An aggregate model for the positive electrode system of the lead/acid cell
I. Model development

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Abstract

An aggregate model for the positive electrode system of the lead/acid cell is developed. This new model uses a network of connected cylinders to represent cell parts involved in the transportation of acid and charge to the PbO_2/solution interface. Represented are three active mass structures in the positive, the separator, the negative and the reservoir. Acid transport is determined from reaction, diffusion, migration and convection mechanisms assuming dilute electrolyte theory. Charge transport is determined from electrical equivalent circuits that are characterized by solution pathway conductivity and exponential or linear current/voltage interface relationships. Structural changes are determined from interface currents using Faraday's law. The model defines voltage, current, acid concentration and active mass distributions for both discharge and charge currents.

The aggregate model is unique in the way it accounts for the detailed structure of the lead/acid cell, has parameters fixed from experimental measurements, and allows for simulation of arbitrary currents. The model has applications in cell and support system design.

Introduction

The aggregate model provides a method for studying the lead/acid cell by computer simulation. The model simulates the positive electrode in a typical traction cell implementation. This means the model has application not only in the study of the positive electrode in isolation but also in the study of the combined effect of all cell components. The model is valid for the practical operating conditions of a cell including discharge and charge currents from zero to $C_{0.5}$ or more. These features make the aggregate model a powerful and convenient tool for practical cell design that complements the traditional approach of prototype testing.

The model presupposes three elemental models [1, 2]. These models represent details of the active mass (AM) structure of the positive.

This paper: (i) discusses the formation of the model; (ii) quantifies component dimensions, electrical and transport effects, and (iii) outlines the practical approach used to operate the model.

A paper that follows gives comprehensive results for a typical lead/acid cell [3].

Aggregate model

The aggregate model reduces the real cell parts of the acid transport system to a network involving six cylinders. The acid transport and electrical characteristics of

this network are then taken to represent the behaviour of the real system. The approach results in a model that resembles a compound single pore model rather than a macrohomogeneous model [4, 5]. The emphasis on structural form is consistent with recent descriptions of the organisation of the AM [6–8].

The generalized acid transport system is a complex three-dimensional network of solution volumes with a variety of structures, electrical characteristics and transport effects. To make the analysis of this system manageable, three simplifying steps are performed:

(i) parts that have distinct structural features are identified;

(ii) a minimum, but representative, set of parts is selected, and

(iii) the minimum set is modelled as a network of connected cylinders.

Transport system parts

Transport system parts for the cell reservoir, separator, negative plate and positive plate regions are readily identified from the cell construction. The positive plate region, however, is known to contain AM in three structural forms, each of which plays an important role in determining the overall cell performance [7–9]. These are the homogeneous nonparticipating AM, the participating AM macrostructure transport channels, and the participating AM porous microstructure. In total, this gives the six distinct transport system parts illustrated in Fig. 1.

Minimum representation of the acid transport system

The acid transport system is simplified by taking a single core sample within the plate area to represent the complete system. This is an approximation that ignores
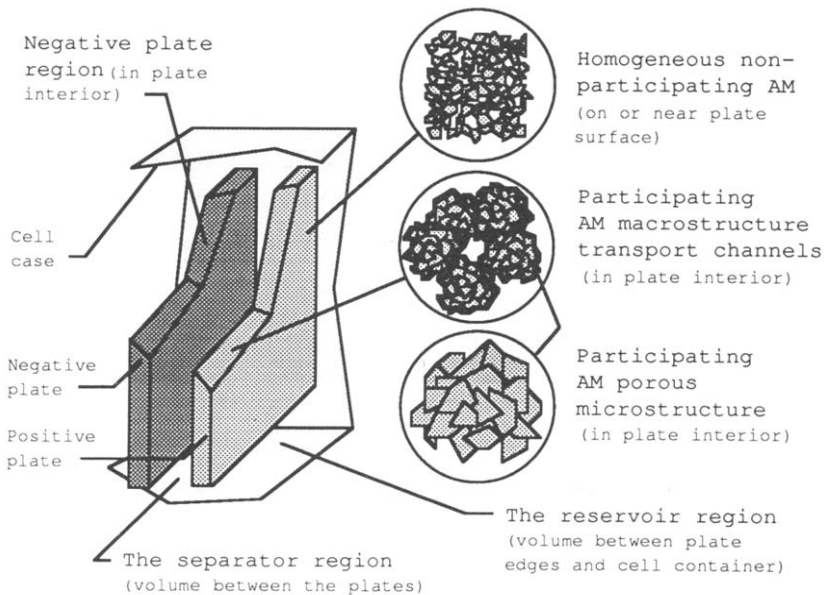

