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Pulse resistance effects due to charging or discharging of high-power lithium-ion cells: A path dependence study

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Abstract

Battery life estimations and state-of-health projections for commercial applications such as hybrid electric vehicles are highly dependent on accurate resistance monitoring. This study examined discharge/charge hysteresis (path dependency) effects on measuring resistance using two different lithium-ion cell chemistries. Cells were either discharged or charged to a target voltage, followed by a rest at open-circuit for electrochemical and thermal equilibration, immediately prior to a resistance measurement using a high-current pulse profile. Results show that a voltage hysteresis effect has an impact on cell resistance measurements, depending on the direction a target voltage is reached. Specifically, charging to a target condition yields different and less consistent resistance measurements compared to discharging to that same condition. Further, using slower rates to approach the target condition has a small impact on resistance on the discharge curve but does give a noticeable improvement on the charge curve. Unfortunately, slow charging and discharging are generally not practical for hybrid electric vehicle applications due to the rapidly changing power demands of the driver. Consequently, these results indicate that life estimates should be primarily based on resistances determined from pulses on the discharge curve.

Keywords: Lithium-ion; Voltage hysteresis; Path dependence; Pulse power; Life estimates

1. Introduction

A significant barrier to the commercialization of high-power lithium-ion batteries for automotive applications is inadequate life prediction. As part of the U.S. Department of Energy's Advanced Technology Development Program [1], the Technology Life Verification Test (TLVT) Manual [2] was developed as a means to verify battery life capability (e.g., 15 years, 150,000-miles) at a target confidence level within 1 or 2 years of accelerated testing. The manual incorporates the goals and requirements determined by the FreedomCAR (Freedom Cooperative Automotive Research) and Vehicle Technologies Program, along with its test procedures and profiles [3]. The goals of TLVT are to estimate life by using Monte-Carlo simulations that randomly varies model parameters, measurement errors and manufacturing variability, and to verify the validity of the estimate by aging cells according to test matrices that account for known stress factors (e.g., temperature, state-of-charge, energy throughput, and pulse power levels).

In the TLVT process, life estimates are based on degradation models. Several models were developed for the second generation of Advanced Technology Development cells (i.e., Gen2 cells), ranging from statistical to empirical approaches [1,4–6]. These models were primarily based on the results of periodic reference performance tests conducted during calendar- or cycle-life aging at various temperatures and states-of-charge (SOC) [4]. However, it has been shown that some components of the reference performance tests actually contributed to cell degradation as well [7]. Consequently, a new reference performance test was created to minimize these deleterious components while still providing sufficient information for accurate life prediction as part of the TLVT methodology [2]. The effects of this new test and profile on cell behavior and life estimation were studied at the Idaho National Laboratory (INL) using two different lithium-ion chemistries.

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Nomenclature

DOD	depth-of-discharge
HPPC	hybrid pulse power characterization (see Fig. 1)
MPPC	minimum pulse power characterization (see Fig. 2)
SOC	state-of-charge
SOC_{MAX}	maximum state-of-charge (see Fig. 2)
SOC_{MIN}	minimum state-of-charge (see Fig. 2)
TLVT	technology life verification test

2. Experimental

A battery's capabilities in regards to the FreedomCAR power and energy goals are typically verified using a $C_1/1$ static capacity test and a hybrid pulse power characterization (HPPC) test [3]. The $C_1/1$ static capacity test consists of a constant current discharge between full charge and the minimum voltage using the 1-h current rate based on rated capacity (e.g., a $C_1/1$ rate for a 1 Ah cell would be 1 A). The HPPC pulse profile is shown in Fig. 1, and consists of 10-s discharge and regen (i.e., regenerative braking) pulses separated by a 40-s rest. The discharge pulse is typically performed at a $5C_1$ rate, and the regen pulse at a $3.75C_1$ rate. This profile is repeated at every 10% depth-of-discharge (DOD) between (but not including) full charge and full discharge. Each DOD increment is reached by removing 10% of the beginning-of-life rated capacity followed by a 1-h rest at open-circuit to reach electrochemical and thermal equilibrium prior to the next pulse profile. From these data, the capacity, resistance, power, and energy can be determined and compared to the FreedomCAR goals [3]. For example, discharge or regen resistances are calculated from each HPPC pulse using Eqs. (1) and (2), respectively (subscripts refer to time points in Fig. 1), where V_{t_0} is the open-circuit voltage immediately prior to the pulse.

