

THE INFLUENCE OF PULSED DISCHARGE ON THE CAPACITY OF LEAD/ACID BATTERIES

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Summary

Measurements of the capacity of lead/acid batteries given pulsed and steady discharges show a small enhancement of capacity by pulsing at high discharge rates. A correlation exists, for both present and previous measurements, between enhanced capacity and the slope of the plot of log (discharge current) against log (discharge time) that is characteristic of the batteries being tested. Comparison with theory indicates that pulsing may allow more effective utilisation of battery electrolyte. The results are significant for chopper control of vehicle speed in electric cars.

Introduction

The lead/acid battery, despite its low energy density, remains at present the only practical power source for electric cars [1]. Since the capacity of such batteries is limited, particularly at the high rates of discharge needed for vehicle acceleration, it is important to ensure that the available energy is used efficiently. It is, in particular, important to know whether the square wave discharge of the battery that results from chopper control of vehicle speed has any effect on battery capacity [2]. A typical pulsed discharge occurs at a frequency of several hundred Hz and, as shown in Fig. 1, draws maximum current I_m from the battery during the conduction or mark period M , and zero current during the off or space period S . The average current is I_a and the pulse repetition frequency $f = 1/(M + S)$, where M/S is the mark-space ratio. The voltage V_m that appears across the battery terminals during the conducting interval M is lower than the average voltage V_a . Vehicle speed is controlled by variation of any or all of the quantities M/S , f and I_m .

Storage capacity C during steady discharge at constant current I is $C = It$, where t is the time for battery voltage to reach a set minimum level. The matter of immediate concern is whether storage capacity C' during

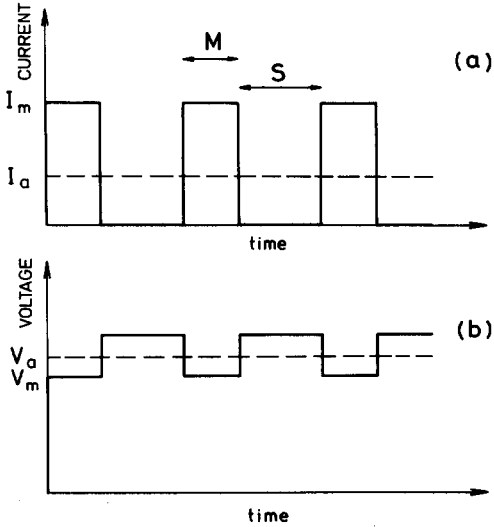


Fig. 1. Idealised waveform of (a) current drawn from battery, (b) voltage across battery, during chopper control.

pulsed discharge is at all different from C in the case where the two values are determined at an equivalent rate of discharge, since capacity is known to decrease with increase of output current. Problems arise from the way in which $C' = I't'$ is determined. The value of I' may be expressed in terms of the mark current as $I_m \Sigma M$ and a comparison made with $C(I_m) = I_m t$ or, alternatively, I' may be expressed in terms of the average current as $I_a \Sigma (M + S)$ and a comparison made with $C(I_a) = I_a t$. The value of C' is the same in both cases, but since $C(I_m) < C(I_a)$ the two comparisons are different [3]. In similar fashion the minimum prescribed voltage that determines t' may be taken to refer to mark voltage, giving a discharge time $t'(V_m)$, or it may be taken to refer to average voltage, giving discharge time $t'(V_a)$. Since $t'(V_m) < t'(V_a)$, different values for C' are obtained.

The above problems are compounded by apparently conflicting reports from previous investigations, where various sets of experiments have shown that pulsing increases capacity [3 - 5], that it sometimes decreases capacity [5, 6], and that it may also produce no change [2]. The inconsistency is, in fact, less than at first appears since testing methods were not identical and the range of variables covered were different. Nevertheless, much uncertainty remains as to just how capacity is affected by pulsing. For this reason, as well as to obtain direct information for a development program on electric vehicles, it was decided to carry out tests that would help in establishing a consistent pattern of battery behaviour. The initial measurements presented here, when combined with previous results, suggest it is possible to relate the variation of capacity to battery properties and thus reach some understanding of the physical processes involved.

Experimental procedure

A square-wave battery test facility was constructed* that provided battery loads of the type shown in Fig. 1 in which the mark-space ratio, maximum current, and pulse repetition frequency were all variable. In this facility, shown in simplified form in Fig. 2, transistors in series acted as a variable resistor whose value depended on the reference voltage, with feedback used to maintain constant average current. The reference square wave was obtained from a function generator, both reference and load signals being monitored by oscilloscope. During pulsed discharge, the values of current and voltage that are most relevant to electric car performance are the average values, and it is therefore important for battery capacities to be reported in terms of I_a and V_a . Voltage V_a across the battery terminals and average current I_a (determined as a voltage drop across the standard resistor) were measured by integrating digital voltmeter.

