Journal of Power Sources, *31* (1990) 271 - 279

INFLUENCE OF ELECTROLYTE TEMPERATURE AND POSITIVE-PLATE THICKNESS ON THE PERFORMANCE OF LEAD/ACID CELLS

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Introduction

Electrolyte temperature and plate thickness are among the parameters most frequently considered, together with the discharge rate, in early [1, 2], and also more recent [3, 4] treatises on lead/acid batteries. A body of experimental data, in the form of tables and curves showing the effect of temperature and plate thickness on the cell capacity, is now available. Although the results have always been qualitatively explained by resorting to the diffusion mechanism, no quantitative relation has ever been proved between discharge performance and temperature through the medium of the diffusion coefficient of sulphuric acid which, as is well known, is strongly dependent on temperature. Similarly, though it is known that thin plates have higher specific performances, no precise correlation is available between cell performance and plate thickness.

The aim of this paper is to demonstrate that such correlations can be obtained by taking advantage of some formal properties of an exact solution of the diffusion equation.

Properties of an exact solution of the diffusion equation

By considering the simple case of a partition of finite length *L*, and section, *S*, containing an electrolyte with diffusion coefficient *D*, the solution of the diffusion equation:

$$\frac{\partial c(x, t)}{\partial t} = D \frac{\partial^2 c(x, t)}{\partial x^2} \tag{1}$$

will be examined for the initial condition

$$c(x, 0) = c_0 \tag{2}$$

and the boundary conditions

$$\left. \frac{\partial c(x, t)}{\partial x} \right|_{x=0} = 0 \tag{3}$$

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$$\left.\frac{\partial c(x, t)}{\partial x}\right|_{x=L} = -\frac{I}{SDnF} \tag{4}$$

which refer to a consumption of solute at one side only of the partition at a constant rate, I.

Defining the maximum capacity as:

$$C_{\max} = c_0 LSnF \tag{5}$$

and, for $c(L, t) = 0$, the limiting current $I = I_L$ and the limiting capacity as:

$$C_{\mathrm{L}} = I_{\mathrm{L}} t \tag{6}$$

and the adimensional time as:

$$\tau = Dt/L^2 \tag{7}$$

the exact solution, for $x = L$ and $c(L, t) = 0$, of the problem is given by two equivalent expressions [5, 6], namely:

$$\frac{C_{\max}}{C_{\mathrm{L}}} = 1 + 2\sum_{n=1}^{\infty} \frac{(1 - \exp(-n^2\pi^2\tau))}{n^2\pi^2\tau} \tag{8}$$

whose infinite series is rapidly convergent for high values of τ (slow discharge rates) and:

$$\frac{C_{\max}}{C_{\mathrm{L}}} = 2\left\{\frac{1}{\sqrt{\pi\tau}} + 2\sum_{n=1}^{\infty}\left[\frac{\exp(-n^2/\tau)}{\sqrt{\pi\tau}} - \frac{n}{\tau}\operatorname{erfc}\left(\frac{n}{\sqrt{\tau}}\right)\right]\right\} \tag{9}$$

whose infinite series is rapidly convergent for low values of τ (fast discharge rates).

Examination of eqns. (8) and (9) yields interesting information, as follows.

From eqn. (8):

$$\lim_{t\to\infty} \frac{C_{\max}}{C_{\mathrm{L}}} = 1 \tag{10}$$

or

$$\lim_{t\to\infty} C_{\mathrm{L}} = C_{\max} = c_0 SLnF \tag{10'}$$

i.e., at infinitely slow discharge rates, the limiting capacity C_{L} does not depend on the diffusion coefficient D (and therefore does not depend on the temperature) and is directly proportional to the thickness, L.

From eqn. (9):

$$\lim_{t\to 0} \frac{C_{\max}}{C_{\mathrm{L}}} = \frac{2}{\sqrt{\pi\tau}} \tag{11}$$

or, using eqns. (5) and (7):

$$\lim_{t\to 0} C_{\mathrm{L}} = nFc_0 S\sqrt{\pi Dt}/2 \tag{11'}$$

i.e., at infinitely fast discharge rates, the limiting capacity C_L does not depend on the thickness L and is proportional to the square root of D and t.

In addition to the above asymptotic properties, eqns. (8) and (9) have other notable properties that are valid at any discharge rate. Both expressions of C_{max}/C_L are functions of the adimensional time $\tau = Dt/L^2$ only. This means that to the same Dt/L^2 values as

$$D_1 t_1/L_1^2 = D_2 t_2/L_2^2 \qquad (12)$$

correspond the same C_{max}/C_L values.
Hence, and by considering that $C_L = I_L t$, the following important properties are derived.

