

Cycle life testing of lithium batteries: The effect of load-leveling

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In the present study, modules of LiNiCoAl and LiFePO₄ cells were cycled at constant current and on dynamic pulse discharge/charge profiles. All the cycling was done at room temperature. Each module consisted of three 18650 cells. The average current for both discharge profiles was C/2. The degradation of the modules was tracked in terms of changes in their Ah capacity and resistance as the cycling proceeded. The modules were cycled for about 750 cycles over a period of six months. For both lithium chemistries, the present data indicated that the modules degraded more rapidly with constant current cycling than using the dynamic pulse profiles. This was an unexpected result as current thinking is that load-leveling the discharge of a battery will increase its cycle life. It is difficult to compare the present data with that from the previous studies because the test conditions, charging algorithms, and discharge profiles of the various studies are quite different. The available data in the literature show large variations in the effect of load leveling on the cycle life of batteries.

Keywords: Cycle life, degradation, dynamic pulse discharge, constant current discharge, LiNiCoAl, LiFePO₄.

1. INTRODUCTION

Li-ion batteries are currently the preferred energy storage technology for plug-in electric vehicles (PEVs) because of their high energy density, good power capability, and high cell working voltage [1]. Limited cycle life and relatively high initial cost have been constraints to their use in mass marketed PEVs. High discharge pulse power demands for vehicle acceleration and large pulse currents during regenerative braking are thought to be factors that can reduce the cycle life of batteries in electrified vehicles [2-6]. The high current pulses experienced by the batteries can be significantly reduced by combining the batteries with supercapacitors (SCs) in the energy storage unit for the vehicle [3]. SCs have very high power density, rapid charging capability with high pulse current, and

very long cycle life (up to one million cycles) [5]. Utilizing the proper control strategy to split the current demand to/from the electric motor between the batteries and the SCs, the current/power experienced by the batteries can ideally approach the average current/power needed to operate the vehicle. Current thinking is that load-leveling the battery will increase its cycle life and in addition, permit the use of batteries with lower power capability and hence higher energy density and lower cost (\$/kWh). The lower currents in the batteries will also reduce the heat generated and the cooling required and thus the round-trip efficiency of the energy storage unit. There have been only a few previous studies [4, 6] that directly seek to determine the effect of battery load-leveling on cycle life utilizing SCs.

The cycle life testing discussed in this paper was intended to quantify the effect on cycle life of load-leveling lithium batteries as they would be used with SCs in PEVs. Specifically, cycle life testing of 18650 cells of the LiNiCoAl and LiFePO₄ chemistries was performed. Three cell, series-connected modules were prepared for both chemistries. One module of each of the two cell chemistries was tested using a dynamic pulsed discharge profile and one module at a constant current equal to the average current of the dynamic pulse profile. The cycles for both modules were terminated when 80% of the cell initial Ah capacity was discharged. The Ah capacity and resistance of the modules were monitored every 30 cycles to assess the degradation of the cells. This test procedure permits the direct assessment of the effect on cycle life of load-leveling the discharge of the cells for the same charge and test termination conditions.

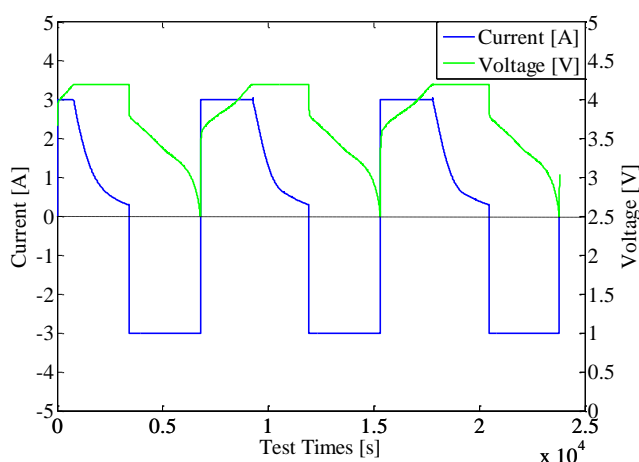
2. OBJECTIVE OF THE PRESENT RESEARCH

As indicated in the previous section, the objective of the present study is to determine the effect of dynamic pulsing of the cells (both charge and discharge power pulses) on cycle life during cell discharge. There have been many experimental studies [7-16] of the factors that affect the cycle life of lithium-ion batteries and the Ah throughput needed to reduce their capacity (Ah or Wh) by 20% and increase their resistance by 50%. There have been far fewer studies [11-13] that compared directly the cycle life of batteries discharged at constant current with the same battery discharged with dynamic charge/discharge pulses. The previous studies [11-13] have shown that the cycle life of lithium batteries depends in a complex manner on many factors and the discharge profile is only one of them. The additional factors include the chemistry and size of the cells, ambient temperature of the tests, the charge algorithm, and the initial and final discharge conditions. For these reasons, special care was taken in this paper to present in detail the test conditions and the pulse test profiles used in these cycling tests so that researchers in future studies can make comparisons of their data with the present results.

