THE INFLUENCE OF MASS TRANSPORT PROCESSES ON THE PERFORMANCE OF THE LEAD–ACID CELL ON PULSED DISCHARGE

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Summary

The effect of pulsed current discharge on lead–acid cell capacity has been examined in the light of the diffusive mass transport limitation of electrolyte to the reaction interface. It is shown that the capacity of a cell on pulsed discharge is expected to be identical with the capacity of the same cell subjected to constant current discharge. This prediction, which arises because the time scale of controller pulses is much shorter than that of diffusion relaxation, is largely supported by data reported in the literature.

It has also been shown that cells subjected to pulsed discharge (pulse width δ, repetition time T) will experience heating effects which are increased by a factor of T/δ over cells discharged at the same mean constant current. In order to preserve cycle life it is recommended that cell cooling be optimized and some capacity be sacrificed to ensure that the cell is not overdischarged.

Introduction

In a previous paper [1] it was shown that electrolyte transport processes exercise a significant influence on the capacity available from a charged lead–acid cell. At low rates ($<C/2.5$) the capacity is limited by acid depletion, and the time of discharge, T, is inversely proportional to the current density, I, while at high rates ($>C/2.5$) the capacity is limited by diffusion in the liquid phase and T is inversely proportional to I^2.

These considerations pertain to the case of a cell undergoing discharge at constant current, but in practice lead–acid batteries are seldom employed in such a well regulated fashion. In the starting, lighting and ignition task, the pattern of current drain is dominated by a heavy discharge of (preferably) short duration at intervals, separated by periods of low current drain or recharge. For motive power use there is great interest in the control of motor speed by chopper systems [2] in which current withdrawal is pulsed at a high frequency.

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The present short paper applies an analytical procedure, similar to that developed previously, to examine the influence of limiting transport processes on the capacity of a cell discharged under pulsed current conditions.

The model

As in the previous analysis [1] the porous electrode is treated as a macrohomogeneous structure in which the physical properties only change in the direction normal to the electrode surface.

The rates of discharge appropriate for electric vehicle operation lie in the range treated as high rate discharge [1] for which liquid phase diffusion processes were found to be exercising control, and the following treatment investigates the effect of pulsed discharge on the available capacity in this regime.

The basic diffusion/migration mass balance equation can be reduced to:

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

which describes the mass transport in response to the consumption of material at the electrode. Under chopper control [2] the battery experiences short pulses of current drain corresponding to $f \cdot I_{pk}$, where the wave-form (f) is shown in Fig. 1, and δ denotes the pulse width and T is the repetition time. Hence, a duty cycle may be defined, $R = \delta/T$, which is the fraction of the time that current is being drawn from the cell.

Equation (1) can be rewritten as

$$\frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial y^2} \quad \text{where } y = \frac{x}{\sqrt{D}}.$$

Taking Laplace transforms [3] of this with respect to time

$$S\bar{c} - c_\infty = \frac{\partial^2 \bar{c}}{\partial y^2}$$

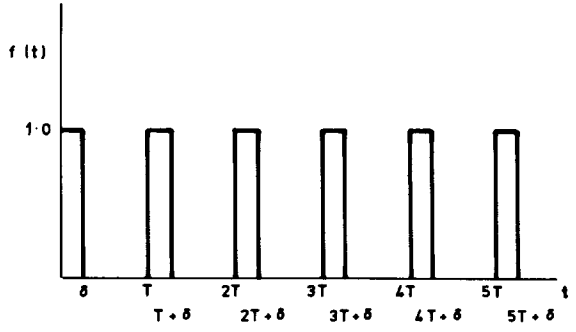

Fig. 1. Schematic representation of pulsed current wave form. δ is the pulse width and T is the repetition time.

where S is the Laplace time variable and c_∞ is the initial uniform acid concentration.

