Characteristics and Behavior of Cycled Aged Lithium Ion Cells

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ABSTRACT
Data collected on "standard" Li-ion cells confirms a change in kinetic behavior as Li-ion cells cycle. The data shows distinct regions through out the cycle life of the cell. The data suggests that the net coulombic output as well as the relative state-of-charge maintained throughout the cells use is as important as total cycles and calendar time when considering cell aging. The data provides a valuable base for both improved charge routines and safety analysis.

INTRODUCTION
The goal of this effort was to examine the kinetic properties of "standard" Li-ion cells throughout their service cycle. Knowledge gained will be used to: Optimize the service cycle and provide the cornerstone for safety analysis. 18650 Cells with representative chemistry of cells contained in current Army procured batteries were cycled at different rates and environmental conditions. The cycle profiles selected for the series of experiments were designed to simulate use profiles used in the field. Results from 2.0 Amp-hr cells form current vintage BB-2590 cells has been previously been reported, however, their relevance to this effort warrants inclusion. [1-3]

EXPERIMENTAL
Representative 18650 cells were cycled at different rates and environmental conditions. The 18650 chemistry used in this effort is a $LiCoO_2$ lithium ion electrochemical cell. The bulk of this effort was conducted with 1.5 Amp-hr cells. The cycling profiles were designed to simulate real life operational conditions and are described below.

Charge
Cells were subjected to a constant current charge to 4.2 volts followed by a constant potential charge at 4.2 volts. The initial charge current was set at 1.0 Amps or 4.0 Amps and the cut off during the constant potential charge was set to 0.1 Amp or 4.0 hours. The 1.0 Amp charge represents a "normal" charge routine typically recommended by the manufacturer and the 4.0 Amp charge represents a "Rapid" charge routine.

Discharge
The cells were discharged at 1.0 A to 2.5 volts.

States-of-Charge
The cells under test were cycled between various states-of-charge in order to simulate different field operational conditions. The state-of-charges the cells were cycled between included 0% to 100%, 50 to 100% and 0% to 50%, representing "Full" use, constant "top-off" and constant drain scenarios. An additional set where the cells were cycled between 25% and 75% was performed for completeness.

Environmental Conditions
Charge/discharge cycles were performed at -20^{o}C, 0^{o}C, 20^{o}C and 40^{o}C simulating cold, normal ambient and hot environments. After 600 half capacity cycles (the equivalent to 300 full cycles) the cells were cycled at 20 ^{o}C and kinetic experiments were conducted.

Kinetic Experiments
Kinetic experiments were performed after each successive 25th full cycle or 50th half capacity cycle on the cells. Environmental conditions were set at 20^{o}C and cell connections were maintained throughout the experiments minimizing the effect of temperature variants and variable contact resistance.

Sweep Voltammetery
Sweep voltammetery was performed using a voltage controlled discharge at -0.01 V / sec for 50 sec. The current at 50 sec. (-0.5V Vs. OCV) was recorded.

Impedance Spectroscopy
Impedance Spectroscopy was performed with a 20 Step/Decade frequency sweep from 65,000 Hz to 0.65 Hz with a 10 mV perturbation.

Please note: Through out this paper each successive 25th full cycle and 50th half capacity cycle will be referred to as the 25th Eq. Full cycle.

RESULTS
Figures 1-7 show the data for a series of experiments where the state-of-charges the cells were maintained at different levels. These levels were intended to simulate various use scenarios. These scenarios include: "Full" use, constant "top-off" and constant drain scenarios. An additional set where the cells were cycled between 25% and 75% was performed for completeness. In addition, cells were maintained at 0^{o}C, 20^{o}C and 40^{o}C simulating cold, normal ambient and hot environments.

Figure 1 and 2 shows the results of 1.0 Amp discharges at 20^{o}C. Figure 1 shows the capacity degradation as a result of cycle aging and Figure 2 show the polarization current. The polarization current is directly proportional to the power capability of the cell.

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14. ABSTRACT
Data collected on ?standard? Li-ion cells confirms a change in kinetic behavior as Li-ion cells cycle. The data shows distinct regions through out the cycle life of the cell. The data suggests that the net coulombic output as well as the relative state-of-charge maintained throughout the cells use is as important as total cycles and calendar time when considering cell aging. The data provides a valuable base for both improved charge routines and safety analysis.