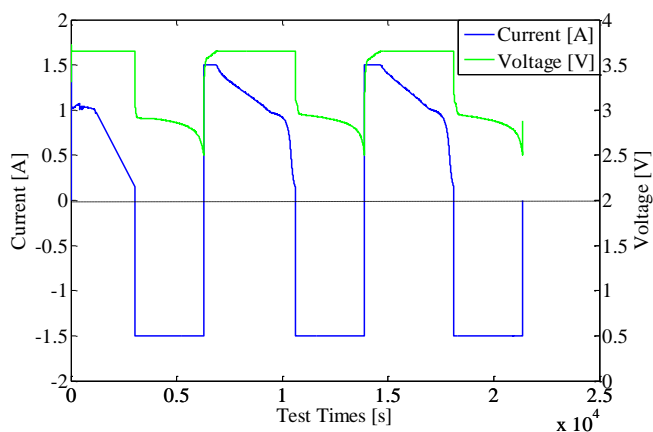
It is difficult and uncertain to compare the life cycle results of the present study with those of previous studies performed under different conditions. In many of the studies that included dynamic discharge profiles, there were not constant current cycling tests for comparison. However, some comparisons of the present cycling test data and that in the literature are made in a later section of the paper.

3. BATTERY CELL/MODULES AND TEST PROCEDURES

In this project, LiNiCoAl cells, Panasonic 3.1Ah 18650A, and LiFePO₄ cells, K2 Energy 1.5Ah 18650E, were tested. Both of these cells are commercially available and can be purchased on the internet. The cells were tested using an Arbin battery tester which can support ±20 A, 20 V for 6 channels in the Vehicle Energy Test Laboratory at the University of California-Davis. The performance characteristics of all the cells were measured before they were connected into 3-cell modules for the life cycle testing. The results of the initial characterization tests of a typical cell of each chemistry are summarized in Fig. 1 and Table 1. Note in Fig. 1 the distinctly different current taper characteristics of the two cell chemistries. In the case of the NiCoAl cell, the current tapers at a near constant rate over a relatively long time and then levels off to taper more slowly. In the case of the LiFePO₄, the current tapers rather slowly for a relatively short time and then rapidly decreases in a short time to the cut-off current. The differences in the cell chemistries are reflected in their C-V charging characteristics and thus their total charging times at specific C rates.



a. Current and voltage profile of LiNiCoAl 18650A Li-ion cell, in which the cell was charged and discharged at 1 C current, 25°C for 3 test cycles between 4.2V to 2.5V.



b. a. Current and voltage profile of LiFePO₄ 18650E Li-ion cell, in which the cell was charged and discharged at 1 C current, 25°C for 3 test cycles between 3.65V to 2V.

Figure 1. Charge and discharge characterization tests of the cells

The cell test results were used to select the cells to combine in the 3-cell modules used in the cycle testing. Since the cell characteristics varied significantly, the selection process was needed to attempt to minimize the differences in the modules for each of the cell chemistries. The two modules of each battery chemistry were tested simultaneously to minimize the impact of calendar life on the cycling performance tests.

Table 1. Performance characteristics of the cells.

Device: Panasonic - LiNiCoAl / Nominal voltage: 3.6 V / Nominal capacity: 3100 mAh						
Constant Current (A)	Time (sec)	Ah	Pulse tests		Steady-state Resistance (mOhm)	Rebound Resistance (mOhm)
			Pulse Current (A)	Pulse Time (sec)		
1	10476	2.91	-9	10	74	76
2	5130	2.85	-6	10	78	77
3	3271	2.73	-3	10	77	78
			7	5	76	75
Device: K2 – LiFePO ₄ / Nominal voltage: 3.1 V / Nominal capacity: 1500 mAh						
0.5	10368	1.44	-6	10	101	101
1	4965	1.38	-4	10	107	108
2	2309	1.28	-2	10	115	115
			4	5	106	101

Table 2. Initial characteristics of the modules.

