

A SIMPLIFIED MODEL OF THE LEAD/ACID BATTERY

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Introduction

Modelling of the lead/acid battery has received increasing attention in recent years. Various treatments have been proposed to predict the behaviour of both a single plate and the complete cell. Among the most significant contributions are those of Newman and Tiedemann [1, 2], Simonsson [3, 4], Micka and Rousar [5-7], and Sunu and Burrows [8-10]. The scope of these studies is to obtain useful information for improving the performance of the battery, to predict its behaviour under particular conditions, and to compare different types of lead/acid cell.

The present work, by continuing previous studies [11, 12], presents a theoretical analysis of the electrical behaviour of the plates. Such an analysis is carried out by considering separately the different contributions of the grid and of the active material to the potential drop within the plate. A simple model, consisting of a resistor network simulating the grid rods, the active material, and the electrolyte, has been considered. The resistors that correspond to the active material are taken as non-linear with an $i(V)$ characteristic derived from porous-electrode theory. This model corresponds to a system in which the positive plate (*i.e.*, where the major potential drop occurs) is immersed in the electrolyte and faces the negative plate, which is assumed to be equipotential.

Behaviour of the grid

The analysis of the electrical behaviour of the grid has been carried out by determining the potential distribution of the grid nodes. The results obtained by considering various geometries and different types of grids are in good agreement with the findings by Tiedemann *et al.* [13]. This approach has led to the definition of a quality coefficient 'CQ' for the grid which can be useful for the evaluation of grid design [11]:

$$CQ = \frac{C}{Pw} \quad (1)$$

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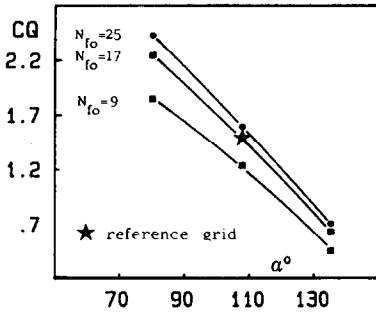


Fig. 1. Effect of the angle between the rods of an expanded grid on the quality coefficient CQ.

where: C is the capacity (in A h) of the plate; P is the weight (in g) of the grid; $w = V_m s / (V_m + s)$ is an electrical parameter that depends on both the mean value V_m and the standard deviation s of the potential distribution at the nodes. The calculation has been carried out by varying the geometric parameters for three different types of grids: rectangular, radial, and expanded. For grids commonly employed in automotive batteries, the following values of the quality coefficient have been found for the standard geometry:

Type	Rectangular	Radial	Expanded
CQ	1.82	1.47	1.43

Figures 1 and 2 show some CQ values for expanded grids. The potential distribution for a rectangular grid with the tab at one end of the frame is given in Fig. 3.

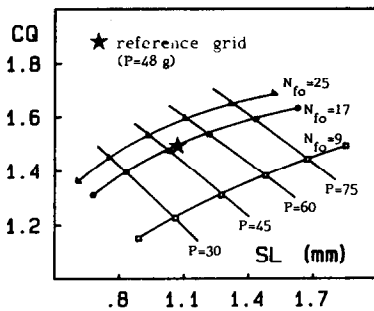


Fig. 2. Effect of the thickness, SL, of the expanded strip on the quality coefficient CQ. N_{fo} is the number of slanting rods and P is the weight of the grid in grams.

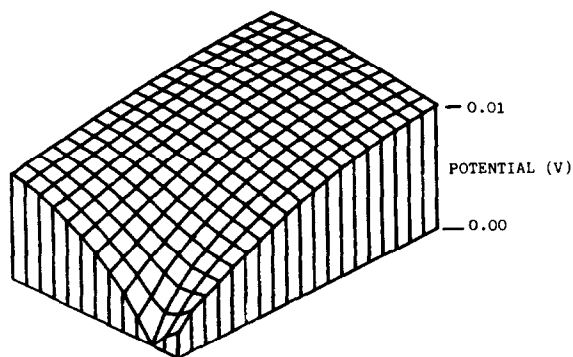


Fig. 3. Potential distribution due to ohmic drop in a rectangular grid.

