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Cycle Life of Lithium-ion Batteries in Combination with Supercapacitors: The effect of load-leveling

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Summary

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. This can be done by combining the batteries with supercapacitors. In the present study, modules of LiNiCoAl cells and LiFePO₄ cells were cycled at constant current and on a dynamic pulse discharge/charge profile. 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 their Ah capacity and resistance as the cycling proceeded. The modules were cycled for about 700 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 profile. One of the difficulties in comparing the data from different studies is that the test conditions, charging algorithms, and discharge profiles are quite different. It is not possible at the present time to identify the reasons for the inconsistencies between the various studies.

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, however, have been constraints to their use in mass marketed PEVs. High pulse power demands for engine start and/or acceleration and large pulse currents during regenerative braking are thought to be prime factors that can reduce the cycle life of batteries in electrified vehicles [2,

3]. 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 [19]. SCs have very high power density, rapid charging capability with high pulse current, and very long cycle life (up to one million cycles) [4]. 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. Load-leveling the battery is expected to 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.

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 cells, 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 that of the dynamic pulse profile. The cycles for both modules were intended to be 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. The purpose of this research was to experimentally determine the cycle life variation of the Ah capacity and resistance of LiNiCoAl and LiFePO₄ cells under constant current and dynamic pulsing discharge profiles as they would experience in an electric vehicle with and without SCs.

2 Background

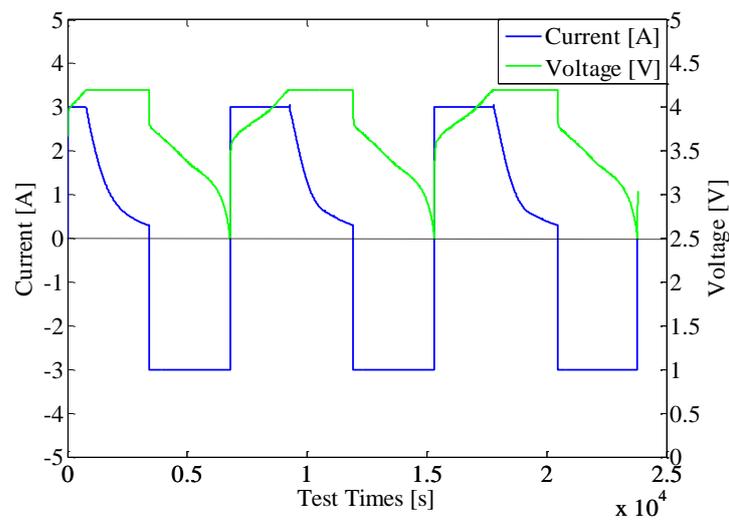
As indicated in the previous section, the present study was intended to determine the effect of dynamic pulsing of the cells via cycling of lithium-ion cells during discharge on cycle life. There have been many experimental studies [3, 5-12] of the factors that affect the cycle life of lithium-ion batteries and the Ah throughput needed to reduce their capacity (Ah or Wh) by about 20% and increase their resistance by about 50%. There have been far fewer studies [3, 6] that compared directly the cycle life of batteries discharged at constant current with the same battery discharged with dynamic charge/discharge pulses and the same average current. The previous studies [5-12] 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, temperature of the tests, the charge algorithm, and the initial and final discharge conditions. Hence it is difficult and uncertain to compare the life cycle results of the present study with those of previous studies performed under different conditions. However, some comparisons are made in a later section of the paper.