Frequencies of 50, 100 and 200 Hz were used, with mark-space ratios of 5/1, 1/1 and 1/3, these values being chosen to give useful comparison with previous work. At the present stage of development the maximum current the vehicle simulator will accept is 100 A, which puts a limit on maximum discharge rate, but this limitation may be circumvented by use of small batteries so that average current during pulsed discharge can reach values that are large relative to steady discharge current at the 5 h rate. Average discharge currents were 15, 25 and 39 A, though current limitation prevented any test at 39 A for the 1/3 mark-space ratio.

Tests were conducted on four model number AP-45 deep-cycle batteries (12 V, 36 A h capacity at the 5 h rate) presented by Besco Batteries, Villawood, N.S.W. The four were chosen from the same production batch to minimise variability, but in fact capacity on discharge to 10.5 V varied by up to 12%, and hence each battery was treated as a separate test unit with C' being compared with C measured on the same battery.

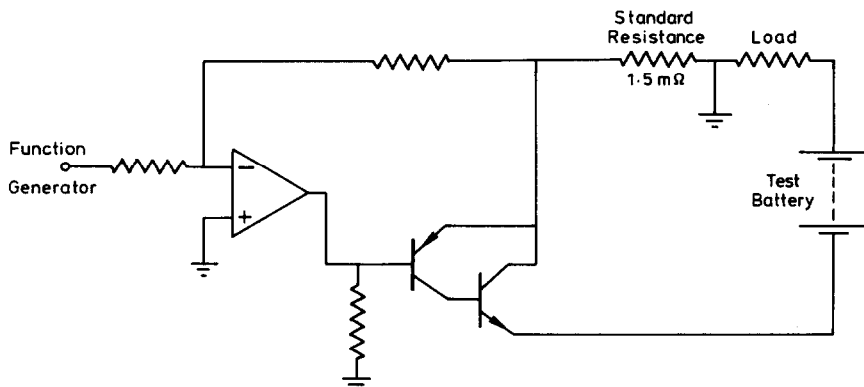


Fig. 2. Schematic representation of battery testing facility.

*Under the supervision of Dr K.C. Daly, Electrical Engineering Department.

After each discharge the battery was allowed to relax to equilibrium voltage and then recharged overnight by a slow taper charge at a starting current of 8 A under an applied voltage of 13.6 V, which is below the voltage needed for gassing. Since such a charge left a vertical concentration gradient in the electrolyte, the electrolyte was then stirred and the battery given a further 3 h charging at an applied 14.5 V in order to reach full charge equilibrium, as determined by specific gravity reading. The battery was then left to relax for one day. After each test discharge the battery was recharged and given a standard discharge at a constant current of 11.3 A, in order to avoid the hysteresis that causes capacity to vary as some inverse function of the previous rate of discharge.

Prior to tests each battery was given repeated steady discharges and recharges of the type just described until a regular pattern of behaviour was reached, as indicated by consistent readings of full charge voltage, specific gravity and capacity. At this stage there was no systematic variation of capacity. To assist stabilisation of temperature, batteries were immersed to above plate level in a water bath kept at a temperature of $20 \pm 2^\circ\text{C}$ over all tests. Experimental error in capacity measurement, determined from irregular variation in capacity measured in repeated tests under identical conditions, had a maximum value of $\pm 5\%$. Errors from inaccuracy in current measurement could extend to $\pm 2\%$, but errors in time measurement were negligible. The estimated errors at different rates of discharge are given in the table of results.

Results

The capacity C' obtained in a pulsed discharge test at average current I_a was compared with capacity C obtained by steady discharge at the same current on the same battery, the two tests being separated by a short time interval. In order to compare tests separated by long time intervals it was convenient to present the change in capacity produced by pulsing as a percentage of steady capacity C , as shown in Table 1, where $\Delta C' = C' - C$. This procedure reduced the scatter arising from systematic differences between batteries and between tests conducted at different stages of a battery's life.

