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# DISCHARGE CHARACTERISATION OF LEAD/ACID BATTERIES

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## Introduction

One of the common problems existing in lead/acid battery development is the lack of accurate mathematical formulae for the characterisation and testing of battery prototypes. The existing methods are difficult and their accuracy is doubtful because the capacity of a battery depends not only on its design, material composition and geometry, but also on the discharge current, ageing effects, temperature and cut-off voltage. The service history of the battery, at least the last charge, discharge and the stand time, greatly influence the capacity.

Several authors have devised empirical equations showing the dependence of capacity on the discharge current, $I$, and the discharge time, $t$ [1 - 4]. Despite these attempts, only Peukert's equation [1] has found wide application

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

where $n$ and $C$ are constants, determined from discharge data. Equation (1) is valid only as an interpolation formula within the range $n \sim 1.3 - 1.4$ for intermediate currents [5].

The chief inadequacies of Peukert's equation are:

(i) temperature effects are not considered;

(ii) capacities are estimated only for interpolated values of the discharge currents, *i.e.*, only those discharge rates that have values between the two rates used to determine $n$ give reliable predictions for the capacity value [5];

(iii) the accuracy decreases drastically at both low and high discharge rates, predicting capacities well above those experimentally obtainable at large currents and infinite capacity at zero current [6].

This work presents results of a research programme aimed to overcome the deficiencies of Peukert's equation and the general lack of accurate mathematical formulae for adequately characterising lead/acid battery performance. The programme has covered a wide range of product types and diverse operational parameters and has allowed the formulation of a new and improved relationship for predicting battery capacity.

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## Theoretical background

### *Battery equation*

The discharge rate most commonly used in the industry to characterise automotive (SLI) batteries is the 20-h rate. Under this condition, the capacity (usually denoted as $C_{20}$) is obtained from the battery at a constant current such that a specified minimum voltage is reached in precisely 20 h. The capacity at other rates of discharge can be interpreted as a function of the discharge current, $I_x$, as follows:

$$C_x = C_{20} - f(I_x) \tag{2}$$

The function $f(I_x)$ can be regarded as a rate-dependent capacity decrement. For a battery of a given $C_{20}$ capacity, this decrement is found to be proportional to the logarithm of the discharge current, $I_x$, *i.e.*,

$$f(I_x) \propto \mathrm{Log}(I_x) \tag{3}$$

or

$$f(I_x) = K\,\mathrm{Log}(I_x) \tag{4}$$

Substituting eqn. (4) in eqn. (2) yields:

$$C_x = C_{20} - K\,\mathrm{Log}(I_x) \tag{5}$$

The value of the constant $K$ in eqn. (5) is associated with the absolute value of $C_{20}$ for a particular battery. The basic characteristics of $K$ have been experimentally ascertained to be as follows:

(i) for the same temperature and same reference capacity, $K$ is constant;

(ii) for the same discharge rate and reference capacity, $K$ is an inverse function of temperature;

(iii) at constant temperature, $K$ is a direct function of the reference capacity and internal resistance of the battery.

Equation (5) can be made universal by normalisation with respect to the relative capacity and corresponding discharge rate, *i.e.*,

$$\frac{C_x}{C_{20}} = 1 - K\,\mathrm{Log}(L)$$

or

$$C_x = C_{20}[1 - K\,\mathrm{Log}(I_x/I_{20})] \tag{6}$$

where $C_x/C_{20}$ is the relative capacity and $L$ is the relative discharge rate $(=I_x/I_{20})$, *i.e.*, the load factor.

Though accurate enough for predicting capacities at a fixed temperature (normally 25 °C) and as an extrapolation formula at both high and low rates of discharge, eqn. (6) still retains some deficiencies, namely,

(i) infinite capacity is predicted at zero discharge rate;

(ii) capacity cannot be determined at different temperatures;

(iii) changing the reference capacity (*e.g.*, $C_5$ for $C_{20}$), the calculated capacity at an absolute discharge rate, $I_x$, is found to differ, even when the relative discharge rate (*i.e.*, $I_x/I_5$) appropriate to the new reference capacity ($C_5$) is used.