$$R_{\text{dis}} = \frac{V_{t_0} - V_{t_1}}{I_{t_1} - I_{t_0}} \quad (1)$$

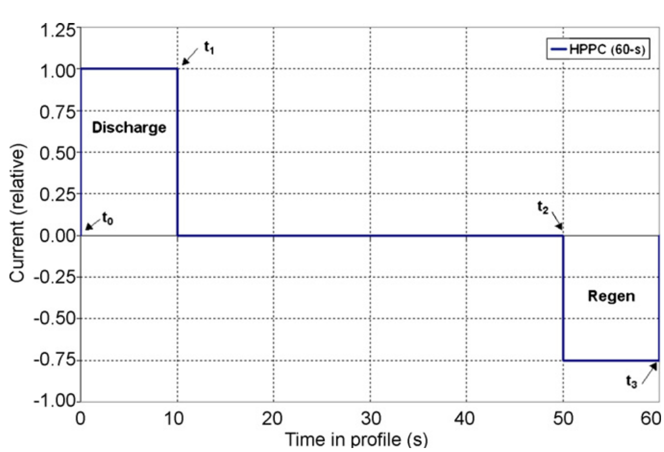

Fig. 1. Hybrid pulse power characterization profile.

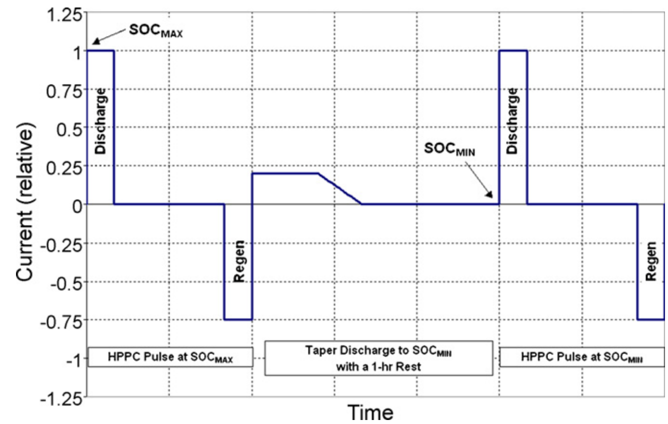

Fig. 2. Minimum pulse power characterization profile.

$$R_{\text{reg}} = \frac{V_{t_3} - V_{t_2}}{I_{t_3} - I_{t_2}} \quad (2)$$

Although it has been shown that the $C_1/1$ and HPPC tests themselves are not a significant source of degradation, the time spent at full charge for these tests can have a deleterious effect [7,8]. Therefore, the new Minimum Pulse Power Characterization (MPPC) test was designed to avoid full discharges and charges while also reducing the time spent away from the calendar- or cycle-life aging conditions due to the reference performance test [2]. The MPPC test profile is shown in Fig. 2, and consists of an HPPC pulse profile performed at only two points with a $C_1/1$ taper discharge in between. The two test conditions, defined as SOC_{MAX} and SOC_{MIN}, represent the anticipated standard operating range of the battery, and are typically specified by the manufacturer. For consistent measurements during aging, the MPPC reference points for SOC_{MAX} and SOC_{MIN} are voltage-based, whereas the HPPC test uses capacity removed as its reference. Consequently, SOC_{MAX} is reached by a taper charge to the appropriate voltage condition, and SOC_{MIN} is reached by a taper discharge.

2.1. Cell testing

A comparative study between the HPPC and MPPC was conducted using two different sets of lithium-ion cells. Initial tests were conducted using four 18650-size Gen2 Baseline cells developed for the Advanced Technology Development Program. These cells consisted of a $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ positive electrode, a MAG-10 graphite negative electrode, and an electrolyte of 1.2 M $LiPF_6$ in EC:EMC [4]. The cells were rated at 1 Ah with maximum and minimum voltages of 4.1 and 3.0 V, respectively. Two of the cells were previously aged at 25 °C to more than 50% power fade with approximately 1.2 million shallow cycles. The other two cells were relatively fresh, uncycled cells (i.e., less than 5% power fade) that had been stored at around 10 °C for about 4 years. The Gen2 test results were subsequently verified using SAFT VL7P lithium-ion cells. Although the chemistry of these cells is not publicly available, it is different from the Gen2 cells. These high-power SAFT cells were rated at 7 Ah with maximum and minimum voltages of 4.0–2.7 V. Testing was conducted on

