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A mathematical model for the porous lead dioxide electrode

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A theoretical model for the porous lead dioxide electrode is proposed on the basis of the macrohomogeneous model for porous electrodes.

The structural changes during discharge, due to precipitation of lead sulphate, are considered.

The two main structural effects, plugging of the pores and gradual insulation of the active electrode surface by the reaction product, lead sulphate, are both considered by relating them to the local degree of discharge.

The numerical results show that, at high current densities, the discharge capacity is limited by both structural and transport restrictions.

At the end of discharge a layer of lead sulphate crystals blocks the electrode surface in the outer layers of the electrode. The current can then neither be transferred across this insulated surface nor reach remaining active material in the inner parts of the electrode because of acid depletion, which is furthermore accelerated by the decreasing porosity.

1. Introduction

The important problems of mass transfer and current distribution within porous electrodes can be successfully treated by application of the theories of porous electrodes. Various mathematical models have been proposed for the theoretical study of the discharge behaviour of porous electrodes. The work up to 1966 has been summarized by de Levie [1].

These early theories did not take into consideration the changes in porous structure during the discharge process.

During the last few years some new models have been developed for the description of porous electrodes undergoing structural changes [2–5]. Even these models must, however, be extended further in the analysis of the dynamic behaviour of actual battery electrodes, in which a reaction product is precipitated, which gradually insulates the active surface and plugs the pores.

Among the practically important electrodes, belonging to this class of porous electrodes, is the lead dioxide electrode, used as the positive plate in the lead-acid cell.

In a previous work [6] it was shown that the initial current distribution in this electrode can be satisfactorily predicted by application of the macrohomogeneous model [7–8]. The experimental results on changes in current distribution during discharge indicated further that the transient discharge behaviour of the porous lead dioxide electrode can be fully understood only when considering together the effects of acid depletion and precipitation of the reaction product, lead sulphate.

An early model for the transient behaviour of this electrode was proposed by Stein [9], who assumed a negligible charge transfer resistance and regarded the structural effects only in a simplified, explicit manner. A more realistic treatment must, however, also take into consideration the kinetics of the electrode process and how the structural changes influence the electrode kinetics and the transport parameters.

In the present work a model is proposed which takes into account these structural effects in the mathematical description of the transient discharge behaviour of the porous lead dioxide electrode.

2. Formulation of the mathematical model

2.1. *The model*

The mathematical model presented below is based upon a porous lead dioxide electrode, in which the accessible pores are completely filled with the electrolyte, a solution of sulphuric acid.

The porous body is regarded as macrohomogeneous. When the electrode is discharged, a cathodic current will cross the matrix-electrolyte interface through the electrode reaction:

$$PbO_2(s)+4H^+ +SO_4{}^{2-}+ 2e \rightleftarrows PbSO_4(s)+2H_2O(l) \qquad (1)$$

This stoichiometric reaction formula indicates two major changes during discharge. The sulphuric acid in the pores is consumed, whereby an acid concentration gradient is established. Simultaneously lead sulphate will precipitate on the shrinking PbO_2-matrix. Because of the lower density of $PbSO_4$, compared to PbO_2, the porosity will decrease in proportion to the increasing amount of $PbSO_4$.

The description of the discharge process must therefore be based upon equations for the transport of mass and charge in the pore electrolyte, for the actual electrode kinetics and for the structural changes.

In order to facilitate analysis a number of simplifying assumptions are first introduced. Although some of these assumptions may seem rather rough, they do not affect the essential features which are of interest.

1. When the discharge is not too deep, the conductivity of the PbO_2-matrix is much higher than that of the pore electrolyte. This also means that the electrode can be regarded as one-dimensional [6].
2. The time constant of the charging of the electrical double layer is small compared to the discharge time.
3. The transport processes in the electrolytic solution can be adequately described by the equations of dilute solution theory.
4. Electrolyte flow in the pores is due only to the decreasing porosity.
5. Bivalent lead ions are transported only over very short distances with respect to the electrode thickness before they precipitate with sulphate ions to form lead sulphate.
6. At the outer surface of the electrode the concentration of sulphuric acid is equal to its value in the bulk of the electrolyte.
7. The system is isothermal.
8. The sulphuric acid can be regarded as a binary electrolyte, completely dissociated into H^+ and $HSO_4{}^-$ ions only.