Problem (i) can be immediately overcome by giving a non-zero limit to the value inside the logarithmic parentheses. That is,

$$C_x = C_{20}\left[1 - K\ \mathrm{Log}\left(\frac{I_x + I_f}{I_f}\right)\right] \tag{7}$$

where $I_f$ is the value of the current that gives the maximum possible capacity of the battery, namely its Faradaic capacity, $C_f$. This is the capacity delivered on the complete utilisation of the active materials in the capacity-limiting plate or the electrolyte. It is independent of temperature. In a given electrochemical reaction, a change in valency by $z$ produces exactly $zF$ coulombs for one mole of reactant, where $F = 1$ Faraday = 96 487.3 C = 26.8 A h. This relationship is used to determine the Faradaic capacity, expressed in A h, that a known weight of active materials can theoretically deliver. The Faradaic capacity does not depend on the inner structure of the masses or the outer discharge parameters. Thus, it is possible to calculate the value of a fixed and temperature-independent reference capacity without performing a discharge.

Since:

$$C_f = C_{20}\left[1 - K\ \mathrm{Log}\left(\frac{I_f}{I_{20}}\right)\right] \tag{8}$$

Solving for $I_f$:

$$I_f = I_{20}\ 10^{[(1 - C_f/C_{20})/K]}$$

$I_f$, the Faradaic rate, is constant at a fixed temperature, $\theta$. Thus,

$$C_x = C_{20}\left[1 - K\ \mathrm{Log}\left\{\left(\frac{I_x + I_f}{I_{20}}\right)\right\}\right] \tag{10}$$

Problem (ii) exists because of the presence of three temperature-dependent terms in eqn. (6), namely, $K$, $I_{20}$ and (hence) $C_{20}$. Though the temperature variation of $C_{20}$ can be taken to be ~1% per °C in the temperature range 15 - 25 °C, the temperature variation of $K$ is more intricate — an inverse relationship exists. Since contributing terms vary differently with temperature, it was decided to minimise the number of these terms.

Problem (iii) arises because on changing the reference capacity, the corresponding change in $K$ has not been considered.

The logical way to circumvent these last two problems is to find a reference capacity that is independent of temperature, or to ascertain the temperature dependence of $K$ and incorporate it in eqn. (10), or both.

*Temperature and reference capacity dependence of K*

The relation between $K^{\theta}$, *i.e.*, the temperature-dependent expression for $K$, and the reference capacity is determined as follows. On short-circuiting the battery terminals, the terminal voltage instantly falls to zero. In other words, the useful capacity of the battery is zero. Using this argument in eqn. (10):

$$\left[1 - K^{\theta}\,\mathrm{Log}\left(\frac{I_{sc} + I_f}{I_{20}^{\theta}}\right)\right] C_{20} = 0 \qquad (11)$$

where $I_{sc}$ is the short-circuit current.
Neglecting $I_f$, because $I_{sc} \gg I_f$, yields:

$$K^{\theta} = 1/\mathrm{Log}(I_{sc}/I_{20}^{\theta}) \qquad (12)$$

If $V_0^{\theta}$ is the voltage intercept at zero discharge current obtained from a linear extrapolation of the discharge $V$–$I$ characteristic of the battery at a given temperature $\theta$ (typically 12 V for a nominal 12 V battery) then:

$$I_{sc} = V_0^{\theta}/r_i^{\theta} \qquad (13)$$

where $r_i^{\theta}$ is the internal resistance of the battery defined as equal to $-\partial V/\partial I$, the slope of the $V$–$I$ curve above.
Thus, combining eqns. (12) and (13) gives:

$$K^{\theta} = 1/\mathrm{Log}(V_0^{\theta}/r_i^{\theta} I_{20}^{\theta}) \qquad (14)$$

For a particular battery type and a given temperature, $r_i$ is constant. Thus, the value of $K^{\theta}$ for a temperature $\theta$ is a direct function of the reference current ($I_{20}$ in eqn. (10)) and, hence, the reference capacity. Thus, the notation for $K^{\theta}$ can be modified to $K_{ref}^{\theta}$, where ref stands for the time rate (in h) corresponding to the reference capacity $C_{ref}^{\theta}$, and $I_{ref}^{\theta}$. Hence,

$$K_{ref}^{\theta} = 1/\mathrm{Log}(V_0^{\theta}/r_i^{\theta} I_{ref}^{\theta}) \qquad (15)$$

