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# High performance plastic lithium-ion battery cells for hybrid vehicles

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**Abstract**

Exploratory studies on small plastic lithium-ion battery test cells with improved cathode material show high pulse power capability and outstanding stability both in a 25 °C pulse cycling test and in a 55 °C calendar life test. Typical discharge pulse power values are 60 mW/cm$^2$. After 50,000 pulse cycles at 5 C rates, cells at 25 °C retain 100% of their initial 1 C capacity and 75% of their pulse power capability. After 60 days at 55 °C, cells measured at 25 °C retain 98% of their initial 1 C capacity and 70% of their pulse power capability. This performance is an excellent basis for the development of long life batteries for hybrid vehicles, as shown by a calculated scale up to a 30 kW hybrid battery for a "Fast Response Engine". © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Plastic lithium-ion cells; Pulse power capability; Hybrid vehicles; Calendar life; Cycle life

## 1. Introduction

Challenging goals [1,2] for the performance of hybrid vehicle batteries are outlined by the US Department of Energy for the partnership for a new generation of vehicles (PNGV) program. Among the many demanding goals are operation over a wide temperature range (−40 to +52 °C), and extended pulse current cycling lifetime (>50,000 cycles) for a battery of relatively low weight, low volume, and low cost. In this paper, we report the basic feasibility of obtaining long pulse cycle life at 25 °C and long calendar life at 55 °C with our high-energy plastic lithium-ion cells containing an improved cathode material.

## 2. Experimental

The small test cells made for this study are based on the PLiON™ technology [3,4] developed by Bellcore (now Telcordia), using a bicell structure as the basic unit [5]. The electrodes of our thin film 100 mAh bicells were 24 cm$^2$ in size, giving 48 cm$^2$ of active area. For these exploratory tests, our bicells were sealed in soft-pack bags. We have studied many other test cell compositions for long periods of time in soft-pack bags, but we have observed better stability with stacks of their bicells sealed in metal cans as 55 Ah cells. For these studies we chose FMC LectroPlus-600 ($LiNi_{0.7}Co_{0.2}Ti_{0.05}Mg_{0.05}O_2$) as the cathode material, with graphite (MCMB-1028) as the anode material. The main features of these test cells are shown in Table 1.

These cells were characterized initially, and periodically during their tests, at 25 °C by "signature" charge and discharge capacities, 1 C discharge capacity, electrochemical impedance spectroscopy (EIS), and by "hybrid pulse power characterization" (HPPC) tests [1]. The signature discharges rates were done sequentially at 1.4, 1, 1/2, 1/4, 1/8, 1/16 and 1/32 C. The EIS studies used a Solatron 1260, and the cell resistance values were calculated from the Nyquist plot values between the crossover point and the value at 10 mHz. The HPPC tests were done with 5 C pulses from 3.7 V, which correspond to 10.4 mA/cm$^2$, using the characterization profile for a "Fast Response Engine" (18 s pulse discharge, and 2 s + 4 s + 4 s pulse charge).

The cycle life stability was studied using the continuous pulse cycling test from 3.7 V at 25 °C corresponding to the 100 Wh Fast Response Engine. The cells were recharacterized each 12,000 cycles. The calendar life was studied at 55 °C, with one charge/discharge pulse per day (at 5 C rate) from 3.7 V according to PNGV test 3.1.8; then the cells were recharacterized at 25 °C after each 28-day storage period at 55 °C.

## 3. Results

One of our initial tests after cell characterization was to study the effect of current density on the HPPC test of one

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Table 1
Features of HRL test bicells

| | |
|---|---|
| Size | 24 $cm^2$ × 0.052 cm |
| Active area | 48 $cm^2$ |
| Active area weight | 2.74 g (including electrolyte) |
| Cathode | FMC LectroPlus-600 |
| Anode | MCMB-1028 |
| Cathode/anode weight ratio | 2/1 |
| Capacity (1 C) | 100 mAh |
| Specific energy | 135 Wh/kg (active area only) |
| Energy density | 296 Wh/l (active area only) |

