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An Experimental Analysis of the Effect of Cell Degradation on Dynamic Charge Acceptance in Lead-Acid Cells

M. J. Smith, D. T. Gladwin and D. A. Stone
Centre for Research into Electrical Energy Storarge & Applications,
Department of Electronic and Electrical Engineering,
University of Sheffield, UK
Email: matt.j.smith@sheffield.ac.uk

***Abstract*—Dynamic Charge Acceptance (DCA) is an important consideration for battery performance, particularly when batteries are used as power buffers within larger systems. This paper presents an experimental analysis of the effects of cycle-related degradation on the DCA performance of lead-acid cells. The results show that capacity loss due to degradation does not provide a reliable indication of the cells DCA performance, in fact for the typical lifetime of the cell DCA performance remains broadly constant, independent of degradation. Only at very severe levels of degradation is DCA performance seen to appreciably reduce. The results show that the more rapid degradation of lead cells need not be such a concern in applications where DCA performance is key. The results also have implications for second-life uses of cells in similar applications.**

I. Introduction

Recent years have seen a major change in the way batteries are used, where once they were an axillary or back-up power source, they are now increasingly becoming a fundamental component of power systems; this change is most readily apparent in the automotive sector.

A. Battery use in Vehicles

Historically a vehicle would carry a single lead-acid battery as a stand-by power source, to be used only for starting, lighting and ignition when the internal-combustion (IC) engine was not running. More recently, with advances in battery technology, together with increasing fuel costs and environmental concerns, vehicles are using batteries to augment the IC engine, or replace it entirely.

This has led to automotive batteries being used in one of two main duties. Where the battery has replaced the IC entirely, as in fully electric vehicles (EV), the duty of the battery becomes very cyclic. Driving the vehicle draws energy from the battery, causing it to discharge; it may be recharged regeneratively during braking but this can never replace all the energy lost. Eventually the vehicle must be plugged into an external power supply to recharge, this leads to a repeating pattern of discharges and charges. Such a duty places a premium on battery capacity, charging time and cycle-life. In these applications lithium-based batteries are the obvious choice, their high energy-density, specific power, long cycle-life and fast-charge ability combine to offset the initial expense and their difficulty of recycling [1]. Even with these properties, however, EV battery packs often have a lifetime significantly shorter than that of the vehicle in which they are installed. The aforementioned difficulty and expense of recycling these packs has lead to growing interest in second-life applications, beyond their original automotive use [2].

Aside from completely replacing the engine, many hybrid electric vehicles (HEV) are now using batteries alongside the existing IC engine. In this application the battery acts as a power buffer, being able to provide short, high-power bursts during rapid acceleration, such as starting or overtaking, more efficiently than the IC could. The battery can also be recharged regeneratively during braking to recover otherwise wasted energy and reduce brake-wear. Unlike in an EV however, the battery can also be charged by the IC should the need arise. This eliminates the need to plug the vehicle in to recharge – although plug-in hybrids (PHEV) retain the ability to do so – and means the user can operate it in the same way as they would a conventional IC-engined vehicle. The duty imposed on a HEV battery is much less predictable than that of an EV and dominated by short, high-power pulses of either discharge during acceleration or charge when braking [3]. The ability to perform reliably under these conditions becomes a crucial factor for HEV batteries, other aspects such as capacity and cycle-life assume a lesser priority.

In such applications lead-acid batteries remain a viable proposition [4]. The physical size of HEV batteries is less as they must share space with the IC, and their capacity need not be as great, so the weight penalty associated with lead is reduced. This is combined with the low initial cost and ready availability of lead recycling infrastructure, which makes lead economically attractive in this application.

B. Beyond Automotive

Outside the automotive sector there are numerous applications where batteries are used as buffers to absorb short high-power transients similar to those seen in HEV applications. Typically these are large grid-connected storage systems, however some applications such as wind or solar photovoltaic

energy storage are candidates for smaller domestic applications using second-life EV batteries [5].