Modules	Charging algorithms	Charging current (A)	Initial Ah capacity	Initial Pulse Resistance (Ohm)
LiNiCoAl (V _{cut-off} :3.0V/cell)	Constant current	1	2.719	0.2436
	Dynamic pulsing	1	2.72	0.2412
LiFePO ₄ (V _{cut-off} :2.5V/cell)	Constant current	0.6	1.389	0.2118
	Dynamic pulsing	0.6	1.286	0.2436

The initial Ah capacity and resistances of the four modules are given in Table 2. As indicated in Table 2, the testing of the K2 module used in the dynamic pulse cycling tests indicated its initial Ah capacity was significantly lower than the module used for the constant current testing. As discussed later, this resulted in the cycle life of the K2 module in the dynamic cycle test being relatively short.

The discharge conditions for the comparative tests of the cells/modules were set as follows. The current and voltage limits were set based on information from the manufacturers of the cells, Panasonic and K2 Energy. In these tests, the maximum charge and discharge pulses were set at 3-4C. The pulse times were set to be appropriate for EV operation. The maximum pulse currents for each chemistry were selected such that the voltage drops during the pulses were compatible with the minimum voltage limits of the cells and their resistance. The discharge profiles with the pulses (charge

and discharge) were configured to yield a constant current of C/2. This discharge time would be reasonable for an EV application. The constant current tests were run at the same average current as experienced by the cells in the dynamic pulsing tests. The dynamic pulse profiles are listed in Tables 3 and 4. The maximum power densities (W/kg) of the pulses were relatively high for the 18650 cells for both the discharge and charge pulses. Hence the cycling with dynamic pulse sub-cycles was relatively demanding.

Table 3. Dynamic pulse sub-cycle steps for life cycling test on LiNiCoAl module*.

Pulse start time (s)	Pulse duration (s)	Pulse Current(A)	Net (As)
0	10	-9	90
10	10	0	90
20	5	6	60
25	25	0	60
50	20	-6	180
70	10	0	180
80	5	6	150
85	15	0	150
100	30	-3	240
130	10	0	240
140	5	6	210
145	37	0	210
170			

*(W/kg)max = 675, Average current: 1.15A (C/2.7-rate)

Table 4. Dynamic pulse sub-cycle steps for life cycling test on LiFePO₄ module*.

Pulse start time (s)	Pulse duration (s)	Pulse Current(A)	Net (As)
0	10	-6	60
10	10	0	60
20	5	4	40
25	25	0	40
50	10	-4	80
60	10	0	80
70	5	4	60
75	15	0	60
90	15	-2	90
105	10	0	90
115	5	4	70
120	25	0	70
145			

*(W/kg)max = 375, Average current: 0.48A (C/3.1-rate)

The cycle testing of the modules was performed as follows. Before each discharge cycle, the module was completely charged to the specified voltage for the two chemistries (12.6V for the NiCoAl cells and 10.95V for the FePO4 cells). The charging current ($C/2$) was then tapered to $1/10$ th the initial value. The modules were rested for 5 minutes before the discharges were initiated. For all the cycles, the cycle was terminated when 80% of the initial Ah capacity of the module had been discharged. The average currents for the dynamic pulse sub-cycles are indicated in Tables 3 and 4. These average currents were used in the constant current cycling of the respective modules. In the dynamic pulse cycle discharges, the sub-cycles were repeated for a specified time to discharge 80% of the module Ah capacity. In the constant current cycling, the cycle was also terminated when 80% of the module capacity had been discharged. After a 5 minute rest, the modules were recharged and then discharged. After each set of 30 cycles, a performance diagnostic test (PDT) was performed to determine the Ah capacity and resistance of the module, shown in Fig.2. The resistance was determined from an 8 sec, 4-5A pulse at 60% SOC; the Ah capacities were determined using a cut-off voltage of 3.0V/cell for the Panasonic NiCoAl module and 2.5V/ cell for the K2 Energy FePO₄ module.