Behaviour of active material

The behaviour of the active material has been studied by considering the porous electrode theory, based on the macroscopic model along the lines given by Newman and Tiedemann [1] and Simonsson [3]. This model takes into account mass and energy conservation, transport equations, and electrochemical kinetics. The derived equations provide the values of the following parameters as a function of time: the electric potential in both the solid phase (Φ_s) and the liquid phase (Φ_e); the overpotential (η); the electronic (i_e) and ionic (i_o) current densities; the faradaic current (I); the sulphuric acid concentration (c); the porosity (ϵ); the degree of discharge (X). The equations are as follows.

Mass conservation for positive active material:

$$\epsilon \frac{\partial c}{\partial t} = \frac{\Delta \hat{V}}{2F} i_e \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) + \frac{3 - 2t_1}{2F} \frac{\partial i_e}{\partial x} \quad (2)$$

where: t is the time; x is the space co-ordinate; t_1 is the transport number for H^+ ; D is the diffusivity. A similar equation can be written for the negative active material.

Charge conservation:

$$\left(1 + \frac{k}{\sigma} \right) i_e = \frac{k}{\sigma} I + k \left(\frac{\partial E}{\partial c} \frac{\partial c}{\partial x} + \frac{\partial \eta}{\partial x} \right) - (D_1 - D_2) F \frac{\partial c}{\partial x} \quad (3)$$

where: k and σ are the electrolyte and solid conductivities, respectively; E is the reversible potential; D_1 and D_2 are the diffusivities for H^+ and HSO_4^- .

Kinetic equation:

$$\frac{\partial i_e}{\partial x} = a_0 \left(1 - \frac{X}{X_m} \right) i_0 \left[\exp \left(\alpha_a \frac{2F}{RT} \eta \right) - \exp \left(-\alpha_c \frac{2F}{RT} \eta \right) \right] \quad (4)$$

where: a_0 is the electrochemically active area per unit volume; X is the degree of discharge; α_a and α_c are the charge-transfer coefficients for the anodic and cathodic reactions, respectively.

Two additional equations refer to the definition of the 'degree of discharge', namely,

$$\frac{\partial X}{\partial t} = -\frac{1}{q_0} \frac{\partial i_e}{\partial x} \quad (5)$$

$$\varepsilon = \varepsilon_0 - k(1 - \varepsilon_0)X \quad (6)$$

where: $k = (r - 1)$ and r is the ratio between molar volumes for PbSO_4 and PbO_2 .

The above system has been solved, after the introduction of the dimensionless parameters $\xi = x/L$ and $J = i_e/I$, by the method of spatial separation. The derivatives with regard to space can be changed to finite differences by means of three-node relationships. A non-linear algebraic system composed of $4N$ equations is obtained, which is linearized and solved by the Newton iteration algorithm.

The following boundary conditions were considered (the system is assumed to be under galvanostatic conditions):

At time $t = 0$

- $c = c_0$, initial acid concentration;
- $\varepsilon = \varepsilon_0$, initial porosity value;
- distribution of ionic current density (i_e) and of overpotential (η) along the pore depends only on ohmic effects in the solid and in the liquid, and on the kinetics of electrochemical reactions.

At time $t \neq 0$

- $\left. \frac{\partial c}{\partial x} \right|_{x=0} = 0$ $\left. \frac{\partial c}{\partial \xi} \right|_{\xi=0} = 0$
- $i_e|_{x=0} = 0$ $J|_{\xi=0} = 0$
- $i_e|_{x=L} = I$ $J|_{\xi=1} = 1$

Figures 4 and 5 show the change of acid concentration *versus* the thickness of the porous electrode at different discharge times for two values of the current density.

The computed value of the ratio V/I as a function of time for different current density values is given in Fig. 6. From these values, the characteristic $V(I)$ is obtained, along with the corresponding $\eta(I)$ values which are used for the non-linear resistor network calculation. A set of equations of the type:

$$I_k = \left(\sum_{\substack{h=0 \\ h \neq k}}^N G_{k,h} \right) V_k - \sum_{\substack{h=1 \\ h \neq k}}^N (G_{k,h} V_h) \quad (7)$$

for the N nodes of the network has been written, where: $G_{h,k}$ is the conductance of the element between the nodes h and k ; I_k is the current-entering node k ; V_k is the potential of node k with regard to node 0. If the nodes h and k are not connected, the conductance $G_{h,k}$ is 0.