C. Dynamic Charge Acceptance

Characterising the performance of batteries under high-rate, partial state-of-charge (HRPSoC) conditions, such as those found in HEV applications has been identified as a key factor in the development of automotive batteries [6]–[8]. One metric, which provides very useful results, Dynamic Charge Acceptance (DCA), has been the subject of much interest in recent years. A standard test procedure exists for determining DCA performance in automotive batteries [9] and detailed investigations have been performed into the individual factors which influence DCA performance [10], and methods by which it may be improved [11]. A full discussion of the DCA test procedure is beyond the scope of this paper, for detailed information see [9], [10]; a brief outline of the salient points is given here for clarity, however.

Fundamentally, DCA is a measure of a battery's ability to accept charge under HRPSoC conditions. The DCA test procedure determines this ability by applying a current waveform as shown in figure 1 to the battery under test, the response to this stimulus is used to determine the DCA performance. The key aspect of the waveform, from which DCA is determined is the initial charge pulse (t_1 – t_2), lasting 10 seconds. During this charge pulse the terminal voltage of the battery will rise, in the ideal case this rise will remain below the maximum voltage allowable (2.47 V per cell for lead-acid), and all of the charge available will be accepted. If, however, the voltage rises above the maximum, the current is reduced to keep the voltage within its limits. In this case, as the current is reduced, the charge acceptance will also be less.

The charge pulse is followed by a rest period of 30 seconds, a discharge pulse and finally another 30 second rest; together these make up one complete DCA microcycle. It is important to note that the microcycle is charge-balanced, this is achieved by dynamically varying the length of the discharge pulse to ensure that all charge accepted in the first step is removed during the discharge, i.e.:

$$\int_{t_1}^{t_2} I(t)\ dt = -\int_{t_3}^{t_4} I(t)\ dt \tag{1}$$

In this way the state-of-charge (SoC) of the battery at the end of the microcycle is the same as at the start. For the purpose of the DCA test, microcycles are not used individually, rather they are grouped into a block of 20 to form a DCA Pulse Profile (DCAPP) which is applied to the battery under test.

DCA is calculated as the average recuperation current, I_{recu}, from all the microcycles in the DCAPP. For each microcycle this is given by

$$I_{recu} = \frac{Ah_{recu} \cdot 3600}{t} \tag{2}$$

where Ah_{recu} is the charge accepted in ampere-hours and t is the length of the charge pulse in seconds. Given that the charge pulse is known to have a length of 10 seconds, the DCA for the complete 20-pulse DCAPP is given by

$$I_{recu} = \sum_{n=1}^{20} (Ah_{recu}(n)) \cdot 18 \tag{3}$$

The DCA test in its standard form normalises all currents to the measured capacity of the battery, C_{exp}, thus giving I_{recu} units of $A \cdot Ah^{-1}$. This is desirable and necessary when comparing the relative performance of different batteries as it removes the effect of differing battery capacities, but has the potential to present a problem when assessing the change in DCA performance over time of batteries which have degraded.

D. DCA and Battery Degradation

As batteries are used, they degrade. This degradation comes from multiple sources, in lead-acid batteries it is primarily due to plate corrosion and sulphation [12]; lithium-based batteries are also affected through cell oxidation and lithium plating of the negative electrode [13]. This degradation has three main effects on battery performance: reduction in capacity, increase in internal resistance and increase in self-discharge. Of these effects, capacity loss is the easiest to determine, this being possible on-line using coulomb-counting [14], it is also the most obvious symptom of degradation to the user, therefore capacity loss alone is commonly used as a measure of battery degradation.

The change in capacity with degradation presents a problem when considering DCA performance, as there are now two variables to consider. Firstly there is the actual loss in performance due to degradation, but there is also the influence of the test procedure itself. As a degraded battery will have a lower capacity, the standard DCA test will apply lower currents during the testing phase. This effectively makes the test easier which may mask the true effects of the degradation. In reality, of course, the demands placed on the battery will not be reduced simply because it has degraded, therefore this should be accounted for when assessing a battery's DCA performance.