To change the reference capacity in eqn. (10) the corresponding $K$ value must be calculated using the appropriate value of $I_{ref}^{\theta}$ in eqn. (15). Accordingly, the latter gives the temperature dependence of $K$, because $r_i^{\theta}$ and $V_0^{\theta}$ are functions of temperature. Equation (10) now becomes:

$$C_x^{\theta} = C_{20}^{\theta}\left[1 - K_{20}^{\theta}\,\mathrm{Log}\left\{\left(\frac{I_x^{\theta} + I_f}{I_{20}^{\theta}}\right)\right\}\right] \qquad (16)$$

By using $C_f$ instead of $C_{20}^{\theta}$ (and hence $I_f$ instead of $I_{20}^{\theta}$) in eqn. (16), the latter achieves a higher degree of universality because $C_f$ is independent of temperature, discharge current, etc. Therefore:

$$C_x^{\theta} = C_f\left[1 - K_f^{\theta}\,\mathrm{Log}\left(\frac{I_x^{\theta} + I_f}{I_f}\right)\right] \qquad (17)$$

$I_f$ is calculated from eqn. (9) and the value is used in eqn. (15) to obtain $K_f$.

Equation (15) is also used for calculating the value of $K$ for a reference current of $I^{\theta}_{\text{ref1}}$, the discharge rate corresponding to ref 1 (in h), at the same temperature $\theta$ as follows

$$K^{\theta}_{\text{ref1}} = 1/\text{Log}(V^{\theta}_{0}/r^{\theta}_{i} I^{\theta}_{\text{ref1}}) \tag{18}$$

Solving eqns. (15) and (18) simultaneously and simplifying:

$$\frac{1}{K^{\theta}_{\text{ref1}}} - \frac{1}{K_{f}} = \text{Log}\left(\frac{I_{f}}{I^{\theta}_{\text{ref1}}}\right) \tag{19}$$

*Estimation of capacity from time rate*

It is sometimes more convenient to calculate the capacity of a battery for a given discharge time rather than for a given discharge current. The relationship between discharge time and the expected capacity of the battery is found by modifying eqn. (17). As the temperature is constant the superscript $\theta$ is omitted.

Since $C = I/T$,

$$C_{x} = C_{\text{ref}}\left\{1 - K_{\text{ref}}\,\text{Log}\left(\frac{C_{x}}{T_{x}} \cdot \frac{T_{\text{ref}}}{C_{\text{ref}}}\right)\right\} \tag{20}$$

where $C_x$ and $C_{\text{ref}}$ are the two capacities for discharge times $T_x$ and $T_{\text{ref}}$, respectively.

With $C_x/C_{\text{ref}} = P$, eqn. (20) becomes:

$$P + K_{\text{ref}}\,\text{Log}(P) = 1 + \text{Log}\left(\frac{T_{\text{ref}}}{T_{x}}\right) \tag{21}$$

To estimate the unknown capacity at a time rate $T_x$, eqn. (21) is solved for $P$. Since this involves $P$ as an inseparable variable, Log($P$) has to be simplified to a first approximation. In this paper, the calculations are accurate and are made possible by using a mathematical computing package called The TK! Solver©*.

*Cut-off voltage equation*

The 'final' or 'cut-off' voltage, $V_{co}$, is the terminal closed-circuit voltage at which it is desirable to stop the discharge. The value of the cut-off voltage varies for different workers and has not been standardised, except by general usage [5, 6]. Without any definite specifications, the shape of the discharge curve generally determines the cut-off voltage. The end of discharge is usually at the knee of the voltage *versus* time curve. The capacity obtained beyond this point is small, and it is not economical to discharge the battery any further. The cut-off voltage is correspondingly lower for higher discharge rates. This is because of the increased voltage drop through

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the battery and the increased degree of plate polarisation. In the present investigation, the 'knee' has been taken as the point where the slope of the voltage–time trace of the discharge becomes equal to 10 times that of the plateau slope. The plateau is the nearly horizontal section of the trace in the initial stages of the discharge.