cell, particularly in regard to the end-of-pulse voltages (EOPV) during charge and discharge. We chose pulse currents of 2.5, 5 and 7.5 C which corresponded to current densities of 5.2, 10.4, and 15.6 mA/$cm^2$, respectively. The HPPC test showed approximately the same power capability results for each of these current densities, namely, about 2.9 W of pulse discharge power and 3.6 W of pulse regeneration power at the cross point (between 30 and 50% DOD) for these HPPC pulse power curves. The effect of current density on the end of pulse voltages in this cell is shown in Fig. 1. Extrapolation of the EOPV points to the voltage limits (4.1 V pulse charging and 3.0 V pulse discharging) gives power capability values corresponding to the HPPC test. A current density of 10.4 mA/$cm^2$ (5 C rate) was chosen for the pulse cycling tests. A 50% higher current density (e.g. 7.5 C rate) in pulse cycling would provide higher real power, but the EOPV would start out much closer to the voltage limits. A 50% lower current density (e.g. 2.5 C rate) in pulse cycling would operate at much more favorable EOPV, but would provide lower real power from the cell (which would result in a weight and volume penalty in a full sized battery).

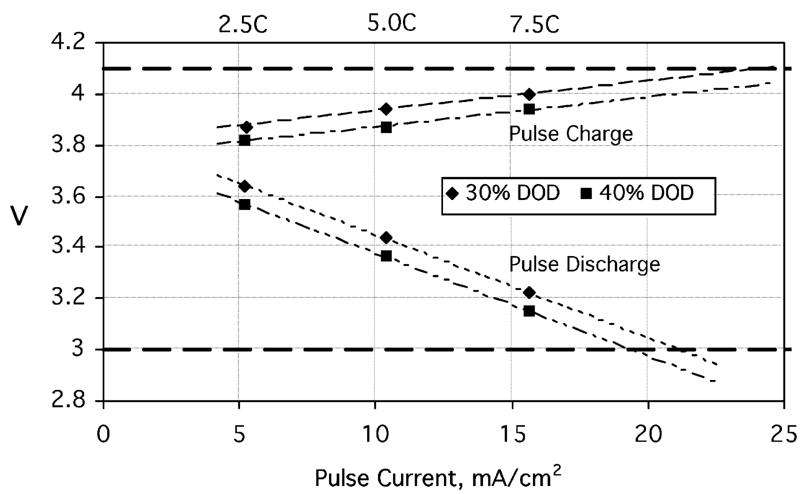


Fig. 1. End of pulse voltages in HPPC tests as a function of pulse current density. The pulse rates are at 2.5, 5.0 and 7.5 times the 1 C capacity of test cell E.

Table 2
Calculation basis for hybrid battery design and HPPC limits

| | |
|---|---|
| Estimated 1 C capacity of 4 in. × 6 in. bicell (mAh) | 646 |
| Active area of 4 in. × 6 in. bicell (2 cm × 155 $cm^2$) | 310 |
| Weight (active area) of 4 in. × 6 in. bicell (g) | 17.7 |
| No. of 4 in. × 6 in. bicells for 40 Ah cell (bicells) | 62 |
| Weight of active stack in 40 Ah cell (kg) | 1.098 |
| Weight per 40 Ah can in battery (estimated as 120% × stack weight) (kg) | 1.32 |
| Volume of active stack in 40 Ah cell (l) | 0.500 |
| Volume per 40 Ah can in battery (estimated as 190% × stack volume) (l) | 0.95 |
| Estimated pulse discharge of 40 Ah cell (40 Ah × 2.9 W[a]/0.1 Ah) (kW) | 1.16 |
| No. of 40 Ah cells at 0.87 kW (75% level) for 25 kW discharge (cells) | 28.7 |
| Estimated pulse regeneration of 40 Ah cell (40 Ah × 3.4 W[a]/0.1 Ah) (kW) | 1.36 |
| No. of 40 Ah cells at 1.02 kW (75% level) for 30 kW regeneration (cells) | 29.4 |
| Maximum allowable 40 Ah cells for 40 kg limit (cells) | 30.3 |
| Maximum allowable 40 Ah cells for 32 l limit (cells) | 33.7 |
| Battery design for 50,000 cycles: no. of 40 Ah cells (cells) | 30 |
| Pulse discharge HPPC limit per 40 Ah cell (25 kW/30 cells) (W/cell) | 833 |
| Pulse discharge HPPC limit per $cm^2$ (833W/(310 $cm^2$ × 62 bicells)) (mW/$cm^2$) | 43.3 |
| Pulse regeneration HPPC limit per 40 Ah cell (30 kW/30 cells) (kW/cell) | 1.0 |
| Pulse regeneration HPPC limit per $cm^2$ (1000W/(310 $cm^2$ × 62 bicells)) (mW/$cm^2$) | 52.0 |

[a] These are average pulse powers at 5 C rates in our 0.1 Ah cells.