The last assumption is justified by the fact that at a concentration of 5 M the sulphuric acid dissociates by about 85% into HSO_4^- ions and by 5% into SO_4^{2-} ions, while about 10% of the molecules are undissociated [10]. These orders of magnitude are approximately valid down to 0·5–1 M. With this assumption the derived system of equations will be much simpler than in the case where also the SO_4^{2-} ions and the neutral H_2SO_4 molecules are considered.

2.2 *Development of the basic equations*

The basic transport equations for the one-dimensional, porous PbO_2 plate can now be derived by application of porous electrode theory [7]. The co-ordinate, x, equals 0 at the centre of symmetry of the electrode and equals L at the outer surface. For symmetry reasons only one half of the electrode needs to be considered.

The H^+ ions are denoted by the index 1 and the HSO_4^- ions by the index 2.

The fluxes of H^+ and HSO_4^- ions may be expressed as a sum of three terms describing diffusion, migration and convection respectively

$$N_i = -D_i\frac{\partial c_i}{\partial x} - c_i l_i \frac{z_i}{|z_i|}\frac{\partial \phi_2}{\partial x} + c_i v \, (i = 1, 2) \qquad (2)$$

where

N_i = flux of species i (kmole m^{-2} s^{-1})
D_i = effective diffusion coefficient of species i (m^2 s^{-1})

c_i = concentration of species i (kmole m^{-3} of electrolyte)
l_i = ionic mobility of species i ($m^2 s^{-1} V^{-1}$)
z_i = charge of species i
ϕ_2 = potential of pore electrolyte (V)
v = electrolyte velocity (ms^{-1})

From the condition of electroneutrality it follows that,

$$c_1 = c_2 = c \tag{3}$$

where c = concentration of sulphuric acid (kmole m^{-3}).

The current density in the electrolyte, i_2, is determined by the flux of ions:

$$i_2 = F \Sigma z_i N_i = F(N_1 - N_2) \tag{4}$$

where

$$i_2 = (Am^{-2})$$

F = Faraday's constant, $96{\cdot}5 \times 10^6$ As (kg equiv.)$^{-1}$ With the use of Equations (2) and (3), Equation (4) can be transformed into

$$i_2 = -\kappa \frac{\partial \phi_2}{\partial x} - F(D_1 - D_2) \frac{\partial c}{\partial x} \tag{5}$$

where

$\kappa = F \Sigma \mid z_i \mid c_i\, l_i$ the effective conductivity of the pore electrolyte (Ω^{-1} m^{-1})

The electrode potential is defined as $E = \phi_1 - \phi_2$ (ϕ_1 = potential of matrix phase (V)). But since the matrix phase can be regarded as equipotential

$$\left(\frac{\partial \phi_1}{\partial x} = 0\right)$$

$$\frac{\partial \phi_2}{\partial x} = -\frac{\partial E}{\partial x} \tag{6}$$

Equations (5) and (6) lead to the final expression for the current density in the pore electrolyte:

$$i_2 = \kappa \frac{\partial E}{\partial x} - F(D_1 - D_2) \frac{\partial c}{\partial x} \tag{7}$$

The local concentration change may be expressed in a differential material balance for species 1:

$$\frac{\partial(\varepsilon c_1)}{\partial t} = -\frac{\partial N_1}{\partial x} + R_1 \tag{8}$$

where

ε = porosity
t = time (s)
R_1 = source term for species 1 (kmol m^{-3} s^{-1})

A suitable expression for N_1 can be obtained from Equation (2) after elimination of c_i and ϕ_2 by application of Equations (3) and (5) respectively. Together with the Nernst-Einstein relation:

$$D_i = \frac{RT}{|z_i|F} l_i \tag{9}$$

where

R = universal gas constant, joule (kmole deg)$^{-1}$
T = temperature, °K

this leads to

$$N_1 = \frac{t_1 i_2}{F} - D \frac{\partial c}{\partial x} + cv \tag{10}$$

where

$$t_1 = \frac{c_1 \mid z_1 \mid l_1}{\Sigma\, c_i \mid z_i l \mid_i}$$

the transference number of the hydrogen ion

$$D = 2 \frac{D_1 D_2}{D_1 + D_2},$$

the binary diffusion coefficient (m^2 s^{-1}).

