

Design Considerations when Disproportionate Heating of Lithium-ion Battery Packs is Present

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ABSTRACT

This paper summarizes a series of papers investigating the, in use, behavior of lithium-ion cells and packs. Initial efforts concentrated on cell data¹⁻⁴ and were reported in 2003 through 2006. Follow-on efforts concentrated on battery pack data⁵⁻⁷ and were reported in 2007 through 2008. In these efforts lithium-ion cells and batteries (4P4S, 2P4S and 4S) were cycled at various conditions. Battery packs, fully augmented with control and monitoring electronics, were subjected to an external heat source at varying intensities which were applied to the base of the battery during both charge and discharge. This heat source effectively heated one cell of the battery string.

INTRODUCTION

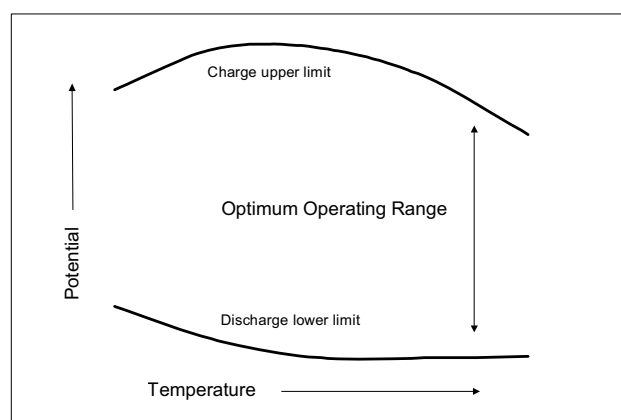
Data collected on Li-ion cells confirms a change in kinetic behavior during cycling. The data shows distinct regions through out the cycle life of the cell. The data suggests that the net coulombic output as well as the relative state-of-charge maintained throughout the cells is as important as total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

During analysis of initial efforts^{3,4} a series of trends stood out. When cells were held at elevated temperatures both the capacity and power capability of the cell decreased significantly. The one notable exception occurred when the cell was maintained at 0% to 50% state-of-charge where the cell tended to maintain their performance at elevated temperatures and performance degradation occurred at reduced temperatures. Additionally, when cells were maintained at a high state of charge, 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. However, the capacity recovered after 300 cycles when the cells were returned to 20°C. The interesting exception here is that when cells were maintained at a low state-of-charge, the decrease of capacity at low temperature was less severe however the cell did not recover. These observations were repeated when analyzing the power capability of the cells.

The following chart shows the charge / discharge profile for optimum service life. The data shows a decrease in capacity at three boundary conditions. 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 least 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.



When considering cases where batteries are, essentially, used as heat sinks for the electronics they are powering, seeded efforts summarized in this paper.

EXPERIMENTAL

Representative 18650 cells were cycled at different rates and environmental conditions. The 18650 chemistry used in this effort is a LiCoO₂ 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 Amperes to 2.5 volts.

STATES-OF-CHARGE - The cells underwent estimated cycles between various states-of-charge in order to simulate

different field operational conditions. The states-of-charge 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% were performed for completeness.

ENVIRONMENTAL CONDITIONS - Charge/discharge cycles were performed at -20°C, 0°C, 20°C and 40°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°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°C and cell connections were maintained throughout the experiments minimizing the effect of temperature variants and variable contact resistance.

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

BATTERY PACK EXPERIMENTS - In the battery pack effort presented here, prototype lithium-ion batteries (4P4S, 2P4S and 4S), fully augmented with control and monitoring electronics, were cycled. The Charge / Discharge Profile for the 4P4S Pack was: Charge, 2.0 A constant current charged to 16.8 volts followed by 16.8 constant voltage charge for 2 hours or 0.2 A, and Discharged at 40 W to 10.0 volts. The 2P4S and the 4S were charged and discharged proportionally.

An external heat source at varying intensities was applied to the base of the battery during both charge and discharge. This heat source effectively heated one cell on the battery string. The external heat source comprised of a thermal-electric heat sink tuned to 20°C or 30°C above ambient (+20°C or +30°C) and heating was maintained throughout the entire charge/discharge profile. The +20°C and +30°C set point represents the maximum and minimum terminal temperature measured on representative equipment.

Prototype battery cases were fabricated in-house with a StataSys® , FDM Vantage rapid prototyping machine. These batteries were designed to accommodate standard 18650 lithium ion cells and simulated common battery configurations. Figure 1 shows the prototype cases used and represent batteries with parallel cells and cells placed end to end. A FLIR Systems ThermoVision® A20M Infrared Camera was used to capture thermal images over time. Figure 2. FLIR Systems ThermoVision® A20M Infrared Camera Set-up.

External heating was accomplished by reversing a thermal-electric heat sink. Figure 3 shows the thermal-electric

element placed on finned aluminum allowing for controlled heating. The finned aluminum was maintained at room temperature resulting in a controlled delta temperature with respect to room temperature. The thermal-electric element was tuned using a water bath.