To achieve a relation between the discharge current and the cut-off voltage, various batteries have been discharged at different rates and their discharge *versus* time curves plotted. The method discussed above has been used to determine the cut-off point. On examining these values against the discharge current, it was found that a linear relationship existed between the two variables. Regression analysis of these variables produced the following equation

$$V_{co} = 10.85 - 0.045L \tag{22}$$

This equation adequately reflects the data of batteries having $K_{20}^{25}$ between 0.36 and 0.40. The exact relationship between $K$ and the slope of eqn. (22) is yet to be ascertained and will be published when available. The slope increases with increasing values of $K$, *i.e.*, with increasing values of the internal resistance and the discharge current. The main deficiency of eqn. (22) is that it is not universal for all batteries and depends upon the choice of the reference current in $L$. However, in the practical range of discharges, *i.e.*, $1 \leqslant L \leqslant 100$, this equation gives satisfactory values of $V_{co}$, that agree with those usually considered for experimental purposes.

## Experimental

To check the validity of the above equations, spot discharges were performed on a typical SLI battery (PS15) at temperatures ranging from −18 to 60 °C and currents from 100 to 1000 A. A Rikadenki R-series multipen recorder was used to plot the current and voltage. Table 1 gives the values of $K$ and $r_i$, as calculated from the experimental data, together with the predicted 20 h rates at the temperatures under discussion.

For characterisation purposes, the battery was discharged at specified temperatures at a constant rate of 25 A using a Thorn-EMI constant-current discharge unit. The temperature of the middle cell of the battery pack

TABLE 1

Spot discharges of PS15 batteries

| Temperature, $\theta$ (°C) | $V_0^\theta$ (V) | $r_i^\theta$ (mΩ) | $K_{20}^\theta$ | $C_{20}^\theta$ (A h) |
|---|---|---|---|---|
| −18 | 11.96 | 8.32 | 0.382 | 69 |
| 0 | 12.15 | 5.66 | 0.374 | 91 |
| 25 | 12.21 | 5.02 | 0.377 | 108 |
| 43 | 12.25 | 4.58 | 0.376 | 117 |
| 57 | 12.33 | 4.62 | 0.377 | 119 |

TABLE 2

Estimated capacities (A h) of a PS15 battery

| Discharge rate (A) | Temperature (°C) | | | | |
|---|---|---|---|---|---|
| | −18 | 0 | 25 | 43 | 57 |
| 5 | 65 | 89 | 109 | 120 | 122 |
| 10 | 57 | 79 | 97 | 106 | 109 |
| 25[a] | 47[a] | 66[a] | 81[a] | 89[a] | 91[a] |
| 50 | 39 | 55 | 69 | 76 | 77 |
| 75 | 34 | 49 | 62 | 68 | 69 |
| 100 | 31 | 45 | 56 | 62 | 64 |
| 150 | 26 | 39 | 49 | 55 | 56 |
| 200 | 23 | 35 | 44 | 49 | 50 |

[a]Experimental data.

TABLE 3

Capacity comparison[a]

| Battery type | $I$ (A) | Discharge capacity (A h) | | | Battery type | $I$ (A) | Discharge capacity (A h) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | exp. | est. | %$E$[b] | | | exp. | est. | %$E$ |
| PS13 | 5 | 101 | 101 | 0 | KS11 | 25 | 44 | 44 | 0 |
| | 15 | 81 | 83 | −1.9 | | 50 | 35 | 37 | −3 |
| | 50 | 62 | 63 | −0.9 | | | | | |
| | 200 | 40 | 41 | −0.9 | | | | | |
| TJ9 | 25 | 447 | 449 | −0.4 | PE27 | 10 | 194 | 194 | 0 |
| | 75 | 341 | 349 | −1.7 | | 25 | 163 | 163 | 0 |
| | 143 | 304 | 291 | 3 | | 50 | 144 | 139 | 2.6 |
| | 195 | 259 | 262 | −0.6 | | 100 | 117 | 115 | 1 |
| | | | | | | 200 | 99 | 91 | 4 |
| | | | | | | 500 | 63 | 60 | 1.5 |
| DCT13 | 6 | 107 | 111 | −3.5 | KN11 | 2.5 | 40 | 40 | 0 |
| | 25 | 96 | 86 | 9 | | 20 | 27 | 27 | 0 |
| | 50 | 80 | 75 | 4 | | 50 | 21 | 21 | 0 |
| | 100 | 64 | 63 | 1 | | 100 | 17 | 16 | 2.5 |
| | 200 | 48 | 51 | −2.5 | | 200 | 12 | 11 | 2.5 |
| DCT11 | 5 | 91 | 93 | −2 | PS15 | 10(−18) | 56 | 57 | −0.9 |
| | 25 | 71 | 68 | 3 | | 200(−18) | 20 | 23 | −2.8 |
| | 50 | 58 | 57 | 1 | | 10(0) | 80 | 79 | 0.9 |
| | 100 | 48 | 47 | 1 | | 100(43) | 63 | 62 | 0.9 |
| | 200 | 34 | 36 | −2 | | 150(57) | 58 | 56 | 1.9 |