Fig. 1. Components of the acid transport system.

dependence on cell height and width [10]. For the simplified situation, the question arises as to how small the single core sample can be. The limit is reached at the size beyond which important structural features are lost. It is determined by the largest structural feature in the positive AM, namely, a single macrostructure transport channel with surrounding porous microstructure. This idea can be extended to include portions of the separator, negative plate and reservoir regions that are likely to exchange acid with the single core sample.

Cylindrical model components

The cylindrical components or channels defined to represent the six transport system parts are:

(i) an m-channel representing the macrostructure transport part within the core sample;

(ii) many small μ-channels representing the agglomerate microstructure transport parts within in the core sample;

(iii) an h-channel representing the homogeneous structure of the nonparticipating AM transport part within the core sample;

(iv) an s-channel representing the separator transport part adjacent to the core sample;

(v) an n-channel representing the negative plate transport part adjacent to the core sample, and

(vi) an r-channel representing the reservoir transport part that affects the behaviour of the core sample.

Together, these components make up the aggregate model illustrated in Fig. 2. The next section presents formulations for dimensions, electrical characteristics and acid transport for the model.
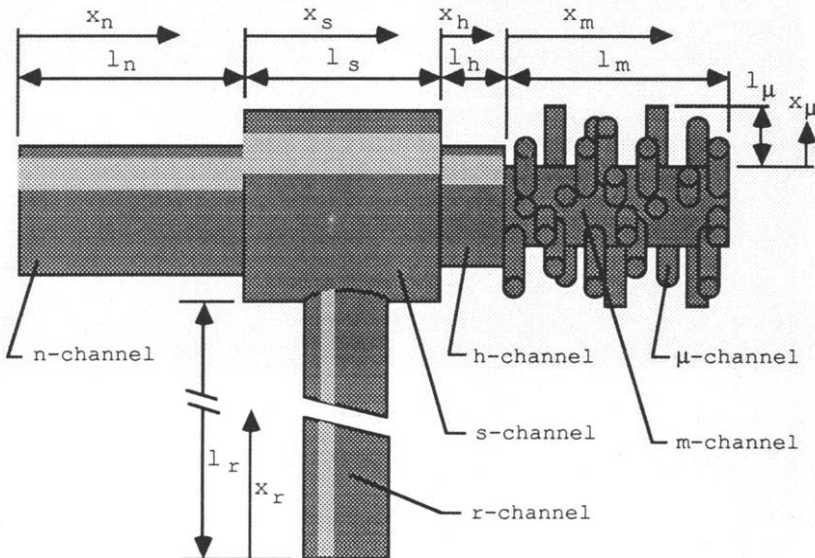

Fig. 2. The aggregate model components.

Physical dimensions of the aggregate model

m-Channel dimensions

The cross-sectional area of th m-channel, a_m (m²), can be defined from the equivalent gram volume and surface area values, assuming a cylindrical form. This gives:

$$a_m = 4\pi (f_m V_m / S_m)^2 \tag{1}$$

where V_m (m³ g⁻¹) is the equivalent gram volume, S_m (m² g⁻¹) is the equivalent gram surface area, and f_m is the surface roughness factor. V_m and S_m make up part of the experimental volume and surface area distribution data after the boundary for the macro- and microstructure has been set and an allowance has been made for the contribution of the nonparticipating AM. The f_m factor is likely to be much greater than unity since the channel is bounded by agglomerates of microstructure crystallites.

The length of an m-channel, l_m (m), can be written as:

$$l_m = \theta_m \chi_m S_p \tag{2}$$

where θ_m is the tortuosity factor, χ_m is the proportion of the positive plate thickness that contains participating AM, and S_p (m) is half the positive plate thickness.