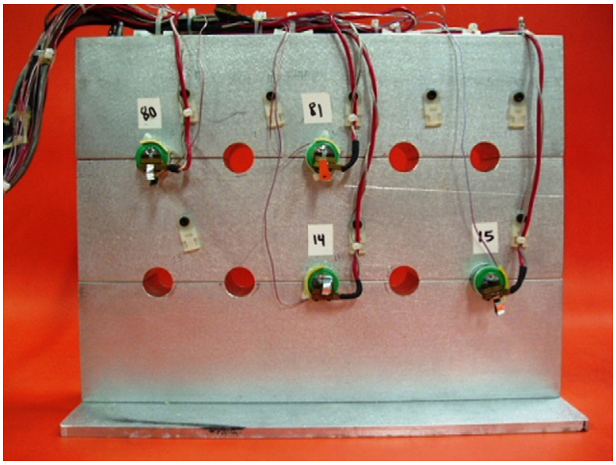

Fig. 3. 18650 cells inside a thermal block.

a Maccor Series 4000 battery tester with full-scale voltage and current ranges of 10 V and 12.5 A, respectively. (Channels were paralleled for a full-scale current range of 25 A for the SAFT cells.) All cells were placed inside aluminum thermal blocks to better control temperature transients, and tested inside a Tenney Junior chamber. Fig. 3 shows the four Gen2 cells placed in a thermal block with the voltage and current sense leads attached to the tabs.

The charging and discharging procedures were based on typical FreedomCAR requirements [3]. Full charge was defined by a $C_1/1$ constant current charge to the maximum voltage, followed by a voltage clamp for a cumulative time of 2.5 h, or until the current fell below a specified threshold (e.g., 50 mA). A particular SOC was reached the same way, with either a $C_1/1$ constant current charge or discharge to the target voltage, followed by the voltage clamp. The cells were then allowed to reach electrochemical and thermal equilibrium with a 1-h rest at open-circuit.

2.2. Measurement uncertainty

Prior to this study, the Maccor test channels were calibrated and checked for accuracy using the process defined in the INL Uncertainty Manuals [9,10]. Accuracy checks were performed over various current and voltage levels within the full-scale range of the test channel. These data, along with the calibration error of the accuracy check equipment (shunt and digital voltmeter), were used to calculate the total channel error. Only voltage and current are directly measured during testing (temperature is also monitored independently), so the uncertainty of derived or calculated parameters such as capacity, energy, resistance, or power is determined using a propagation of Taylor Series partial derivatives. The resulting uncertainty expressions are based on the standard deviations determined from the accuracy check and the calibration errors due to the measurement equipment. The total parameter error is usually expressed as a percent of reading.

For example, the uncertainty expression for the resistance determined from an HPPC test profile is shown in the following equation:

$$\%R_S = \left[2\left(\frac{\%\text{err}V_{STD}}{V(t_a)-V(t_b)}V_{FS}\right)^2 + 2\left(\frac{\%\text{err}I_{STD}}{I(t_a)-I(t_b)}I_{FS}\right)^2 + (\%\text{err}V_{CAL})^2 + (\%\text{err}I_{CAL})^2\right]^{1/2} \quad (3)$$

where $\%\text{err}V_{STD}$ and $\%\text{err}I_{STD}$ are the standard deviations for voltage and current, respectively (as determined from the accuracy check), $\%\text{err}V_{CAL}$ and $\%\text{err}I_{CAL}$ the equipment calibration errors, V_{FS} and I_{FS} the full-scale voltage and current levels for the test channel, and $V(t)$ and $I(t)$ are the voltage and current measurements taken during the discharge or regen pulse. The subscripts "a" and "b" correspond to "t_0" and "t_1" for the discharge resistance shown in Eq. (1), and to "t_2" and "t_3" for the regen resistance from Eq. (2).

This methodology was applied to the resistances calculated from both the MPPC and HPPC tests performed in this study. For example, Table 1 shows the discharge resistances and their associated uncertainties at SOC_{MAX} and SOC_{MIN} from an MPPC test (as a percent of reading) using the Gen2 cells. The uncertainties of the regen resistance for these cells were similar. Note that while all four cells have a very small uncertainty, the aged cells (A and B) have a lower uncertainty than the fresh cells (C and D). This is primarily due to the larger ΔV from the discharge pulse that results from the higher resistance in an aged cell compared to a fresh cell (i.e., "$V(t_a) - V(t_b)$" in the numerator of Eq. (3)).