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Figures 3-6 show additional capacity data where cells were cycle aged at 0 °C and 40 °C. These figures display the data for cells cycled between states-of-charge values of 0% to 100%, 50 to 100%, 25% to 75% and 0% to 50%, representing "Full" use, constant "top-off" and constant drain scenarios.

After 600 half capacity cycles (the equivalent to 300 full cycles) the cells were cycled at 20°C and kinetic experiments were conducted. Figures 3-6 show the capacity data and Figure 7 displays the sweep voltammetery results.

Figure 8-12 shows data from cell from current vintage Army procured batteries. Figures 8 and 9 show impedance spectroscopy of cells cycled at 20°C. Figure 8 shows the impedance when the cell is in the charged state and Figure 9 shows the impedance data when the cell is in the discharged state.

Figure 10-12 show the capacity, open circuit voltage and polarization current for cells cycled at various conditions. These conditions include different temperatures and high rates charge. Figure 10 shows the capacity delivered during the conditioning of the cells. Figure 11 and 12 shows the open circuit voltage and polarization current of the cells after each 25th successive cycle. The open circuit voltage and sweep voltammetery were preformed at 20°C.

DISCUSSION

During analysis of the data a series of trends stood out. The first being, whenever the cell was held at an elevated temperature both the capacity and power capability of the cell decreased significantly (Figures 3-5). The one notable exception is when the cell was maintained at 0% to 50% state-of-charge (Figure 6).

The second is when the cell was maintained at a high state of charge (Figures 3 and 4). The capacity of these cells faded at an increased rate. This is especially true for the cells maintained at a state-of-charge of 50% to 100%.

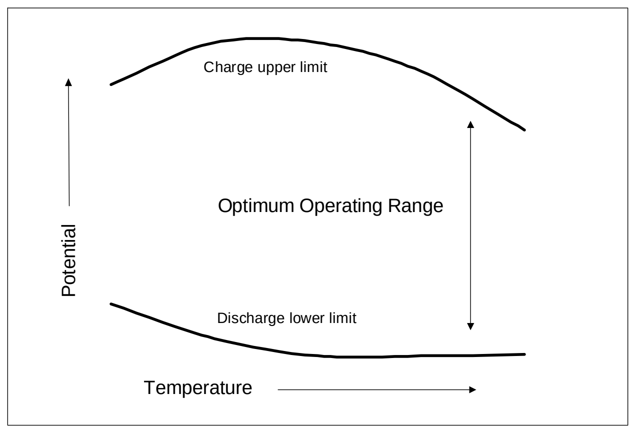
The cells cycled at cold temperature all showed continual decrease in capacity while being cycled at temperature. However, after 300 cycles and the cells were brought to 20°C the capacity recovered (Figures 3-5). The interesting exception here is that when the cell was maintained at a low state-of-charge (Figure 6) the decrease of capacity at low temperature was less severe but the cell did not recover.

These observations were repeated when analyzing the power capability of the cells (Figure 7). The impedance spectroscopy data in Figures 8 and 9 shows the gradual increase in impedance as the cells cycle age. This data also reveals periods where the increase is lower followed by a rapid transition to the next region.

The data confirms change in kinetic behavior as Li-ion cells cycle age. The data shows distinct regions through out the cycle life of the cell. The data suggests that the net coulombic output as well as the relative state-of-charge maintained throughout the cells use is as important as total cycles and calendar time when considering cell aging. The data has provided a valuable base for both improved charge routines and safety analysis.

The following chart shows the charge / discharge profile for optimum service life, as suggested by the data presented here. The data shows a decrease in capacity at three boundary conditions on the charge / discharge profile. The first and most severe is elevated temperature and charging to 100% state of charge. The second is cold temperatures and discharging the cell to a 0% state-of-charge. The third, and lest severe, is cold temperatures and maintaining the cell at a full state-of-charge. Additionally a loss in power capability is observed for the same conditions.

The chart shows the relative charge / discharge conditions for maintaining performance. The chart shows a suppressed charge voltage is required at elevated temperatures and a suppressed charge and elevated discharge cut-off is required at low temperatures.



In order to fully understand the processes affecting the behavior of cycle aged cells the thermodynamic properties will be studied further.

