A new equation for the limiting capacity of the lead/acid cell

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Abstract

As an alternative to the empirical Peukert equation, whose validity is restricted to intermediate discharge rates, a new equation for the limiting capacity of the lead/acid cell is proposed, formally derived from an approximate closed form solution of a two finite compartment diffusion problem. The four parameters of the equation are evaluated through a non-linear least-squares method. The resulting capacity curve fits the typically undulating experimental data closely throughout their range.

1. Introduction

The strong influence of discharge rate on the capacity of the lead/acid cell has been observed since the early years of the battery industry. Though a number of equations relating capacity and discharge time or current have been developed, the equations by Peukert [1] and Liebenow [2], both published in the year 1897, are still the best known examples.

The Peukert equation, which relates the discharge current I to the discharge time t:

$$I^n t = K \tag{1}$$

can be linearized as

$$\log t = \log K - n \log I \tag{2}$$

permitting an easy evaluation of the constants n and K.

The Liebenow equation, which relates the capacity $C = It$ to the discharge time t:

$$C = C_{\text{max}}/(1 + \gamma/\sqrt{t}) \tag{3}$$

can also be linearized as

$$C = C_{\text{max}} - \gamma I\sqrt{t} \tag{4}$$

supplying an even easier way for evaluating the two constant parameters C_{max} and γ. The Liebenow expression, however, is definitely a much less popular equation.

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Though the Peukert equation is still used in the battery industry, it has been recognised in recent years [3–5] that it only fits the experimental data reasonably well in the intermediate rates region. When the exponent n lies between 1 and 2, as is the rule, the capacity at low discharge rates tends to infinity, which is a physical absurdity. A less-stressed point is that at high discharge rates it is the quantity $I\sqrt{t}$ which tends to infinity: an equally absurd behavior.

The situation of both Peukert and Liebenow equations is clearly illustrated by a comparison with typical experimental data for a lead/acid cell extended over a wide range of discharge rates in the C versus $I\sqrt{t}$ plot of Fig. 1.

The experimental data show three distinct regions:

at low discharge rates the capacity manifestly tends to a constant value (C_{max}). The curve is concave downwards;

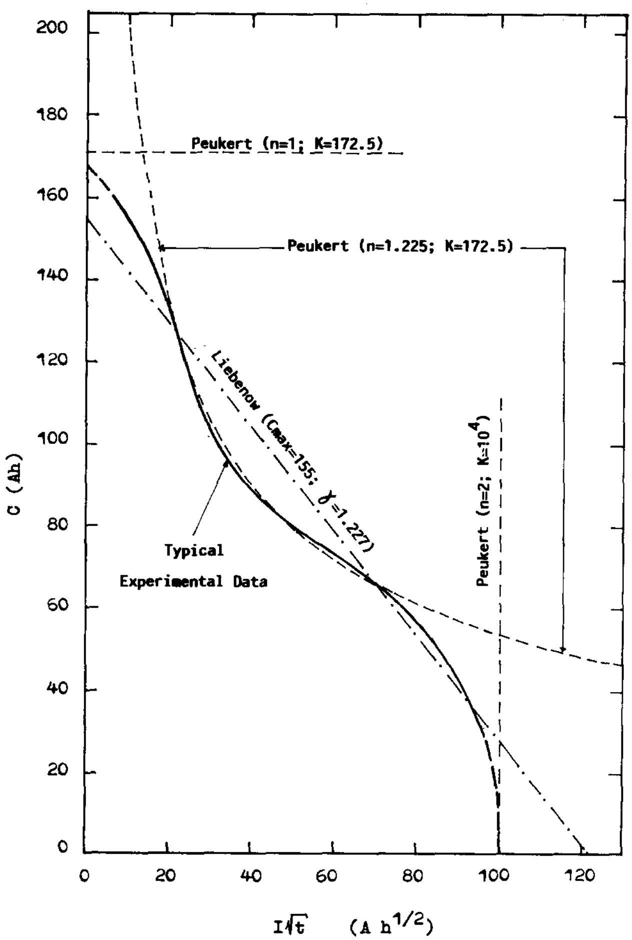

Fig. 1. Comparison of Peukert and Liebenow equations with typical experimental data of a lead/acid cell in a C vs. $I\sqrt{t}$ plot.

at intermediate discharge rates the curve is concave upwards;

at high discharge rates the curve tends to a constant value $(I\sqrt{t})_{max}$ again with a downward concavity.

The Peukert equation operates well in the intermediate region but requires different values of n (from $n=1$ to $n=2$) for each region, whereas the Liebenow straight line covers the entire range with a rather crude fit. However, both equations fail to match the well marked two-wave profile of the experimental curve.

A comparatively more recent equation, admittedly of empirical origin, relating capacity and current and involving a single hyperbolic function, has been proposed by Selim and Bro [6] for primary batteries. However, at high discharge rates it shows the same behavior as the Peukert equation. The same remark can be made for an equation proposed by Kappus and Voss [7] with the additional objection that the capacity does not vanish at $t=0$.