In accordance with the bisulphate electrolyte model, the stoichiometry of the electrode reaction (1) may now be described in the equivalent form:

$$PbO_2(s) + 3H^+ + HSO_4^- + 2e$$
$$\rightleftarrows PbSO_4(s) + + 2H_2O(l) \tag{11}$$

From this stoichiometric formula it follows that the source term in Equation (8) can be related to the local discharge rate per unit volume, $\frac{\partial i_2}{\partial x}$ according to Faraday's law:

$$R_1 = \frac{3}{2F} \frac{\partial i_2}{\partial x} \tag{12}$$

The transference number of the H^+ ion, t_1, is fairly constant in the concentration interval which is of interest, and Equations (3), (10) and (12) may thus be inserted into Equation (8) to give

$$\frac{\partial(\varepsilon c)}{\partial t}=\frac{3-2t_1}{2F}\frac{\partial i_2}{\partial x}+\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)-\frac{\partial}{\partial x}(cv) \quad (13)$$

2.3 *The kinetics of the electrode reaction*

It has been previously reported [6] that in the region −30 to −100 mV, the current-overvoltage relation for the electrode reaction in 5 M H_2SO_4 can be expressed by a Tafel equation in which the prelogarithmic coefficient has a value of about 30 mV per decade. When these experiments were repeated for successively lower concentrations down to 1.0 M, it was found that – within the experimental limits of error – the same relation holds for the whole concentration range of interest, 1–5 M H_2SO_4.

The overvoltage, η (V), is here defined as the difference between the maximum, rather constant electrode potential, E, obtained after the initial drop of voltage at the beginning of discharge and the equilibrium, open circuit potential at the actual concentration, E_c (V).

In this specific case, it is thus possible, as an approximation, to express the local electrode potential as a sum of two additive terms

$$E=E_c+\eta \quad (14)$$

where η is independent of the concentration of sulphuric acid.

The potential gradient $\frac{\partial E}{\partial x}$ appearing in Equation (7) may consequently be written

$$\frac{\partial E}{\partial x}=\frac{\partial E_c}{\partial c}\frac{\partial c}{\partial x}+\frac{\partial \eta}{\partial x} \quad (15)$$

The kinetic expression for the reaction rate per unit volume is then, approximately

$$\frac{\partial i_2}{\partial x}=-Sj_0\exp(-2F\eta/RT) \quad (16)$$

where

S = specific active surface (m^{-1})

j_0 = exchange current density ($A\,m^{-2}$)

2.4 *Consideration of the structural effects*

The effective transport coefficients in Equations (7) and (13) will decrease during the discharge process, which leads to a continuous plugging of the pores, since PbO_2 is converted into $PbSO_4$ with a larger molar volume. In addition the free active surface, available to the charge transfer process, S, which appears in Equation (16), depends on the fraction of the surface not yet covered by insulating lead sulphate crystals. It is thus necessary to introduce equations describing the structural changes in the electrode. A simple way to do this is to relate these structural changes to the local degree of discharge, X, which may be defined as proportional to the amount of charge which has been consumed up to the actual time, t:

$$X=-\frac{1}{q_0}\int_0^t\frac{\partial i_2}{\partial x}\,dt \quad (17)$$

where

q_0 = initially available quantity of charge per unit volume ($As\,m^{-3}$)

A relation between the local porosity, ε, and the local degree of discharge, X, can now be easily derived:

$$\varepsilon=\varepsilon_0-k(1-\varepsilon_0)X \quad (18)$$

where

ε_0 = initial porosity, prior to any discharge

k = 0.917, a constant determined by the difference in specific volume between PbO_2 and $PbSO_4$ (see Table 1)

The simplest way to take into account how the structural changes affect the transport coefficients is to assume that they vary in proportion to the porosity. Thus, as an example, the diffusion coefficient, D, can be expressed as

$$D=\frac{\varepsilon}{\varepsilon_0}D_c \quad (19)$$

where the index c denotes pure concentration dependence.

In the absence of detailed knowledge, the free active surface is assumed to be linearly related to the quantity X:

$$S=S_0\left(1-\frac{X}{X_{\max}}\right) \quad (20)$$

S_0(m^{-1}) is the initially available active surface in the fully charged electrode, while $X_{\max}$ is the maximum fraction of the electrode material which can be utilized at the actual current density. It may be expected from previous experimental results [6] that this quantity depends on the applied current density. This seems reasonable also in view of the decreasing capacity of flat PbO_2 electrodes with increasing current density.