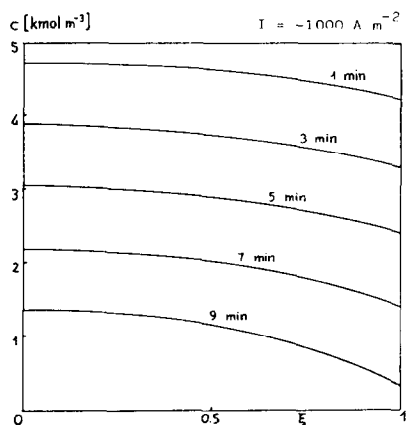


Fig. 4. Change of acid concentration with thickness of porous electrode at different discharge times for positive active material at 1000 A m^{-2} .

The results of such calculations for two values of the plate current intensity are presented in Figs. 7 and 8. One of the most interesting aspects to emerge from these calculations is that, apart from a small region near the plate tab, the current distribution through the plate can be considered as uniform, in spite of the fact that the resistors simulating the active material are a function of the electric current. This can be explained by concluding that the ratio between the resistances of the elements that in the model correspond to the electrolyte, and those corresponding to the active material, is very high, thus rendering the electrolyte a very effective distributor of the current through the plate. This observation also suggests that the potential distribution along a vertical plane close to the positive plate is mainly dependent on the ohmic drop in the grid bars.

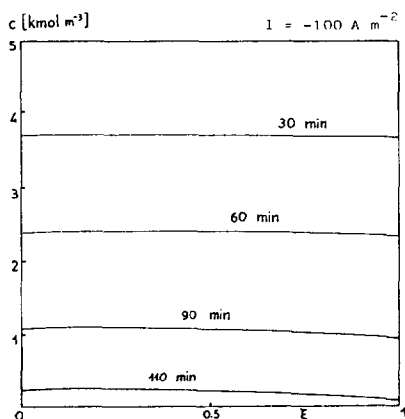


Fig. 5. Change of acid concentration with thickness of porous electrode at different discharge times for positive active material at 100 A m^{-2} .

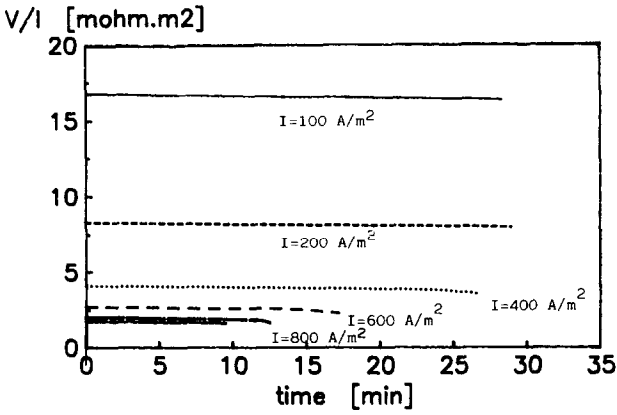


Fig. 6. Ratio V/I of the potential difference between the solid phase (a.m.) and the liquid, vs. current density for different discharge times.

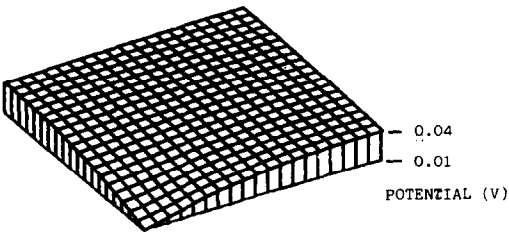


Fig. 7. Potential distribution for the resistor network model at 5 A.

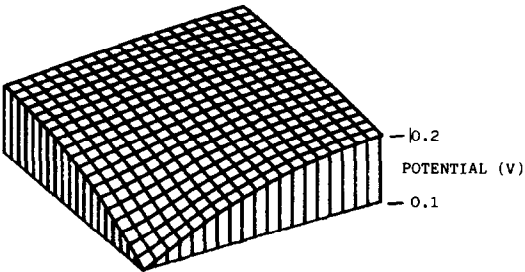


Fig. 8. Potential distribution for the resistor network model at 12 A.

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