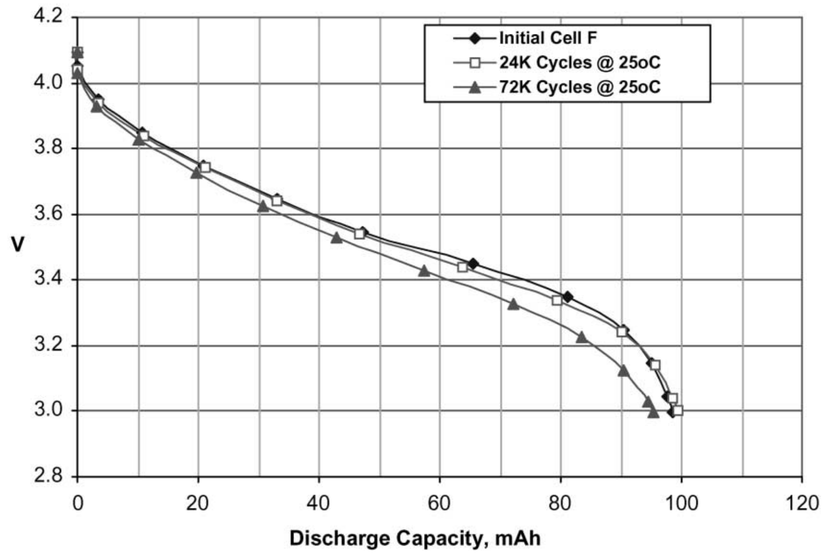


Fig. 2. Effect of pulse cycling on the 1 C discharge capacity curves of cell F at 25 °C.

The minimum pulse power capability limits calculated for our cycling and calendar HPPC tests on small cells are based on our extrapolation to a battery for a "Fast Response Engine". We used the minimum PNVG battery goals of 25 kW pulse discharge, 30 kW regeneration pulse, 40 kg weight limit, and 32 l volume limit for our calculations. We forecast the use of stacks of bicells, each about 4 in. × 6 in. in size for 40 Ah cells. This is similar to our previous actual scale up work. We then estimated the weight and volume of combining these 40 Ah cells into a battery for the Fast Response Engine, with the added goal of retaining the pulse power goals after 25% degradation of the initial pulse power capability. The calculations and related estimates are summarized in Table 2. This shows a design using 30 cells of 40 Ah each, resulting in a pulse discharge limit (for 25 kW) of 43.3 mW/cm$^2$ and in a regeneration pulse limit (for 30 kW) of 52.0 mW/cm$^2$. These are the limits shown in the plots of our HPPC test results. Our test cells begin with pulse power capability 25% higher than these 25 and 30 kW limits.

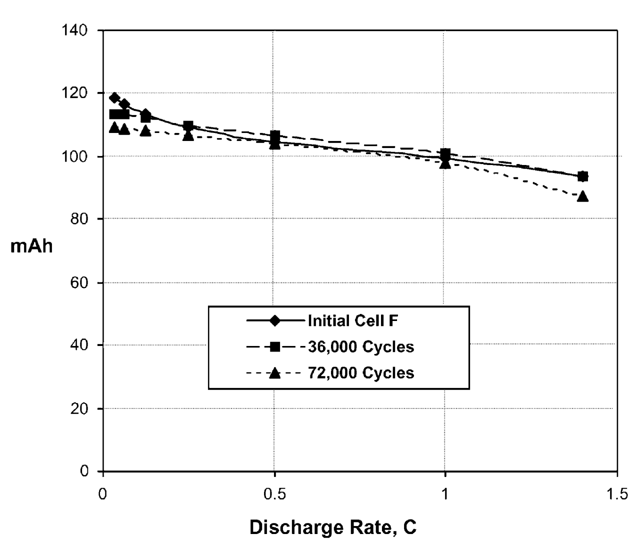


Fig. 3. Effect of pulse cycling on the discharge capacity Peukert plot of cell F at 25 °C.