Influence of temperature

At equal discharged limiting capacity C_L, the ratio of the limiting currents I_{L_1} at the temperature T_1 and I_{L_2} at the temperature T_2, is equal, for the same cell ($L_1 = L_2$), to the ratio of the diffusion coefficients $D(T_1)$ and $D(T_2)$ of the sulphuric acid solution

$$(I_{L_1}/I_{L_2})_{C_L} = D(T_1)/D(T_2) \qquad (13)$$

or

$$(t_2/t_1)_{C_L} = D(T_1)/D(T_2) \qquad (13')$$

Influence of plate thickness

At equal C_L/C_{max} or, if S is the same, at equal C_L/L, the ratio of the limiting currents I_{L_1} and I_{L_2} for the plate thicknesses L_1 and L_2 is equal, at the same temperature ($D_1 = D_2$), to the ratio of L_2 and L_1:

$$(I_{L_1}/I_{L_2})_{C_L/C_{max}} = L_2/L_1 \qquad (14)$$

or

$$(I_{L_1}/L_1/I_{L_2}/L_2)_{C_L/C_{max}} = (L_2/L_1)^2 \qquad (14')$$

or

$$(t_2/t_1)_{C_L/C_{max}} = (L_2/L_1)^2 \qquad (14'')$$

or

$$(\sqrt{t_2}/\sqrt{t_1})_{C_L/C_{max}} = L_2/L_1 \qquad (14''')$$

Comparison with published experimental data

Influence of temperature

The property described by eqn. (13) may be tested directly by using the discharge characteristics in the form $C(I)$ for different temperatures published by Bode (see ref. 4, page 288, Fig. 4.2) and Witte (see ref. 7, page 50, Fig. 25/2).

TABLE 1

$I_L(T)/I_L(25\ °C)$ ratios for different constant discharge capacities and electrolyte temperatures

C_L (A h)	$(I_L(T)/I_L(25\ °C))_{C_L}$					
	T (°C)					
	50	$\bar{T}=25$	0	−20		
(a)						
90	1.500	1.000	0.570	–		
80	1.593	1.000	0.550	–		
70	1.729	1.000	0.563	0.146		
60	1.583	1.000	0.479	0.146		
50	1.405	1.000	0.560	0.178		
40	–	1.000	0.677	0.268		
Mean	1.562	1.000	0.567	0.185		
	$\bar{T}=25$	20	10	0	−10	−20
(b)						
90	1.000	0.891	0.703	–	–	–
80	1.000	0.914	0.710	0.516	–	–
70	1.000	0.902	0.714	0.511	0.331	–
60	1.000	0.915	0.707	0.521	0.330	–
55	1.000	0.911	0.721	0.522	0.332	0.181
Mean	1.000	0.907	0.711	0.518	0.331	0.181

Data derived from: (a) Bode (ref. 4, p. 288, Fig. 4.2); (b) Witte (ref. 7, p. 50, Fig. 25/2).

For each discharge capacity, the ratio of the discharge current at each temperature to the current at the reference (interpolated) temperature of 25 °C can be measured. By repeating the measures for different discharge capacities, the data shown in Table 1 are obtained.

Another source of data may be found in the paper by Baikie *et al.* [8]. According to these authors, the experimental results can be described by the relationship:

$$I^n t = k_0(1+\alpha T) \tag{15}$$

where: $k_0 = 0.32$ and $\alpha = 0.021$ for the negative electrode; $k_0 = 0.24$ and $\alpha = 0.015$ for the positive electrode; $n = 1.4$ for both electrodes. According to eqn. (15), the $I_L(T)/I_L(25\ °C)$ ratio at equal It is given by:

$$I_L(T)/I_L(25\ °C) = \left(\frac{1+\alpha T}{1+25\alpha}\right)^{2.5} \tag{16}$$

The values obtained by using this relationship for the positive plate, together with the mean values of the measured $I_L(T)/I_L(25\ °C)$ ratios according to