It is obvious that an alternative equation is needed. In this paper a new equation is proposed which, though not having the simple structure of the Peukert and Liebenow equations, is more able to reproduce all the peculiarities of the real curve.

The new equation is a closed form (i.e., not containing infinite series or definite integrals), approximate solution to the diffusion problem for two planar, finite compartments of different lengths, simulating the porous electrode and the inter-plate space occupied by electrolyte of different apparent diffusion coefficients, $D1$ and $D2$. A similar problem was studied by Stein [8] for two compartments, one of which, however, was semi-infinite. The case of two finite compartments has probably never been considered before.

Though the fact that the reaction is supposed to be concentrated on the plate surface is an obvious simplification, the more realistic geometry of the model is of decisive importance, as will be apparent, for generating the typical, often very deep, inflection shown by the real curve at intermediate rates.

In general terms, if a simple result suitable for direct practical use is required, a simplification of the physical model is unavoidable: the problem is transferred to the choice of what is convenient to simplify and what is not.

The explicit exact solution, in two forms, of the problem for the general case $D_1 \neq D_2$ will be not given here because it is too cumbersome. Some relevant properties only will be demonstrated and used to check the exact and approximate solutions for the special case $D_1 = D_2$ and the approximate solution for the general case.

2. The two-compartment diffusion problem

With reference to the double compartment system of cross section S, schematically represented in Fig. 2, the problem is to determine the concentration profiles $c_1(x, t)$ and $c_2(x, t)$ satisfying the two diffusion equations:

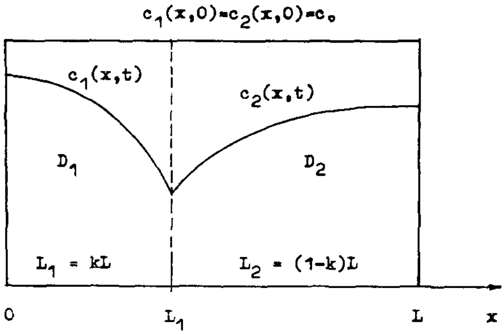

Fig. 2. Schematic representation of a two partition diffusion problem.

$$\partial c_1(x,\, t)/\partial t = D_1\ \partial^2 c_1(x,\, t)/\partial x^2 \tag{5}$$

$$\partial c_2(x,\, t)/\partial t = D_2\ \partial^2 c_2(x,\, t)/\partial x^2 \tag{6}$$

with the initial conditions:

$$c_1(x,\, 0) = c_2(x,\, 0) = c_0 \tag{7}$$

the continuity condition:

$$c_1(L_1,\, t) = c_2(L_1,\, t) \tag{8}$$

and the boundary conditions:

$$\partial c_1(0,\, t)/\partial x = 0;\ \partial c_1(L_1,\, t)/\partial x = -I_1(t)/nFSD_1 \tag{9}$$

$$\partial c_2(L_1,\, t)/\partial x = I_2(t)/nFSD_2;\ \partial c_2(L,\, t)/\partial x = 0 \tag{10}$$

with $I_1(t)$ and $I_2(t)$ satisfying the condition:

$$I_1(t) + I_2(t) = I \tag{11}$$

where I is the applied constant discharge current.

3. The Laplace-Transform of the exact solution

It is possible to verify that the Laplace-Transform of the exact solution to the problem stated in eqns. (5)–(11) for $x = L_1$ is given by:

$$y_1(L_1,\, p) = y_2(L_1,\, p) =$$

$$= \frac{c_0}{p} - \frac{I}{nFSL}\left\{\frac{L}{p\sqrt{p}\left[\sqrt{D_1}\tanh\left(\sqrt{\frac{p}{D_1}}\,kL\right) + \sqrt{D_2}\tanh\left(\sqrt{\frac{p}{D_2}}\,(1-k)L\right)\right]}\right\} \tag{12}$$

where $k=L_1/L$ and $(1-k)=L_2/L$ or, in an alternative form:

$$y_1(L_1, p)=y_2(L_1, p)$$

$$=\frac{c_0}{p}-\frac{I}{nFSL}\left\{\frac{\sqrt{\lambda}L}{(\sqrt{D_1}+\sqrt{D_2})p}\left[\frac{\cosh\sqrt{\lambda p}}{\sqrt{\lambda p}\sinh\sqrt{\lambda p}}+\frac{\cosh(2v-1)\sqrt{\lambda p}}{\sqrt{\lambda p}\sinh\sqrt{\lambda p}}\right]\right.$$

$$\left.\times\left[1+\sum_{s=1}^{\infty}(2\alpha-1)^s\left(\frac{\sinh(2v-1)\sqrt{\lambda p}}{\sinh\sqrt{\lambda p}}\right)^s\right]\right\} \tag{13}$$

where

$$\sqrt{\lambda}=L_1/\sqrt{D_1}+L_2/\sqrt{D_2} \tag{14}$$

$$-1\leqslant 2\alpha-1=\frac{(1/\sqrt{D_1}-1/\sqrt{D_2})}{(1/\sqrt{D_1}+1/\sqrt{D_2})}\leqslant 1 \tag{15}$$

$$-1\leqslant 2v-1=\frac{(L_1/\sqrt{D_1}-L_2/\sqrt{D_2})}{(L_1/\sqrt{D_1}+L_2/\sqrt{D_2})}\leqslant 1 \tag{16}$$

The explicit exact solution $c_1(L_1, t)=c_2(L_1, t)$ should be obtained by inverting eqns. (12) or (13). This is not a simple matter, save, comparatively, for the special case $D_1=D_2$ whose solution will be given later.