### 3.1. *Pulse cycling test results*

The long term pulse cycling tests at 25 °C had relatively small effect on the discharge curves of these cells, as shown in Figs. 2 and 3. The discharge capacity versus voltage plots in Fig. 2 shows a decrease of 1 C capacity of only about 3% after 72,000 cycles. The Peukert plot in Fig. 3 shows that after 72,000 cycles the discharge capacity changed more at lower and higher rates than at 1 C, with an 11% decrease at 1/32 C and a 7% decrease at 1.4 C. The temporary gain of capacity at 0.5–1.0 C rates at 36,000 cycles is a real effect. We have also observed similar related effects with other mixed oxide cathodes when using a high cathode/anode ratio (such as the 2/1 weight ratio used in the present cells).

The pulse cycling tests are done at 5 C rates, and their effect on the cells is also indicated by periodic observations

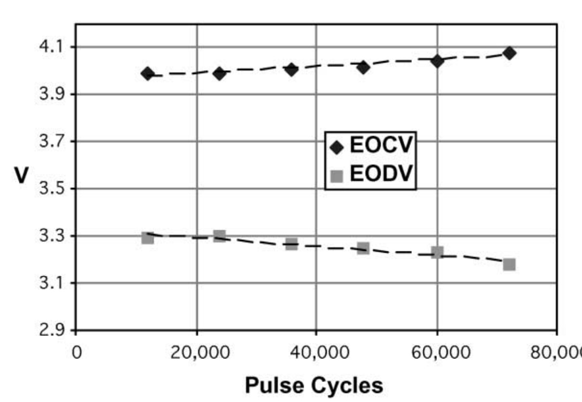


Fig. 4. End of pulse voltages during pulse cycling test (cell F).

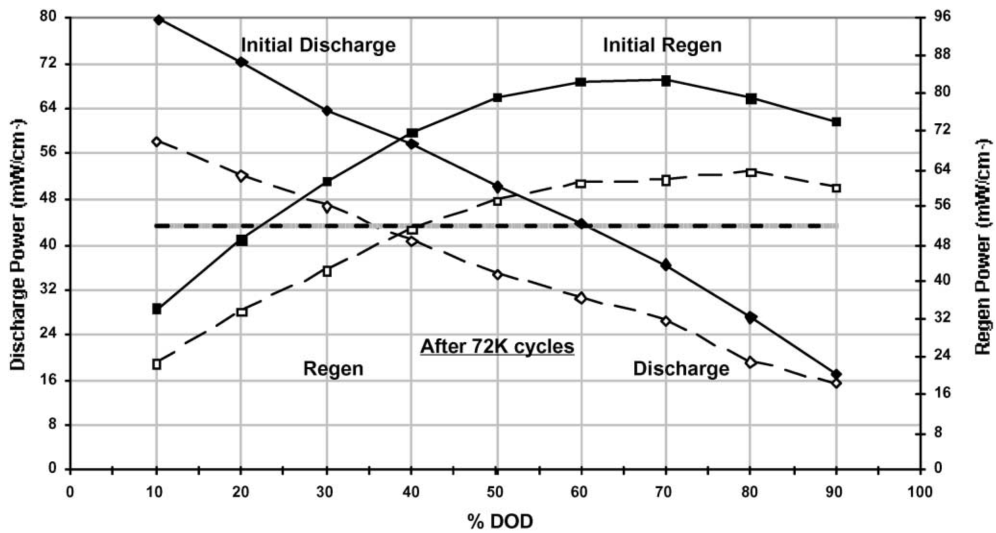


Fig. 5. HPPC curves before (solid lines) and after (dashed lines) 72,000 pulse cycles at 25 °C on cell F. The horizontal line is the limit goal for 75% of initial power.

of the voltages at the end of the charge and discharge pulses. These results are given in Fig. 4, which shows a gradual small increase in the end of charge voltage (EOCV) and a corresponding decrease in the end of discharge voltage (EODV). Because we used a rest point voltage of 3.7 V for these pulses, the EOCV approaches the 4.1 V voltage limit more closely than the EODV approaches the 3.0 V limit after 72,000 cycles.

In Fig. 5, the HPPC test results after 72,000 pulse cycles are compared with the initial values. The dashed horizontal line shown with these plots indicates the limits which we have calculated for the retention of 75% of the initial HPPC values. At 48,000 cycles, our cells had a crossover point (the crossing of the pulse discharge and pulse regenation curves) above this limit, and at 60,000 cycles they were just below this limit. The 1 C capacity of these cells changed very little with cycling, as shown in Fig. 6 which compares the cycling effects on the retention of 1 C capacity with the retention of the HPPC discharge values at the crossover points. Our EIS studies showed that the cell resistance changed appreciably with the pulse cycling. Fig. 7 shows that the percent increase in cell resistance was approximately equivalent to the percent decrease in HPPC values. On the other hand, the 1 C capacity remained nearly constant even up to a 44% increase in the cell resistance.