Taking the distance transform of this

$$S\bar{\bar{c}} - \frac{c_\infty}{\sigma} = \sigma^2\bar{\bar{c}} - \sigma\bar{c}_0 - \bar{c}_0'$$

where σ is the Laplace distance variable, $\bar{c}_0 = \mathcal{L}^t_{c_0}$, the surface concentration and $\bar{c}_0' = \mathcal{L}^t(\partial c/\partial y)_0$, the surface flux.

On rearrangement,

$$\bar{\bar{c}} = \frac{\sigma\bar{c}_0}{(\sigma^2 - s)} + \frac{\bar{c}_0'}{(\sigma^2 - s)} - \frac{c_\infty}{\sigma(\sigma^2 - s)}$$

where $\bar{c}_0' = \mathcal{L}^t(\partial c/\partial y)_0 = \mathcal{L}^t_{j \cdot f_{\text{pulse}}}$ (see Fig. 1), and j is the peak value of $(\partial c/\partial y)_0$, which is related to the current density I_{pk} by

$$\frac{I_{\text{pk}}}{nF} = D\left(\frac{\partial c}{\partial x}\right)_0^{\text{pk}} = \sqrt{D}\left(\frac{\partial c}{\partial y}\right)_0 = \sqrt{D}j$$

or

$$j = I_{\text{pk}}/nF\sqrt{D}.$$

$$\text{So } \mathcal{L}^t_{j \cdot f} = \int_0^\infty e^{-st} j \cdot f\,dt = \left\{ \int_0^\delta e^{-st}dt + \int_T^{T+\delta} e^{-st}dt \ldots + \int_{nT}^{nT+\delta} e^{-st}dt \ldots \right\} j$$

$$= j\sum_0^\infty \left\{ \int_{nT}^{nT+\delta} e^{-st}dt = -j \sum_0^\infty \frac{[e^{-st}]_{nT}^{nT+\delta}}{s} \right. \quad nT$$

$$= \frac{-j}{s} \sum_0^\infty \left\{ e^{-snT}e^{-\delta s} - e^{-snT} \right\} = \frac{j}{s}(1 - e^{-\delta s}) \sum_0^\infty e^{-snT}$$

$$= \frac{j(1 - e^{-\delta s})}{s(1 - e^{-sT})}$$

since if $e^{-sT} = x$, then $\sum_0^\infty x^n = 1 + x + x^2 \ldots = (1 - x)^{-1}$ for $-1 < x < +1$.

Thus

$$\bar{\bar{c}} = \frac{\sigma\bar{c}_0}{(\sigma^2 - s)} + \frac{j(1 - e^{-\delta s})}{s(\sigma^2 - s)(1 - e^{-sT})} - \frac{c_\infty}{\sigma(\sigma^2 - s)}.$$

Inverting the distance transform gives

$$\bar{c} = \bar{c}_0 \cosh(\sqrt{s}y) + \frac{j}{s\sqrt{s}} \frac{\sinh(\sqrt{s}y) \cdot (1 - e^{-\delta s})}{(1 - e^{-sT})} + \frac{c_\infty}{s} - \frac{c_\infty}{s}\cosh(\sqrt{s}y).$$

Now since $\bar{c}$ does not $\to \infty$, as $y \to \infty$, all the coefficients of $e\sqrt{s}y$ contained in cosh and sinh terms must sum to zero.
Thus

$$\bar{c}_0 + \frac{j(1 - e^{-\delta s})}{s\sqrt{s}(1 - e^{-sT})} - \frac{c_\infty}{s} = 0.$$