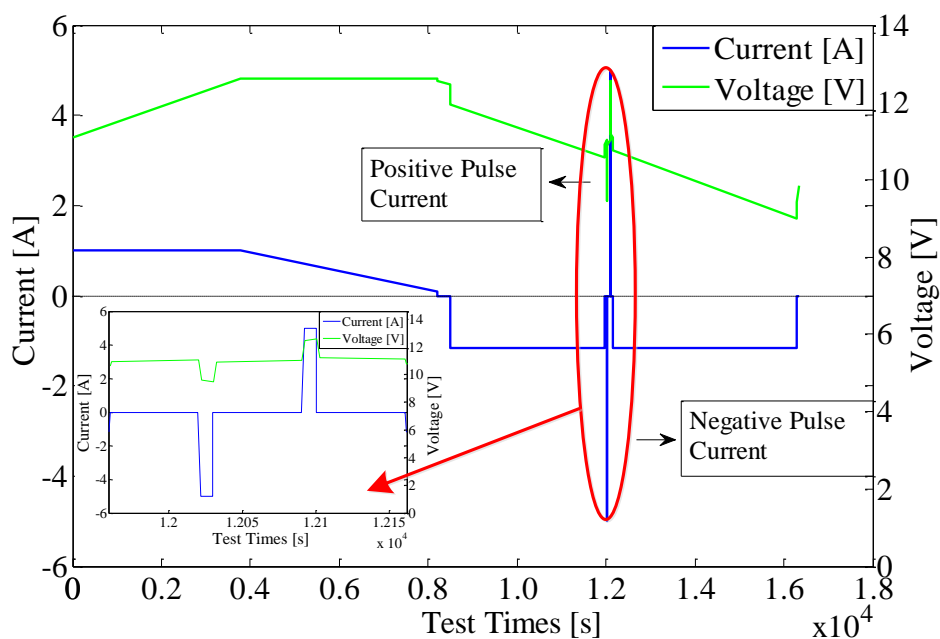


Figure 2. Performance diagnostic test after each 30 deep discharge cycles (Supplementary note: PDT comprises a fully charge, SOC=100%, and then a capacity-examination via constant current discharge at $C/2.7$ -rate for LiNiCoAl battery module and $C/3.1$ -rate for LiFePO₄ battery module is implemented. Discharge and charge pulse tests are performed to obtain the steady-state resistance, and rebound resistance of the battery modules [27].

4. RESULTS AND DISCUSSION

The primary objective of the experimental study was to determine the effect of dynamic pulse cycling on the cycle life of lithium-ion cells. To accomplish this objective, one module of each chemistry was cycled on the dynamic discharge/charge profiles shown in Tables 3 and 4, and the other

module was cycled at the constant average current of the respective dynamic cycles. All the cycling was done at room temperature. The degradation of the cells is described in terms of the change in the Ah capacity and resistance of the modules as the cycling proceeded. The results of the cycling are shown in Fig. 3 for the Ah capacity and in Fig. 4 for the resistance.

The test results shown in Fig. 3a indicate that the Ah capacity of the NiCoAl module decreased more rapidly for the constant current cycling than with dynamic cycling, but the difference was not large. The test results for the FePO₄ modules given in Fig. 3b indicate that the degradation was more rapid with the dynamic pulse cycling, but this interpretation is uncertain because the module used for dynamic cycling was discharged to 87% of its original Ah capacity rather than to 82% as was the case for the module being cycled at constant current. If one extrapolates the curves in Fig. 3 to estimate the number of cycles to reach a 20% reduction in Ah capacity, one obtains the estimated cycle life values given in Table 5, which show that dynamic cycling does not have a significant negative effect on cycle life for either lithium battery chemistry and in fact for the NiCoAl chemistry, the effect of dynamic cycling on Ah degradation is positive. Due to the unplanned deep discharges of the K2 module being dynamic cycled, its cycle life was much shorter than the other modules, but it seems likely its cycle life would have been comparable to that of the K2 module being cycled at constant current if its discharge level had been 80%.

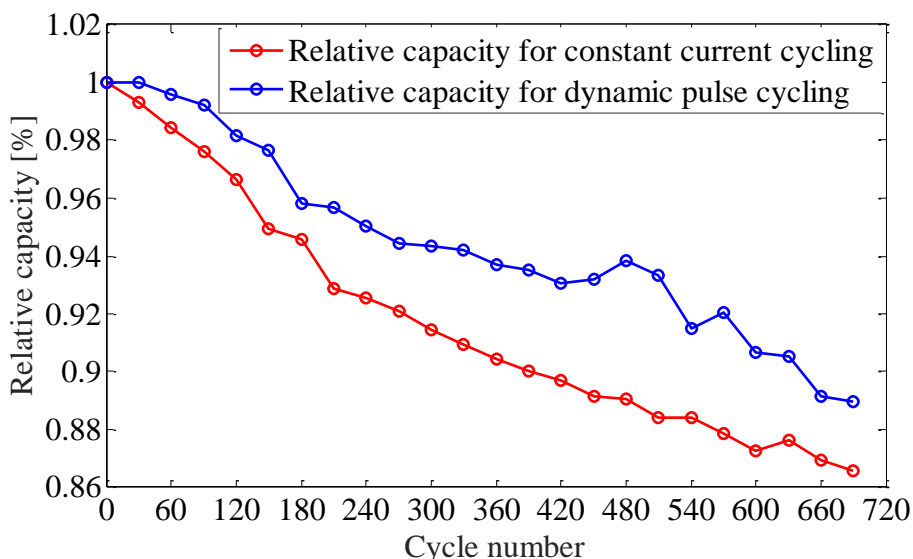
Table 5. Estimated cycle life for the LiNiCoAl and LiFePO₄ for constant current cycling and dynamic pulse cycling.