It is evident from Table 1 that the effect of pulsing on capacity over the range of conditions studied is relatively small, but there is also evidence of a systematic increase in $\Delta C'$ with discharge current. Minus signs in column 5 are bunched together at the top of the Table, while plus signs collect together at the bottom. Capacity also varies with mark-space ratio, the overall trend being for $\Delta C'$ to increase with decrease of M/S , which is again an effect of increased current since when mark-space ratio is reduced at constant average current, the battery is required to deliver current at a higher maximum rate I_m (see Fig. 1). These trends are of the same order of magnitude as the un-

certainty in the measurements, however, and it was therefore considered appropriate to carry out a statistical analysis in order to determine their significance.

TABLE 1
Percentage change in capacity produced by pulsing

Battery	I_a (A)	M/S	f (Hz)	$\Delta C'/C$ (%)	Error in $\Delta C'/C$ (%)
2	15	5/1	50	-3	± 4
3	15	5/1	100	-7	± 4
1	15	5/1	200	-3	± 4
1	15	1/1	50	-6	± 4
4	15	1/1	100	-5	± 4
4	15	1/1	200	-1	± 4
2	15	1/3	50	0	± 4
1	15	1/3	100	0	± 4
3	15	1/3	200	0	± 4
1	25	5/1	50	+1	± 4
4	25	5/1	100	+4	± 4
2	25	5/1	200	+12	± 4
1	25	1/1	50	-1	± 4
3	25	1/1	100	-1	± 4
4	25	1/1	200	0	± 4
4	25	1/3	50	+11	± 4
3	25	1/3	100	+5	± 4
2	25	1/3	200	+5	± 4
3	39	5/1	50	+4	± 6
1	39	5/1	100	0	± 6
2	39	5/1	200	+2	± 6
3	39	1/1	50	+7	± 6
1	39	1/1	100	+19	± 6
2	39	1/1	200	+10	± 6

Analysis of variance established that changes in frequency, over the limited range of values studied, had markedly less influence on results than mark-space ratio and that any residual variation with frequency could safely be ignored. Application of Student's t test to the mean value of pulsing capacity C' at a given value of I_a , ignoring changes in mark-space ratio, showed that there was a better than 95% probability that C' was different from steady capacity C at each of three currents used. When the influence of mark-space ratio was included in an analysis of variance that also incorporated the experimental error given in Table 1, the difference between mean pulsing capacity C' and mean steady capacity C was significant, at the 0.05 level, for both the $I_a = 25$ A, $M/S = 1/3$ test and the $I_a = 39$ A, $M/S = 1/1$ test. It is thus seen that a small but genuine increase in capacity can be

produced by pulsing as current is increased and mark-space ratio is reduced. On this basis a test at $I_a = 39$ A, $M/S = 1/3$, prevented by current limitation of the test facility, would be expected to show further increase in capacity.

A comparison was made with previous observations that covered the 'regions' of frequency and discharge current shown in Fig. 3. Differences in the size and type of batteries tested is allowed for in Fig. 3 by dividing the discharge rate I_a during pulsing by the steady discharge current I_5 at the 5 h rate on the same type of battery. As stated earlier, a variety of behaviour has been reported, but direct disagreement is small. A result that could not be conveniently shown in Fig. 3 is that an increase in frequency from 100 to 1000 Hz, over the range of I_a/I_5 from 0.9 to 3.6, reduced capacity C' by 7% [4].

The change in capacity reported in Table 1 occurred under the frequency and current conditions indicated by points in Fig. 3, and careful study shows that though these results span much of the gap left by previous observers they do not give any immediately clearer picture of behaviour. Tests at higher discharge rates (crosses) show some agreement with reports of enhancement of capacity [5], while tests at lower current (circles) are similar to other work that reports no change [2], but there is no obvious overall consistency. Figure 3, in fact, does little more than confirm the earlier conclusion that enhancement of capacity is to be obtained at high rather than low discharge currents. It therefore appears necessary to look more closely at how capacity varies with discharge current, and at how this variation is affected by battery properties. This is considered in the discussion below.

Attention is sometimes drawn [1] to the significant increase in capacity (up to 30%) reported at low discharge rates [3], but it needs to be noted

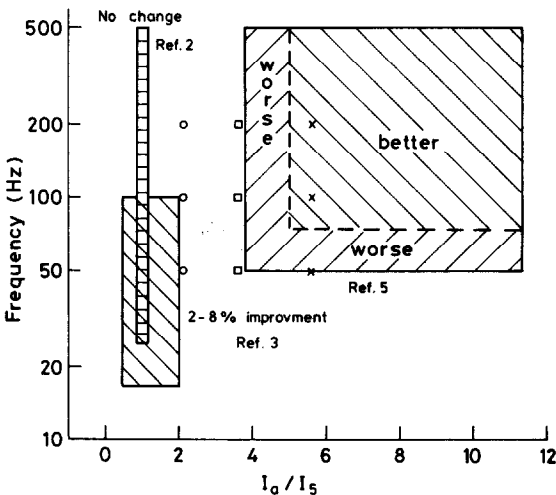


Fig. 3. The type of change in capacity produced by pulsing in the regions of frequency and discharge current at which tests were carried out. Shaded areas represent previous work; results in Table 1 indicated by points.