3 Battery cell/modules and test procedures

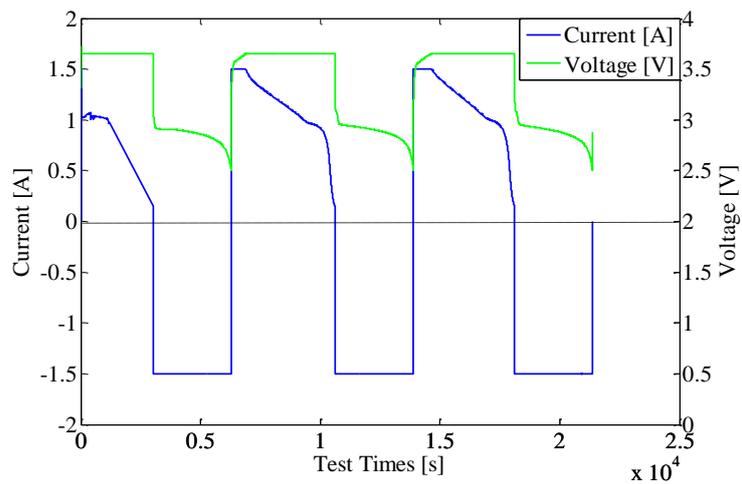
In this project, the LiNiCoAl cells, Panasonic 3.1Ah 18650A, and LiFePO₄ cells, K2 Energy 1.5Ah 18650E, were tested. The cells were tested using a 6-channel, 20A, 20V Arbin battery tester in the Battery Test Lab at the University of California-Davis. The performance characteristics of all the cells were measured before they were connected into 3-cell modules for the life cycle testing. The results of the initial characterization tests are summarized in Fig. 1 and Table 1. The cell test results were used to select the cells to combine in

the 3-cell modules used in the cycle testing. The objective of the selection process was to minimize the differences in the modules for each of the cell chemistries. The two battery modules were tested simultaneously to minimize the impact of calendar life on the cycling performance tests.

The initial Ah capacity and resistances of the four modules are given in Table 2. Photographs of the modules are shown in Fig.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 significant 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.



a. LiNiCoAl 18650A Li-ion cells



b. LiFePO4 18650E Li-ion cells

Fig. 1: Charge and discharge characterization tests of the cells.

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 Pulse Current (A)	Pulse Time (sec)	Steady-state Resistance (mOhm)	Rebound Resistance (mOhm)
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

Module Panasonic NiCoAl (V _{cutoff} =3.0V/cell)	Charging current (A)	Initial Ah capacity	Initial Pulse Resistance (Ohm)
Constant current tests	1	2.719	.2436
Dynamic pulsing tests	1	2.72	.2412
Module K2 Energy FePO ₄ (V _{cutoff} =2.5V/cell)			
Constant current tests	.6	1.389	.2118
Dynamic pulsing tests	.6	1.286	.2436



constant current

Dynamic pulsing

Panasonic NiCoAl cells



constant current

Dynamic pulsing

K2 Energy FePO₄ cells

Figure 2: Photographs of the test modules

Table 3: Dynamic pulse sub-cycle steps for life cycling test on NiCoAl-based module*

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

*(W/kg)_{max} = 675, Average current: 1.15A (C/2.4-rate)

Table 4: Dynamic pulse sub-cycle steps for life cycling test on LiFeP-based module*

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

*(W/kg)_{max} = 375, Average current: 0.48A (C/2.7-rate)

The discharge conditions for the comparative tests of the cells/modules were developed as follows. The current and voltage limits were set based on information from the manufacturer, Panasonic and K2 Energy, of the cells. For EV applications, the battery must provide relatively high power pulses for both acceleration and braking of the vehicle. The pulse times were set to be appropriate for EV operation. The maximum currents 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 about 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 and shown graphically in

Fig. 3 and 4.