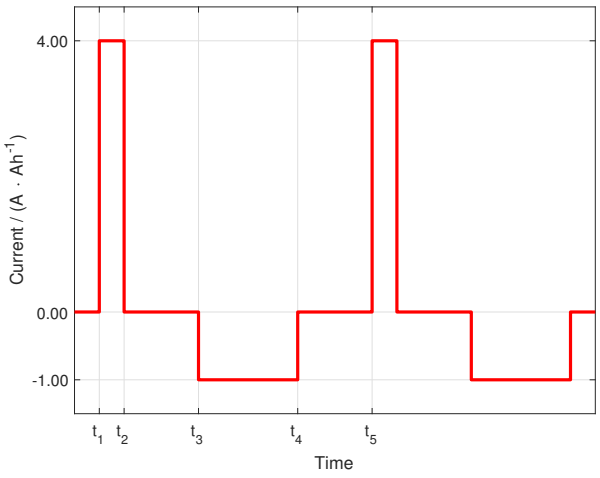

Fig. 1: DCA Test Microcycle Current Profile (t_1 – t_5)

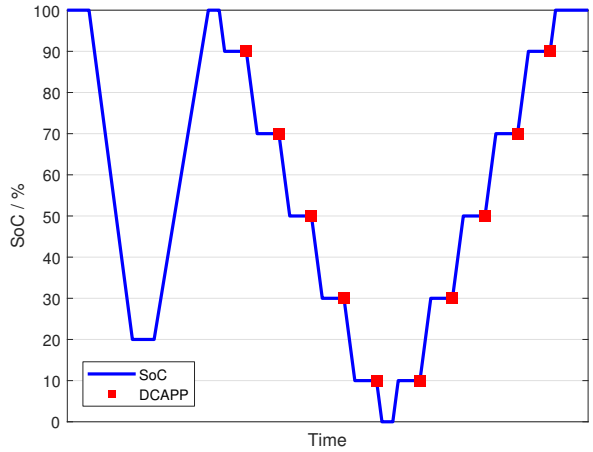

Fig. 2: DCA Test SoC Profile & DCAPP Locations

II. Test Procedure

A test procedure has been developed to determine the effects of degradation on DCA performance, as well as to assess the effect the DCA test itself has on the results. The test procedure consists of two main components, the DCA testing phase and the cycling phase.

Within a battery there will be differences in individual cell performance and rate of degradation. These differences, and their effect on overall battery performance, can often be hard to determine, as access to individual cells for measurement is difficult or impossible. To overcome this, single cells have been used for this study; these were EnerSys Cyclon 2 V, VRLA type, with a nominal capacity, C_{nom}, of 2.5 Ah.

A. DCA Testing

Previous work by the authors has shown that the standard A3 DCA test as outlined in [9] has some shortcomings when measuring performance under HRPSoC conditions [10]. The chief concerns are that it only measures DCA performance in a narrow SoC window and makes the assessment of the influence of history difficult to assess.

SoC has a large impact on DCA performance so this must be accounted for during the test procedure, particularly where cells will be operated across a wide SoC range, such as those in HEVs. The history of a cell, that is, whether it has previously been charged or discharged, also significantly affects DCA performance. The standard DCA test accounts for this, but measures charge and discharge history at different SoC levels, making any analysis of the effects of history alone more complex. Both of these shortcomings have been addressed for this study; the DCA test has been performed using the SoC profile shown in figure 2.

Starting from 100 % SoC the cell is initially discharged to 20 % SoC, from this C_{exp} is calculated. The cell is then recharged for the beginning of the DCA test proper. This consists of 10 DCAPPs applied across the SoC range from 90 % – 10 % SoC, the first five of these assess performance when the cell has discharge history, whilst the second five account for charge history. The SoC levels are the same for both allowing the effect of history to be easily compared, and cover a wide SoC range more typical of that encountered in HRPSoC applications. Upon completion of the DCA test procedure the cell is returned to 100 % SoC in preparation for continued testing. All charges and discharges (except those within the DCAPP) are performed at 0.5 A ($0.2C_{nom}$ A) and all rest periods are 1 hour in duration.

Within the DCAPP, the A3 test applies only a modest charge current of $1.67C_{exp}$ A, this is quite low in comparison to the actual currents seen in HRPSoC applications [3]. It has been shown that increasing this current to $4C_{exp}$ A yields results which are more representative of real-world performance [10]. This change is reflected in the microcycle current profile given above in figure 1, and is the profile used for this investigation.