The convective term in Equation (13) will, for simplicity, be related only to the decreasing porosity during discharge, which leads to a net flow of electrolyte out of the volume element.

Thus, neglecting the density changes:

$$\frac{\partial v}{\partial x} = -\frac{\partial \varepsilon}{\partial t} \tag{21}$$

However, the rate of change in porosity is also proportional to the rate of conversion of PbO_2 to $PbSO_4$ and to the difference in molar volume between products and reactants:

$$\frac{\partial \varepsilon}{\partial t} = \frac{1}{2F}\frac{\partial i_2}{\partial x}(V_p - V_r) \tag{22}$$

where

V_p = molar volume of $PbSO_4$, $48{\cdot}9 \times 10^{-3}$ m^3 kmole^{-1}

V_r = molar volume of PbO_2, $25{\cdot}5 \times 10^{-3}$ m^3 kmole^{-1}

Thus, after elimination of $\partial\varepsilon/\partial t$ in Equation (21)

$$\frac{\partial v}{\partial x} = -\frac{1}{2F}\frac{\partial i_2}{\partial x}(V_p - V_r) \tag{23}$$

Since at $x = 0$, $v = i_2 = 0$ (because of symmetry reasons) Equation (23) can easily be integrated:

$$v = -\frac{i_2}{2F}(V_p - V_r) \tag{24}$$

When the structural equations above together with Equation (15) are inserted into the basic equations (7), (13) and (16), the following equations are obtained, which describe the dynamic behaviour of the electrode.

$$i_2 = \frac{\varepsilon}{\varepsilon_0}\kappa_c\left(\frac{\partial E_c}{\partial c}\frac{\partial c}{\partial x} + \frac{\partial \eta}{\partial x}\right) - F\frac{\varepsilon}{\varepsilon_0}(D_1 - D_2)_c\frac{\partial c}{\partial x} \tag{24}$$

$$\frac{\partial c}{\partial t} = \frac{3 - 2t_1}{2F\varepsilon}\frac{\partial i_2}{\partial x} + \frac{1}{\varepsilon}\frac{\partial}{\partial x}\left(\frac{\varepsilon}{\varepsilon_0}D_c\frac{\partial c}{\partial x}\right) + \frac{i_2}{2F\varepsilon}(V_p - V_r)\frac{\partial c}{\partial x} \tag{25}$$

$$\frac{\partial i_2}{\partial x} = -S_0 j_0\left(1 - \frac{X}{X_{\max}}\right)\exp(-2F\eta/RT) \tag{26}$$

Where ε is defined by Equation (18) and X by Equation (17).

These equations can be transformed into the more convenient dimensionless form through the following transformations:

$$z = x/L;\ C = \frac{c}{c_0};\ \tau = \frac{D_0 t}{L^2}$$

$$\eta' = \frac{F(\eta - \eta_{x=0})}{RT};\ E' = \frac{FE_c}{RT};\ i = \frac{i_2}{I}$$

where

L = the thickness of one symmetric half of the porous electrode (m)

c_0 = the initial concentration of sulphuric acid (kmole m^{-3})

D_0 = the diffusion coefficient at the initial conditions (m^2 s^{-1})

$\eta_{x=0}$ = activation overvoltage at $x = 0$, (V) (time dependent)

The equations representing the electrode model then become

$$i = a\frac{\varepsilon}{\varepsilon_0}\frac{\kappa_c}{\kappa_0}\left(\frac{\partial E'}{\partial C}\frac{\partial C}{\partial z} + \frac{\partial \eta'}{\partial z}\right) - b\frac{\varepsilon}{\varepsilon_0}\frac{\partial C}{\partial z} \tag{27}$$

$$\frac{\partial C}{\partial \tau} = (3 - 2t_1)\frac{f}{\varepsilon}\frac{\partial i}{\partial z} + \frac{1}{\varepsilon}\frac{\partial}{\partial z}\left(\frac{\varepsilon}{\varepsilon_0}\frac{D_c}{D_0}\frac{\partial C}{\partial z}\right) + \frac{f}{\varepsilon}c_0(V_p - V_r)i\frac{\partial C}{\partial z} \tag{28}$$

$$\frac{\partial i}{\partial z} = g\left(1 - \frac{X}{X_{\max}}\right)\exp(-2\eta') \tag{29}$$