3. Results and discussion

3.1. Gen2 cells

Since the MPPC test is voltage-based, a modified HPPC test was defined for comparison and verified using the Gen2 cells. Instead of removing 10% of the rated capacity prior to each pulse, the cells were discharged to the open-circuit voltage corresponding to each 10% SOC instead (using the procedure defined

Table 1
Gen2 discharge resistance uncertainty from an MPPC test

	SOC_{MIN}		SOC_{MAX}	
	Resistance (mΩ)	Uncertainty (%)	Resistance (mΩ)	Uncertainty (%)
Gen2 cell A (aged)	56.64	0.138	62.08	0.127
Gen2 cell B (aged)	57.32	0.141	63.23	0.130
Gen2 cell C (fresh)	29.79	0.409	32.01	0.381
Gen2 cell D (fresh)	33.45	0.294	36.10	0.273

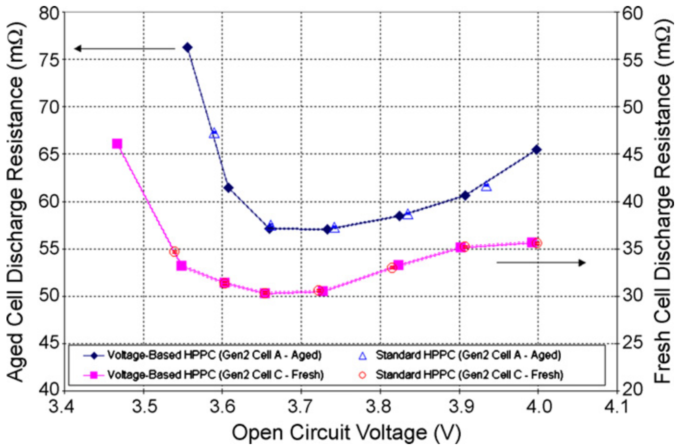

Fig. 4. Comparison between a capacity- and voltage-based HPPC test.

above). In other words, for a standard HPPC, the cells were discharged in 10% capacity increments regardless of the voltage drop; for the modified HPPC test, the cells were discharged to pre-determined voltage increments regardless of the capacity removed. The open-circuit voltages corresponding to each 10% SOC increment were determined by a slow discharge (i.e., $C_1/25$ rate) between full charge and the cell minimum voltage at beginning of life, and remained fixed regardless of cell age [4]. The cells were initially fully charged prior to the start of these tests.

Fig. 4 compares the discharge resistance from the standard capacity-based HPPC test (open symbols) to that of a voltage-based HPPC test (closed symbols) for representative aged and fresh Gen2 cells (cells A and C, respectively). Dashed lines represent the uncertainty band determined from Eq. (3), though in some cases it may be hard to see them due to the high-data quality. These data show that both versions of the HPPC test yield the same resistance curve as a function of voltage. Consequently, the voltage-based HPPC test is considered a valid basis for comparison with the MPPC test.

Fig. 5 shows the discharge resistance for a voltage-based HPPC test (closed symbols) and a standard MPPC test (open symbols) for a representative aged and fresh Gen2 cell. Table 2 shows the percent difference in resistance between these two tests at both SOC_{MAX} (90% SOC, 3.99 V) and SOC_{MIN} (50% SOC, 3.65 V). The MPPC and HPPC resistances are reasonably similar at SOC_{MIN} (within test-to-test cell variability), but very different at SOC_{MAX}. The approach towards the voltage corresponding to SOC_{MAX} from alternate directions (i.e., charging for the MPPC and discharging for the HPPC) is the most significant difference in the test sequence. At SOC_{MIN}, the cells were discharged to the target voltage for both tests, and the differences in resistance were minimal. This voltage hysteresis effect has been observed before with various lithium-ion cell chemistries [11–18], and it has been argued that the mechanism responsible for hysteresis is present in all lithium-ion cells [16], though its extent and location will be dependent on cell chemistry and the cycling conditions. Many have attributed the source of the hysteresis to the negative electrode for both hard and graphitic carbons [11–15], though others have attributed it to the positive electrode instead [16–18].

Table 2
Difference between the MPPC- and voltage-based HPPC discharge resistances

	SOC_{MIN} (%)	SOC_{MAX} (%)
Gen2 cell A (aged)	0.47	4.63
Gen2 cell B (aged)	0.21	4.55
Gen2 cell C (fresh)	2.42	8.90
Gen2 cell D (fresh)	1.67	8.02

The effect of voltage hysteresis was verified with a sequence of four consecutive MPPC tests using the Gen2 cells. The cells were fully charged prior to the first and fourth MPPC tests, followed by a discharge to SOC_{MAX}. The cells were fully discharged prior to the second and third MPPC tests, followed by a charge to SOC_{MAX}. Fig. 6 shows the resulting discharge resistances at SOC_{MAX}, and Table 3 shows the percent difference between the averages of the charging path (i.e., MPPC 2 and 3) and discharging path (i.e., MPPC 1 and 4). These data also demonstrate that the approach to a target voltage has an effect on cell resistance, with a smaller resistance when SOC_{MAX} is reached by a charge. Srinivasan and Newman [18] have used the shrinking core model to describe path dependence on a $LiFePO_4$ electrode, and that may also help describe what is happening to the Gen2 cell chemistry. Using this model, a fully charged cell under discharge conditions will have cathode particles characterized by a lithium-deficient core that is covered with a