Also δ and T will be small ($\leqslant$10 ms) [4], especially when compared with the total discharge time ($\sim$1 h) represented by s.
Thus

$$(1 - e^{-\delta s}) \sim (1 - 1 + \delta s) = \delta s$$

and

$$(1 - e^{-sT})^{-1} \sim (1 - 1 + sT)^{-1} = \frac{1}{sT}$$

so that

$$\frac{j(1 - e^{-\delta s})}{s\sqrt{s}(1 - e^{-sT})} \sim \frac{j}{s\sqrt{s}} \frac{\delta}{T} = \frac{jR}{s\sqrt{s}}$$

where R, the duty cycle = δ/T.
So

$$\bar{c}_0 = \frac{c_\infty}{s} - \frac{jR}{s\sqrt{s}}.$$

Inverting the time transform gives

$$c_0 = c_\infty - 2jR\sqrt{\frac{t}{\pi}}.$$

The condition for termination of discharge is $c_0 = 0$ at $t = \mathrm{T}$ [1].
Thus

$$c_\infty = 2jR\sqrt{\frac{\mathrm{T}}{\pi}}$$

As $j = \dfrac{I_{\mathrm{pk}}}{nF\sqrt{D}}$

then

$$\frac{c_\infty nF\sqrt{D\pi}}{2} = RI_{\mathrm{pk}}\sqrt{\mathrm{T}} = \bar{I}\sqrt{\mathrm{T}},$$

where $\bar{I}$ is the mean current, $\dfrac{\delta}{T} \cdot I_{\mathrm{pk}}$.

For continuous discharge under constant current density, I, the corresponding eqn. (1) at $t = \mathrm{T}'$ is

$$\frac{c_\infty nF\sqrt{D\pi}}{G} = I\sqrt{\mathrm{T}'}$$

where $G = G_+ + G_- = 2$, since $G_+ = 3 - 2t_+$, $G_- = 2t_+ - 1$ and t_+ = transport number for H_3O^+.
Hence

$$I\sqrt{T'} = \frac{c_\infty nF\sqrt{D\pi}}{2}$$

and the ratio of discharge capacities is

$$\frac{\bar{I}\cdot T}{IT'} = \frac{I}{\bar{I}} .$$

In other words, when a battery is pulse discharged with a peak current density I_{pk} then it will give the same capacity as if it were discharged at a constant current density, I, given by

$$I = \delta/TI_{pk} = \bar{I}.$$

Basically, the concentration depletion produced in the "on" part of the the cycle is relaxing to some extent during the "off" part (see Fig. 2). The pulse time durations are so short compared with the coarse time scale of the battery discharge time, that the average current and electrolyte depletions will look the same as in the continuous case.

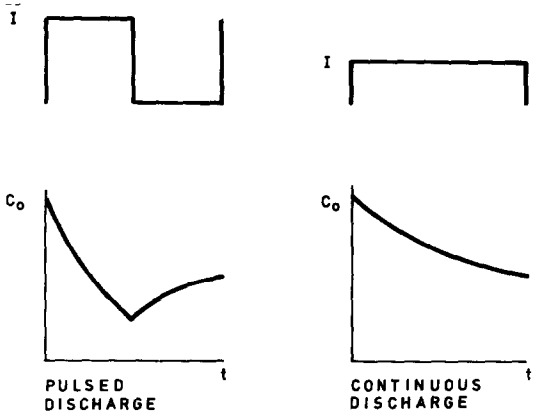

Fig. 2. Schematic representations of responses of current and surface concentration to pulsed and continuous discharge, respectively.

The conclusion that the battery capacity is unchanged whether discharge is pulsed or constant is supported by data in the literature [5, 6]. Curves for capacities of various frequencies and mark/space ratios plotted against mean current [5] are all bunched together (see Fig. 3), showing the expected lack of difference in capacity between pulsed and constant discharge. However, as illustrated in Fig. 4, the choice of end of discharge voltage is very important in the comparison between pulsed and continuous discharge capacities. As far as the Laplace transform method used here is