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2) Terrill B. Atwater and Laura M. Cristo, "Kinetic Properties of Cycle Aged Lithium Ion Cells", P. 9th Workshop for Battery Exploratory Development, (2005)
3) Laura M. Cristo and Terrill B. Atwater, "Low Temperature Behavior Phenomenon of 1M LiPF6 1EC:1DMC Electrolyte", P. 8th Workshop for Battery Exploratory Development, (2003)

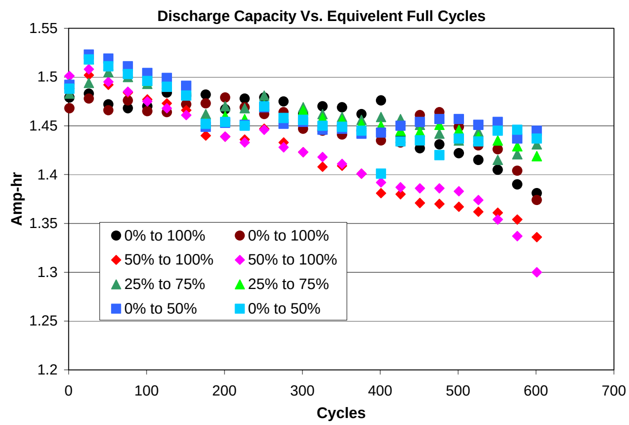

Figure 1. Discharge capacity as a function of maintained state of charge. Full cycle every 25th Eq. full cycle. Cells cycled at 1 Amp, 20^{o}C

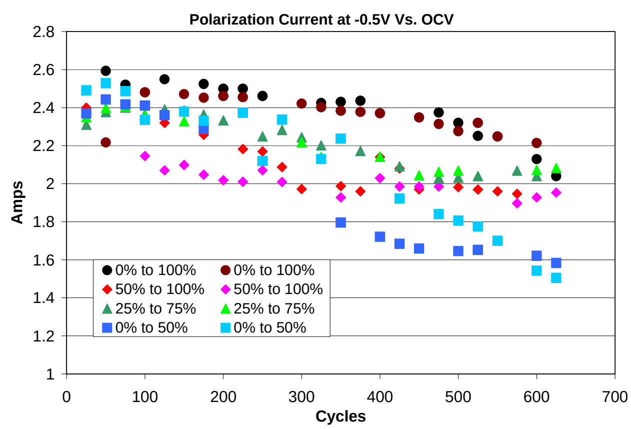

Figure 2. Polarization current as a function of maintained state of charge. Sweep Voltametery every 25th Eq. full cycle. Cells cycled at 1 Amp, 20^{o}C

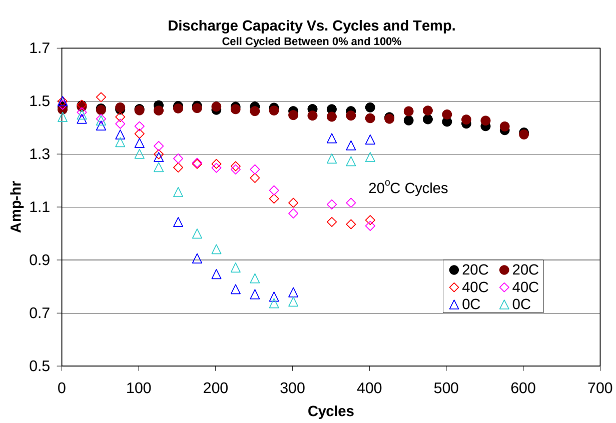

Figure 3. Discharge capacity as a function of cycles and temperature. Full cycle every 25th Eq. full cycle. Cells cycled at 1 Amp between 0% and 100% state-of-charge at 0^{o}C, 20^{o}C and 40^{o}C

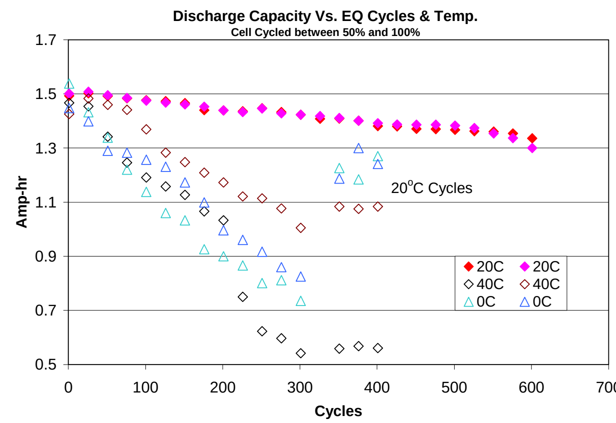

Figure 4. Discharge capacity as a function of cycles and temperature. Full cycle every 25th Eq. full cycle. Cells cycled at 1 Amp between 50% and 100% state-of-charge at 0^{o}C, 20^{o}C and 40^{o}C