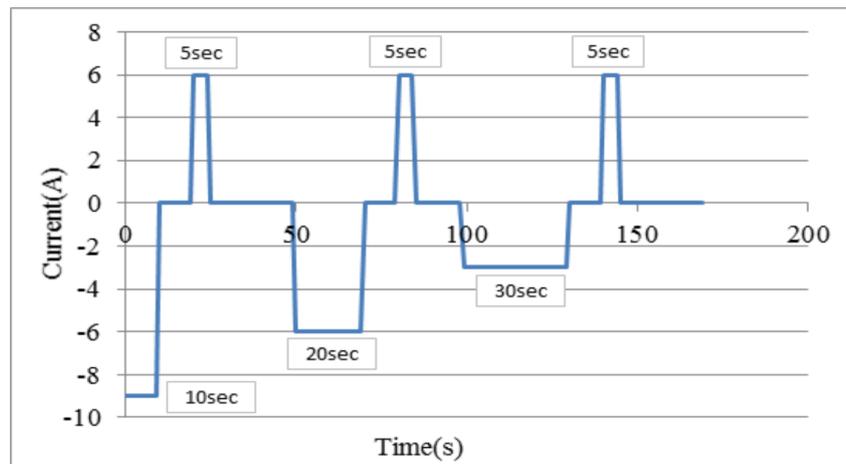


Figure 3: Dynamic pulse sub-cycles for the Panasonic cells

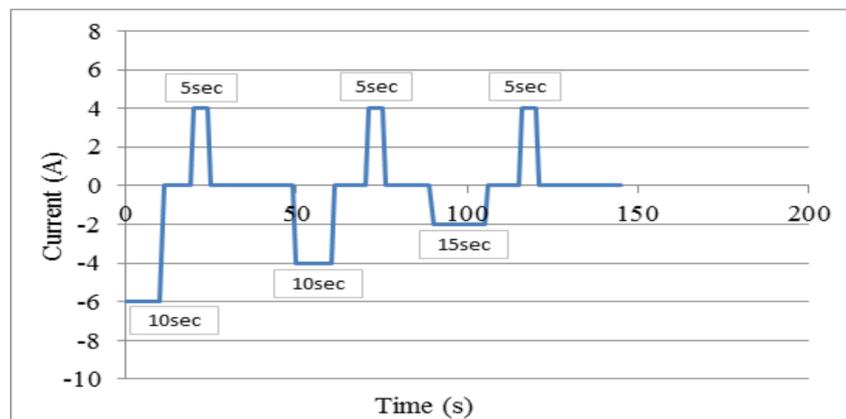


Figure 4: Dynamic pulse sub-cycles for the K2 Energy cells

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 was then tapered to 1/10th 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 discharged. After each set of 30 cycles, a diagnostic test was performed to determine the Ah capacity and resistance of the module. The resistance was determined from an 8 sec 4-6A 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. The cycling tests are being continued until the modules reach their respective cut-off voltages during a cycle before 80% of their initial capacity is discharged.

4 Experimental Results

The primary objective of the experimental study was to determine the effect of dynamic pulse cycling on the cycle life of lithium batteries. To accomplish this objective, one module of each chemistry was cycled on the dynamic discharge/charge profiles shown in Figures 3 and 4 and the other module was cycled at the constant current of the respective dynamic cycle. All the cycling was done at room temperature. The degradation of the battery 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 Figures 5 for the Ah capacity and in Figure 6 for the resistance.

The test results shown in Figure 5a 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 figure 5b indicate that the degradation was more rapid with the dynamic pulse cycling, but the 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 Figure 5 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%. Further testing of FePO₄ is planned.

The test results shown in Figure 6 indicate that the resistances of the modules increase with cycling and for both the NiCoAl and FePO₄ chemistries, the increase is greater with constant current cycling than for dynamic pulse cycling. The data indicate that 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 Figure 6 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. 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.