4. Properties of the C_{max}/C_L ratio obtainable by investigating the L-Transform of the exact solution

It is known that many properties of a function can be discovered by studying its L-Transform [9–11].

Let us first define the following quantities:

$c_0 nFSL=C_{max}=$ maximum capacity

and, for $c_1(L_1, t)=c_2(L_1, t)=0$

$I=I_L$ = limiting current
t = transition time
$C=I_L t=$ limiting capacity C_L

The inverse of eqn. (12) or eqn. (13) can be indicated in terms of the defined quantities as follows:

$$C_{max}/C_L=\mathcal{L}^{-1}[f(p)]/t=\mathcal{L}^{-1}[f(p)]/\mathcal{L}^{-1}(p^{-2}) \tag{17}$$

By using as $f(p)$ the expression between the curly brackets of eqns. (12) or (13), it is possible to prove, by taking advantage of the 'Final Value' Theorem, that:

$$\lim_{t\to\infty} C_{max}/C_L=1 \tag{18}$$

and, by taking advantage of the 'Initial Value' Theorem, that:

$$\lim_{t \to 0} C_{\max}/C_{\mathrm{L}} = \begin{cases} 2L/\sqrt{\pi D_1 t} & \text{for} \quad k=1 \\ 2L/\sqrt{\pi D_2 t} & \text{for} \quad k=0 \\ 2L/(\sqrt{D_1}+\sqrt{D_2})\sqrt{\pi t} & \text{for} \quad 0<k<1 \end{cases} \tag{19}$$

while, by using as $f(p)$ the expression between the curly brackets of eqn. (12) it is possible to detect another interesting property of the exact solution in the time domain, namely, that the derivative of $C_{\max}/C_{\mathrm{L}}$ with regard to the 'geometric partition coefficient' k, vanishes for

$$k=\sqrt{D_1}/(\sqrt{D_1}+\sqrt{D_2}) \tag{20}$$

i.e., when

$$L_1/L_2=\sqrt{D_1}/\sqrt{D_2} \tag{21}$$

the $C_{\max}/C_{\mathrm{L}}$ ratio has an extreme value (a maximum or a minimum). It will be shown later that this extreme value is a minimum, namely, $C_{\mathrm{L}}/C_{\max}$ has a maximum for all discharge rates t.

5. The exact solution to the special case $D_1=D_2=D$

For this special case, eqns. (14), (15), and (16) become:

$\sqrt{\lambda}=L/\sqrt{D}$; $2\alpha-1=0$; $2v-1=2k-1$

and the L-Transform [13] becomes:

$$y_1(L_1, p)=y_2(L_1, p)$$

$$=\frac{c_0}{p}-\frac{I}{2nFSp\sqrt{D}}\left[\frac{\cosh\sqrt{p/D}L}{\sqrt{p}\sinh\sqrt{p/D}L}+\frac{\cosh\sqrt{p/D}(2k-1)L}{\sqrt{p}\sinh\sqrt{p/D}L}\right] \tag{22}$$

For $c_1(L_1, t)=c_2(L_1, t)=0$, the exact solution can be expressed in terms of $C_{\max}/C_{\mathrm{L}}$, as a function of the dimensionless time $\tau=Dt/L^2$, in two equivalent ways corresponding to the two equivalent expressions of the θ_3 Jacobi function [10], the inverse of the terms between the square brackets of eqn. (22):

$$\frac{C_{\max}}{C_{\mathrm{L}}}=1+2\sum_{n=1}^{\infty}\frac{(1-\exp(-n^2\pi^2\tau))}{n^2\pi^2\tau}\cos^2(kn\pi) \tag{23}$$

whose infinite series is rapidly convergent for large values of τ (low discharge rates), and

$$\frac{C_{\max}}{C_{\mathrm{L}}}=\frac{1}{\sqrt{\tau}}\left\{\frac{1}{\sqrt{\pi}}+\mathrm{ierfc}\left(\frac{k}{\sqrt{\tau}}\right)\right.$$
$$\left.+\sum_{n=1}^{\infty}\left[2\,\mathrm{ierfc}\left(\frac{n}{\sqrt{\tau}}\right)+\mathrm{ierfc}\left(\frac{n+k}{\sqrt{\tau}}\right)+\mathrm{ierfc}\left(\frac{n-k}{\sqrt{\tau}}\right)\right]\right\} \tag{24}$$

whose infinite series is rapidly convergent for small values of τ (high discharge rates).

