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Life cycle Testing of Lithium Batteries for Fast charging and Second-use Applications

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Abstract

Two aspects of the life cycle testing of lithium-ion batteries were studied- (1) the effect of fast charging (4C) on cycle life and (2) extended cycling of cells beyond first-use requirements for second-use applications. In the case of the fast charging studies, the test data indicate that the Ah capacity of the lithium titanate oxide (LTO) cells is essentially independent of charge rate up to 6C with no current taper at the end of charge. This means that the LTO cells can be fully charged at the fast charge rates. The life cycle tests of a 24V module (10 cells in series) at the 4C charge rate and C/2 discharge rate showed negligible degradation in Ah capacity or resistance (voltage response) in over 1000 cycles. The temperature response of the module without cooling showed a maximum interior temperature of 40C that remained unchanged over the 1000 cycles of the testing.

The second-use studies involved the life cycle testing of new and used 20 Ah prismatic cells (Lithium Manganese Oxide) obtained from EIG, Korea. Testing was done at room temperature and 45 deg C. The new and used cells were cycled (4.15V to 3.0V) about 850 times at room temperature and about 350 times at 45 deg C. The way in which the new and used cells degraded in terms of the decrease in Ah capacity and increase in the resistance were compared with second-use of the cells in mind. As expected it was found that the resistance degraded (%/100 cycles) more rapidly with cycles than the Ah capacity and that for both new and used cells the degradation was much more rapid at 45 deg C than at room temperature. The test results indicate second-use batteries will be best suited for applications requiring relatively high energy density, but relatively low power capability. The degradation of the used cells was gradual (no sudden failures), but accelerated with increasing cycles especially at 45 deg C.

Keywords: battery, life cycle, second-use

Introduction

This paper is concerned with life cycle testing of lithium batteries. In Part 1, the life cycle testing of a lithium titanate oxide (LTO) module with fast charging (4C) is discussed for a transit bus application. In Part 2, the life cycle testing of 20Ah, lithium manganese oxide (LMO) cells from EIG, Korea is discussed as related to second-use applications. In both parts, detailed test data are presented and the performance of the cells/modules tracked during the cycling.

Part 1: Fast charging of a lithium titanate oxide module

1. Introduction

There has been much discussion [1-3] of fast charging of lithium-ion batteries as a means of extending the practical daily range of electric vehicles making them more competitive with engine-powered conventional vehicles in terms of range and refueling time. It has been recognized [4-7] that the lithium titanate oxide (LTO) chemistry is the most capable of fast charging of the various lithium battery chemistries. However, there has been limited test data [8] available in which the batteries have been fast charged and their response to fast charging determined. In this paper, extensive data for fast charging of LTO cells and modules are presented. The electrical and thermal responses during fast charging were measured as well the effect of fast charging on cycle life.

2. Cells and modules tested

The modules tested in this study utilized 50Ah cells from Altairnano, United States. The 24V modules consisted of 10 cells connected in series. The characteristics of the cells are given in Table 1-1. The Ah capacity of the cell varied little with discharge rate up to 6C. The cell resistance was .9 mOhm. Based on these test results, it is reasonable to expect that the 50Ah cell would have good fast charging characteristics.

The module characteristics are summarized in Table 1-2. The energy density of the module for a 1C discharge is 49 Wh/kg, 85 Wh/L. The corresponding cell values are 70 Wh/kg, 128 Wh/L. The modules were instrumented such that the voltages of the individual cells could be recorded and the cell resistances calculated. The cell resistances for the module are given in Table 1-3 for both discharge and charge currents from 100-300A. The standard deviation of the cell-to-cell variability of the resistance is about 9%. The cell and module resistances do not vary significantly with current and in all cases, the module resistances are close to the sum of the resistances of the 10 cells. The Ah capacity of the modules for charge rates up to 6C are also given in Table 1-3. As expected for the lithium titanate oxide battery, the Ah capacity of the module varies only slightly with charge rate even without current tapering.