$$X = -\frac{IL}{D_0 q_0}\int_0^\tau \frac{\partial i}{\partial z}\,d\tau \tag{30}$$

where κ_0 is the initial conductivity and where the new dimensionless parameters have the following definitions:

$$a = \frac{\kappa_0 RT}{ILF}$$

$$b = \frac{F(D_1 - D_2)c_0}{IL}$$

$$f = \frac{IL}{2F\,D_0\,c_0}$$

$$g = -\frac{S_0 j_0 L}{I} \exp\left(-2F\,\eta_{x=0}/RT\right)$$

Before any discharge of the electrode the acid concentration in the pores is uniform and equal to the concentration in the bulk. The electrode is assumed to be fully charged. Thus the initial conditions are:

$$\text{at } t = 0,\ c(x) = c_0 \text{ or, equivalently, } C = 1$$
$$X(x) = 0$$

Since mass transfer resistances exterior to the porous electrode are assumed to be negligible, the following boundary condition exists:

$$\text{at } z = 1,\ c = c_0 \text{ or } C = 1$$

Also, at this surface the current density in the electrolyte must be the total current density applied.

$$\text{At } z = 1,\ i_2 = I \text{ or } i = 1$$

At the plane of symmetry of the electrode, symmetry conditions may be expressed as:

$$\text{At } z = 0,\ \frac{\partial C}{\partial z} = \frac{\partial \eta'}{\partial z} = \frac{\partial \varepsilon}{\partial z} = 0;\ i = 0$$

Also, by the choice of reference voltage, $\eta' = 0$ at $z = 0$.

The equations above represent a rather compilcated non-linear problem of the boundary value type.

Solution of these equations requires the application of suitable numerical methods. Before these calculations can be carried out, the actual values of the parameters appearing in the equations must be determined.

3. Determination of the actual parameters in the model

The transport parameters appearing in the formulation of the model can be determined from experiments and from suitable data given in the literature.

The initial effective conductivity of the sulphuric acid in the fully charged PbO_2 plate has been reported earlier [6].

The diffusion coefficients in the free electrolyte can be found in the literature. These values can be corrected by the same factor as used for the conductivity to give the effective values with respect to the porous electrode.

The individual ionic diffusion coefficients are calculated from the formula for the binary diffusion coefficient and known transport numbers.

The values of $X_{\max}$ at various current densities can be estimated from experimental results in [6] and from discharge experiments with electrolyte flow through the electrode to remove transport restrictions. Thus $X_{\max}$ was found to be approximately 0·45 at $-1{\cdot}0 \times 10^3$ A m^{-2} and 0·60 at $-0{\cdot}50 \times 10^3$ A m^{-2}.

The dependence of e.m.f. on acid concentration was evaluated from the reported e.m.f. values of Wynne-Jones *et al.* [11] for the cell

$$\text{Pt}\,|\,\text{H}_2(\text{g})\,|\,\text{H}_2\text{SO}_4(\text{m})\,|\,\text{PbSO}_4(\text{s})\,|\,\text{PbO}_2(\text{s})\,|\,\text{Pt}$$

Since $E_{\text{cell}} = E_c - E_{\text{H}}$.

Where

E_{cell} = e.m.f. of the cell, (V)

E_{H} = electrode potential of hydrogen electrode, (V)

We may now write

$$\frac{\partial E_c}{\partial c} = \frac{\partial E_{\text{cell}}}{\partial c} + \frac{\partial E_{\text{H}}}{\partial c}$$

An approximate expression for $\frac{\partial E_{\text{cell}}}{\partial c}$ can be calculated from the tabulated values for the e.m.f. at various concentrations [11]. Assuming a constant activity coefficient in the concentration range of interest we may write, according to Nernst's formula:

$$\frac{\partial E_{\text{H}}}{\partial c} = \frac{RT}{F}\frac{1}{c}$$

After transformation into corresponding dimensionless quantities we finally arrive at the dimensionless equation

$$\frac{\partial E'}{\partial C} = \frac{\partial E'_{\text{cell}}}{\partial C} + \frac{1}{C}$$

$$\text{where } E'_{\text{cell}} = \frac{F\,E_{\text{cell}}}{RT}$$

The data used in the calculations (for 20°C) are summarized in Table 1.