The equivalent gram number of m-channels, N_m (g⁻¹), is:

$$N_m = V_m / (a_m l_m) \tag{3}$$

μ-Channel dimensions

The cross-sectional area of a μ-channel in fully charged AM, $a_{\mu 0}$ (m²), can be defined as for the m-channel. That is:

$$a_{\mu 0} = 4\pi (f_\mu V_\mu / S_\mu)^2 \tag{4}$$

where V_μ (m³ g⁻¹) is the equivalent gram volume, S_μ (m² g⁻¹) is the equivalent gram surface area, and f_μ is the surface roughness factor. The quantities V_μ, S_μ and f_μ can be qualified in the same way as the corresponding quantities for the m-channel. In general, the cross-sectional area must vary to account for microstructure changes that depend on charge state. Assuming the channel length is constant, the cross-sectional area, $a_\mu(X)$ (m²), for a general charge state X ($X = 1$ for fully charged AM) is:

$$a_\mu(X) = a_{\mu 0} X \tag{5}$$

The μ-channel length can be defined if the core sample microstructure volume is taken as being contained in a cylindrical sleeve around the m-channel, and the μ-channels are arranged as radial cylinders that extent throughout the thickness of this sleeve. This gives a μ-channel length, l_μ (m), of:

$$l_\mu = \theta_\mu (\sqrt{a_c} - \sqrt{a_m}) / \sqrt{\pi} \tag{6}$$

where $a_c = a_m + (V_\mu + 1/\rho_{PbO_2})/(N_m l_m)$ (m²) is the core sample cross section, and θ_μ is the μ-channel tortuosity factor.

The number of μ-channels per m-channel ($N_{m\mu}$) is:

$$N_{m\mu} = V_\mu / (N_m a_{\mu 0} l_\mu) \tag{7}$$

For the purposes of this model, it is necessary to relate the charge state to the PbO_2/solution interface current in the μ-channel. This can be done by writing the

equivalent gram capacity [1, 2] in terms of the time integral of the equivalent gram interface current. This gives the charge state at time t_1 as:

$$X(x_\mu, t_1) = 1 - \frac{N_m N_{m\mu} l_\mu}{q_0 \, dx_\mu} \int_{t=0}^{t_1} dI_\mu(x_\mu, t) \, dt \tag{8}$$

where dx_μ (m) is the increment of μ-channel length over which the charge state is defined, and dI_μ (A) is the current flowing through the solution/PbO_2 boundary within that increment.

h-Channel dimensions

The length of the h-channel, l_h (m), can be written as:

$$l_h = \theta_h (1 - \chi_m) S_p \tag{9}$$

where θ_h is the tortuosity factor.

Deriving the volume of the h-channel from the positive AM porosity (ρ_p) gives a cross-sectional area, a_h (m^2), of:

$$a_h = \rho_p a_c / \theta_h \tag{10}$$

s-Channel dimensions

The s-channel length, l_s (m), is equal to the separator thickness, S_s (m) and the s-channel cross-sectional area, a_s (m^2), is equal to the core sample cross-sectional area when corrected for the area of the plate grid members. That is:

$$l_s = S_s \tag{11}$$

and

$$a_s = a_c \frac{H_p W_p}{(H_p - H_g)(W_p - W_g)} \tag{12}$$

where H_p (m) is the plate height; W_p (m) is the plate width and H_g (m) and W_g (m) are the combined thickness of horizontal and vertical plate grid members, respectively. The s-channel cross-sectional area also defines the number of m-channels per unit plate area, N_{ma} (m^{-2}). That is:

$$N_{ma} = 1/a_s \tag{13}$$

n-Channel dimensions

The n-channel is defined to account for the acid in the porous negative plate that affects the behaviour of the adjacent components in the positive plate. The structure is assumed to be made from porous uniformly-distributed crystallites and the n-channel dimensions are found as for the h-channel. That is:

$$l_n = \theta_n S_n \tag{14}$$

and,

$$a_{n0} = \rho_n a_c / \theta_n \tag{15}$$

where l_n (m) is the length, S_n (m) is half the negative plate thickness, θ_n is the tortuosity factor, a_{n0} (m^2) is the cross-sectional area for full charged AM, and ρ_n is the negative