Table 1-1: Characteristics of the Altairnano 50Ah cell

Constant current discharge (2.8-1.5V)

Current (A)	nC	Time (sec)	Ah
50	.96	3773	52.4
100	1.95	1847	51.3
200	4.0	904	50.2
300	6.1	588	49.0

Constant power discharge (2.8-1.5V)

Power (W)	W/kg	Time (sec)	nC	Wh	Wh/kg
100	62	3977	.9	111	69
200	125	1943	1.85	108	67
300	188	1244	2.9	102	64
400	250	849	4.2	94	59
500	313	636	5.66	88	55
600	375	516	7.0	86	54

weight: 1.6 kg

3. Test procedures

The life cycle testing of the 24V module involves fast charging at the 4C rate (200A) and discharging at C/2. The voltage at the end of the charge (26.45V) corresponds to a state-of-charge of 90% and the voltage at the end of the discharge (21.72V) corresponds to a state-of-charge of 24% resulting in the use of 33.3 Ah (66%) from the module. The charging is done at 200A and the discharge at 25A. The charging time is 10 minutes and the discharge time is 80 minutes. This test cycle is meant to mimic the use of the module in a transit bus application with fast charging.

Table 1-2. Characteristics of the 24V Lithium Titanate Oxide module.

Parameter	
Module configuration	Ten 50Ah cells in series
Weight (kg)	23.2 module, 16 cells alone
Volume (L)	13.25 module, 8.9 cells alone
Ah capacity	50.5 at 50A, 44.2 at 200A
Energy density (Wh/kg)	70.6 at 1C, 66.4 at 2C
Resistance (mOhm)	7.0
Pulse power (W, W/kg)	6.7 kW, 420 W/kg cells alone, 90% efficiency.
Fast charging capability	Up to 6C with 96% of rated Ah

Table 1-3: Cell-to-cell variability of the 24V module

50Ah Module 005 R (mOhm)

	Pulse Current						
cell #	-300A	-200A	-100A	100A	200A	300A	ave R
0	0.5976	0.5893	0.5841	0.5832	0.5764	0.5712	0.583633
1	0.675	0.6686	0.6609	0.6561	0.6512	0.6422	0.659
2	0.802	0.7957	0.7856	0.7778	0.7695	0.7575	0.78135
3	0.7456	0.7368	0.7328	0.7257	0.7157	0.7039	0.72675
4	0.7011	0.6944	0.6915	0.6859	0.6762	0.6667	0.685967
5	0.7396	0.7315	0.727	0.7174	0.7112	0.6988	0.720917
6	0.7126	0.7058	0.6989	0.695	0.6869	0.677	0.696033
7	0.7129	0.7037	0.6997	0.695	0.6877	0.6776	0.6961
8	0.7865	0.7769	0.7691	0.7704	0.7522	0.7366	0.765283
9	0.6333	0.6228	0.6113	0.6064	0.6084	0.5979	0.61335
Average	0.71062	0.70255	0.69609	0.69129	0.68354	0.67294	0.692838
St Dev	0.063501	0.063799	0.06382	0.063063	0.0597737	0.057575	0.061894
module R	7.109349	7.201439	6.840243	6.89108	7.016456	6.739212	(mOhm)

Room Temperature: 24.739899 °C

Module Internal Temperature: 28.558503 °C

Charge Current	50A	150A	200A	250A	300A
module Ah	50.5	50.4	50.1(49.9)	49.5(49.3)	48.7(48.3)

(fan cooling)

4. Life cycle test results

The life cycle testing was done in blocks of 30 cycles which takes about 2 days per block. The tests were run without the cooling fan. Samples of the life cycle results are shown in Figures 1-1 and 1-2. Figure 1-1 shows the voltage and maximum temperature interior to the module are stable over repeated cycles of the module. As indicated, the maximum temperature stabilizes at about 40C without active fan cooling. The tests results shown in Figure 1-2 indicate that the module shows no degradation in Ah capacity over the 1000 cycles. The only small variations in the test data occur when the life cycle testing is resumed after stoppage due to the need to use the battery tester for other research.