It is possible to verify, by using eqn. (23), that:

$$\lim_{\tau \to \infty} C_{max}/C_L = 1 \tag{25}$$

and, by using eqn. (24), that:

$$\lim_{\tau \to 0} C_{max}/C_L = \begin{cases} 2/\sqrt{\pi\tau} & \text{for } k=0 \text{ and } k=1 \\ 1/\sqrt{\pi\tau} & \text{for } 0<k<1 \end{cases} \tag{26}$$

Furthermore, by calculating the first and second derivatives of eqn. (23) with regard to k, it is possible to verify that for

$$k=\sqrt{D_1}/(\sqrt{D_1}+\sqrt{D_2})=1/2 \tag{27}$$

namely, for $L_1=L_2$, the ratio C_L/C_{max} has a maximum for any discharge rate τ.

All the formal properties anticipated by studying the L-Transform have thus been confirmed for the exact solution to the special case $D_1=D_2=D$.

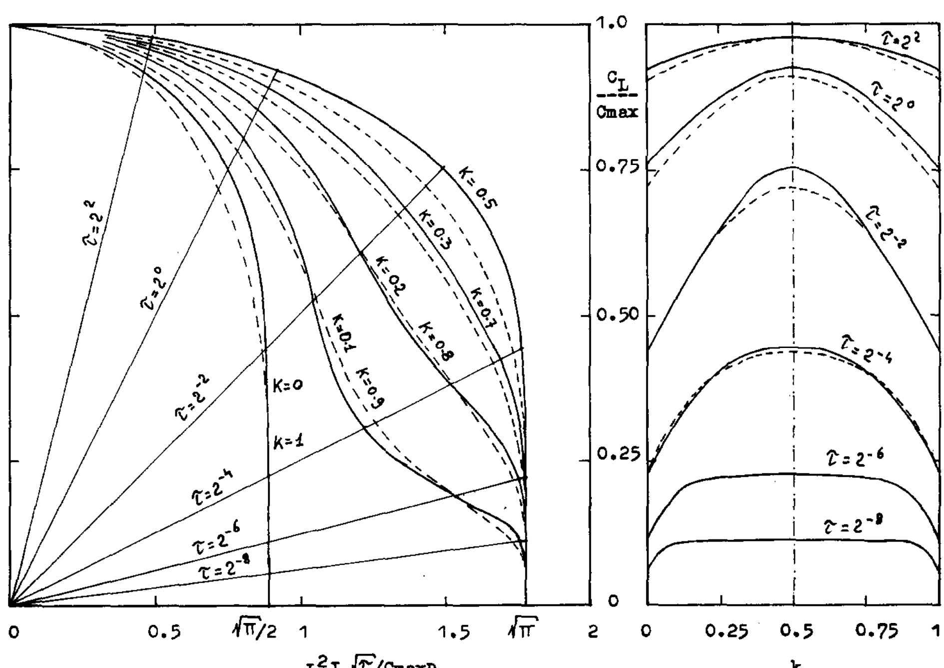

Fig. 3. C_L/C_{max} vs. $L^2I_L\sqrt{\tau}/C_{max}D$ for different values of k, and C_L/C_{max} vs. k for different values of τ according to the exact (——) and approximate (-----) solutions for the special case $D_1=D_2=D$.

6. An approximate solution to the special case $D_1=D_2=D$

As an approximate solution to the special case the following expression is proposed:

$$\frac{C_L}{C_{max}} = \frac{\sqrt{\pi\tau}}{2}\,[\tanh(2k/\sqrt{\pi\tau}) + \tanh(2(1-k)/\sqrt{\pi\tau})] \qquad (28)$$

It is possible to verify that even for this approximate solution all the properties of the exact solution are preserved. As shown in Fig. 3, the proposed approximation is acceptable even outside the asymptotic regions.

7. An approximate solution to the general case $D_1 \neq D_2$

As an approximate solution to the general case $D_1 \neq D_2$, the following equation is proposed:

$$\frac{C_L}{C_{max}} = \frac{\sqrt{\pi t}}{2L}\left[\sqrt{D_1}\,\tanh\left(\frac{2kL}{\sqrt{\pi D_1 t}}\right) + \sqrt{D_2}\,\tanh\left(\frac{2(1-k)L}{\sqrt{\pi D_2 t}}\right)\right] \qquad (29)$$

Again, it is possible to verify that even for the proposed approximate solution for the general case, all the formal properties anticipated by studying the Laplace Transform of the rigorous solution are exactly maintained.

Equation (29) in the condensed form:

$$C_L = \sqrt{t}\,[A\,\tanh(B/\sqrt{t}) + C\,\tanh(D/\sqrt{t})] \qquad (30)$$

or

$$I_L\sqrt{t} = A\,\tanh(B/\sqrt{t}) + C\,\tanh(D/\sqrt{t}) \qquad (31)$$

where

$$A = C_{max}\sqrt{\pi D_1}/2L \qquad (32)$$

$$B = 2kL/\sqrt{\pi D_1} \qquad (33)$$

$$C = C_{max}\sqrt{\pi D_2}/2L \qquad (34)$$

$$D = 2(1-k)L/\sqrt{\pi D_2} \qquad (35)$$

is proposed as a new equation for the limiting capacity of the lead/acid cell.