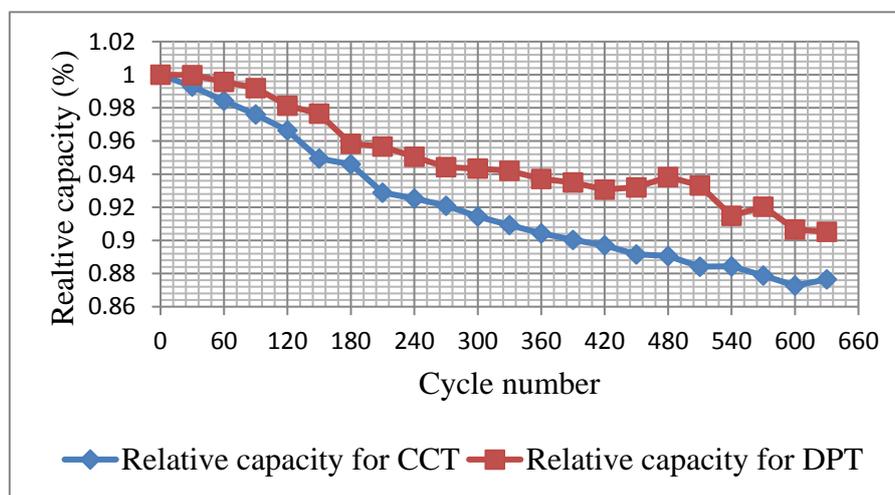
Whether these results can be generalized to apply to other batteries of the same chemistry and/or different discharge profiles, temperatures, and charging conditions will require much additional testing as it is well known that the cycle life of any battery depends in a complex way on many factors [5, 7, 11, 13-15]. The present test results may apply only for the test conditions of the present study and thus should be applied carefully. Some comparisons of the present data with other studies are given in the following section.

An indicator of battery health (SOH) can be the open-circuit voltage (OCV) at the end of the discharge and before the start of charging [16-18]. Of particular interest is the OCV when the battery is completely discharged after each cycle, because changes in the OCV as the battery is cycled will indicate the extent to which the battery Ah capacity is being degraded. 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.

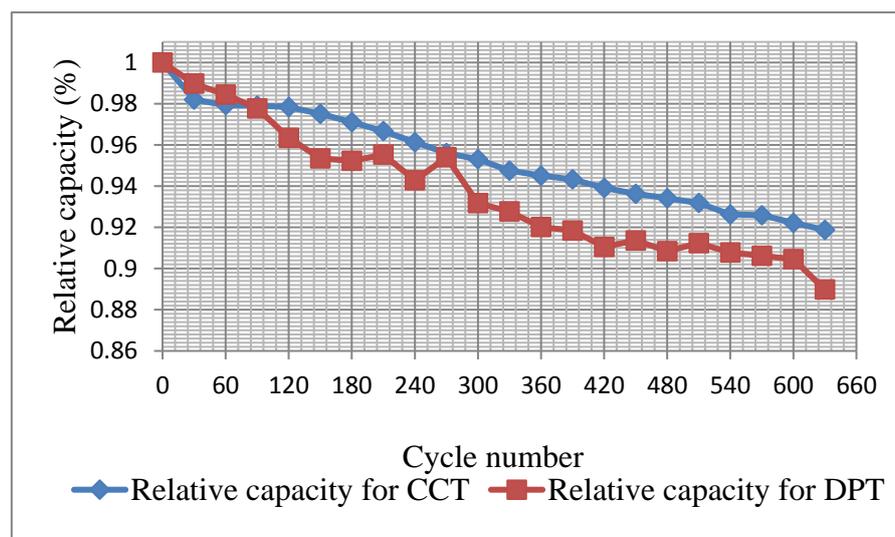
Table 5: Estimated cycle life for the NiCoAl and FePO₄ for constant current and dynamic pulse cycling

Lithium battery Chemistry	Estimated cycle life for a 20% degradation in Ah capacity	Estimated cycle life for a 50% increase in resistance
Panasonic NiCoAl *		
Constant current cycling	1000	1750
Dynamic pulse cycling	1500	3050
K2 Energy FePO ₄ *		
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 82%.