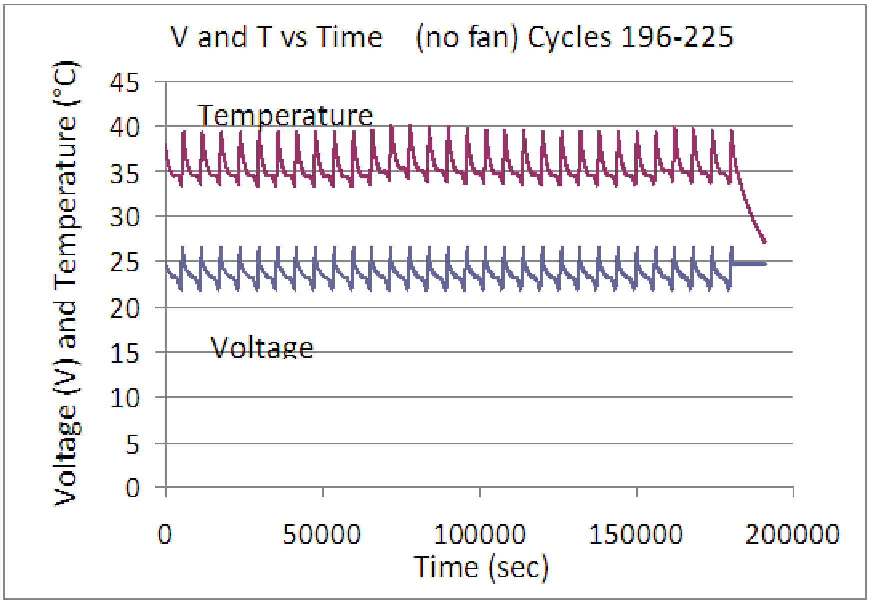

Figure 1-1: Voltage and maximum interior temperature data for the 24V module with fast charging (one 30cycle block).

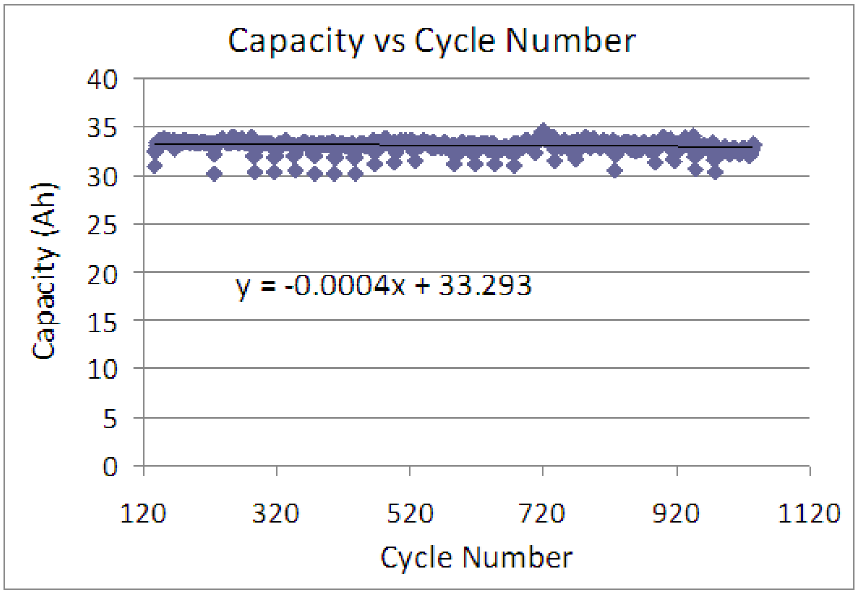

Figure 1-2: Life cycle (cell Ah capacity) data for the 24V module

5. Summary and conclusions (Part 1)

The module characteristics and life cycle test data presented confirmed the fast charging capability of lithium titanate oxide batteries. The test data indicate that the Ah capacity of the LTO cells is essentially independent of charge rate up to 6C with no current taper at the end of charge. The voltage at the end of charge was 2.8V/cell for all the charging tests. This means that the LTO cells can be fully charged at the fast charge rates. The life cycle tests of a 24V module (10 cells in series) at the 4C charge rate and C/2 discharge rate showed almost no degradation in Ah capacity or resistance (voltage response) in over 1000 cycles. The temperature response of the module without cooling showed a maximum interior temperature of 40C that remained unchanged over the 1000 cycles of the testing.