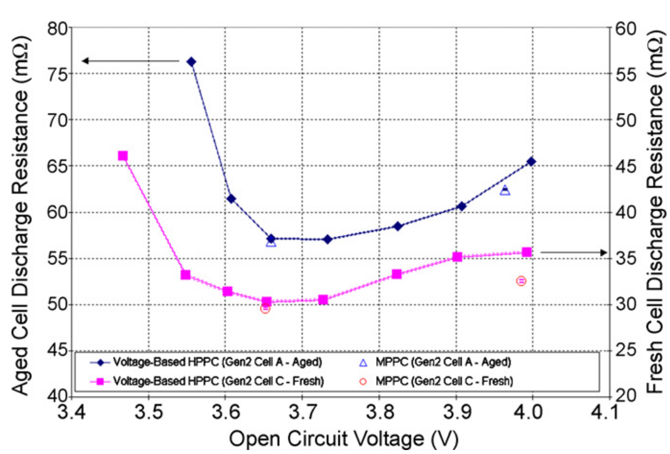

Fig. 5. Comparison between the MPPC- and voltage-based HPPC tests.

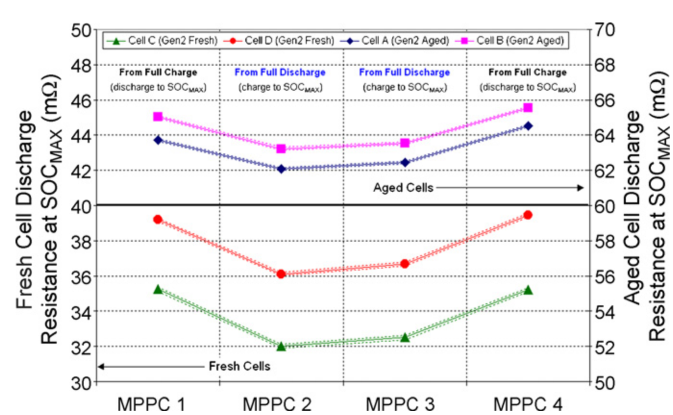

Fig. 6. MPPC path dependence effects on resistance at SOC_{MAX}.

Table 3
Percent difference between MPPC tests at SOC_{MAX}

	Average of MPPC 1 and 4 (mΩ)	Average of MPPC 2 and 3 (mΩ)	Difference in averages (%)
Gen2 cell A (aged)	64.12 ± 0.56	62.26 ± 0.26	2.90
Gen2 cell B (aged)	65.29 ± 0.36	63.38 ± 0.22	2.93
Gen2 cell C (fresh)	35.23 ± 0.02	32.26 ± 0.35	8.45
Gen2 cell D (fresh)	39.32 ± 0.19	36.39 ± 0.41	7.46

lithium-rich shell that increases as current is applied. Conversely, anode particles might experience depletion of lithium-ions from outer radii, while maintaining a higher lithium population in their core. This is the condition for MPPC 1 and 4, where the cells were discharged to SOC_{MAX}, then (after a 1-h rest), were subjected to the HPPC discharge pulse. A fully discharged cell (i.e., MPPC 2 and 3) under charge conditions will have cathode particles characterized by a lithium-rich core that is covered with a lithium-deficient shell that increases as current is applied. However, once the cells were charged to SOC_{MAX} and rested for 1 h, they were subjected to the HPPC discharge pulse. This would form an additional lithium-rich shell over the lithium-depleted shell and the lithium-rich core. Srinivasan and Newman have demonstrated that forming these new shell regions yield lower ohmic drops compared to the expansion of existing shells since the diffusion length will be smaller, resulting in smaller activation energies. Consequently, since the path towards SOC_{MAX} resulted in the formation of additional shells for MPPC 2 and 3, the resistances are lower.