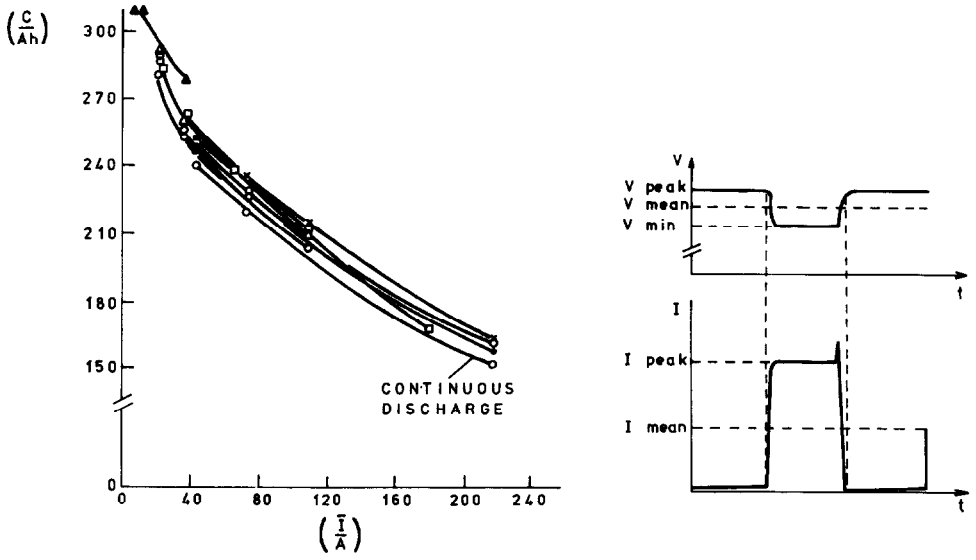

Fig. 3. Variation of cell capacity with mean current for V_{mean} cut-off condition, at a variety of duty cycles. Data taken from ref. 5.

Fig. 4. Effect of pulsed current on cell voltage.

concerned, the time scale is that of the total battery discharge, so that the appropriate condition is when V_{mean} reaches the predetermined end voltage. But the life of the battery may well be endangered by applying this end voltage in practice. When V_{mean} is at the end voltage (equivalent to $c_0 = 0$), V_{min} may well have dropped to quite a low value. It is well known [7] that if the voltage of a cell is allowed to fall too low (*e.g.*, below 1.75 for a 5 h rate discharge or pulsed equivalent), then the cycle life drops dramatically. The reason for this is that in order to maintain the passage of current after $c_0 = 0$, other electrode processes will take over at these lower potentials and it is the effect of these processes that can damage the battery. For this reason consideration should be given to the use of V_{min} reaching the cut-off voltage as the termination of discharge criterion, particularly for multi-cell batteries. Figure 5 shows the effect that this has on cell capacity as a function of discharge current and duty cycle. This Figure presents the V_{min} data from ref. 5 plotted against I_{mean} instead of against I_{peak}.

At high rates, and duty cycles of 0.5 or less, the capacity available is somewhat reduced. In effect, although the capacity available in pulsed discharge is the same as for continuous discharge, a portion of that capacity must be sacrificed in order to preserve the battery's life. In addition, though, it is well known that high current density discharge reduces cell cycle life, due to local conditions on a microscopic scale in the battery plates being significantly perturbed from a reversible situation. Super-saturation and other changes in electrolyte composition can lead to active material migration and

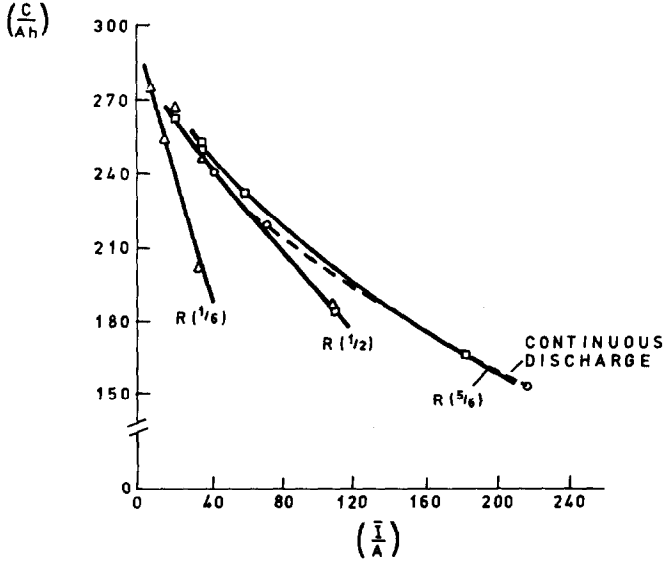

Fig. 5. Variation of cell capacity with mean current for V_{min} cut-off condition at 3 values of duty cycle (R). Data taken from ref. 5.