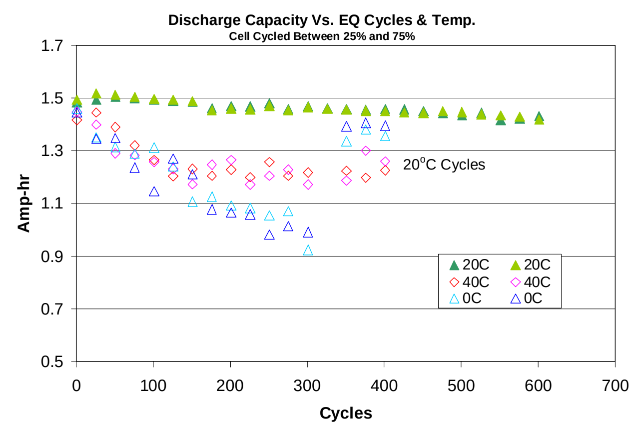

Figure 5. Discharge capacity as a function of cycles and temperature. Full cycle every 25th Eq. full cycle. Cells cycled at 1 Amp between 25% and 75% state-of-charge at 0^{o}C, 20^{o}C and 40^{o}C

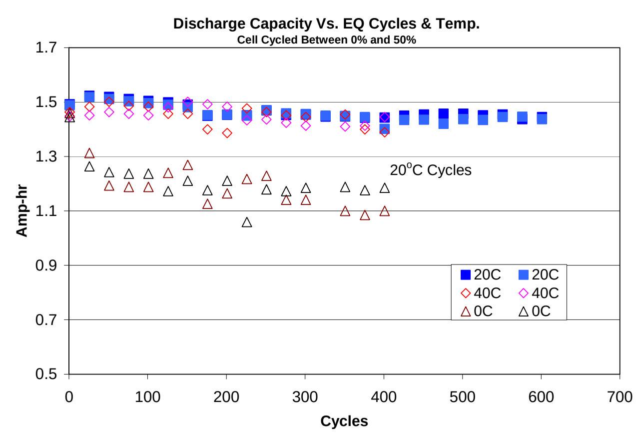

Figure 6. Discharge capacity as a function of cycles and temperature. Full cycle every 25th Eq. full cycle. Cells cycled at 1 Amp between 0% and 50% state-of-charge at 0^{o}C, 20^{o}C and 40^{o}C

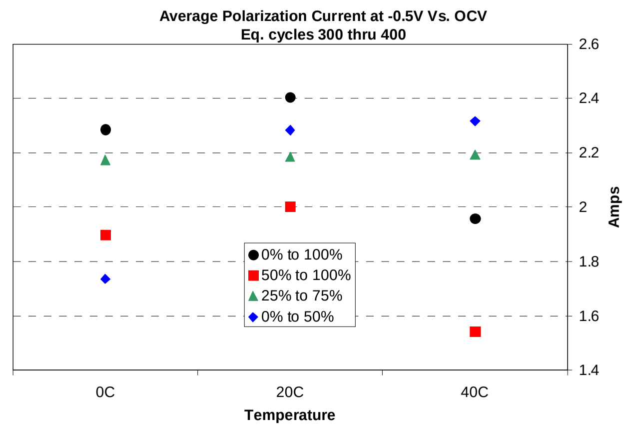

Figure 7. Polarization current as a function of maintained state of charge and Temperature. Sweep Voltammetery every 25th Eq. full cycle from cycle 300 to 400. Cells cycled at 1 Amp, 20°C after 300 conditioning cycles at 0°C, 20°C or 40°C.

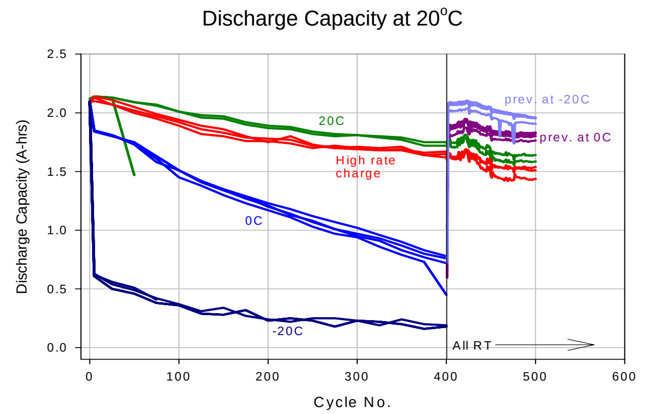

Figure 10. Discharge Capacity as a function of preconditioning and cycles. Cells cycled at 1 Amp or 4.0 Amps at 20°C, 0°C, and -20°C.