The other concern here is the normalisation itself, as discussed above the choice of normalising value may have a significant influence on the apparent DCA performance of the cell. To account for this two versions of the test procedure were conducted, the first with currents normalised to $4C_{exp}$. For the second, normalisation was to $4C_{nom}$, in this case there was no change in applied DCAPP current as the cell degraded.

B. Cycling

The second phase of the test procedure was that of cycling to degrade the cells. The objective was to cause an accelerated ageing process to occur, thereby degrading the cell more quickly than would be the case in reality, but maintaining its relevance to real-world scenarios by the method of degradation being the same. To this end a procedure was developed to subject the cell under test to 24 cycles at a rate of $1C_{nom}$ A, with a SoC range from 100 % – 20 %, and a 1-hour rest period between discharging and charging.

This cycle profile is not intended to represent the duty a cell would be subjected to in HRPSoC conditions, rather it serves to degrade the cell in a timely manner whilst avoiding the very low SoC regions where a real-world system would not be operated. Operation at very low SoC causes additional

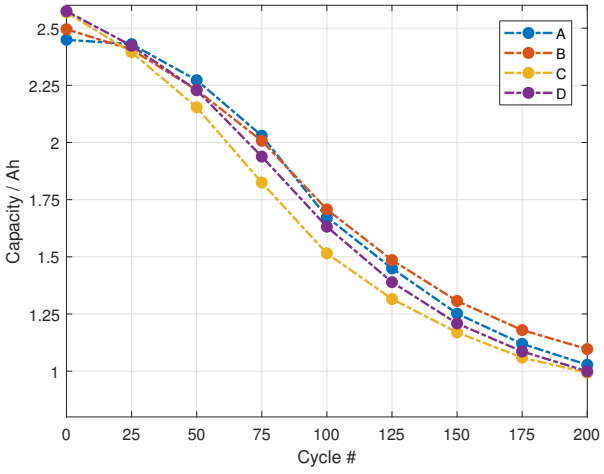

Fig. 3: Capacity Loss with Ageing

stresses on the cell and is likely to lead to forms of degradation which would not be seen in real-world applications.

The complete test procedure consisted of an initial DCA test to establish baseline values for DCA performance and C_{exp}. This was then followed by repeated applications of Cycling and DCA testing, the initial discharge within the DCA test making for 25 effective cycles between each analysis of DCA performance. The testing was continued until 200 cycles had been completed, and was conducted using a MACCOR Series 4000 test unit. The cells were placed in an environmentally-controlled test chamber with the ambient temperature maintained at 25 °C ±2 °C throughout.

III. Results & Discussion

The test procedure described above was applied to four cells: A, B, C & D, all of which were new and unused. For cells A and B the DCA test was normalised to the nominal capacity of the cells, C_{nom}, for the entirety of the investigation; cells C and D meanwhile, were tested using the standard C_{exp} normalisation.

A. Degradation

Figure 3 shows the change in cell capacity throughout the test, as measured from the $0.2C_{nom}$ A discharge prior to the DCA testing phase. All four cells are seen to have similar baseline capacities and all follow a similar trend of capacity loss as they age, this indicates that the four cells are well matched. It also shows that the differing currents used during the DCA testing phase do not have any significant effect on the rate at which the cells degrade.

The results show the typical cycle-life performance trend expected for lead-acid cells: initial capacity loss within the first 25 cycles was modest, after this however the rate increased, becoming roughly linear for a time between cycles 25 and 150, where a typical loss of around 10 % per 25 cycles or 0.4 % per cycle was seen, before gradually reducing as the cells became seriously degraded. This shows that whilst the test procedure has caused the cells to age more quickly than would be seen in service, it has not changed the way in which they degrade, therefore the results can be considered representative of real-world conditions.