Note that at low discharge rates:

$$\lim_{t\to\infty} C_L = AB + CD = C_{max} = (It)_{max} \qquad (36)$$

while at high discharge rates:

$$\lim_{t\to 0} I_L\sqrt{t} = A + C = \sqrt{\pi}\,\frac{(\sqrt{D_1}+\sqrt{D_2})}{2L}\,C_{max} = (I\sqrt{t})_{max} \qquad (37)$$

8. Estimation of the parameters of the new equation

Expression (31), which will be used for determining the four unknown parameters A, B, C, and D, is a non-linear equation with regard to B and D.

The parameter estimation can be carried out by minimizing the objective function:

$$\varphi(A,B,C,D)=\sum_{i=1}^{N}(y_i-A\tanh Bx_i-C\tanh Dx_i)^2 \tag{38}$$

where N is the number of couples of experimental data $x_i=1/\sqrt{t_i}$ and $y=I_i\sqrt{t_i}$.

The problem can be solved by using a multidimensional non-linear least-squares technique as the Levenberg–Marquardt algorithm [12] or the so called 'damped Newton's method' [13].

Both methods converge very quickly provided that good initial values A_0, B_0, C_0 and D_0 are used. Good initial values can be obtained by following the graphic procedure shown in Fig. 4. In Figs. 5–8 some examples of curve fitting to experimental data regarding lead/acid cells of different sizes and constructions are shown. The performance data are derived from manufacturers' catalogues [14], technical handbooks [4, 15], and a monograph [16].

It is necessary to point out that the experimental data must be derived from discharges carried out at different constant discharge currents on an

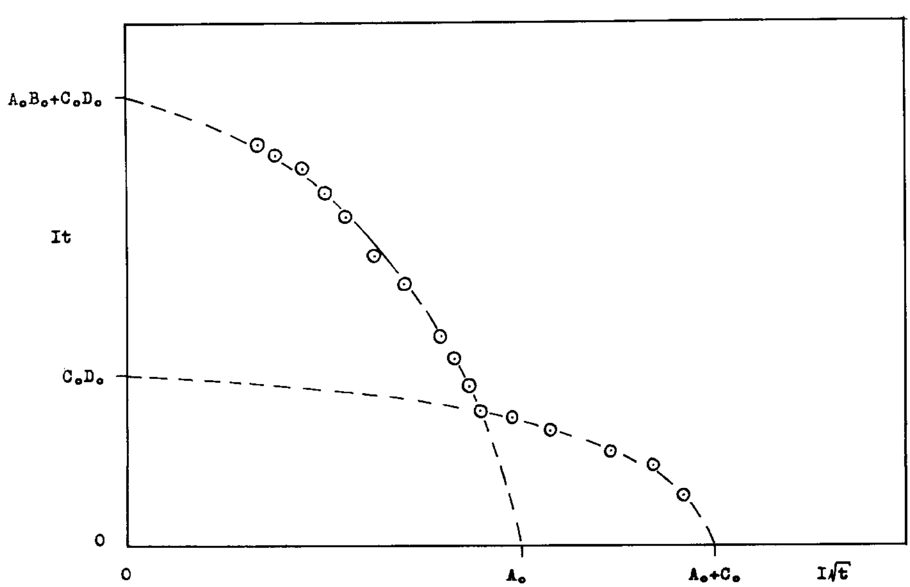

Fig. 4. Suggested procedure for evaluating the initial values A_0, B_o, C_o and D_o to be used in the Marquardt's or Newton's parameter estimation techniques for eqn. (31).

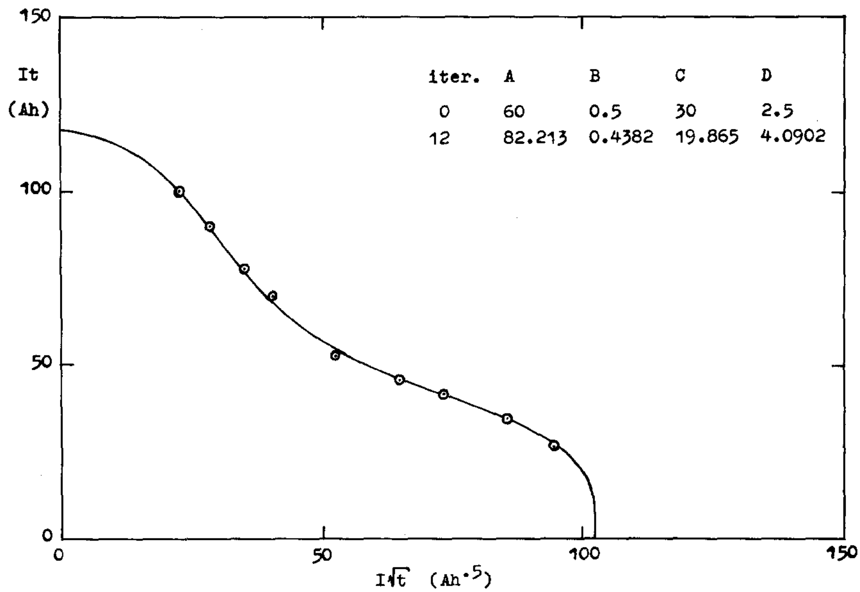

Fig. 5. Capacity It as a function of $I\sqrt{t}$ for a 12 V 100 A h SLI battery. Initial values and best fitting values of the parameters for eqn. (31), obtained at the 12th iteration of the 'damped Newton's' method, are also indicated.