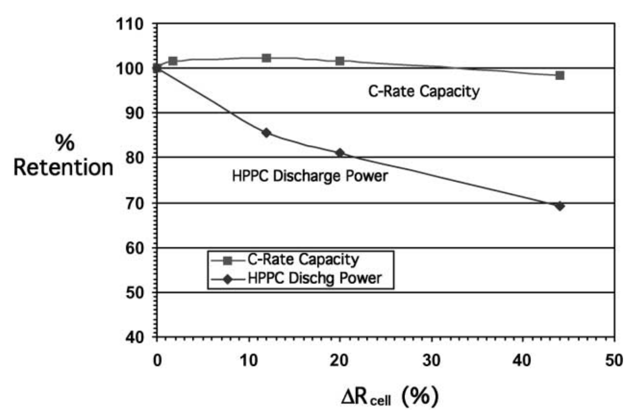


Fig. 7. Pulse cycling effects (25 °C) on retention of capacity and of HPPC correlated with the resistance increase of cell F, as measured by EIS. Data at 0,12, 24, 36, and 72 kcycles.

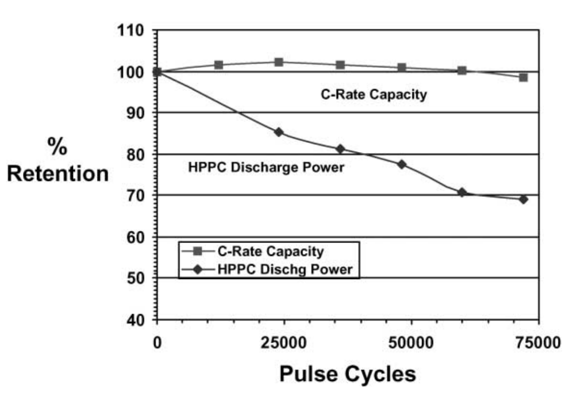


Fig. 6. Effects of pulse cycling at 25 °C on the relative retention of capacity and of HPPC for cell F.

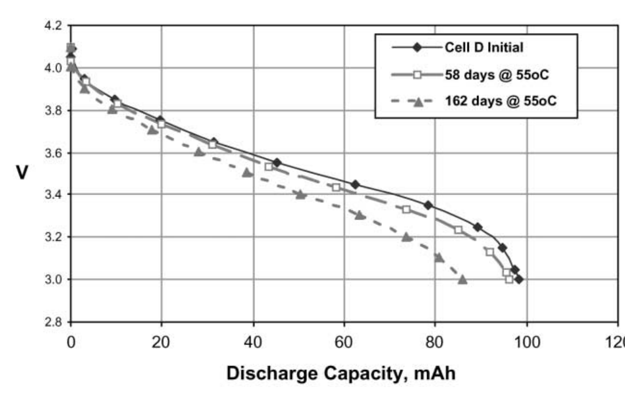


Fig. 8. Effect of 55 °C calendar life test on the 1 C discharge capacity curves of cell D at 25 °C.