Part 2: Life cycle testing for second-use applications

1. Introduction

There is considerable interest in using lithium-ion cells in second-use applications (primarily stationary [9-12]) after they have been degraded in a vehicle application, in which their Ah capacity has decreased by about 20% and/or their resistance has increased by about 50%. Hence the degraded batteries still have reasonably good energy storage and power capability. A key question in evaluating a second-use application is how fast the cells will continue to degrade when they are cycled well beyond the vehicle application limits. In order to investigate this problem, several cells (Lithium Manganese Oxide) which had been cycled over 1000 times at the 1C rate were obtained from EIG, Korea. The Ah capacity of these cells had degraded about 10% and their resistance had increased 50-60%. Hence the used cells had degraded in a manner similar to that expected in a vehicle. New cells of the same technology and Ah capacity as the cycled cells were also obtained from EIG. This paper is concerned with further life cycle testing of the used cells to determine the character of their continued degradation.

2. Cells tested

Both the used and new cells were tested prior to starting the life cycle testing. The results of the tests for both the new and used cells are shown in Table 2-1. The cells were discharged from 4.15V to 3.0V. The testing indicated that the Ah and Wh capacity of the new and old (those with 1000 cycles at EIG) cells differed by only 6%, but the resistances differed by a much greater factor (1.5-2.5). Hence the used cells had degraded much more in resistance and power capability than in energy storage capacity.

Table 2-1: Characteristics of the new and used cells at the beginning of the life cycle testing

		Constant current (Ah)			Constant power (Wh)			R mOhm
Device number		6.5A	20A		21W	50W		
New								
226		19.3	18.8		71.7	69.5		2.2
227		19.4	18.8		71.9	69.3		2.3
228		19.4	18.6		71.6	67.8		2.3
Used *								
194		18.6	18		67.6	64.7		4.5
253		18.2	17.5		66.1	62.9		5.9
793		17.9	17.3		65.4	62.5		4.5

* 1000 cycles at 1C by EIG

Table 2-2: Cycling tests performed on the new and used cells

Cell Number	Initial cond. Before testing	Current (Amps)	Temperature (C)
226	New	15	Room Temp
793	Cycled	15	Room Temp
227	New	5	Room Temp
194	Cycled	5	Room Temp
228	New	5	45 deg C
253	Cycled	5	45 deg C

3. Test procedure

As indicated in Table 2-2, a series of tests were performed to compare the cycling characteristics of the new and used cells. The cycling testing was done on a 6 channel, Arbin tester (20V, 20A). The 45 deg C tests were performed using a Test Equity temperature chamber.

4. Life cycle test results

The Ah and resistance of the cells were measured during the cycling. Figures 2-1 and 2-3 show data for the new and used cells cycled at room temperature and Figure 2-2 and Figure 2-4 show data for cycling at 45 deg C. The resistances were calculated from the rebound (I=0) of the voltage after a 5 sec pulse.

Ah cycling characteristics

In all cases, the Ah capacity of the used cells decrease linearly with cycling and showed no tendency for a sudden degradation or failure up to about 900 additional cycles. In the case of the new cells, the Ah capacity increased slightly and then leveled off during the early cycling. This pattern was consistent with cycling data received from EIG for the used cells. The degradation measured for the used cells was the following:

Room temperature	1.7%/100 cycles
45 deg C	6. %/100 cycles

It is clear from Figure 2-1 that the degradation of the used cells at room temperature is much higher than that of new cells.

The effect of temperature on degradation of the Ah capacity is evident from Figure 2-2. Measuring the slope of the degradation curves after the initial level portion, one can calculate the following degradation values for 45 deg C:

	45 deg C		Room temperature
New cell	3.2%/100 cycles	New cell	1.4%/100 cycles
Used cell	6.5%/100 cycles	Used cell	1.7%/100 cycles

As expected, the degradation is much higher for the used cell than for the new cell and the difference is significantly greater at 45 deg C than at room temperature.

Resistance cycling characteristics

The increase of cell resistance with cycling is shown in Figures 2-3 and 2-4. The data indicate that the resistance of the used cell is much higher than the new cell and increases faster than that of the new with additional cycling. This is especially true at 45 deg C where the resistance increases very fast with cycling. Cycling data at room temperature is difficult to understand as both the new and used cells seem to maintain a constant resistance for about 400 cycles before a rather rapid increase starts. There seems little doubt that for the EIG cells (Magnesium Oxide chemistry) that the resistance degrades much more rapidly than the Ah capacity and that both resistance and capacity degrade more rapidly at 45 deg C than at room temperature.