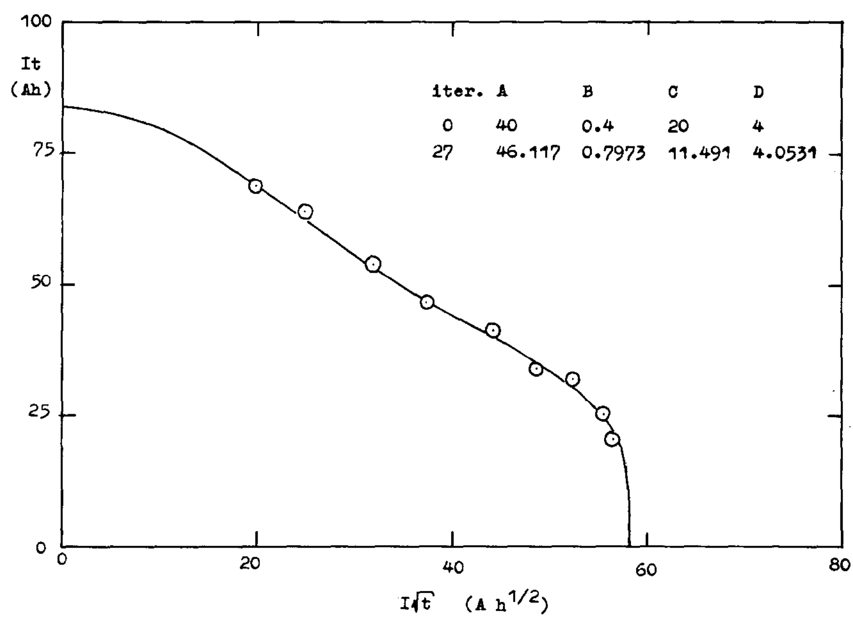

Fig. 6. Capacity It as a function of $I\sqrt{t}$ for a 55 A h stationary cell with multitubular positive plates. Initial values and best fitting values of the parameters for eqn. (31), obtained at the 27th iteration of the 'damped Newton's' method, are also indicated.

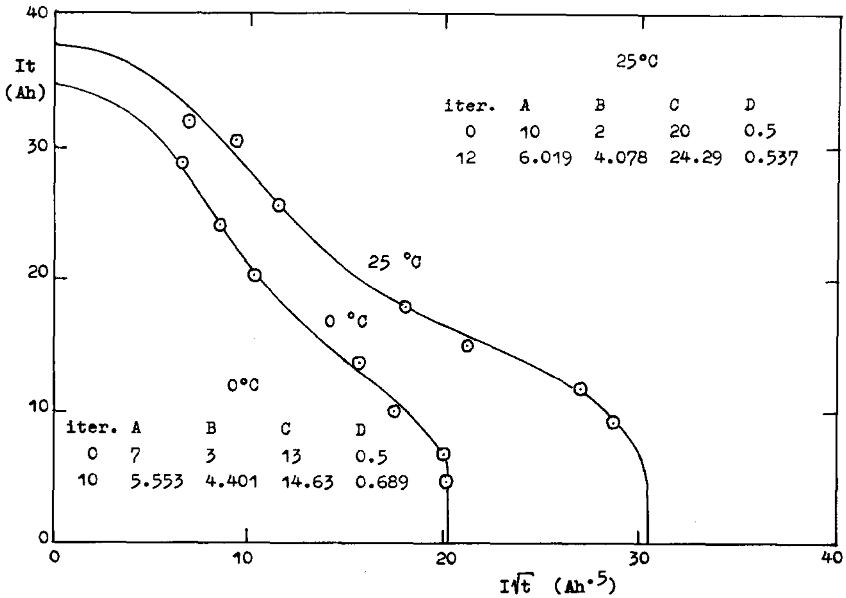

Fig. 7. Capacity It as a function of $I\sqrt{t}$ at 0 °C and 25 °C of a 12 V 30 A h sealed-type battery. Initial values and best fitting values of the parameters used for eqn. (31), obtained at the 12th iteration, are also indicated.