that this reference is to experiments in which capacity C' during pulsing was compared with capacity $C(I_m)$ obtained for steady discharge at a rate equal to maximum pulse current I_m and, as already indicated, such results are not relevant to electric car use [4]. In any case, when a comparison with $C(I_m)$ is made for the results in Table 1 obtained for $I_a = 15$ A, the enhancement in capacity obtained for $M/S = 1/1$ and $M/S = 1/3$ is also found to be large, and hence no contradiction exists in this respect with the earlier work [3].

Discussion

The variation of battery capacity with discharge current I is conveniently represented by the inverse Peukert equation

$$I = Kt^{-\nu} \quad (1)$$

where K is a constant. The exponent ν , which is an index of battery performance, is obtained from the slope of a log-log plot, though when such a plot is extended to high discharge rates it is found to consist of two linear segments separated by a knee. This is illustrated in Fig. 4, where manufacturer's data for batteries of the type used in the present work are combined with observations at steady discharge rates made in this laboratory. Since data in Fig. 4 are expressed in terms of current density J instead of current I , where J is represented by the quantity I/I_5 , it has been possible to include all observations from previous work on the same plot. Two lines have been drawn in Fig. 4 with slopes corresponding to $\nu = 1.0$ and $\nu = 0.5$, which are values obtained from a recent theory of battery capacity [7] and whose

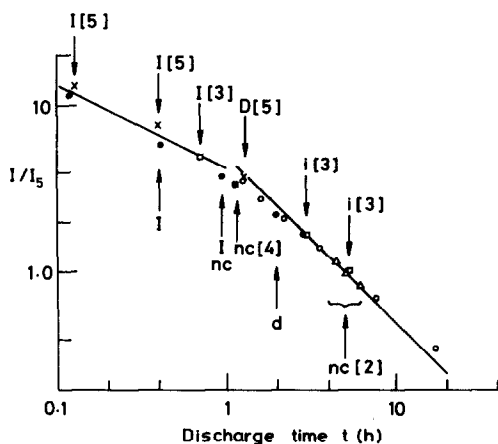


Fig. 4. Ratio of steady discharge current I to discharge current I_5 at 5 h rate against time t for all batteries tested. ●, present experiments; ○, manufacturer's data on batteries used in present work; Δ, from ref. 2; □, from ref. 3; ■, from ref. 4; x, from ref. 5. Location of pulsing experiments indicated by arrows. Effect of pulsing on capacity shown as follows: I, increase; i, small increase; D, decrease; d, small decrease; n.c., no change.

significance is discussed later. For convenience in what follows ν is taken to be the magnitude of the slope, without reference to the minus sign in eqn. (1).

The curve of Fig. 4 represents battery behaviour under steady discharge conditions. To show how such behaviour is related to pulsing experiments, arrows have been drawn at the discharge times measured in pulsing experiments, with captions attached to indicate the change in capacity that was observed. This treatment shows the expected link between capacity change $\Delta C'$ and discharge time that corresponds to the relation found earlier with discharge current, but a more useful way of looking at the pulsing results is to examine the correlation with ν . Since ν is determined by physical processes within the battery, this correlation provides insight into factors that influence $\Delta C'$, and hence enables some physical explanation to be given of why pulsing produces changes.

The existence of two slopes in Fig. 4 means that different mechanisms control capacity at low and high discharge rates, though theory suggests that both mechanisms are determined by mass transport processes in the electrolyte [7]. A value $\nu = 1.0$ at low discharge rates is obtained when capacity is limited by acid depletion that leaves just sufficient concentration between the plates for the battery to function to the discharge cut-off point. It is thus assumed that the battery is efficiently discharged. By contrast, the value $\nu = 0.5$ at high rates results from a diffusion-limited reaction that is confined to a narrow layer of electrolyte at the electrode surface, which means that the discharge point is reached when there is substantial unused capacity in the remainder of the electrolyte. The fact that data in Fig. 4 fit closely to lines with these slopes indicates that capacity was controlled by one or other of these mechanisms, and it thus becomes necessary to explain why, in general, capacity is increased by pulsing when ν is low, but not when ν is high.