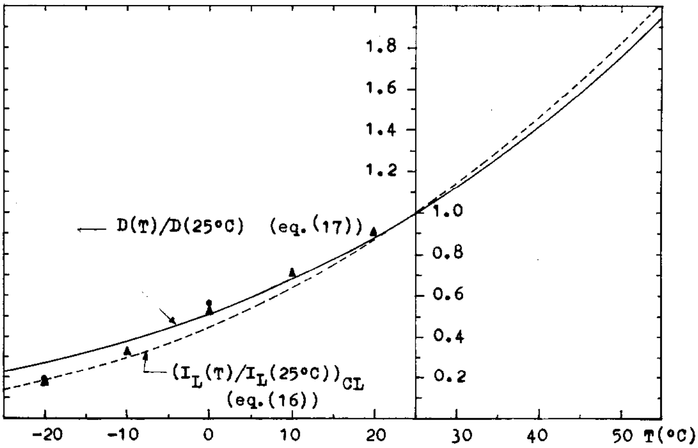


Fig. 1. Comparison of $D(T)/D(25\ ^\circ C)$ with $I_L(T)/I_L(25\ ^\circ C)$ at constant discharge capacity C_L for a complete cell: ●, according to Fig. 4.2 of ref. 4; ▲, according to Fig. 25/2 of ref. 7; ---, for a positive plate according to eqn. (16) derived from ref. 8.

Table 1 for a complete cell, are compared in Fig. 1 with the adimensional, concentration-independent, diffusion coefficient of the sulphuric acid solution $D(T)/D(25\ ^\circ C)$ given by [9]:

$$D(T)/D(25\ ^\circ C) = \exp(2174(1/298.15 - 1/(273.15 + T))) \qquad (17)$$

The comparison shows a good agreement for $T \geqslant 0\ ^\circ C$. The divergence of behaviour at temperatures below 0 °C may be due to: (i) a progressively larger part of the electrolyte freezes so that C_{max} cannot be taken as constant; (ii) a different and higher activation energy must be used in the expression for the diffusion coefficient (see ref. 10).

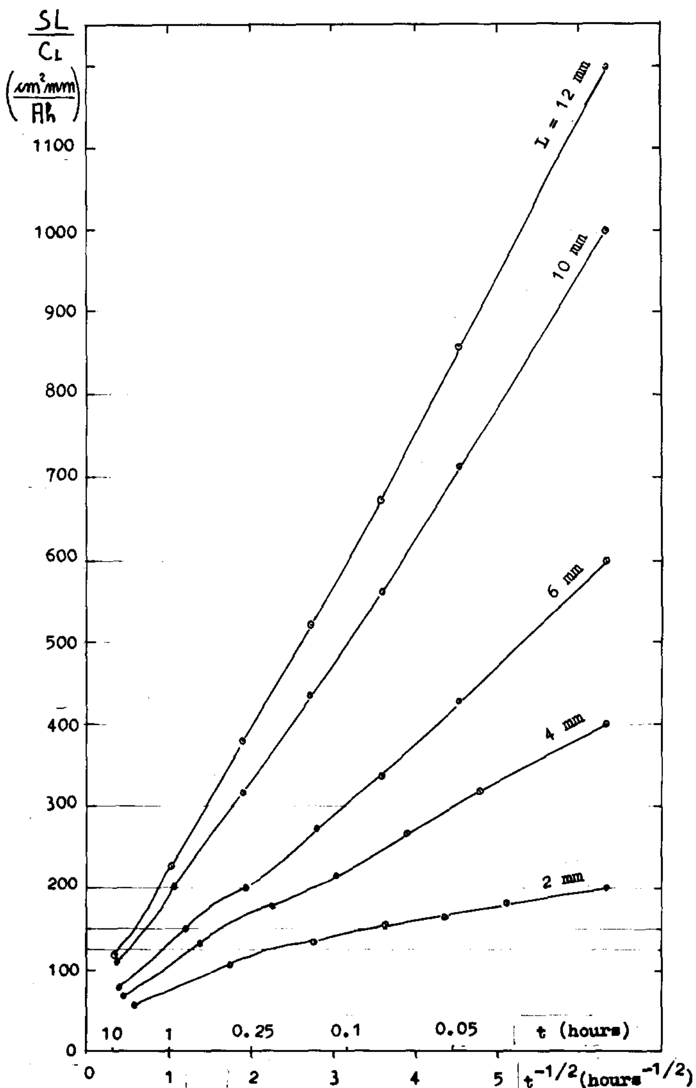
Influence of positive-plate thickness

The property described in the form of eqn. (14‴) may be tested by using the measured values of the capacities obtained by Stein (Fig. XIIb, ref. 11) and Bode (ref. 4, page 302, Fig. 4.12) for wide ranges of discharge rates and positive plate thicknesses. Both series of data are shown in the form SL/C_L *versus* $1/\sqrt{t}$ in Fig. 2. For each SL/C_L value the ratios of $1/\sqrt{\bar{t}}$ and $1/\sqrt{t}$ are measured for different positive-plate thicknesses assuming a reference thickness of $\bar{L} = 10$ mm for the Stein data and $\bar{L} = 1$ mm for the Bode data.