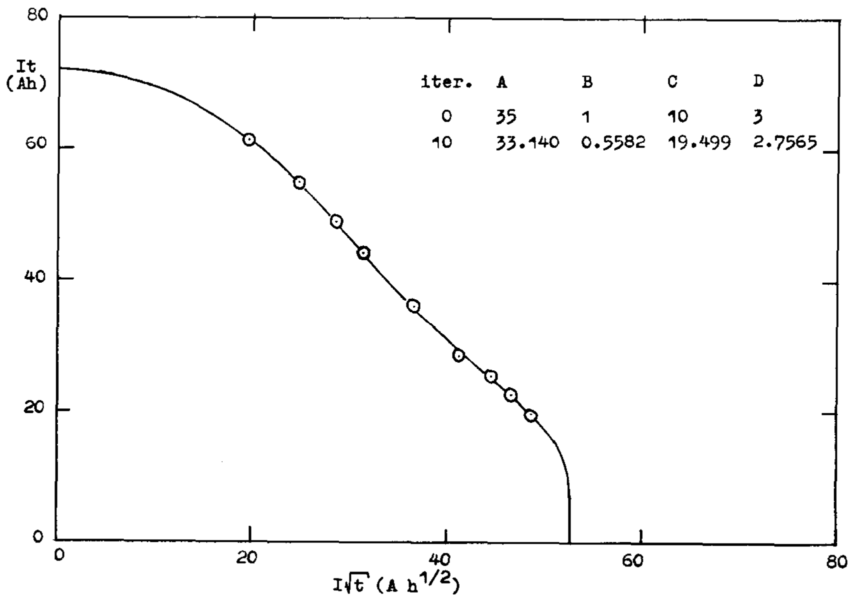

Fig. 8. Capacity It as a function of $I\sqrt{t}$ of a traction-type cell. Initial values and best fitting values of the parameters for eqn. (31), obtained at the 10th iteration of the 'damped Newton's' method, are also indicated.

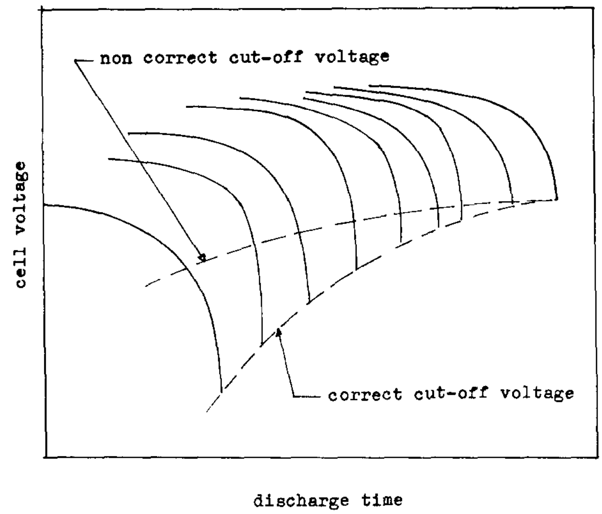

Fig. 9. Correct and non-correct cut-off voltages used for evaluating the transition times and limiting capacity of a lead/acid cell (immobilized electrolyte type).

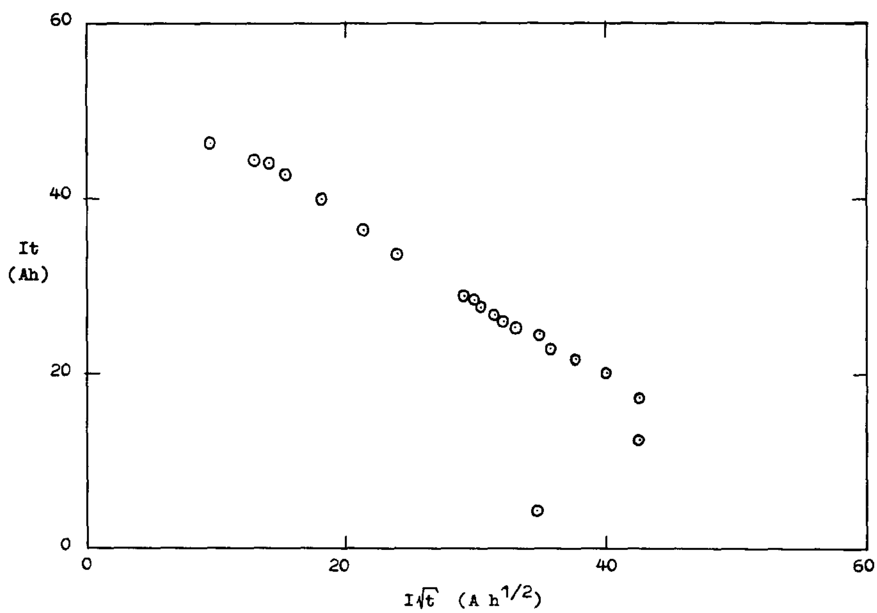

Fig. 10. Consequences on the It vs. $I\sqrt{t}$ profile of a non-correct choice of the cut-off voltage at high discharge rates for a sealed, maintenance-free lead/acid cell.

initially fully-charged cell. The cut-off voltage corresponding to the transition times t that are evaluated in order to obtain the limiting capacity $C_L = I_L t$ must be chosen carefully for each discharge curve (see Fig. 9) in the region of vertical descent of the voltage curve. An incorrect choice of the cut-off voltage, especially at high discharge rates, results in an It versus $I\sqrt{t}$ plot of the type illustrated in Fig. 10.

9. Possible uses of the new equation

(a) Obviously, the new equation can be used instead of the Peukert or Liebenow equations to describe the limiting capacity of a lead/acid cell when a better accuracy is required over a more extended range of discharge rates.