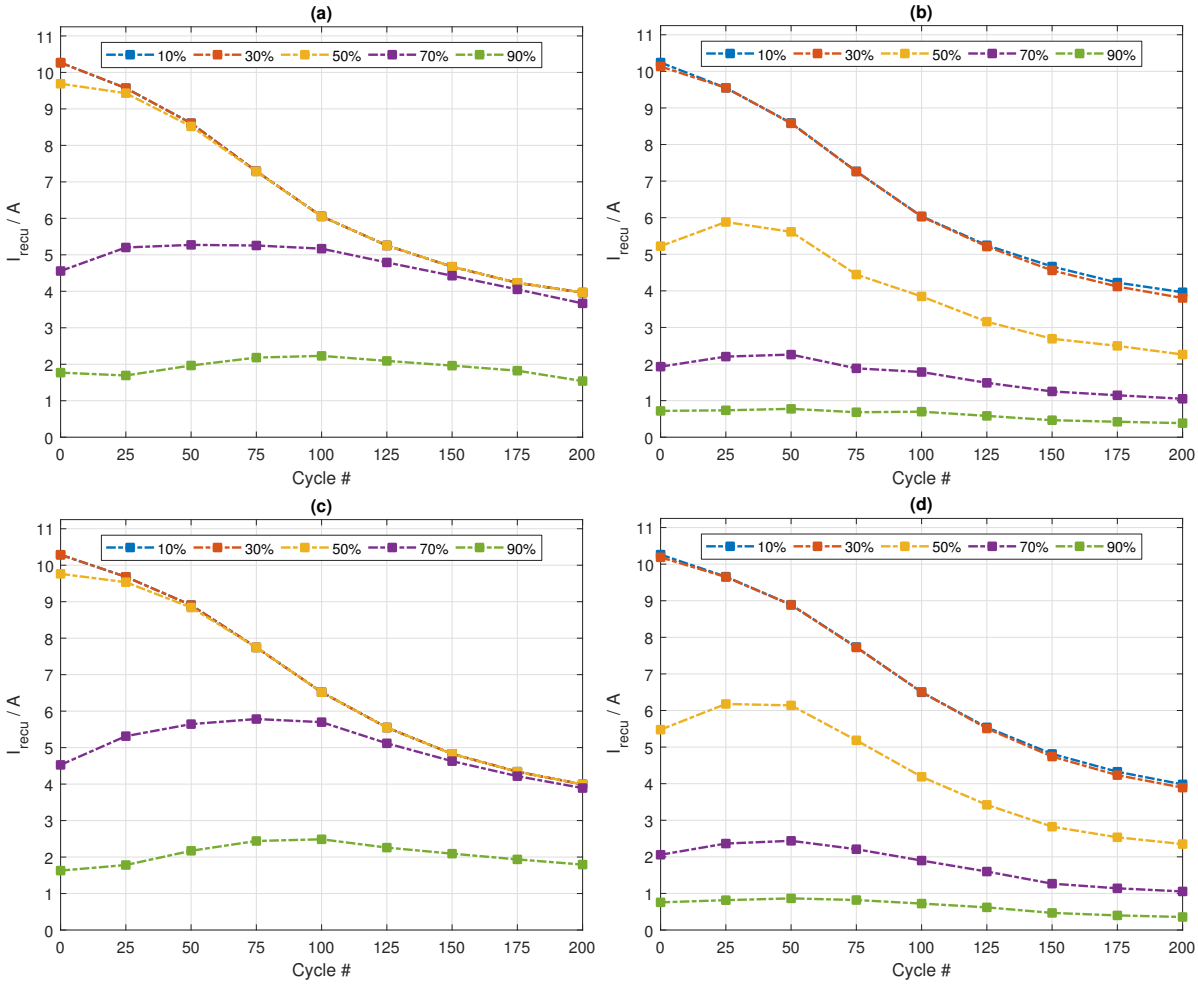

Fig. 4: DCA Performance at Various SoC Levels with C_{exp} Normalisation. (a) Cell C with Discharge History, (b) Cell C with Charge History, (c) Cell D with Discharge History, (d) Cell D with Charge History