[a]Capacities at 25 °C except for PS15 where temperatures are shown in parentheses.
[b]The %$E$ (percent. error) is calculated relative to the 20-h capacity at 25 °C. The formula used is $\%E = 100(C_{exp} - C_{est})/C_{20}^{25}$ where $C_{exp}$ = measured capacity and $C_{est}$ = capacity determined from eqns. (15) and (16).

TABLE 4

Catalogue specifications of batteries under test[a]

| Battery code | Battery type | Voltage (V) | Number of plates/cell | $C_{20}^{25}$ (A h) | CC (A) |
|---|---|---|---|---|---|
| PS13 | SLI | 12 | 13 | 95 | 450 |
| PS15 | SLI | 12 | 15 | 110 | 510 |
| KS11 | HMF | 12 | 11 | 65 | 420 |
| KN11 | HMF | 12 | 11 | 40 | 350 |
| DCT11 | DCAP | 12 | 11 | 90 | NA |
| DCT13 | DCAP | 12 | 13 | 115 | NA |
| PE27 | SLI | 6 | 27 | 190 | 800 |
| TJ9 | Tr | 2 | 9 | 340 | NA |

[a]SLI = automotive, HMF = hybrid maintenance free, DCAP = deep cycle auxiliary power, Tr = traction, CC = cold crank.

TABLE 5

Experimental summary

| Battery | Temperature (°C) | $r_i^\theta$ (mΩ) | $C_{20}^\theta$ (A h) | $K_{20}^\theta$ |
|---|---|---|---|---|
| PS13 | 25 | 4.96 | 101 | 0.373 |
| PS15 | 25 | 5.02 | 108 | 0.377 |
| KS11 | 25 | 6.61 | 65 | 0.364 |
| KN11 | 25 | 1.19 | 40 | 0.370 |
| DCT11 | 25 | 5.87 | 94 | 0.379 |
| DCT13 | 25 | 2.82 | 114 | 0.348 |
| PE27 | 28 | 4.18 | 195 | 0.405 |
| TJ9 | 28 | 3.44 | 341[a] | 0.458 |

[a]5-h rate.

was recorded with other discharge parameters. The cut-off voltage was determined using eqn. (22) and the capacity obtained was used as a reference for further calculations. The predicted capacities at specified discharge rates and temperatures are given in Table 2.

To test the accuracy of these predictions, discharges were performed for the underlined values in Table 2. These experimental results together with the predicted data are summarised in Table 3, which shows the comparison between the predicted and the experimentally obtained capacities of these batteries. The average difference between the predicted and experimental values is within ±5%.

The results show an excellent agreement between the predicted and experimental values, thereby proving the validity of the proposed equations not only for different discharge rates but also for an appreciable range of temperature. Similar results are obtained when these experiments are repeated on different battery types, ranging from low-capacity automotive to high-capacity traction batteries. Table 4 gives the catalogue specifications of these batteries. Table 5 summarises the characterisation results of these batteries using the proposed equations.

## Conclusions

A new set of equations is formulated to simplify lead/acid battery characterisation. These equations overcome the fundamental limitations of the widely used Peukert equation and give a greater degree of accuracy in predicting the battery capacity for a particular rate and temperature. To get a complete estimate of the battery performance, extensive experimental procedures are not necessary. The active material mass determines the reference capacity, which, with the battery performance constant $K$, predicts the capacities at different rates. The numerical value of this constant gives a good measure of battery capacity reduction at higher discharge rates.

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