By repeating the measures for different SL/C_L values, the data collected in Table 2 are obtained. In the last two rows of each series of data the mean values of the $(\sqrt{t}/\sqrt{\bar{t}})$ ratios are compared with the $L/\bar{L}$ ratios: the agreement is excellent. Thus, the hypothesis formulated through eqns. (14), (14′), (14″) and (14‴) is fully verified.

Graphic method and a third property

The two properties involving the temperature and the plate thickness effects can be used in a simple graphic method for predicting the discharge characteristics of a cell at a temperature T, or with a positive plate of thickness L, when the discharge characteristics of the same cell at the reference temperature $\bar{T}$, or the discharge characteristics of a positive plate having reference thickness $\bar{L}$, are known. The method is demonstrated in Fig. 3.

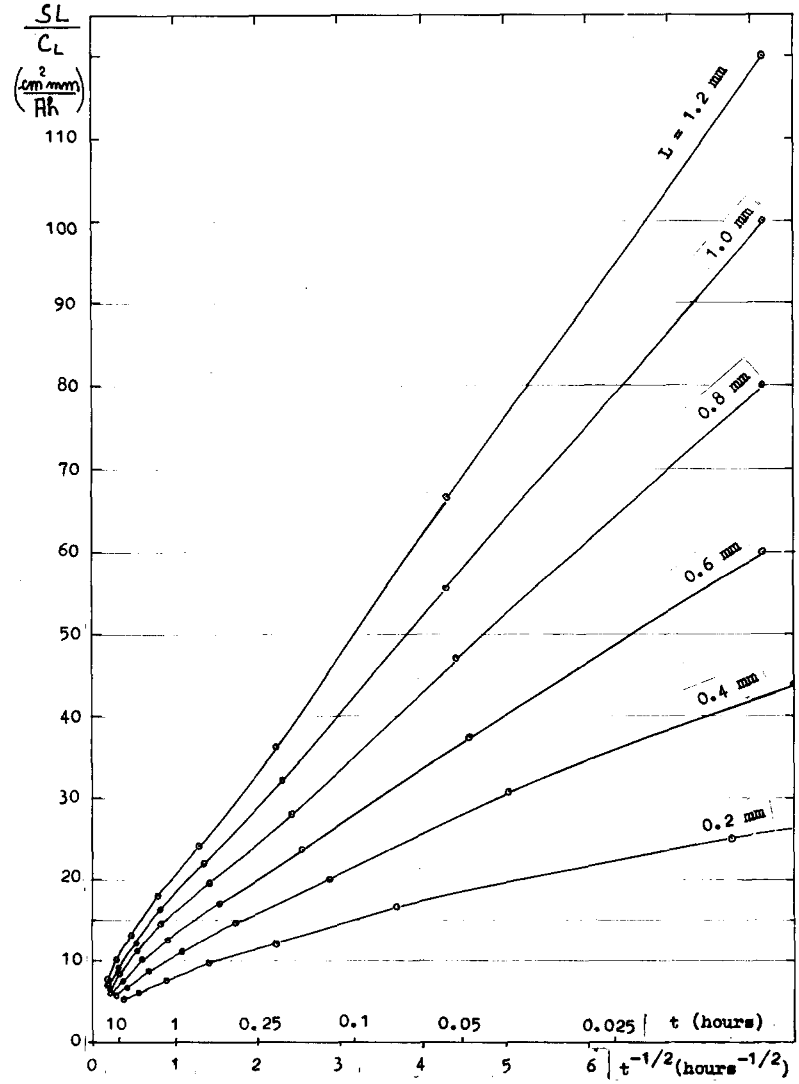


(a)

Fig. 2. Representation of SL/C_L *vs.* $1/\sqrt{t}$ for different thicknesses of the positive plate according to data derived from: (a) Stein (ref. 11, Fig. XIIb); (b) Bode (ref. 4, p. 302, Fig. 4.12).