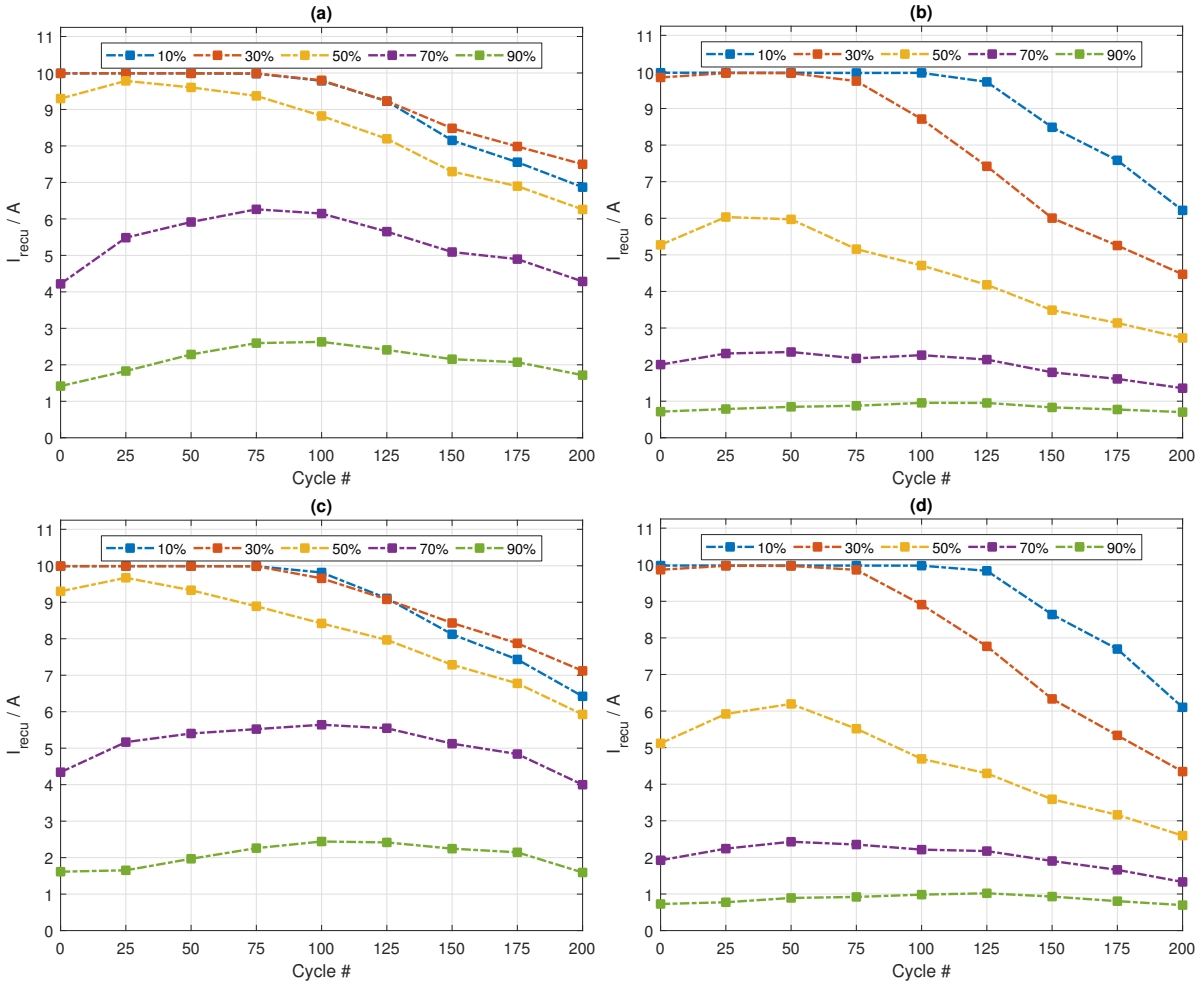

Fig. 5: DCA Performance at Various SoC Levels with C_{nom} Normalisation. (a) Cell A with Discharge History, (b) Cell A with Charge History, (c) Cell B with Discharge History, (d) Cell B with Charge History

Three of the cells took 75 cycles to degrade to around 80 % of their initial capacity, this is the point at which they would usually be considered too degraded to continue in an EV application, and hence can be considered as the starting condition of cells in second-life applications. The final cell (cell C) had degraded slightly quicker but remained above 70 % capacity at this point. By the end of the test, after 200 cycles, all four cells had degraded to around 40 % of their initial capacity. This is a very severe level of degradation and it is unlikely that they would remain in use much beyond this point in any real-world application.

B. DCA Performance

Figure 4 shows the DCA performance for cells C and D. Note that all results are shown in terms of absolute current, rather than being normalised to either C_{nom} or C_{exp}.