AM porosity. In this simple representation, the area varies uniformly with length to account for volume changes in the negative AM. The general cross section, a_n (m^2), at time t_1 found by applying Faraday's law is:

$$a_n = a_{n0} - \frac{1}{l_n} \frac{V_{mPbSO_4} - V_{mPb}}{2F} \int_{t=0}^{t_1} I_h(t) \, dt \tag{16}$$

where V_{mPbSO_4} and V_{mPb} (m^3 mol^{-1}) are the molar volumes for PbSO$_4$ and Pb, respectively, and I_h (A) is the current in the h-channel (equal to the current in the n-channel).

r-Channel dimensions

The r-channel is defined to account for acid in the reservoir region that affects the behaviour of the associated single cores sample. The r-channel length, l_r (m), is defined for a core sample area average plate position. That is:

$$l_r = (H_{c0} W_c / \pi)^{1/2} - (H_p W_p / \pi)^{1/2} / \sqrt{2} \tag{17}$$

where H_{c0} (m) is the full charge solution height, and W_c (m) is the case width.

The cross-sectional area at full charge, a_{r0} (m^2), can be found from the total reservoir volume. This gives:

$$a_{r0} = \frac{H_{c0} W_c S_c - H_p W_p (N_p S_p + N_p S_s + (N_p + 2) S_n)}{N_p H_p W_p N_{ma} l_r} \tag{18}$$

where N_p is the number of positive half plates in the cell, and S_c (m) is the cell case thickness. The cross-sectional area must vary to account for the inflow of solution caused by volume changes in the positive and negative AM. The general cross section, a_r (m^2), at time t_1 found by applying Faraday's law is:

$$a_r = a_{r0} + \frac{1}{l_r} \frac{2V_{mPbSO_4} - V_{mPbO_2} - V_{mPb}}{2F} \int_{t=0}^{t_1} I_h(t) \, dt \tag{19}$$

where V_{mPbO_2} (m^3 mol^{-1}) is the molar volume of PbO$_2$.

Electrical formulations

The electrical characteristics of the aggregate model are defined by the channels that pass current. This includes all but the r-channel. Time dependence is due to acid movement in all six channels and dimension changes in the μ-channels and n-channel.

The electrical characteristics can be analyzed using a distributed network of equivalent circuit components. For current through electrolyte solution, a simple resistance component is used to represent the current induced solution potential drop. For current through a PbO$_2$/solution interface, an ideal cell and nonlinear resistance component are used to represent the interface equilibrium potential and the current induced overpotential, respectively. The latter effect involves the surface area defined previously [1, 2]. For current through solid phase PbO$_2$, a zero resistance component is used since PbO$_2$ conductivity is very high compared with that for sulfuric acid solution. In all but the last case, the circuit components are time dependent.

In the formulations that follow, current flowing from the solution towards the solid phase PbO$_2$ is taken as positive and the potential at the s-channel/h-channel junction is arbitrarily taken as zero.

h-Channel equivalent circuit

In the h-channel, current passes in electrolyte solution with no divergence into the surrounding AM (i.e., it is inactive). This means that the h-channel can be represented by a single equivalent resistance (R_h (Ω)) given by:

$$R_h(t) = \frac{1}{a_h} \int_{x_h=0}^{l_h} \rho_h(x_h, t) \, dx_h \tag{20}$$

where ρ_h (Ω m) is the solution resistivity.

Assuming a uniform current distribution over the plate area, the current in the h-channel (I_h (A)) is related to the total cell current, I_{cell} (A), by:

$$I_h(t) = \frac{I_{cell}(t)}{N_p H_p W_p N_{ma}} \tag{21}$$

m-Channel equivalent circuit

Here, current passes in electrolyte solution but diverges into the surrounding μ-channels. This means the m-channel circuit is best represented by a series of resistances with side branches at the μ-channel openings. Assuming the μ-channels are equally spaced, the m-channel naturally divides into $N_{m\mu}$ discrete series resistances and branches. This arrangement is illustrated in Fig. 3. Taking the solution resistivity (concentration) to be constant over the small lengths involved, the series resistances, R_m (Ω), are defined by:

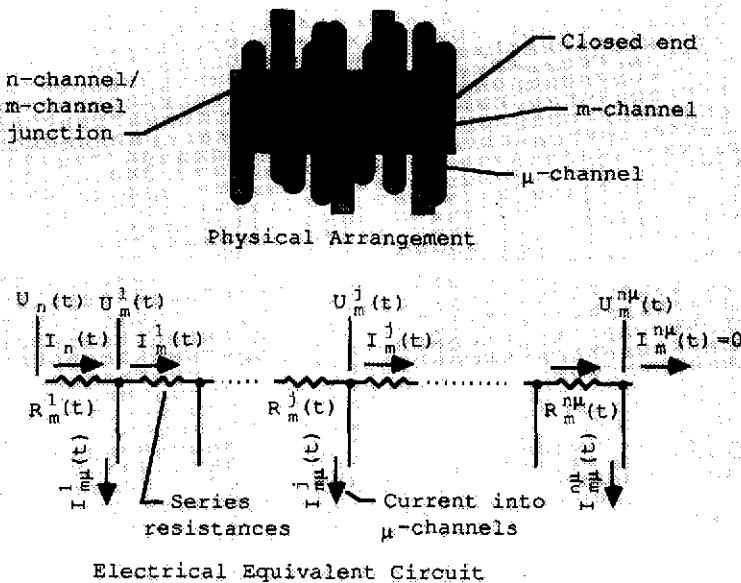$$R_m{}^j(t) = \frac{l_m \rho_m{}^j(t)}{a_m N_{m\mu}} \tag{22}$$

Fig. 3. The m-channel equivalent circuit.

where the superscript 'j' defines the position on the m-channel ($j=1$ at the n/m-channel junction and $j=N_{m\mu}$ at the closed end), and ρ_m (Ω m) is the solution resistivity.

μ-Channel equivalent circuit

Current passes in solution along the axis of the μ-channel and through the PbO$_2$/solution interface at the surface of the μ-channel where the electrochemical reaction occurs. This situation can be treated in a similar way to the m-channel by dividing the μ-channel into incremental segments of length dx_μ. This arrangement is illustrated in Fig. 4. The value of the series incremental resistances, dR_μ (Ω), is given by:

$$dR_\mu(x_\mu, t) = \frac{dx_\mu \rho_\mu(x_\mu, t)}{a_{\mu 0} X(x_\mu, t)} \tag{23}$$

where x_μ (m) defines the position on the μ-channel, and ρ_μ (Ω m) is the solution resistivity.

An ideal cell, representing the local equilibrium potential of the solution/PbO$_2$ interface, and a nonlinear resistance, representing the current/overpotential characteristic of the interface can be assigned to the side branches. The ideal cell potential, E_μ (V), can be obtained from tabulated data given the acid concentration. At high overpotential, the nonlinear resistances are implied by Tafel equations written for current through the PbO$_2$/solution interface of an μ-channel segment. That is:

$$dI_\mu(x_\mu, t) = \frac{2i_{01} \, dx_\mu S_{PbO_2}}{N_m N_{m\mu} l_\mu} \exp(\alpha_1 F \, dU_\mu(x_\mu, t)/RT) \tag{24a}$$

and

$$dI_\mu(x_\mu, t) = -\frac{2i_{02} \, dx_\mu S_E}{N_m N_{m\mu} l_\mu} \exp((1-\alpha_2)F \, dU_\mu(x_\mu, t)/RT) \tag{24b}$$
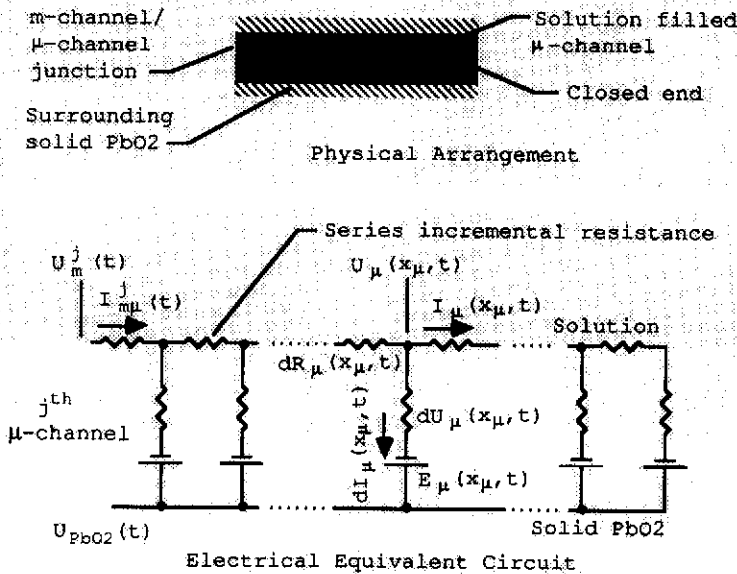