A third property correlating plate thickness and electrolyte temperature can be easily derived from eqn. (12) for $t_1 = t_2$. In order to obtain at temperature T, the same specific performances C_L/C_{max} *versus* I_L/C_{max} obtainable at temperature $\bar{T}$ with plate thickness $\bar{L}$, the plate thickness L must satisfy the relation:

$$L/\bar{L} = \sqrt{D(T)/D(\bar{T})} \tag{18}$$



(b)

TABLE 2

$(\sqrt{t}/\sqrt{\bar{t}})$ ratios for different SL/C_L values and positive plate thicknesses

SL/C_L (cm^2 mm (A h)$^{-1}$)	$(\sqrt{t}/\sqrt{\bar{t}})_{SL/C_L}$ L (mm)					
	12	$\bar{L} = 10$	6	4	2	
(a)						
125	1.250	1.000	0.541	0.400	0.222	
150	1.217	1.000	0.583	0.431	0.200	
200	1.200	1.000	0.538	0.382	0.166	
300	1.203	1.000	0.568	0.399	–	
400	1.235	1.000	0.588	0.395	–	
500	1.219	1.000	0.552	–	–	
600	1.203	1.000	0.609	–	–	
700	1.201	1.000	–	–	–	
800	1.206	1.000	–	–	–	
900	1.199	1.000	–	–	–	
1000	1.199	1.000	–	–	–	
Mean	1.212	1.000	0.568	0.401	0.196	
$L/\bar{L}$	1.200	1.000	0.600	0.400	0.200	
	1.2	$\bar{L} = 1.0$	0.8	0.6	0.4	0.2
(b)						
10	1.310	1.000	0.800	0.626	0.411	0.240
15	1.252	1.000	0.823	0.588	0.395	0.225
20	1.210	1.000	0.767	0.568	0.400	0.219
30	1.183	1.000	0.792	0.609	0.428	–
40	1.200	1.000	0.811	0.600	0.402	–
50	1.222	1.000	0.810	0.586	–	–
60	1.208	1.000	0.795	0.572	–	–
70	1.214	1.000	0.789	–	–	–
80	1.218	1.000	0.791	–	–	–
90	1.217	1.000	–	–	–	–
100	1.208	1.000	–	–	–	–
Mean	1.222	1.000	0.798	0.593	0.407	0.228
$L/\bar{L}$	1.200	1.000	0.800	0.600	0.400	0.200

Data derived from: (a) Stein (ref. 11, Fig. XIIb); (b) Bode (ref. 4, Fig. 4.12, p. 302).

Conclusions

The above graphic method, which can be usefully employed in sizing and designing lead/acid batteries, suggests the possible reason for the lack of success of past attempts to correlate performance and temperature or plate thickness in a quantitative way. That is, performance must not be compared at equal discharge current or time but at equal discharge capacity or fraction

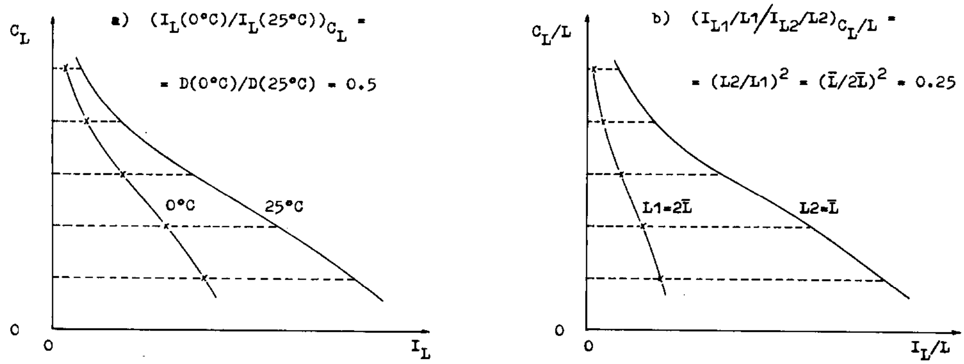


Fig. 3. Graphic method for obtaining the discharge characteristics of: (a) a cell at 0 °C when the discharge characteristics of the same cell at 25 °C are known (see eqns. (13) and (17)); (b) a positive plate of thickness $2\bar{L}$ when the discharge characteristics for a thickness $\bar{L}$ are known (see eqn. (14′)).

of C_{max}. This simple change of perspective, prompted by the observation of the formal structure of an exact solution of the diffusion equation, yields the required results.

The property described by eqn. (18) may be considered a by-product that can be used to design the positive-plate thickness needed to counterbalance the effect of a low electrolyte temperature on the cell performance.

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