a change of morphology, resulting in capacity loss. Thus it is expected that the intrinsically higher instantaneous current densities found in chopper control systems will cause some unavoidable reduction in battery cycle life from that expected with constant current discharge. This situation, therefore, presents a challenge to electric vehicle control gear designers to devise a motor circuit that draws a steadier current from the battery.

Temperature rise

Although the discharge capacity remains essentially unaltered in pulsed discharge, the heat output will increase. If R' is the cell resistance, then the heat dissipated under continuous discharge will be

$$\Delta H_{cont} = I^2 R'.$$

Under pulsed discharge the heat generated will be

$$\Delta H_{pulse} = I_{pk}^2 R' \cdot \frac{\delta}{T}.$$

If $I = \delta(I_{pk}/T) = \bar{I}$; that is the same mean current is being used in the pulsed case, then this latter will produce more heat by a factor

$$\frac{\Delta H_{pulse}}{\Delta H_{cont}} = \frac{T}{\delta}.$$

This additional heating, which has been observed in practice [5], will lead to faster grid corrosion and thus to shorter cell life.

Conclusions

Consideration of the effects of the diffusional/migration limitation on electrolyte mass transport leads to the conclusion that, at a given mean current, pulsed discharge produces the same cell capacity as continuous discharge to the $V_{mean} = V_{cut\text{-}off}$ end of discharge condition. As a consequence of this result it should be possible to predict the capacity of a battery which is to be pulsed discharged at a peak current density of I_{pk} on the basis of a continuous discharge at a constant current density of I, where I is given by $I_{pk}\delta/T$. Practical evidence in the literature is in agreement with these conclusions.

The use of the $V_{mean} = V_{cut\text{-}off}$ end voltage may result in reduced cycle life so it is recommended that a $V_{min} = V_{cut\text{-}off}$ condition should be used for pulsed discharge of batteries even though this will lead to a reduction in capacity by comparison with continuous discharge.

Increased heat output can be expected on pulsed discharge and improved battery cooling will be required in order to minimize grid corrosion.

Acknowledgement

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List of symbols

c	Electrolyte concentration (mole cm^{-3})
c_0	Electrolyte concentration at electrode surface
c_∞	Initial uniform acid concentration
D	Diffusion coefficient ($cm^2\ s^{-1}$)
δ	Duration of current pulse (s)
F	The Faraday
ΔH_{cont}	Heat generated during continuous discharge
ΔH_{pulse}	Heat generated during pulsed discharge
I	Constant current density during continuous discharge (A cm^{-2})
I_{pk}	Peak current density during pulsed discharge
$\bar{I}$	Mean current density of pulsed discharge = RI_{pk}
j	Normalized peak current density value = $I_{pk}/nF\sqrt{D}$
n	Number of electrons consumed or released in an electrochemical reaction
R	Duty cycle of current pulsation

R'	Cell resistance (Ω)
s	Laplace transformed time variable
σ	Laplace transformed distance variable
T	Pulsed current discharge time
T'	Constant current discharge time
t	Time (s)
T	Repetition time of current pulse (s)
V_{mean}	Mean cell voltage during a pulsed discharge cycle (V)
V_{min}	Minimum cell voltage during a pulsed discharge cycle
x	Distance perpendicular to a plane electrode surface (cm)
y	Normalized distance variable $x/\sqrt{D}$

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