Table 1. Numerical values of the parameters used for the calculations

Parameter	*Ref.*	*Note*
$L = 0{\cdot}9\times10^{-3}$ m		
$c_0 = 5{\cdot}0$ kmole m^{-3}		
$\varepsilon_0 = 0{\cdot}60$		
$D_0 = 2{\cdot}62\times10^{-10}$ m^{2}s^{-1}	Thovert [12 a]	Modification of value for free electrolyte at 5 M
$D_c/D_0 = 0{\cdot}706+0{\cdot}294\ C$	Thovert [12 a]	Least square approximation
$(D_1-D_2)_c = 3{\cdot}5\times10^{-10}$ m^{2}s^{-1}		Average value
$\kappa_0 = 7\ \Omega^{-1}$m^{-1}	[6]	
$\kappa_c/\kappa_0 = \begin{cases} 0{\cdot}20+2{\cdot}10c-1{\cdot}3C^2 \\ (0{\cdot}2\leqslant C\leqslant 1) \\ 2{\cdot}84\ C\ (C<0{\cdot}2) \end{cases}$	Kolrausch [12 b]	Least square approximation
$t_1 = 0{\cdot}80$	[12 b]	Average value
$\dfrac{\partial E'}{\partial C} = \begin{cases} 5{\cdot}32+1/C(0{\cdot}2\leqslant C\leqslant 1) \\ 0{\cdot}13+2{\cdot}04/C\ (C<0{\cdot}2) \end{cases}$	[11]	Least square approximation
$M_{\mathrm{PbO_2}} = 239{\cdot}19$ kg kmole^{-1}	[13]	
$M_{\mathrm{PbSO_4}} = 303{\cdot}25$ kg kmole^{-1}	[13]	
$\rho_{\mathrm{PbO_2}} = 9{\cdot}375\times10^3$ kg m^{-3}	[13]	
$\rho_{\mathrm{PbSO_4}} = 6{\cdot}2\times10^3$ kg m^{-3}	[13]	
$V_p = \dfrac{M_{\mathrm{PbSO_4}}}{\rho_{\mathrm{PbSO_4}}} = 48{\cdot}9\times10^{-3}$ m^3 kmole^{-1}		
$V_r = 25{\cdot}5\times10^{-3}$ m^3 kmole^{-1}		
$q_0 = 2F(1-\varepsilon_0)\ 39{\cdot}2$ As m^{-3}		
$k = \dfrac{\rho_{\mathrm{PbO_2}}}{M_{\mathrm{PbO_2}}}(V_p-V_r) = 0{\cdot}917$		

4. Numerical procedure

The partial differential equation system was first solved by an implicit finite difference method and the quasi-linearization technique [14].

Only Equation (28) was linearized. It was decoupled from Equations (27) and (29) by solving for the concentration in the $(k+1)$th iteration using the values from the kth iteration for the other dependent variables. With the calculated concentration profile the current distribution and potential profile were calculated from Equations (27) and (29) by a Runge-Kutta method. The boundary value problem was treated as an initial value problem, in which the missing initial condition, $g(t)$ was guessed, and iteration continued until the given condition at the other boundary was satisfactorily fulfilled (relative error less than 10^{-5}). The calculations were repeated in this cyclic manner until the required accuracy was obtained for each dependent variable.

However, this application of the implicit method requires a very large number of arithmetic operations. For the most interesting case as regards transient behaviour, the high rate discharge, the explicit difference-method actually proved to be more advantageous in spite of its restrictive stability conditions [15]. For very rapid discharges the larger number of time steps required with this method was more than compensated by the smaller number of arithmetic operations required at each time step.

Therefore the explicit method was preferred in the calculations for very rapid discharges, while the implicit method was used only to check the results from the explicit method.

The calculations were tested for convergence and stability by successively decreasing the length and time steps until the results did not change appreciably.

5. Results and discussion

Numerical calculations for rapid discharges were carried out for two different current densities, $-1{\cdot}0\times10^3$ A m^{-2} and $-0{\cdot}50\times10^3$ A m^{-2}, corresponding to about 7–8 min discharge and 20–22 min discharge respectively. The calculations were conducted until a local concentration of 0·5 M was reached, since the approximation of a binary electrolyte becomes too rough below this point.