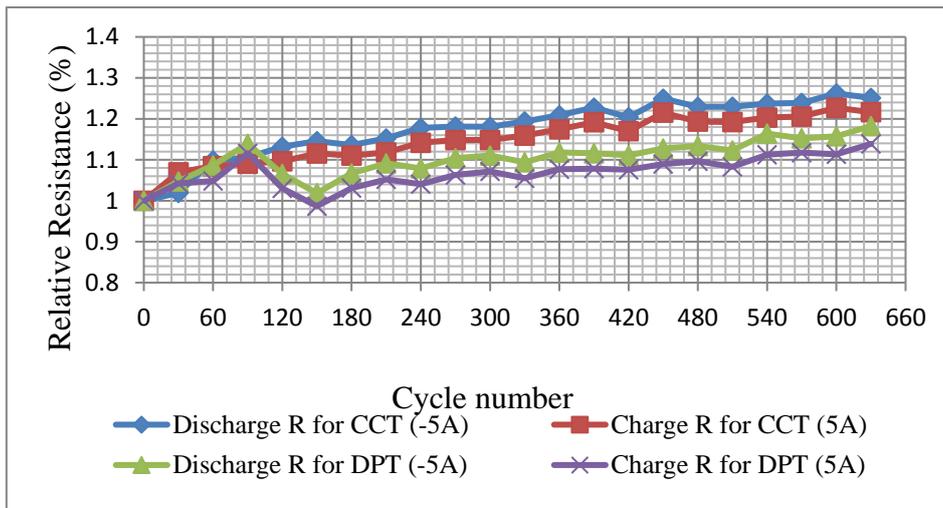


a. Capacity degradation curves for LiNiCoAl module

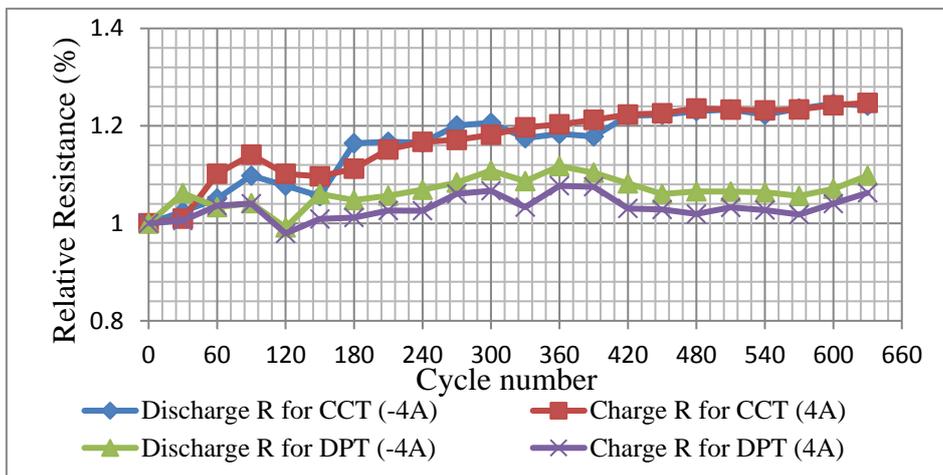


b. Capacity degradation curves for FePO₄ module

Figure 5: Ah capacity degradation curves for the NiCoAl and FePO₄ modules



a. Resistance increase curves for LiNiCoAl module



b. Resistance increase curves for LiFePO4 module

Fig. 6: Resistance increase curves for the NiCoAl and FePO₄ modules

Table 6: Changes in the end of discharge OVC after cycling
Panasonic NiCoAl module (3 cells)

Constant current cycling *			Dynamic pulse cycling*		
cycle	OCV at end of discharge	Ah Degradation factor	cycle	OCV at end of discharge	Ah Degradation factor
150	10.384	.956	120	10.28	.985
210	10.32	.932	240	10.228	.954
390	10.246	.903	330	10.198	.945
510	10.207	.887	540	10.135	.918
600	10.176	.875	630	10.104	.908
690	10.160	.869	720	10.075	.891
750	10.154	.865	780	10.047	.888

*2.21 Ah discharged on each cycle

K2 Energy (3 cells)

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	.975		90	9.608	.99
240	9.617	.961		180	9.600	.949
360	9.602	.943		300	9.532	.933
480	9.595	.934		420	9.414	.910
630	9.564	.918		540	9.305	.905
720	9.548	.912		630	9.00	.889
810	9.521	.903		750	8.546	.879
840	9.515	.900				

** 1.14 Ah discharged each cycle

The data for the NiCoAl module show a systematic variation in the OCV as the battery 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 will complicate 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 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.