Lithium battery Chemistry	Estimated cycle life for a 20% degradation in Ah capacity	Estimated cycle life for a 50% increase in resistance
Panasonic NiCoAl-based*		
Constant current cycling	1000	1750
Dynamic pulse cycling	1500	3050
K2 Energy FePO ₄ -based*		
Constant current cycling	1620	2000
Dynamic pulse cycling	600**	Resistance increase less than 10% until Ah limit was reached

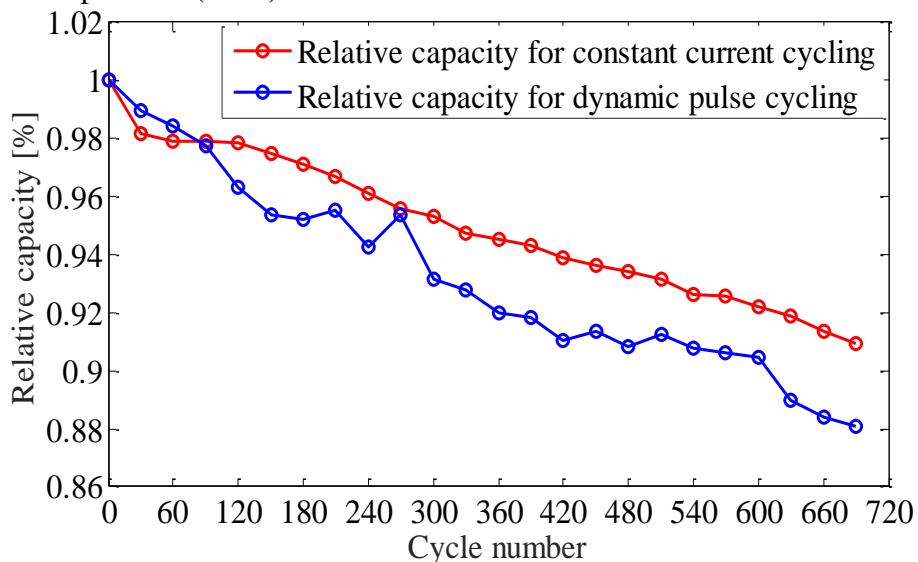
*all the modules consisted of 18650 cells

** module was discharged to 87% of its original Ah capacity rather than about 80%.

The test results shown in Fig. 4 indicate that the resistances of the modules increase with cycling and for both the NiCoAl and FePO₄ chemistries. The magnitude of the increase is greater for the constant current cycling than for the dynamic cycling particularly for the FePO₄ chemistry. If the curves in Fig. 4 are extrapolated to estimate the number of cycles to reach a 50% increase in the resistances, one obtains the values shown in Table 5. The estimates in Table 5 indicate that dynamic pulse cycling results in an increase in cycling life by a factor of 1.5-2 if an increase in resistance is the determining factor for determining cycle life. However, it appears that for both the lithium chemistries the degradation in Ah capacity and not an increase in resistance will be the primary factor in determining cycle life.



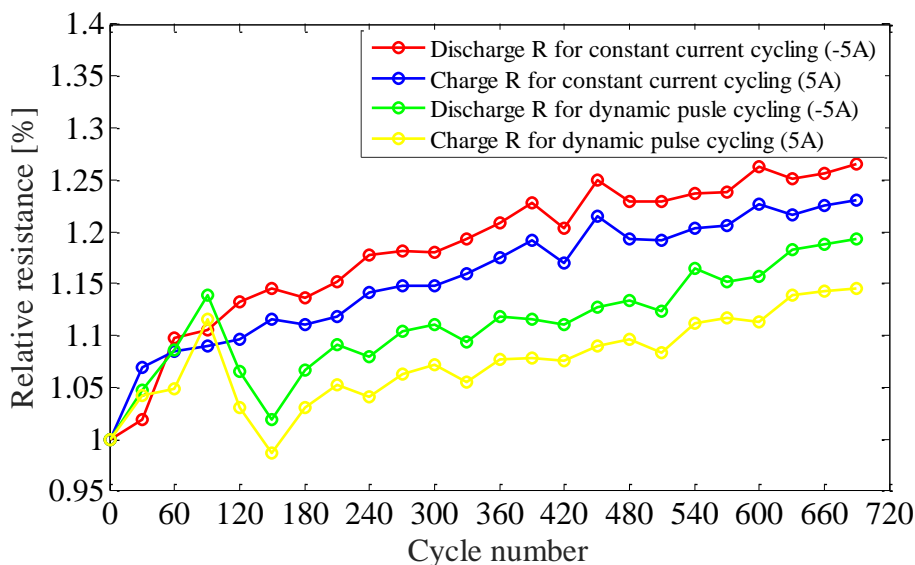
a. Capacity degradation curves for LiNiCoAl module, in which the module was discharged at C/2.7-rate, room temperature (25°C)