Interestingly, as shown in Fig. 6, the aged cells have a smaller path-dependent resistance effect than the fresh cells, but Zimmerman and Quinzio [16] have shown that the voltage hysteresis between charge and discharge increases with cell age. The explanation for this apparent inconsistency lies in the voltage recovery behavior. Table 4a shows the Gen2 cell voltage recovery during the 1-h rest immediately prior to the MPPC pulse. In all cases, the aged cells show a larger voltage recovery than the fresh cells, indicating that the hysteresis is indeed larger as expected (i.e., more voltage depolarization as a function of rest time). Further, the hysteresis also appears to have a dramatically larger effect when charging. The aged cells show almost five times as much voltage recovery when approaching SOC_{MAX} from a charge (i.e., MPPC 2 and 3) compared to only about twice as much recovery when discharging to SOC_{MAX}. The differences are further clarified when looking at the ratio of the voltage recovery during the 1-h rest (Table 4a) and the voltage drop during the MPPC discharge pulse at SOC_{MAX}, as shown in Table 4b. When approaching SOC_{MAX} from a discharge (i.e., MPPC 1 and 4), the relative ratios are similar for all fresh and aged cells (approximately 2%). However, approaching SOC_{MAX} from a charge (i.e., MPPC 2 and 3), the relative ratios increase to approximately 3% and 8% for the fresh and aged cells, respectively. Thus, the aged cells appear to show a larger percent recovery than the fresh cells during the 1-h rest following a charge, indicating that they may have reached a more equilibrated state as a result. This observation may help to explain the smaller difference in resistance for the aged cells compared to the fresh cells in Table 3. Furthermore, this observation also suggests that using the discharge curve will yield more consistent and repeatable results throughout life, because the voltage recovery for the aged cells is more comparable to the recovery from the fresh cells under discharge conditions. This is further verified with the discharge resistances at SOC_{MIN}, where the percent difference in discharge resistance for both the fresh and aged cells was less than 1% for all cells (not shown in this paper).

The stronger voltage hysteresis effect on the charge curve was further confirmed by a modified MPPC test. The modified MPPC test consisted of an HPPC pulse profile at SOC_{MAX} (after a charge to the appropriate voltage), followed by pulse at each 10% DOD increment until the voltage corresponding to SOC_{MIN} was reached. Fig. 7 shows the resulting discharge resistances compared to the voltage-based HPPC and standard

Table 4a
Voltage recovery after 1-h rest at open-circuit voltage at SOC_{MAX}

	MPPC 1 (mV)	MPPC 2 (mV)	MPPC 3 (mV)	MPPC 4 (mV)
Gen2 cell A (aged)	5.80	−27.01	−25.64	5.34
Gen2 cell B (aged)	8.24	−25.02	−23.80	6.10
Gen2 cell C (fresh)	3.05	−5.80	−4.43	2.75
Gen2 cell D (fresh)	4.43	−7.32	−5.04	3.81

Table 4b
Relative voltage recovery between the 1-h rest at OCV and the voltage drop during the MPPC discharge pulse

	MPPC 1 (%)	MPPC 2 (%)	MPPC 3 (%)	MPPC 4 (%)
Gen2 cell A (aged)	1.82	−8.70	−8.21	1.66
Gen2 cell B (aged)	2.53	−7.92	−7.49	1.86
Gen2 cell C (fresh)	1.73	−3.62	−2.72	1.56
Gen2 cell D (fresh)	2.26	−4.06	−2.75	1.93

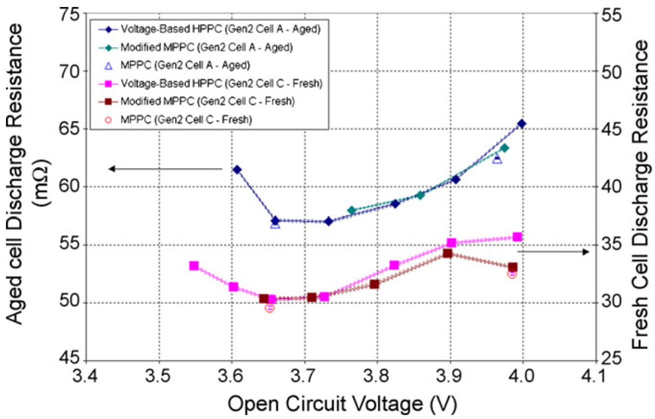

Fig. 7. Comparison between the modified MPPC- and voltage-based HPPC test.

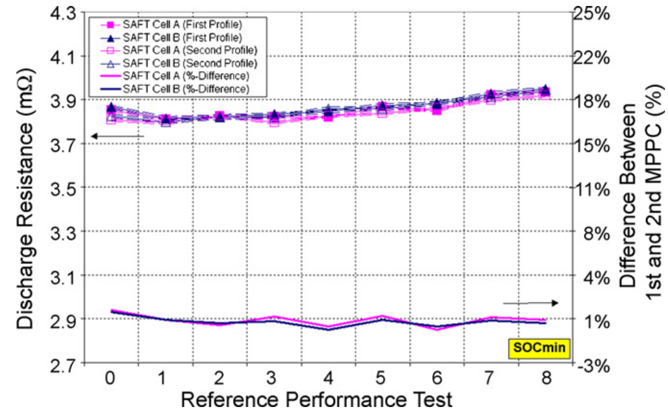

Fig. 9. Discharge resistance at SOC_{MIN} for 30 °C cells.