(b) As has been shown, a physical meaning can be assigned to the parameters A, B, C, and D. This allows the possibility of studying the influence of the involved quantities on the cell performance. For example, $C_{max} = AB + CD = c_0 nFSL$ is independent of diffusion coefficients and therefore is independent of temperature, while $I\sqrt{t}_{max} = A + C = C_{max}\sqrt{\pi}(\sqrt{D_1} + \sqrt{D_2})/2L$ is proportional to the square roots of D_1 and D_2. In effect, as shown by Fig. 7, C_{max} is almost independent of temperature whereas

$$I\sqrt{t}_{max,\ 0\ °C}/I\sqrt{t}_{max,\ 25\ °C} \simeq 2/3$$

which is very near to the concentration independent ratio $\sqrt{D_{0\ °C}}/\sqrt{D_{25\ °C}} = \sqrt{1/2}$ for sulfuric acid [17].

Another example: the formal property concerning the 'geometric partition coefficient' k suggests an investigation into the real existence of an optimum value of plate distance (pitch) for maximum capacity (see Fig. 11). Such a possibility has been predicted by Micka and Rousar on the basis of a theoretical model of the lead/acid cell [18].

(c) The battery system as a whole cannot be considered as a linear system. However, the concentrations of the reactants obey a linear diffusion equation. Therefore the proposed equation can be included in a mathematical model where the linearity of the diffusion mechanism is used for predicting the concentration polarization response to a step-varying discharge-current profile I_1 until time t_1, I_2 until time t_2, ... I_n until time t_n.

The cell voltage during step n is given by:

$$V_n = V_0 - (1/\alpha)\ \ln(I_n) + (\alpha/\beta)\ \ln(OX_n) - RI_n \tag{39}$$

where V_0, α, β and R are constant parameters which can be evaluated as shown elsewhere [19] and OX_n is given in terms of a convolution summation [20]:

$$OX_n = 1 - \sum_{i=1}^{n} \frac{I_i - I_{i-1}}{I_L(t_n - t_{i-1})} \tag{40}$$

where for $I_L(t)$, the expression derived from eqn. (31):

$$I_L(t) = [A\ \tanh(B/\sqrt{t}) + C\ \tanh(D/\sqrt{t})]/\sqrt{t} \tag{41}$$

can be profitably used.

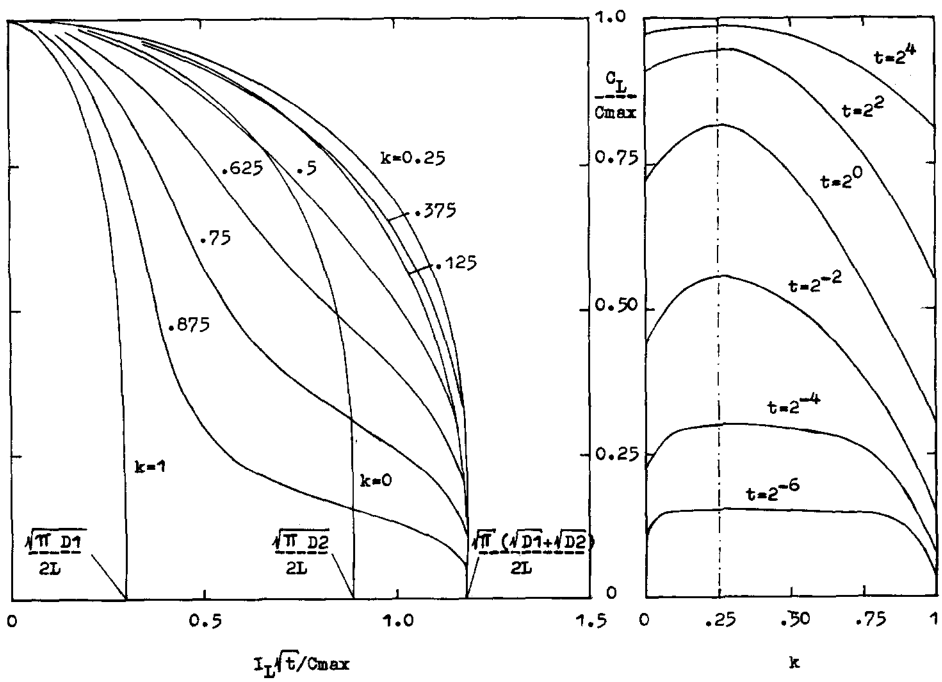

Fig. 11. C_L/C_{max} vs. $I_L\sqrt{t}/C_{max}$ for different values of k, and C_L/C_{max} vs. k for different values of t according to the approximate solution for the exemplifying case $D_1=1/9$, $D_2=1$, $L=1$.

10. Conclusions

The proposed new equation contains four parameters which must be determined through a much more sophisticated technique than the simple log–log plot required by the Peukert equation.

Notwithstanding this drawback (which can hardly be called so when the present availability of effective algorithms and high speed computers is considered), the new equation offers the advantage of a better fit over a wider range of discharge rates and, possibly, a chance to understand the mechanisms better and to improve the performance of the lead/acid cell.

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