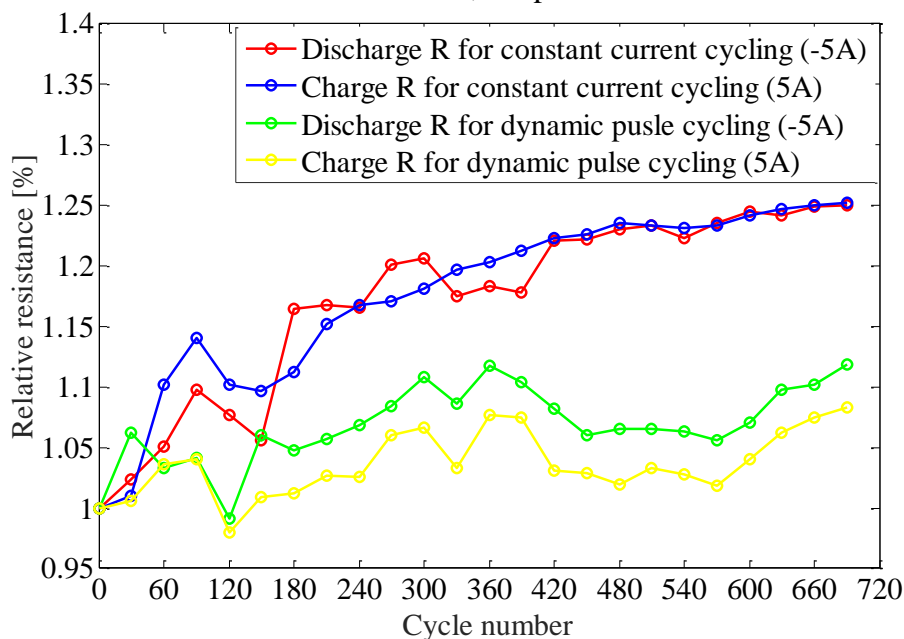
b. Capacity degradation curves for LiFePO₄ module, in which the module was discharged at C/3.1-rate, room temperature (25°C)

Figure 3. Ah capacity as a function of cycle number for the LiNiCoAl and LiFePO₄ modules

It seems unlikely that these results can be generalized to apply to other cells/batteries of the same chemistry and/or for different discharge profiles, temperatures, and charging conditions. It is well known that the cycle life of any battery depends in a complex way on many factors [11-21]. The present test results may apply only for the test conditions of the present study and should be applied with care. Some comparisons of the present data with other studies are given in the following section.



a. Resistance increase curves with cycle number for LiNiCoAl module, in which the resistance was determined from an 8 sec, 5A pulse at 60% SOC



b. Resistance increase curves with cycle number for LiFePO₄ module, in which the resistance was determined from an 8 sec, 4A pulse at 60% SOC

Figure 4. Module resistance as a function of cycle number for the LiNiCoAl and LiFePO₄ modules at room temperature (25°C)

4.1. Indication of the State-of-health of the battery

An indicator of battery health (SOH) during the cycling can be the open-circuit voltage (OCV) at the end of the discharge and before the start of charging [22-24]. Of particular interest is the OCV when the module is completely discharged after each cycle, because changes in the OCV as the module is cycled will indicate the extent to which the battery Ah capacity is being degraded.

Table 6. Changes in the end of discharge OCV after cycling. a. Panasonic LiNiCoAl module*.

Constant current cycling			Dynamic pulse cycling		
Cycle	OCV at end of discharge**	Degradation factor	Cycle	OCV at end of discharge**	Degradation factor
150	10.384	0.956	120	10.28	0.985
210	10.32	0.932	240	10.228	0.954
390	10.246	0.903	330	10.198	0.945
510	10.207	0.887	540	10.135	0.918
600	10.176	0.875	630	10.104	0.908
690	10.16	0.869	720	10.075	0.891
750	10.154	0.865	780	10.047	0.888

*2.21 Ah discharged on each cycle

**after a 5 minute rest

b. K2 Energy LiFePO₄ module*.