When ν is exactly 1.0, battery capacity $C = It$ is a constant that is independent of discharge current. This represents an ideal situation in which the battery is so efficiently discharged that there is no possibility of any increase in capacity. Practical values of ν will be less than 1.0 since battery design inhibits complete utilisation of electrolyte, and the extent to which ν falls below 1.0 is a measure of available capacity left behind in unused electrolyte, as represented schematically in Fig. 5. A battery would have constant capacity independent of discharge current if test data fitted on the line with slope $\nu = 1.0$ shown in Fig. 5. Actual data fit on lines with lower slope, such as that shown with slope $\nu = 0.88$ obtained at low discharge rates for the batteries used in the present work. In this case the width of the shaded area between the lines $\nu = 1.0$ and $\nu = 0.88$ is a measure of capacity in unused electrolyte, capacity that is potentially available during pulsing experiments. This width is small, so it is not surprising that no increase in capacity with pulsing was observed (see Table 1 and Fig. 4 for $I_a = 15$ A, $t = 2$ h). Pulsed discharge has no effect because potential capacity resides in concentration gradients in bulk electrolyte that need

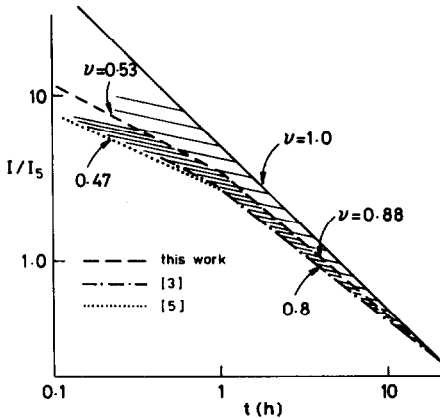


Fig. 5. Representation of data in Fig. 4 in terms of slopes obtained from the experimental results. Shaded area represents available electrolyte capacity.

times longer than the discharge test time in order to disperse and supply energy.

Above the knee at approximately $t = 1$ h, the value of ν obtained experimentally drops to 0.53, which corresponds to an increase in unused capacity, particularly in electrolyte adjacent to electrodes, and it is in this low- ν region that significant enhancement by pulsing has been observed. The conclusion that the value of ν characteristic of a battery is an indication of capacity available for use by pulsed discharge is confirmed by data from other work, such as the observation [2] that capacity is unchanged when $\nu \cong 0.9^*$, but may be significantly increased when $\nu = 0.47$ [5]. Such a conclusion is even consistent with the apparently anomalous report of increased capacity C' observed at low discharge rates [3], since this result was obtained with $\nu = 0.8$, a value which indicates moderate unused capacity after a steady discharge (see Fig. 5). Values of ν plotted in Fig. 5 are only approximate, since data is sparse, but the overall trend is reliable.

The empirical fit of data in Figs. 4 and 5 provides some explanation of why capacity may be enhanced by pulsing, but details of the mechanism involved have not been given. In general, it is expected that pulsing enhances capacity by operating on diffusion mechanisms to reduce concentration gradients and polarisation, the extra local heating produced by pulsing [4, 5] being one factor that promotes mixing. This leads naturally to a variation with mark-space ratio, as observed in this work and elsewhere [3 - 5], especially at high discharge rates where non-linear diffusion down steep concentration gradients is more likely to occur. When steep concentration gradients are not adequately dispersed, however, pulsing can have deleterious effects on plate microstructure [8].

*A very approximate value based on data that is not fully self-consistent [2].

It is significant that variable values of $\Delta C'$, such as seen in the results for $I_a = 25$ A in Table 1 or in the reduced values of C' obtained at $I_a = 100$ A by Cataldo [5], were obtained near the knee, where the operating point for a pulsed discharge may not be sufficiently well defined in terms of a definite value of ν for a reliable comparison to be made with a steady discharge test.

Conclusion

The general conclusion of this work is that pulsing enhances battery capacity by promoting greater utilisation of electrolyte, and that its use is beneficial in electric cars since it operates most effectively at the high discharge rates needed in such cars. The extent of the enhancement is relatively modest, however, and probably less than that obtained by a simple method of electrolyte stirring, if such were available. The interpretation given here has pragmatic value in giving a direction to future investigations and in pointing out the need to take account of the value of ν , an index of battery performance. Even though low ν may not always be a desirable battery characteristic, it has bonus value for batteries used with chopper control in electric vehicles.

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