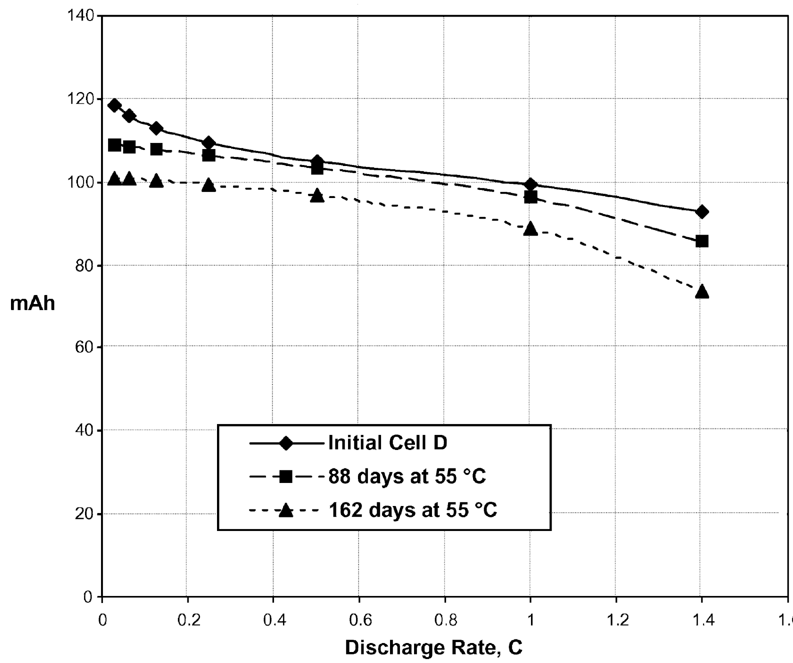


Fig. 9. Effect of 55 °C calendar life on the discharge capacity Peukert plot of cell D at 25 °C.

### 3.2. Accelerated storage tests at 55 °C

Calendar life tests at 55 °C changed the 1 C discharge capacity curves (at 25 °C) noticeably, as shown in Fig. 8. Corresponding changes were observed in the Peukert plots (taken from the signature capacities) shown in Fig. 9. These data show that the 55 °C storage decreased the cell capacities at both low and higher discharge rates, with the larger effects in the 1.0–1.4 C range. This corresponds to a loss of total capacity along with increased cell impedance.

In Fig. 10, the HPPC test results after 58 days at 55 °C are compared with their initial values. The dashed horizontal line indicates the limits which we have calculated for the retention of 75% of the initial HPPC values. After 58 days at 55 °C, the HPPC crossover for our cells reached this limit, although their 1 C capacity was virtually unchanged. As shown in Fig. 11, after 162 days at 55 °C, the 1 C capacity of these cells had decreased by only 10%, while the HPPC discharge power at the crossover had decreased by 50%. Our EIS studies showed that the cell resistance measured

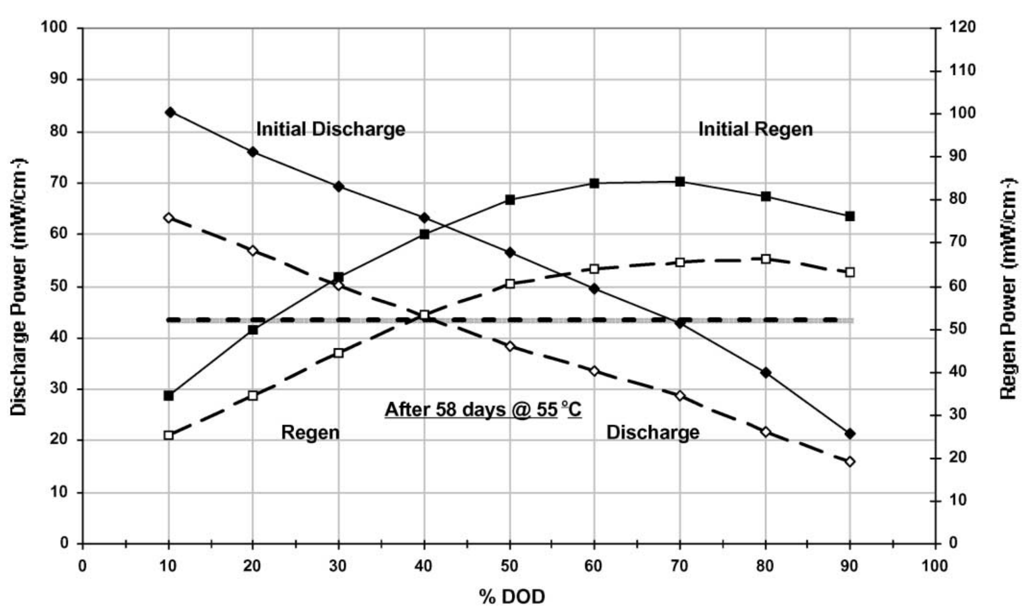


Fig. 10. HPPC curves before (solid lines) and after (dashed lines) 58 days of the 55 °C storage test on cell D at 25 °C. The horizontal line is the limit goal for 75% of initial power.