Constant current cycling			Dynamic pulse cycling		
Cycle	OCV at end of discharge**	Degradation factor	Cycle	OCV at end of discharge**	Degradation factor
150	9.617	0.975	90	9.608	0.99
240	9.617	0.961	180	9.6	0.949
360	9.602	0.943	300	9.532	0.933
480	9.595	0.934	420	9.414	0.91
630	9.564	0.918	540	9.305	0.905
720	9.548	0.912	630	9	0.889
810	9.521	0.903	750	8.546	0.879

*1.14 Ah discharged on each cycle

**after a 5 minute rest

This effect is shown in the data presented in Table 6 for the two lithium battery chemistries. Data are shown for constant current and dynamic pulse discharges of the modules.

The data for the NiCoAl module show a systematic variation in the OCV as the module is cycled and the Ah capacity of the module slowly degrades. There is a reasonable variation of the OCV with the state-of-the degradation, but there are also differences due to the type of discharge. This complicates the application of this approach to determine the cell degradation from OCV data. A further complication is accounting for variations in the depth-of-discharge before each recharge of the battery.

The data for the FePO₄ module also shows a variation in the OCV as the battery is cycled, but the variation with change in Ah capacity is much smaller than for the NiCoAl chemistry. It is well known that the OCV curve vs depth of discharge (DOD) is relatively flat for a significant range of DOD for the FePO₄ chemistry. The data for the dynamic pulse discharge shows clearly that the module had reached complete discharge at about 600 cycles when the total Ah capacity of the module approached the 1.14 Ah discharged in the dynamic cycle. This result indicates that tracing changes in the OCV at the end of discharges can be an indicator of battery health.

4.2. Mechanisms of the degradation

In the present study there was no attempt to determine the mechanisms that caused the degradation in the Ah capacity and the resistance of the batteries as they were cycled. The mechanisms [17-23] would be of considerable interest especially if they are different for the constant current and dynamic pulse cycling. These differences can be studied by applying the differential voltage technique [25] to the charging data and the constant current discharge data. This technique involves tracking (-Q₀, dV/dQ) during the charging and noting the SOC at which there are large changes in the parameter. As discussed in [11, 13 16, 26], these changes can be related to particular mechanisms of degradation.

4.3. Comparisons with previous life cycle testing of lithium-ion batteries

As indicated in the Introduction, the present testing of lithium batteries was undertaken to evaluate the effect of load leveling on the cycle life of the two lithium battery chemistries. It was expected that the testing would show that load-leveling the power demand, as can be done using SCs, would significantly increase the cycle life of the batteries. As noted in the previous section, this was not the outcome of the present testing. The test results indicated that the performance of the modules tested degraded more rapidly for constant current (load leveled) discharges than for dynamic pulsed discharges at the same average current. This was found most clearly in the case of the NiCoAl battery chemistry for both the degradation of the Ah capacity and the resistance. In the case of the LiFePO₄ battery chemistry, the resistance clearly degraded more rapidly in the constant current cycling than for the dynamic pulse cycling of module. In general, in the present testing, constant current cycling did not indicate an increase in battery cycle life as expected for either battery chemistries, but the effect on the cycle life of the discharge profile was not large for either battery chemistry.

Table 7. Summary of life cycle test data from various sources.

Battery tested	Test conditions and profiles	Capacity fade With cycles (%)		Resistance increase with cycles (%)		Reference
LiFePO ₄ 12Ah	SOC 80% - 30% 45°C	600	1200	600	1200	China [6]
	Without ultracaps	7.7	17	5	10.5	
	Moderate leveling	7.5	14	7	9	
	Load -leveled	7.5	13.7	0	4.5	
LiMn ₂ O ₄ 5Ah	SOC 90% - 30% 40°C	250	500	250	500	Argonne Nat. Lab.[4]
	Full DST	4.5	12	27	57	
	Modified DST	0	4	5	10	
LiNiCoAl 3.1Ah	SOC 100% - 20% 25°C	300	600	300	600	Present study
	Dynamic pulsing	6	9.6	8	16	
	Load-leveled	8.4	12.4	18	26	
LiFePO ₄ 1.5Ah	SOC 100% - 12% 25°C	300	600	300	600	Present study
	Dynamic pulsing	7	10	15	14	
	Load-leveled	4	8	20	24	