Leaving aside the effects of degradation for a moment, it is apparent that the results for the two cells are well correlated and the results clearly show the importance of considering multiple SoC levels and cell history when assessing DCA performance; in general terms, DCA is improved at lower SoC and when the cell has discharge history.

Considering the effects of degradation, is clear that the results may be divided into two broad regions, depending on the baseline performance. Above 70 % and 50 % SoC for discharge and charge history respectively, the result is determined by charge acceptance alone; it can be seen that under these conditions DCA performance is always below the maximum current provided by the test, therefore the charge acceptance of the cell is the only limiting factor. As the cell degrades, the effects of cell history become important, the results with discharge history (figures 4a & c) show performance improving to reach a maxima around the 75-cycle mark, before falling back gradually to end with no significant loss of performance after the entire 200 cycles. With charge history (figures 4b & d) the rise is again present, but is less pronounced with the maximum being reached after 50 cycles; following this however, the loss of performance is much more pronounced, with charge acceptance falling to around 50 % of the baseline performance after 200 cycles. For the remaining

SoC levels, DCA performance follows a consistent downward trend for the entirety of the test, regardless of history. In this case performance is limited by the maximum current provided by the test procedure, which reduces in line with C_{exp}. From these results it is impossible to determine the actual cell performance as it is being masked by the effects of the DCA test procedure. This clearly demonstrates the shortcomings of using the standard DCA testing methodology to characterise cells as they degrade.

Figure 5 shows the DCA performance for cells A and B, again there is a good correlation between the results for the two cells. It can be seen that there is a demarcation depending on SoC as before, and the DCA performance at high SoC levels is very similar to that previously observed for cells C & D. This further confirms that the results seen in these cases is due to the effects of cell degradation alone and not an artefact of the DCA test.

At lower SoC, however, the true picture now becomes more apparent. In this case performance remains broadly constant up to the 75-cycle mark, regardless of history, this must be due to charge acceptance being limited by the DCA test itself. In this region greater charge acceptance would be possible if the DCA current were increased. Beyond this point the performance begins to decrease in all cases, this decrease can only be caused by the degradation of the cell as the maximum available current remained the same as for the baseline case.

It may be seen that history has a significant effect on performance. As seen at higher SoC, charge acceptance reduces much more quickly when the cell has charge history. Taking 30 % SoC as an example, performance drops from 10 A at 75 cycles to around 4.5 A at 200 cycles, with charge history; a loss of around 0.45 % per cycle. Over the same period with discharge history, performance had only fallen to around 7.5 A; a loss of 0.20 % per cycle. Again, this illustrates the importance of ensuring that the test procedure fully reflects the operating conditions of the cell if the results are to be accurate and informative.

It is also interesting to consider the results after 75 cycles. At this point the cells had degraded to 80 % of their baseline capacity, the point at which they would usually be considered too degraded to continue in EV use. At this point however, DCA performance in all cases was at least as good as the baseline case, and in some cases it was better. This suggests that in situations where DCA performance is more important than absolute capacity, such as HEV applications or energy storage buffers, effective cell lifetime could be greater than would be predicted from capacity loss measurements. It also suggests that the DCA performance on-delivery of second-life batteries is likely to be little changed from the performance when they were new; although they will begin to show signs of degradation more rapidly.

IV. Conclusions

It is apparent from this investigation that the effects of cell degradation on DCA performance are complex, and not well correlated to capacity loss alone. It is also clear that the DCA test procedure itself has a significant influence on the observed performance. Together these factors highlight the importance of ensuring that the DCA test procedure accounts for the actual operating SoC window, and maintains a constant charge current as the cell degrades if an accurate assessment of DCA performance is to be achieved. In this investigation the best results were achieved with the current normalised to the nominal cell capacity, but it is likely that similarly valid results could be achieved by normalising to an experimentally determined baseline capacity, if this were more convenient.

The results suggest that reduction in capacity may not be the best indication of the end-of-life point for cells. In applications where DCA performance is more important than capacity, it is possible that the useful life of the cell may be much longer than would be suggested by capacity loss alone. This also has implications for second-life applications; in these situations, although the cell has degraded and lost capacity, its DCA performance may be very similar to that of a new cell.

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