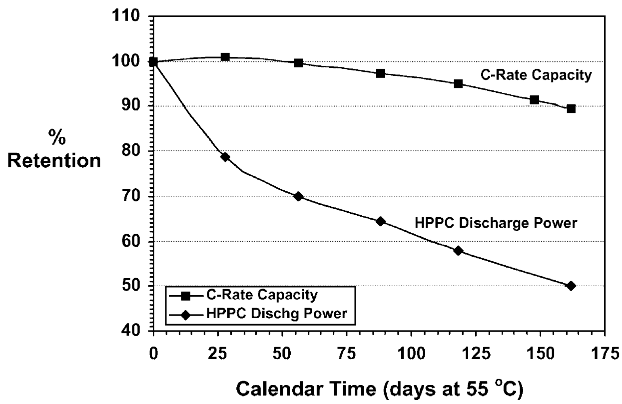


Fig. 11. Effects of 55 °C storage on the relative retention of capacity and of HPPC for cell D.

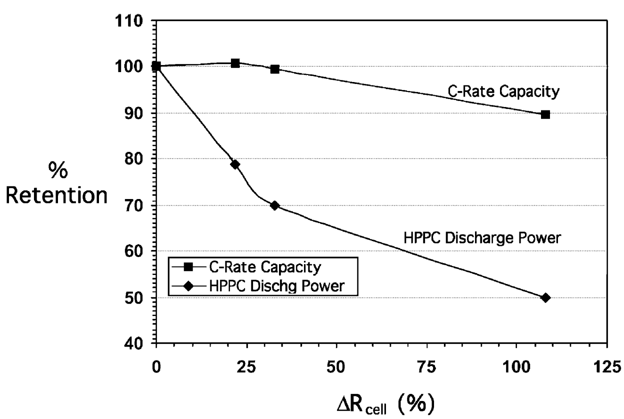


Fig. 12. Effect of 55 °C calendar test on retention of capacity and of HPPC correlated with the resistance increase of cell D, as measured by EIS. Data at 0, 28, 56 and 162 days at 55 °C).

at 25 °C was changed substantially by the 55 °C storage. Fig. 12 indicates that with continued storage up to 162 days at 55 °C, the cell resistance increased by 108%. In this same period, the HPPC values dropped by 50% while the 1 C capacity loss was only 10%.

## 4. Discussion

Excellent performance results pertinent to hybrid vehicle type applications are shown here on our exploratory plastic lithium-ion battery test cells containing improved cathode material. Our HPPC tests are evaluated in terms of a conservative calculation for the scale up of these cells to a large battery with the weight and volume limits corresponding to the minimum PNVG goals for a "Fast Response Engine" capable of a 25 kW pulse discharge and 30 kW regeneration pulses at the end of life. Our accelerated tests show that this HPPC limit is reached only after 50,000 pulse test cycles, or after about 40 days of the 55 °C calendar test. Longer period tests show that the HPPC discharge power decreased only about 30% after a total of 72,000 cycles and decreased about 50% after 162 days at 55 °C.

All of our tests were made in soft-pack bags, although the scale up calculations assume use of a metal can for each 40 Ah cell in the battery. These would be prismatic cells containing stacks of bicells larger than the small bicells studied in this paper. We expect that hermetically sealed metal can cells would substantially improve the lifetime of the cycling and calendar tests observed in our soft-pack cells, especially when operating at elevated temperatures such as 55 °C. In other studies, we have observed improved cycle life at 25 °C in metal-can cells of 55 Ah as compared to the small test cells in soft-packs. Optimization of the designs of the basic bicell, the 40 Ah cells, and the battery are all expected to provide improvements in the weight, volume, and performance of the scaled-up battery as compared to our calculations based on the small test cells.

Our test results reported, here, indicate there is probably some difference in the failure mechanism from thousands of pulse cycles at 25 °C as compared to one pulse cycle per day of calendar testing at 55 °C. The pulse cycling tests cause little change in the 1 C capacity, small changes in the total capacity, and a decrease of cell pulse power capability nearly proportional to the increase in cell resistance. The 55 °C calendar tests cause more loss in both the 1 C and total capacity, and after long periods the cell resistance increases substantially more than the loss of pulse power capability. We speculate that the pulse cycling tests cause some loss of lithium from the cathode to the anode, and that the impedance probably increases in both the anode and cathode. The elevated temperature storage tests probably cause relatively more changes in the cathode, both in capacity and resistance. This may be due to electrolyte decomposition at 55 °C, especially if impurities (oxygen and moisture) diffuse into the cells through the soft-packs.

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