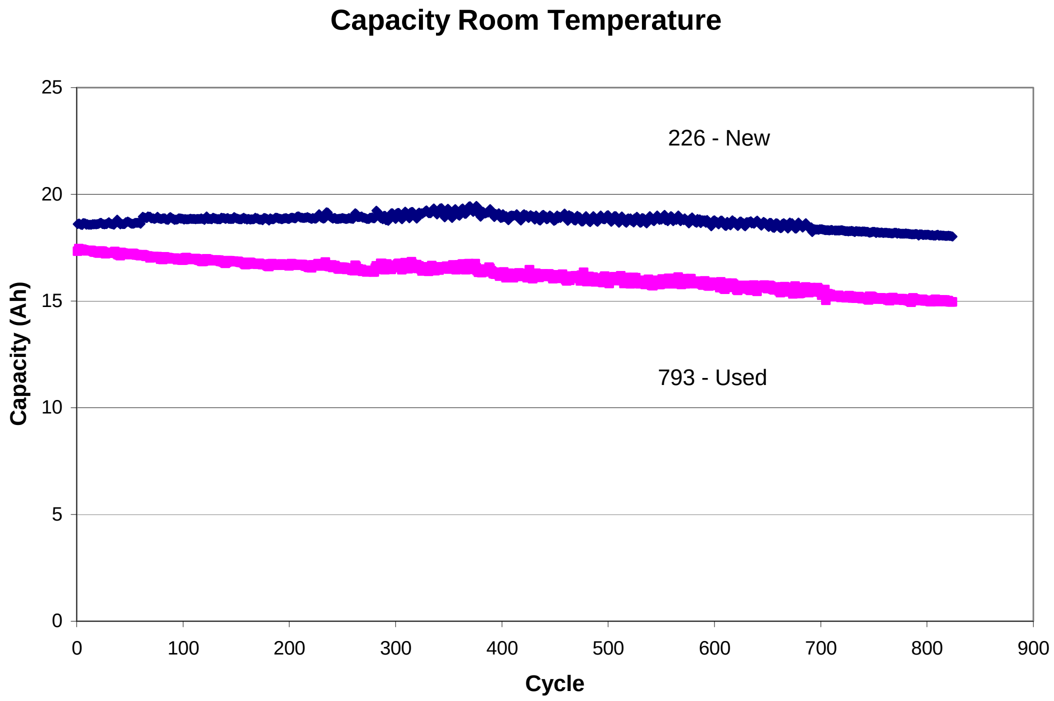

Figure 2-1: The Ah capacity of the new and used cells at room temperature

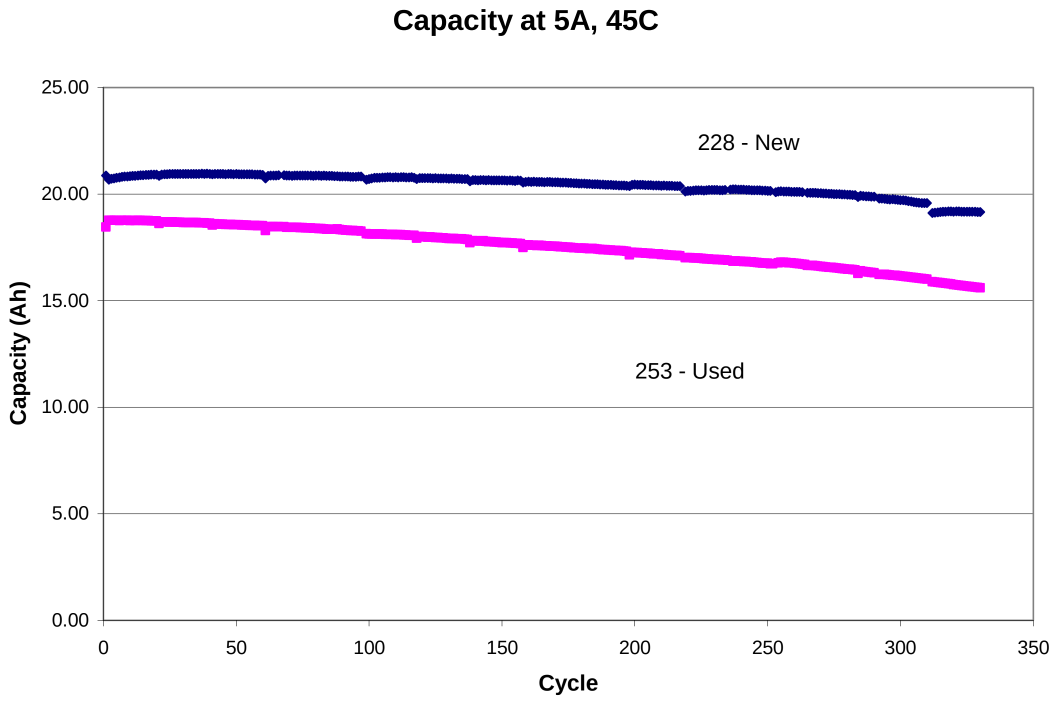

Figure 2-2: The Ah capacity of the new and used cells at 45 deg C temperature

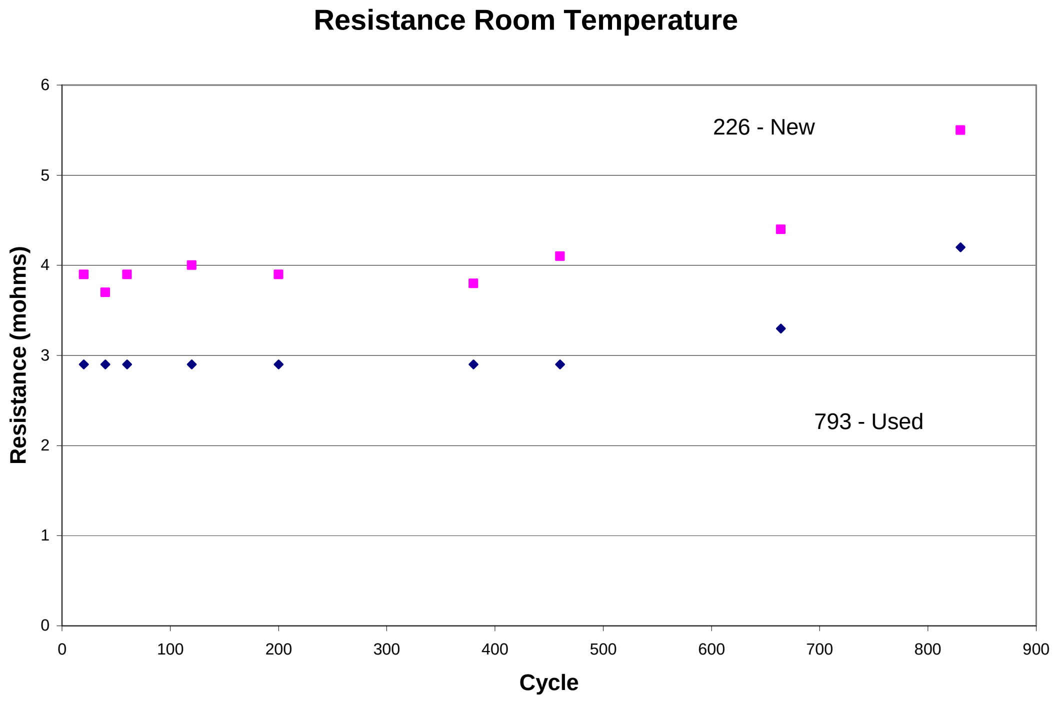

Figure 2-3: The resistance of the new and used cells at room temperature

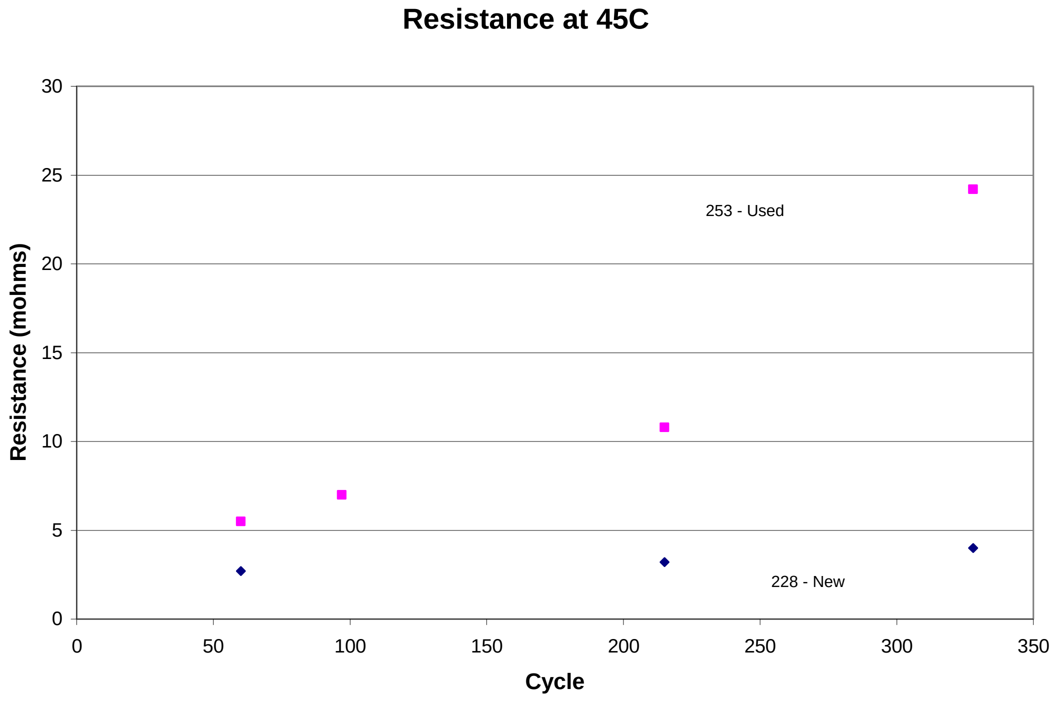

Figure 2-4: The resistance of the new and used cells at 45 deg C

5. Second-use implications of the life cycle results

In assessing whether any cell/battery is suitable for a particular application, the energy density, power capability, and cycle life of the cell must be known. This approach would not be different for the second-use of a battery than for the first-use except that the battery characteristics used in the assessment would be those at the end of the first-use of the battery. Also it is likely that the requirements for the second-use would be less demanding than the first-use. The cycle testing discussed in Section 4 indicates that the Ah capacity and thus the energy density of the battery would be only 10-20% less than when the battery was new after 1-2k cycles in the first first-use