A comparison between experimental and theoretical discharge curves seems to be the most natural way to judge the relevancy of the model. This comparison cannot however be made straightforwardly since the potential in the model is referred to the potential at $z = 0$ taken as zero. In addition the initial drop of potential in the experimental discharge curves, due to supersaturation of lead sulphate [16], is not considered in the model. The comparison between the experimental and theoretical discharge curves are therefore made relative to the potential at $z = 0$ and $t = 0$. In order to disregard the phenomenon in the very beginning of discharge, the curves are adjusted to fit each other at the maximum after the initial drop of voltage, Fig. 1.

These comparisons show rather good agreement at the lower current density, while the deviations are larger at the higher current density. This discrepancy may be expected when bearing in mind the approximate formulation of the structural changes, especially in Equation (26), and the fact that the exponential factor in this equation was experimentally established only for overvoltages less than 100 mV. The discharge mechanism may change at higher overvoltages. In that case it is also possible, in view of the non-uniform current distribution, that different parts of the electrode operate under different mechanisms.

Another important factor, the discharge capacity, could be predicted within the variability of electrode performance. This agreement can only be reached when considering the struc-

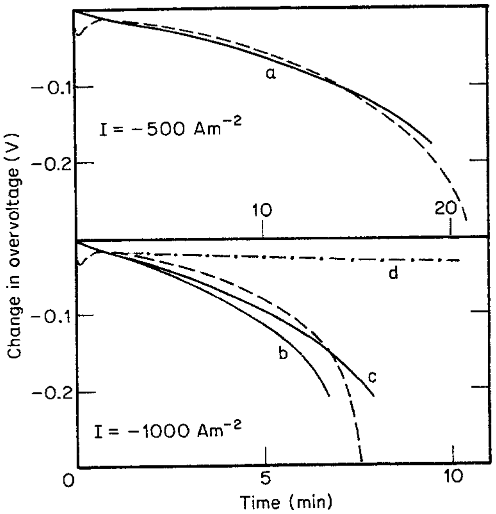

Fig. 1. Comparison between theoretical (solid lines) and experimental (dashed lines) discharge curves. Changes in overvoltage during discharge with the initial overvoltage taken as zero.
(a) $X_{max} = 0{\cdot}60$; (b) $X_{max} = 0{\cdot}45$; (c) $X_{max} = 0{\cdot}60$; (d) model without consideration of the structural effects ($X(x,t) = 0$).

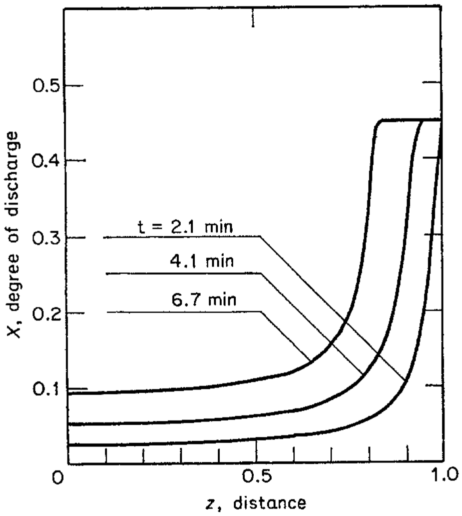

Fig. 2. State of discharge distribution during discharge of porous lead dioxide electrode with -1000 A m^{-2}. ($X_{max} = 0{\cdot}45$).

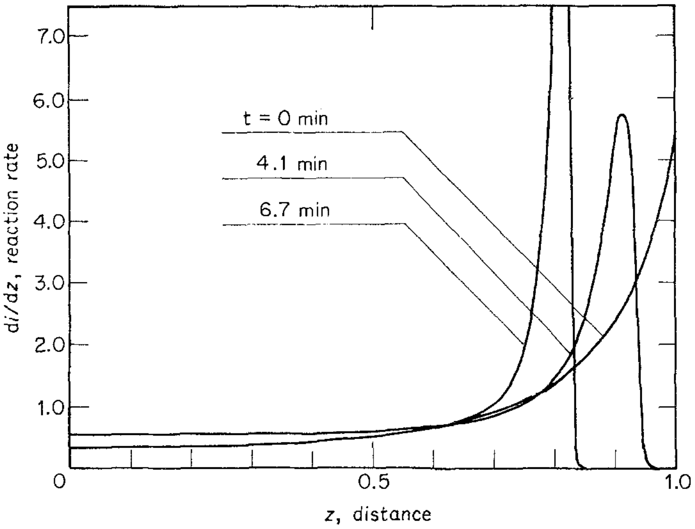

Fig. 3. Changes in current distribution during discharge. ($I = -1000$ A m^{-2}, $X_{max} = 0{\cdot}45$).