Fig. 4. The μ-channel equivalent circuit.

for the discharge and charge, respectively; where dU_μ (V) is the overpotential, and dI_μ (A) is the current through the PbO_2/solution interface area within the segment. At low overpotential, the nonlinear resistances are approximated by linear forms that pass through the zero current/overpotential point and meet the exponential forms at a tangent. An explicit form for the nonlinear resistance is not required.

The surface areas S_{PbO_2} and S_E are defined by elemental models elsewhere [1, 2]. S_{PbO_2} is a simple function of charge state. S_E can be adequately treated as a function of charge state and charge current only.

The potential at the solid phase PbO_2 boundary of the μ-channel is independent of position (since this phase is taken as having zero resistance) and is equal to the potential difference across the positive electrode U_{PbO_2}.

Complete equivalent circuit

The complete equivalent circuit is formed by combining the individual circuit components defined above. In principle, this circuit can be solved by writing voltage loop and current node circuit equations and evaluating these simultaneously. The independent variable is the cell current. The solution gives the current in all the equivalent circuit components and the potential at all component junctions in the system. These results enable the evaluation of the state-of-charge and the acid transport formulations given in the following section. These, in turn, control the time dependence of the circuit components and therefore the complete electrode system.

Acid transport formulations

In the formulations that follow 'i' and 'i_a' are used as subscripts to indicate a first and second (adjacent) general channel case, respectively, and the channel prefix is used as a subscript to indicate a particular case. When the m-channel is under consideration, it is assumed to be divided into $N_{m\mu}$ discrete segments of length Δx_m and continuous space derivatives are replaced by finite differences equivalents.

General transport, initial and boundary condition equations

The general transport equation is formed assuming the theory of dilute electrolytes and writing a mass balance for an acid channel of incremental length, d_{xi} (m), and time and space dependent circular cross section, a_i (m^2). This gives:

$$\frac{\partial c_i(x_i, t)}{\partial t} = L_i(x_i, t)\frac{\partial^2 c_i(x_i, t)}{\partial x_i^2} + M_i(x_i, t)\frac{\partial c_i(x_i, t)}{\partial x_i} + N_i(x_i, t)c_i(x_i, t) + O_i(x_i, t) \tag{25a}$$

where

$$L_i(x_i, t) = D_i(x_i, t) \tag{25b}$$

$$M_i(x_i, t) = \left(\frac{1}{a_i(x_i, t)}\frac{\partial a_i(x_i, t)D_i(x_i, t)}{\partial x_i} - v_i(x_i, t)\right) \tag{25c}$$

$$N_i(x_i, t) = \left(\frac{-1}{a_i(x_i, t)}\left(\frac{\partial a_i(x_i, t)v_i(x_i, t)}{\partial x_i} + \frac{\partial a_i(x_i, t)}{\partial t}\right)\right) \tag{25d}$$

and,

$$O_i(x_i, t) = \frac{P_i(x_i, t)}{a_i(x_i, t)} \tag{25e}$$

where c_i (mol m^{-3}) is the acid concentration, D_i (m^2 s^{-1}) is the acid binary diffusion coefficient, v_i (m s^{-1}) is the bulk solution velocity, and P_i (mol m^{-1} s^{-1}) is the rate of reaction per unit length. From left to right, the terms in eqn. (25a) represent accumulation, diffusion, convection, expansion and reaction.

The initial condition equation assumes the acid transport system is at equilibrium. This gives:

$$c_i(x_i, 0) = c_0 \text{ (for all } x_i) \tag{26}$$

where c_0 (mol m^{-3}) is the full charge equilibrium acid concentration. This equation applies to all channels.