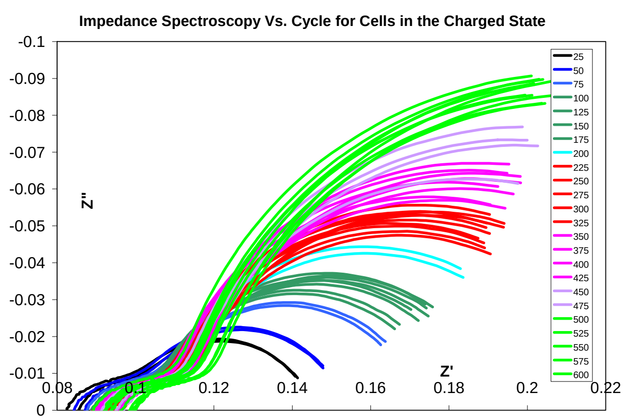

Figure 8. Impedance spectroscopy of cells cycled at 20°C. Impedance for cells is in the charged state.

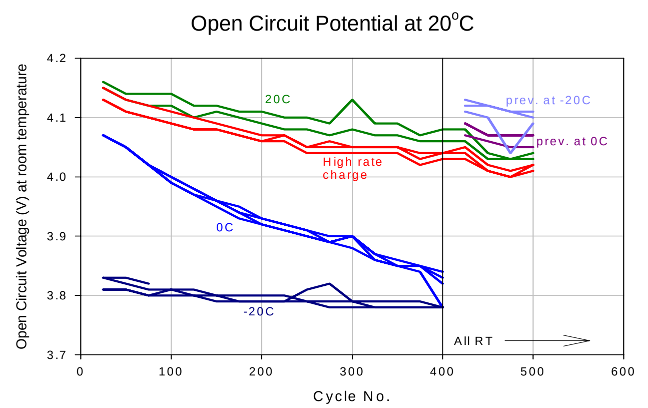

Figure 11. Open Circuit Potential as a function of preconditioning and cycles. Cells cycled at 1 Amp or 4.0 Amps at 20°C, 0°C, and -20°C.

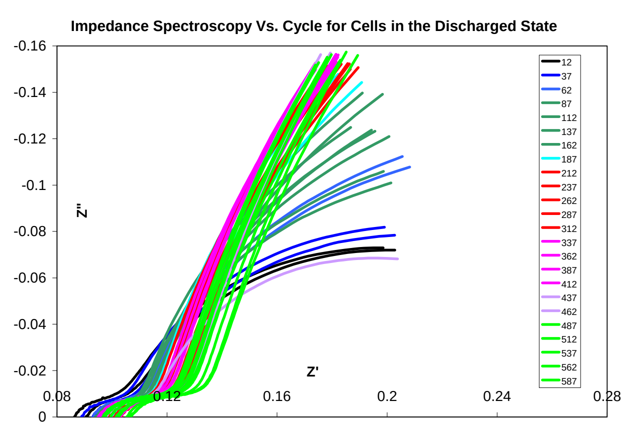

Figure 9. Impedance spectroscopy of cells cycled at 20°C. Impedance for cells is in the discharged state.

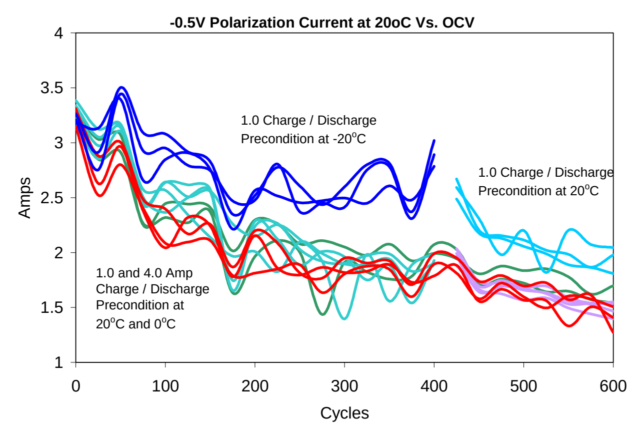

Figure 12. Polarization current as a function of preconditioning and cycles. Sweep Voltammetery every 25th cycle. Cells cycled at 1 Amp or 4.0 Amps at 20°C, 0°C, and -20°C.