application. It seems likely that the power capability that is proportional to the cell resistance will be degraded by a much larger factor than the energy density. In the same 1-2k cycles, the resistance could be more than double the value of the new cell (see Figure 2-3) and as a result the pulse power of the battery would be about ½ that of the new battery. Assessing the cycle life of the second-use battery is even more uncertain than its power capability. In fact, it is likely that assigning a value for the cycle life will depend on deciding how large an increase in resistance is acceptable for the second-use application. This will depend to an important degree on the temperature expected in the second application (see Figure 2-4) as the degradation of the resistance is strongly dependent on the temperatures during the cycling. The test results discussed in Section 4 indicate second-use batteries will be best suited for applications requiring relatively high energy density, but relatively low power capability. Fortunately a number of stationary applications [10, 11] fall in this category.

6. Summary and conclusions (Part 2)

Life cycle testing of new and used 20 Ah prismatic cells obtained from EIG, Korea. Testing was done at room temperature and 45 deg C. The chemistry of the cells was Lithium Manganese Oxide. The charge and discharge currents were 15A for the room temperature tests and 5A for the 45 deg C tests. The new and used cells were cycled (4.15V to 3.0V) about 850 times at room temperature and about 350 times at 45 deg C. The way in which the new and used cells degraded in terms of the decrease in Ah capacity and increase in the resistance were compared with second-use of the cells in mind. As expected it was found that the resistance degraded (%/100 cycles) more rapidly with cycles than the Ah capacity and that for both new and used cells the degradation was much more rapid at 45 deg C than at room temperature. The test results indicate second-use batteries will be best suited for applications requiring relatively high energy density, but relatively low power capability. The degradation of the used cells was gradual (no sudden failures), but accelerated with increasing cycles especially at 45 deg C.

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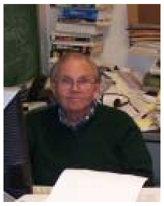

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