5. 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 two lithium battery chemistries. It was expected that the testing would show that load-leveling the power demand, as can be done using supercapacitors, 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. For the most part, the differences in the rates of degradation were not large. It is of interest to inquire as to whether the present test results are consistent with those available in the literature for cycle life testing of lithium batteries of the same chemistry. As discussed in the **Introduction**, there is much literature on life cycle testing of lithium batteries [3, 5-12] and the modeling of battery degradation [13-15]. 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 a limited number of studies [3-6] 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.

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

Battery tested	Test conditions and profiles	Capacity fade (%)		Resistance increase (%)		Reference
LiFePO₄ 12 Ah	SOC 80-30%, 45 degC	600	1200 cycles	600	1200 cycles	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	
LiMnO 5 Ah	SOC 90-30% 40 degC	250	500 cycles	250	500 cycles	Argonne Nat. Lab. [3]
	Full DST	4.5	12	27	57	
	Modified DST	0	4	5	10	
LiNiCoAl 3.1 Ah	SOC 100-20 % 25 degC	300	600 cycles	300	600 cycles	Present study
	Dynamic pulsing	6	9.6	8	16	
	Load-leveled	8.4	12.4	18	26	
LiFePO₄ 1.5 Ah	SOC 100-12% 25 degC	300	600 cycles	300	600 cycles	Present study
	Dynamic pulsing	7	10	15	14	
	Load-leveled	4	8	20	24	

One of the difficulties in comparing the data from different studies is that the test conditions, charging algorithms, and discharge profiles are quite different. The state-of-charge range and the temperature utilized in the cycling are particularly important. As indicated in Table 7, they vary significantly between the various studies. 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. It is clear from Table 7 that the differences in test conditions and profiles can have a significant effect on the cycling data and consequently whether load-leveling increases the cycle life of the batteries. In general, the test results from the present study are not in agreement with results from the previous studies regarding whether load leveling increases the cycle life for complex discharge cycles like those encountered in vehicle applications. This is particularly true of the results from the Argonne Lab tests which show that load-leveling significantly reduces the cell degradation with cycling. It is not possible at the present time to identify the reasons for this disagreement. Clearly more cycle test data are needed under controlled test conditions to clarify this important topic.

6. Summary and Conclusions

Lithium-ion batteries are currently the preferred energy storage technology for plug-in electric vehicles 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. This can be done

by combining the batteries with supercapacitors 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 on a dynamic pulse discharge profile. 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 about 80% of the initial Ah capacity of the cells. The dynamic pulse profile consisted of a sequence 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 700 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 profile. The cycling results in the literature from related previous studies of lithium batteries indicated that load-leveling the battery reduced the rate of degradation for both Ah capacity and resistance. 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. 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. 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.

In general, the test results from the present study are not in agreement with results from the from previous studies regarding whether load leveling increases the cycle life for complex discharge cycles like those encountered in vehicle applications. It is not possible at the present time to identify the reasons for this disagreement. Clearly more cycle test data are needed under controlled test conditions to clarify this important topic.

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Authors



Andrew Burke, Research faculty, ITS-Davis. Ph.D., 1967, Princeton University. Since 1974, Dr. Burke's research has involved many aspects of electric and hybrid vehicle design, analysis, and testing. He was a key contributor on the US Department of Energy Hybrid Test Vehicles (HTV) project while working at the General Electric Research and Development Center. He continued his work on electric vehicle technology, while Professor of Mechanical Engineering at Union College and later as a research manager with the Idaho National Engineering Laboratory (INEL). Dr. Burke joined the research faculty of the ITS-Davis in 1994. He directs the EV Power Systems Laboratory and performs research and teaches graduate courses on advanced electric driveline technologies, specializing in batteries, ultracapacitors, fuel cells and hybrid vehicle design. Dr. Burke has authored over 80 publications on electric and hybrid vehicle technology and applications of batteries and ultracapacitors for electric vehicles.