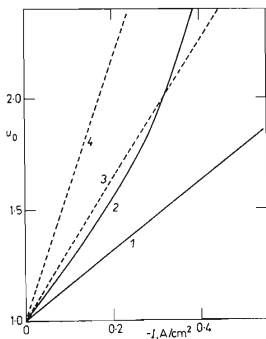
FIG. 2

Dependence of Dimensionless Concentration of KOH in the Pores on Current Density

1, 2 Exact theory; *3, 4* approximate theory; *1, 3* electrode without cover layer; *2, 4* with cover layer. Critical value of $u_0 = 2\cdot67$; 93°C.

(20°C) according to tabulated data[4], the critical value of u_0 is 2·07. This is surpassed by the curve *4* calculated from the approximate theory, whereas the more exact theory (curve *2*) eliminates this difficulty. (Curves *1* and *3* for an electrode without cover layer are shown merely for comparison since real electrodes were always provided with a cover layer). Hence, in the considered range of current densities the deposition of a solid phase in the pores cannot be expected. At a higher temperature of 90°C, the solubility of KOH is[4] about 18·7M, hence the critical value of u_0 is higher, 2·67. However, the electrode performance increases considerably and the electrolyte concentration can be read from Fig. 2. The deposition of the solid phase should occur only at $I = -0.43$ A/cm² (curve *2*, the critical point lies beyond the diagram) and not at -0.29 A/cm² (curve *4*). Even when we take into consideration that the more exact theory has also a limited validity, especially with regard to concentrations approaching saturation, the calculated concentrations of KOH are probably more correct than the values from the approximate theory.

In a more detailed analysis, it can be shown that the main part of the difference between the exact and approximate theories consists in the expression for the diffusion coefficient of KOH: the correction for the activity of KOH is $d \ln a_{\pm}/du > 1$ and indeed by this factor the quantity D_{12} introduced earlier is multiplied. Other correction for changes of water concentration acts in the same sense as the preceding one but is smaller.

Since the Eq. (1) of the local polarization curve is the same as in the approximate theory, a larger difference in the calculated polarization curves cannot be expected (Fig. 3). The deviations are caused mainly by the fact that the conductivity of KOH changes only little in the concentration range considered here (*cf.* tabulated data
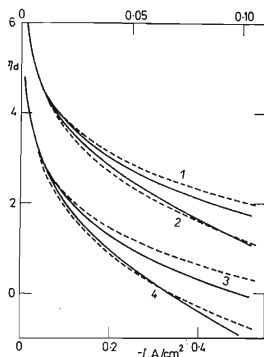

FIG. 3

Dependence of Dimensionless Polarization of the Electrode on Current Density

1, *2* $\eta_d = 19.67(E_d - E_0)$, 22°C (upper scale); *3*, *4* $\eta_d = 15.85(E_d - E_0)$, 93°C (lower scale); *1*, *3* electrode without cover layer; *2*, *4* with cover layer. Dashed curves according to ref.[1], full curves according to the present theory.

in ref.[3]), whereas in the approximate theory the assumption of direct proportionality between conductivity and concentration (*i.e.* of constant mobility of ions) was involved. For this reason the more exact (full) curves in Fig. 3 indicate a somewhat larger ohmic voltage drop in the pores than the approximate curves (dashed). For the same reason the current distribution in the pores is calculated as more unequal. The difference between the curves calculated for electrodes without and with cover layer ("correction for the cover layer") is smaller than would correspond to our previous estimate based on an empirical extrapolation formula[1], which however gave obviously much too high values at the lower temperature. It should be emphasized that the mentioned correction includes not only the voltage drop in the cover layer but also the change in polarization of the operating layer caused by increasing concentration of KOH. This latter effect is represented in our theory mainly by the dependence of conductivity on concentration of KOH, whereas the exchange current i'_{0c} in Eq. (*1*) was assumed[1] in accord with other authors to be independent of the concentration of KOH although an experimental evidence is lacking. It seems therefore that a further improvement of the theory would be possible only by replacing Eq. (*1*) by a more exact one whereas a further modification of the transport equations would have no sense.

Burštejn and coworkers[5] derived a theory of the porous oxygen electrode in 7m-KOH based on similar equations and assumptions as in our preceding work[1] except that they consider the concentration of KOH in the pores as constant. They also arrived at the conclusion that the electrode reaction proceeds mainly in the drowned pores and that the film of electrolyte on the walls of gas pores plays only a very small role. The authors stated that their silver catalyst generates current in a situation where the oxygen concentration in the drowned pores is more or less exhausted, hence an intermediate case between the "internal diffusion" (our[1] case A) and "kinetic" (case[1] B) regime. It can be shown that their criterion $(l/l_d) \exp (\bar{\varphi}/2)$ for distinguishing between these extreme cases is equivalent to our criterion[1] d_c/λ_c: the condition $(l/l_d) \exp (\bar{\varphi}/2) \geqq 1 \cdot 6$ corresponds approximately to our $d_c/\lambda_c \geqq 1 \cdot 3$ (case A) and $(l/l_d) \exp (\bar{\varphi}/2) \ll 1$ corresponds to $d_c/\lambda_c \ll 1$ (case B).* With our (relatively more active) catalyst the situation approaches more the kinetic regime (case B) apparently because of a larger content of shorter pores of a greater specific surface area; the internal diffusion regime would be manifested by a higher polarisation resistance, $|dE/dI|$, and hence by disagreement with measurements, as already stated[1].

Most recently, the Soviet authors[6,7] arrived at the conclusion that the approximate transport equations valid for diluted electrolytes lead in the case of hydrogen–oxygen fuel cells with a membrane to much too high calculated concentration gradients of KOH since the measured gradients were much lower. This is in support of the theory presented above.

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* In ref.[1], p. 3208 below, d_c/λ_c is given erroneously as $\leqq 1 \cdot 3$ instead of $\geqq 1 \cdot 3$.

REFERENCES

1. Micka K.: This Journal *34*, 3205 (1969).
2. Micka K.: Ber. Bunsenges. Physik. Chem. *72*, 60 (1968).
3. Micka K.: This Journal *34*, 3197 (1969).
4. *Handbook of Chemistry and Physics* (C. D. Hodgman, Ed.). Chem. Rubber Publ. Co., Ohio 1962.
5. Burštejn R. Ch., Vachonin V. A., Tarasevič M. R., Chruščeva E. I., Čizmadžev Ju. A., Čirkov Ju. G.: Elektrochimija *6*, 939 (1970).
6. Volfkovič Ju. M., Bagockij V. S.: Elektrochimija *8*, 1179 (1972).
7. Kukuškina I. A., Štejnberg G. V., Volfkovič Ju. M., Bagockij V. S.: Elektrochimija *8*, 1451 (1972).

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