MPPC tests, and the corresponding uncertainties based on Eq. (3). As expected, the initial resistance at SOC_{MAX} (approximately 3.99 V) is lower for the MPPC and modified MPPC tests due to the initial charge. The fresh cell resistance from the modified MPPC then rapidly approaches the voltage-based HPPC resistance curve after just the first 10% discharge prior to the next pulse. The hysteresis effect due to the initial charge, however, still appears to have a smaller effect on the resistance curve for the second and third pulses before it starts to match up with the voltage-based HPPC more closely on the fourth and fifth pulses. For the aged cells, the voltage recovery is much larger (as shown in Table 4a), and the modified MPPC recovers very quickly to the voltage-based HPPC curve between the first and second pulse profiles.

3.2. High-power SAFT cells

The SAFT VL7P high-power cells also showed a voltage hysteresis effect from the MPPC test. Two cells were calendar-life aged at SOC_{MAX} and 30 °C for approximately 8 months. Calendar-life aging included a daily taper charge to SOC_{MAX}, with the remaining time spent resting at open-circuit condition. Reference performance tests were conducted every 31.5 days during aging and consisted of two back-to-back MPPC tests [2]. Fig. 8 shows the discharge resistances from both the first and second profiles at SOC_{MAX} for the two SAFT cells over

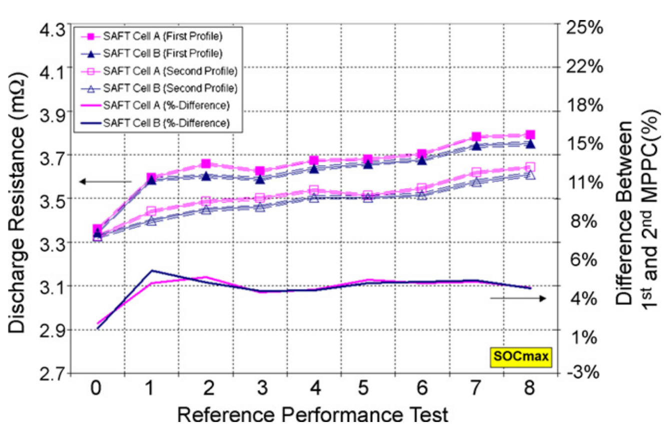

Fig. 8. Discharge resistance at SOC_{MAX} for 30 °C cells.

time, along with the corresponding measurement uncertainty as determined from Eq. (3). The percentage differences between the resistances for each pair of MPPC tests are also shown. Except for the very first test, the back-to-back MPPCs consistently yield about a 4% difference in resistance through 8 months of aging (although this may start decreasing as the cells age and hysteresis rises, as discussed above). A significant difference between the back-to-back MPPCs is the amount of taper charge required to reach the voltage corresponding to SOC_{MAX}. Since the cells are already calendar-life aging at SOC_{MAX}, the required charge prior to the first MPPC pulse profile is very small (approximately 2.8 mAh). Much more charge is required for the second profile (approximately 2700 mAh) since the cell voltage is closer to SOC_{MIN} after performing the first profile. At beginning of life (i.e., time = 0), the discharge resistances were similar since the cells had previously been fully discharged from the preceding HPPC test. Consequently, the first MPPC test also required an initial charge from full discharge to SOC_{MAX} (approximately 4500 mAh). The data at SOC_{MIN} clearly have less variation, as shown in Fig. 9. In all cases, the cells were discharged from SOC_{MAX} to SOC_{MIN}, and the difference in the back-to-back MPPCs was only about 1%, compared to 4% at SOC_{MAX}.

It was considered possible that these differences were due to the cells not reaching full equilibrium prior to the pulses. Intercalation efficiency (as measured by lithium ordering within the solid state) is greater for cycling rates approaching equilibrium conditions. Thus, lithium distribution within a particle is rate-dependent, and differences therein should be minimized as that rate is reduced. Fast-rate hysteresis effects could also be related to differences in the intrinsic rate capabilities between cathode and anode. Consequently, a comparison of different charge/discharge rates was also made using two additional SAFT VL7P cells. These cells had been previously characterized with various HPPC and MPPC tests, some thermal performance testing, and about 2000 shallow cycles. The six test sequences are described in Table 5. The "standard" MPPC test uses the procedure typically adopted for reaching equilibrium for the FreedomCAR Program. The "fast" and "slow" rates (i.e., using $C_1/1$ and $C_1/5$ currents, respectively) maintain constant voltage for an additional 1.5 h (4 h total) followed by a 5-min rest at open-circuit voltage.