The general boundary condition equation assumes conservation of acid flux. Applying Fick's first law gives:

$$\left(-a_i(x_i, t)D(x_i, t)\frac{\partial c_i(x_i, t)}{\partial x_i} \right)_{x_i - l_i} = \left(-a(x_{i_a}, t)D_{i_a}(x_{i_a}, t)\frac{\partial c_{i_a}(x_{i_a}, t)}{\partial x_{i_a}} \right)_{x_{i_a} = 0} \tag{27}$$

Qualifications and simplifications that apply to particular channels are given below.

Acid transport in the μ-channels

Electrochemical reaction occurs throughout the μ-channels and, as a result the cross-sectional area, bulk solution velocity and reaction rate terms vary in the general way. The expansion term is zero since volume changes are determined by the net volume flow through the segment cross sections.

The μ-channel bulk solution velocity at some arbitrary position $x_{\mu 1}$ is determined by the rate of change of volume between $x_{\mu 1}$ and the closed end of the μ-channel. That is:

$$v_\mu(x_{\mu 1}, t) = -\frac{V_{mPbSO_4} - V_{mPbO_2}}{2Fa_\mu(x_{\mu 1}, t)} \int_{x_\mu - l_\mu}^{x_{\mu 1}} dI_\mu(x_\mu, t) \tag{28}$$

The acid reaction rate term can be found using Faraday's law. Taking account of the coupled ion pair and assuming the transport number is constant, gives:

$$P_\mu(x_\mu, t) = \frac{3 - 2t_+}{2F} \frac{\partial i_\mu(x_\mu, t)}{\partial x_\mu} \tag{29}$$

where t_+ is the transport number for the H$^+$ ion.

The boundary condition equation for the closed end of the μ-channel is defined by setting the right-hand side of the general equation to zero. The boundary condition equation for the open end of the μ-channel is given by the general equation, where the left-hand side refers to the m-channel segment into which the μ-channel opens. Here, the area parameter is not the m-channel cross-sectional area but rather the m-channel area at the segment circumference through which flux flowing radially into the attached μ-channel passes ($a_{m\mu}$ (m^2)). This is defined by:

$$a_{m\mu} = 2\sqrt{(\pi a_m)}l_m/N_{m\mu} \tag{30}$$

Acid transport in the m-channel

The acid and bulk solution exchanged with the μ-channels are treated using the reaction rate and expansion terms, respectively. This means that all parameters except the constant cross section vary in the general way in the m-channel.

The m-channel bulk solution velocity at some arbitrary position j_1 can be found in a similar way to that for the μ-channel. Here, this gives:

$$v_m^{j_1}(t) = -\frac{V_{mPbSO_4} - V_{mPbO_2}}{2Fa_m} I_m^{j_1}(t) \tag{31}$$

The m-channel acid reaction term is determined from the acid flux through the μ-channel opening as defined by the boundary condition equation for the open end of the μ-channel. The required quantity per unit length is:

$$P_m^j(t) = \frac{N_{m\mu}}{l_m} \left(-a_\mu(x_\mu, t)D_\mu(x_\mu, t)\frac{\partial c_\mu(x_\mu, t)}{\partial x_\mu} \right)^j_{x_\mu = 0} \tag{32}$$

The boundary equation for the closed end of the m-channel is defined in the same way as that for the μ-channel. The general boundary condition equation applies for the h/m-channel junction.

Acid transport in the h-channel

In the h-channel, the expansion and reaction terms are zero, the cross section is constant, and the bulk solution velocity is dependent only on time.

The bulk solution velocity is determined by the velocity of solution leaving the attached m-channel. That is:

$$v_h(t) = v_m^1(t)a_m/a_h \tag{33}$$

The general boundary condition equation applies for both ends of the h-channel.

Acid transport in the r-channel

In the r-channel, the expansion and reaction terms are zero and the cross-sectional area depends on time only to account for volume changes in the positive and negative AM.