tural effects, since a model with invariant electrode matrix gives an almost infinite discharge curve (Fig. 1, curve d). (This is obvious, since reactants are always available as long as the current density does not exceed the value where the external mass transfer becomes limiting.) Fig. 1 shows also how an improved mass utilization (higher X_{max}) would improve the capacity. The parameter X, to which the structural parameters, porosity and active surface are related, is thus of dominating importance. The changes in this parameter during discharge are illustrated in Fig. 2. By definition, this parameter is also a measure of the time-integral current distribution, and Fig. 2 may thus be compared with the experimental determinations reported previously [6]. The theoretical and experimental results show qualitative agreement. The quantitative deviations are difficult to interpret since even the experimental determinations must be considered as approximate.

Fig. 3 demonstrates how the structural changes during discharge affect the current density distribution. As the insulation of the electrode surface proceeds inwards into the electrode, the maximum of the current distribution is similarly moving inwards.

The acid depletion during rapid discharge is very difficult to measure experimentally, but an interpretation of this process is given from the solution of the equations in the model.

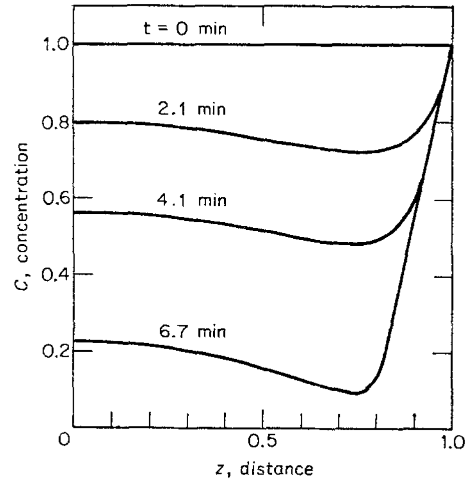

Fig. 4. Changes in concentration distribution duriug discharge. ($I = -1000$ A m^{-2}, $X_{max} - 0{\cdot}45$).

The concentration profile in the pore electrolyte at different stages of discharge is illustrated in Fig. 4. It is apparent from this figure, that the acid concentration in the layer next to the zone of passivated electrode material tends to zero at the end of discharge.

A comparison of Figs. 2, 3 and 4 indicates that the current density distribution exhibits a maximum just behind the zone of unreactive material. According to Fig. 3 this maximum increases during discharge, while it simultaneously moves inwards into the electrode. The reason for this increase is the decreasing conductivity due to acid depletion (Fig. 4) and increasing structural hindrance (Fig. 2).

The slight minimum in the concentration profile becomes more accentuated during discharge. Just before the voltage drops rapidly at the end of discharge this minimum almost coincides with the maximum of the current distribution. It may thus be assumed that the discharge capacity is limited by an acid depletion where this minimum tends to zero. The physical picture of this process is illustrated in Fig. 5.

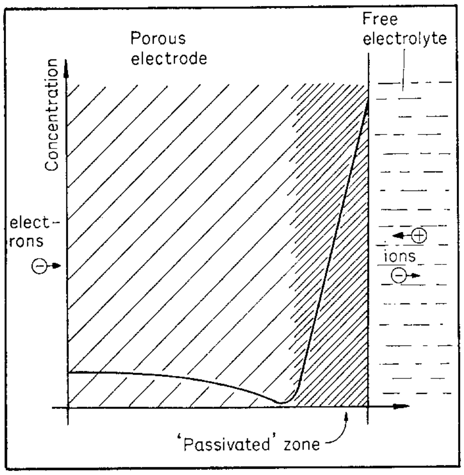

Fig. 5. Illustration of acid depletion and structural effects at the end of discharge with high current density.

Conclusions

The theoretical model presented here rests necessarily upon rough approximations concerning the rather complicated discharge behaviour of the porous PbO_2 electrode. The purpose of this model is to give a qualitative analysis rather than an exact, detailed description. An exact treatment would require more knowledge about electrolytic data and about the details of the discharge mechanisms and the structural effects in the porous electrode. The present model gives a good explanation of the discharge behaviour of the porous lead dioxide electrode, especially the limited discharge capacity. The relative importance of the various variables may be estimated from the model to suggest how improvements in performance can be reached.

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