Table 5
Equilibrium study

MPPC test	Description for reaching SOC_{MAX}
Standard	$C_1/1$ *charge*; maintain constant voltage until current ≤ 50 mA or total time ≤ 2.5 h, rest at open-circuit voltage for 1 h $C_1/1$ *discharge*; maintain constant voltage until current ≤ 50 mA or total time ≤ 2.5 h, rest at open-circuit voltage for 1 h
"Fast" rate	$C_1/1$ *charge*; maintain constant voltage for a total of 4 h, rest at open-circuit voltage for 5 min $C_1/1$ *discharge*; maintain constant voltage for a total of 4 h, rest at open-circuit voltage for 5 min
"Slow" rate	$C_1/5$ *charge*; maintain constant voltage for a total of 4 h, rest at open-circuit voltage for 5 min $C_1/5$ *discharge*; maintain constant voltage for a total of 4 h, rest at open-circuit voltage for 5 min

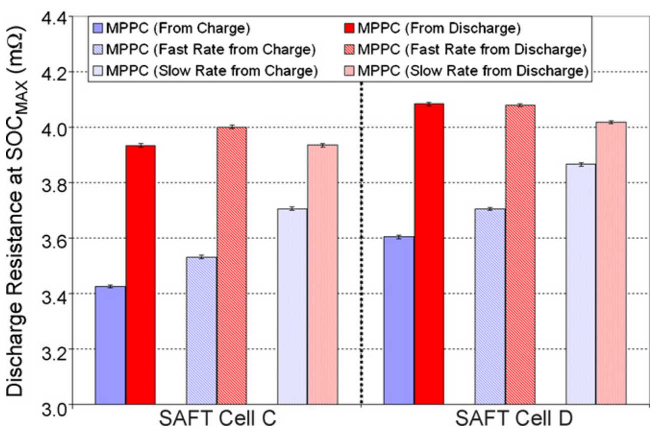

Fig. 10. Discharge resistance at SOC_{MAX} at different rates.

Fig. 10 shows the resulting discharge resistances at SOC_{MAX} for the six different test conditions along with the associated uncertainty bands as determined from Eq. (3). Resistance does not appear to be significantly affected by the rate when approaching SOC_{MAX} from a discharge. However, the resistance noticeably changes as a function of rate when SOC_{MAX} is reached by charging. As the charging rate is reduced, the resistance increases towards the corresponding discharge value. However, the resistances between charge and discharge do not match very well even at the slower rate. Table 6 shows the percent-differences in resistance when approached from different directions. At the slowest rate, the difference is still 4–6%, which is significantly greater than the measurement uncertainty (approximately 0.14%). These data suggest that equilibrium does play a role in the determination of resistance (as expected), but even at the slower rates, a voltage hysteresis is still present. Further, slow discharges and charges are generally not practical for hybrid electric vehicle applications since driving profiles usually require high-power pulsing during operation. Consequently, these data also support the observation that life estimates should primarily be based on the discharge curve since it appears to be less affected by current rate.

Table 6
Percent difference of discharge resistance at SOC_{MAX} between approaches

	Standard rate (%)	"Fast" rate (%)	"Slow" rate (%)
SAFT cell C	14.85	13.27	6.18
SAFT cell D	13.31	10.10	3.95

4. Summary and conclusions

Battery technology life verification is a key component to the development of lithium-ion chemistries for hybrid electric vehicle applications. Towards that end, cells are aged at various temperatures and states-of-charge with periodic reference performance tests that are used to measure degradation rates and predict life. A newly developed minimum pulse power characterization test was designed to avoid some of the commonly known degradation factors such as time spent at full charge. However, the application of this test to lithium-ion cells revealed a voltage hysteresis (i.e., path dependence) that has an impact on resistance measurement. Different resistance values are observed when approaching a target voltage condition from a charge compared to a discharge. The resistance was more consistent and repeatable when determined from a discharge step. Approaching a target condition at different rates does not appear to significantly effect resistance measured after discharging, but does have a noticeable effect after charging. However, slow charging and discharging rates are generally not practical for hybrid electric vehicles. Therefore, it is recommended that life modeling and estimating should be based on discharge behavior since the data appear more consistent and repeatable throughout life.

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