The bulk solution velocity is zero at the closed end and is defined by the rate of change of volume in the positive and negative AM at the open end of the r-channel. This gives:

$$v_r(x_r, t) = -\frac{x_r}{a_r(t)l_r} \frac{2V_{mPbSO_4} - V_{mPbO_2} - V_{mPb}}{2F} I_h(t) \tag{34}$$

The boundary condition equations for the r-channel are comparable with those for the μ-channels. The equation for the closed end is formed by setting the left-hand side of the general equation to zero. The equation for the open end is given by the general equation where the right-hand side refers to the s-channel parameters that control the flow of flux from the r-channel opening. The s-channel parameters for the concentration and diffusion coefficient are defined midway along the s-channel and the area parameter, a_{sr} (m^2), defined to account for the r-channel connection over the entire length of the s-channel. The area parameter is:

$$a_{sr} = 2\sqrt{(\pi a_s)}l_s \tag{35}$$

Acid transport in the n-channel

Because of the simplified representation of the negative plate, the expansion term is zero and the cross-sectional area and reaction rate are dependent on time only.

The bulk solution velocity is found in a similar way as that for the r-channel above. Here, this gives:

$$v_n(x_n, t) = \frac{x_n}{a_n l_n} \frac{V_{mPbSO_4} - V_{mPb}}{2F} I_h(t) \tag{36}$$

The acid reaction rate in the n-channel is found from the reaction rate for the overall lead/acid less the reaction rate in the μ-channels. The reaction rate per unit length is:

$$P_n(t) = \frac{-1 + 2t_+}{2F} I_h(t) \tag{37}$$

The boundary condition equations for the n-channel are comparable with those for the m-channel.

Acid transport in the s-channel

The s-channel is, in all but one region, similar to the h-channel and the same simplifications and corresponding boundary equations apply. The exception is the region where the r-channel connects. Here, bulk solution and acid exchanged with the r-channel are accounted for by the expansion and reaction terms, respectively.

The bulk solution velocity on the h-channel side of the r-channel (v_{sh}) attachment is determined by the velocity of solution leaving the h-channel. That is:

$$v_{sh}(t) = v_h(t)a_h/a_s \tag{38}$$

The bulk solution velocity on the n-channel side of the position of r-channel attachment (v_{sn}) is determined by the velocity of solution leaving the n-channel. That is:

$$v_{sn}(t) = v_n(l_n, t)a_h/a_s \tag{39}$$

The acid reaction term for the s-channel is determined from the flux defined by the boundary condition equation for the open end of the r-channel. If the r-channel attachment position covers an s-channel segment of length Δx_s, then the required quantity per unit length is:

$$P_s(t) = \frac{1}{\Delta x_s} \left(-a_r(t)D_r(x_r, t) \frac{\partial c_r(x_r, t)}{\partial x_r} \right)_{x_r = l_r} \tag{40}$$

Operating the aggregate model: a practical approach

Operating the aggregate model amounts to solving the set of simultaneous algebraic and partial differential equations. The nonlinear equations involved do not allow solution by analytical methods. The solution was obtained by numerical methods using discrete approximations for the space and time intervals. To reduce the number of equations, the m-channel segments were made to accommodate a group of many identical μ-channel connections. The equation set representing the μ-channels could be reduced

from the order of 10^6 to 10^1 by this approach. The simultaneous nature of the equations was simplified by decoupling in time. The latter allowed the reduced set of equations to be solved in three stages at each time step:

(i) solution of electrical equations as a nonlinear algebraic set using last time step parameter values;

(ii) solution of transport equations as a partial differential and algebraic set using last time step parameter values, except those derived from present time step electrical results, and

(iii) update of structural and other parameters using present time step results.

Two levels of iterative procedures were used to solve the electrical equations: an inner level for one μ-channel and an outer level for the entire m-channel. The solution procedure for the transport equations involved the formation of three tridiagonal matrix equations that were solved in sequence by Gauss elimination. All the last time step parameter values were for transport or structural quantities that exhibit very little change over the time step used.

Conclusions

An new aggregate model has been developed to represent the positive electrode in a practical lead/acid cell. The model formation and details describing the dimensions, electrical and transport effects have been set out. The model takes account of the electrode structure and electrochemical behaviour, together with the influence of surrounding cell components. It determines the current, potential and acid concentration distributions within the electrode for discharge, rest (zero) and charge currents.

The electrode voltage and plate AM distribution results are in good agreement with experimental data. Detailed results are given in a later paper [3].

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