It is of interest to compare the findings of the present tests with those available in the literature for cycle life testing of lithium batteries. As discussed in the Introduction, there is much literature on life cycle testing of lithium batteries [7-16] and modeling of battery degradation [17-22]. This is particularly true for the lithium iron phosphate chemistry [10-14]. Most of the previous studies were concerned with batteries undergoing constant current discharges at different rates and did not consider pulsed discharges with sequences of charge and discharge pulses. However, there have been several studies [4, 6] that are closely pertinent to the present cycle life testing. These studies have involved extensive cycle life testing of lithium batteries using pulsed profiles with both charge and discharge steps. A summary of the life cycle data pertinent to the present study is given in Table 7. In general, the test results from the present study are not in agreement with results from the [4, 6] regarding whether load leveling increases the cycle life for dynamic discharge cycles like those encountered in vehicle applications. The reasons for this disagreement are considered in the following paragraphs.

One of the difficulties in comparing the data from different studies is that the test conditions, charging algorithms, and discharge profiles are quite different as shown in Table 7. The state-of-charge range and the temperature utilized in the cycling are particularly important. There are also large differences in the discharge profiles used in the cycling particularly in the terms of the C-rates of the charge and discharge pulses, the average current of the discharge, and the contribution of the charge pulses in the profile to recharging the batteries. Most of the life cycle testing in the literature has been done using the DST (Dynamic Stress Test) cycle [27] used in USABC testing procedures. The DST cycle is specified based on the maximum power density (W/kg) assumed for the cell being tested. The fraction of the charge (Ah) returned to the cell in charge pulses in the DST is relatively low (less than 20%). In some of the cycling studies using the DST profile, it was found that the effect of the discharge profile on the cell cycle life was large [12, 13] and in others it was small [10, 11]. In all cases, the effect of temperature (40-45deg C compared to 25deg C) was large and the degradation of the cells with dynamic cycling significantly increased at the higher temperatures. This could explain the large difference between the Argonne Laboratory tests results and the present data shown in Table 7. As noted previously, all the present testing was done at room temperature.

5. SUMMARY AND CONCLUSIONS

Lithium-ion batteries are currently the preferred energy storage technology for PEVs because of their high energy density, good power capability, high cell working voltage, and relatively good cycle life. Current thinking is that reducing the high current pulses experienced by the batteries in both charge and discharge will reduce the stress on the batteries and thus increase cycle life [27]. This can be done by combining the batteries with SCs in the energy storage unit for the vehicle. In addition to increasing cycle life, load-leveling the battery will permit the use of batteries with lower power capability and hence higher energy density and lower cost (\$/kWh). In the present study, modules of LiNiCOAl cells and LiFePO₄ cells were cycled at constant current and also on dynamic pulse charge/discharge profiles. Each module consisted of three 18650 cells. The objective of the testing was to determine the effect of load-leveling on the cycle life of the two lithium battery chemistries. The

modules were fully charged before each cycle and were discharged to 80% of the initial Ah capacity of the cells in each cycle. The dynamic pulse profiles consisted of sequences of charge/discharge pulses at currents up to 3-4C. The average current for both discharge profiles was C/2. The degradation of the modules was tracked in terms of their Ah capacity and resistance as the cycling proceeded. The modules were cycled for about 750 cycles over a period of about six months.

The cycling results of the present study were unexpected. For both lithium chemistries, the present data indicated that the modules degraded more rapidly with constant current cycling than using the dynamic pulse profiles. The cycling results in the literature from related previous studies of lithium batteries indicated that load-leveling the battery reduced to varying degrees the rate of degradation for both Ah capacity and resistance [4, 6]. However, the rate of degradation varied significantly between those studies (see Table 7).

One of the difficulties in comparing the data from different studies is that the test conditions, charging algorithms, and discharge profiles are quite different as shown in Table 7. Most of the life cycle testing in the literature has been done using the DST (Dynamic Stress Test) cycle used in USABC testing procedures [28]. In some of the cycling studies using the DST profile, it was found that the effect of the discharge profile on the cell cycle life was large and in others it was small. In all cases, the effect of temperature (40-45deg C compared to 25deg C) was large and the degradation of the cells with dynamic cycling significantly increased at the higher temperatures. This could explain the large difference between the Argonne Laboratory tests results at 40 deg C and the present data at room temperature shown in Table 7. It is clear that the differences in test conditions and profiles can have a significant effect on the cycling results and consequently whether load-leveling increases the cycle life of the batteries. Clarification of the uncertainty of the effect of load-leveling on battery cycle life is particularly important in connection with the use of SCs in vehicle applications.

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