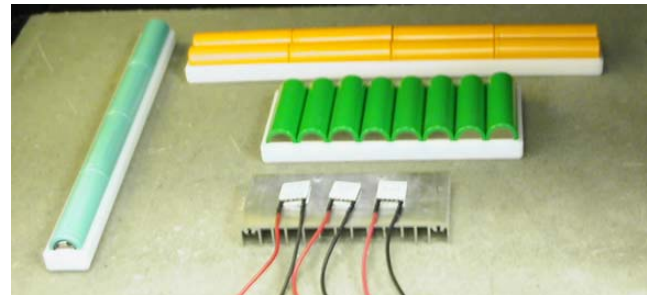


Figure 1. Prototype batteries.



Figure 2. FLIR Systems ThermoVision® A20M Infrared Camera Set-up.

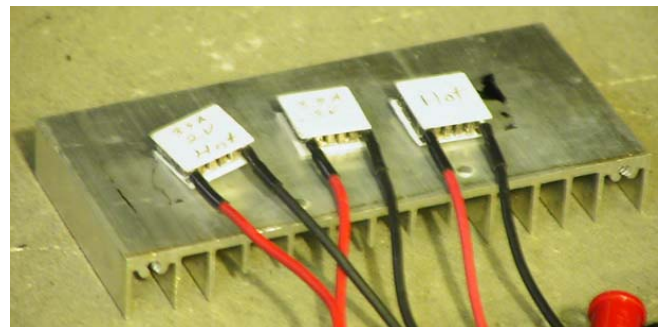


Figure 3. Thermal Electric Element

Heat flow experiments were conducted by placing the prototype battery on the thermal-electric element. Placement of the battery was done to simulate various in use configurations. After initiation of the thermal imaging camera the element was energized. The heat was maintained for at least 3 hours, and the system monitored during both heating and cool down.

RESULTS

Figures 4-8 displays data from initial efforts^{3,4} described in the introduction section of this paper. In these experiments the cell states-of-charge were maintained at different levels to simulate various use scenarios. These scenarios include: "full" use, constant "top-off" and constant drain scenarios. The cells were maintained at 0°C, 20°C and 40°C.

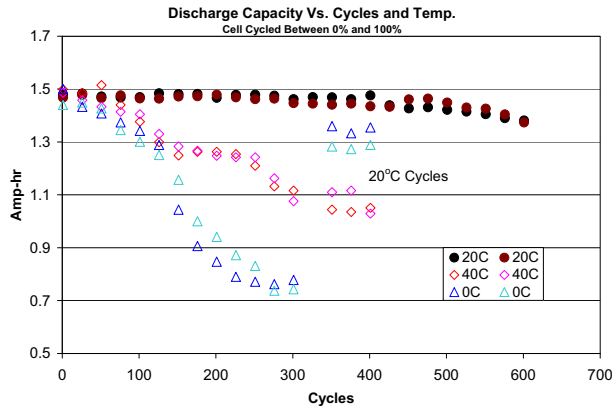


Figure 4. Discharge capacity as a function of cycles and temperature. Cells cycled at 1 Amp between 0% and 100% state-of-charge at 0°C, 20°C and 40°C.

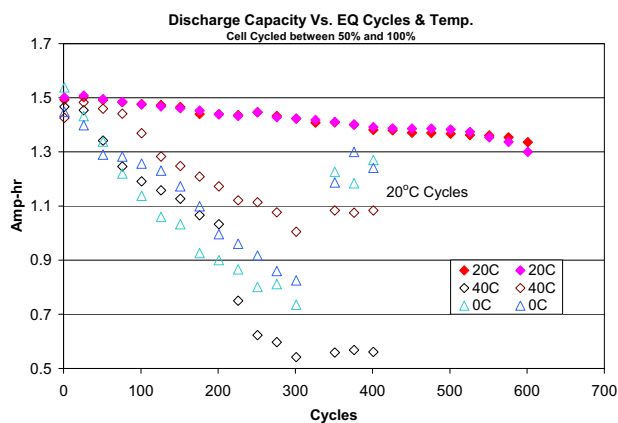


Figure 5. Discharge capacity as a function of cycles and temperature. Cells cycled at 1 Amp between 50% and 100% state-of-charge at 0°C, 20°C and 40°C.

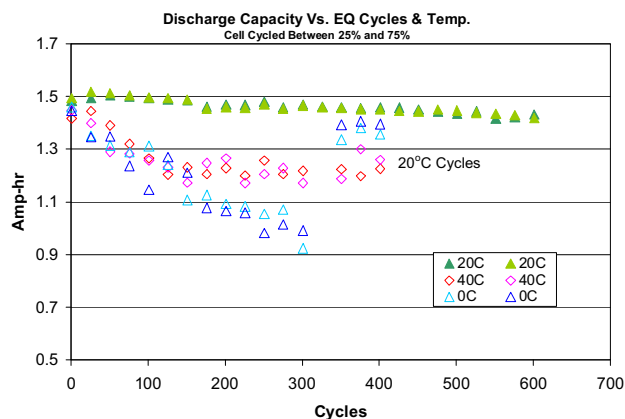


Figure 6. Discharge capacity as a function of cycles and temperature. Cells cycled at 1 Amp between 25% and 75% state-of-charge at 0°C, 20°C and 40°C.

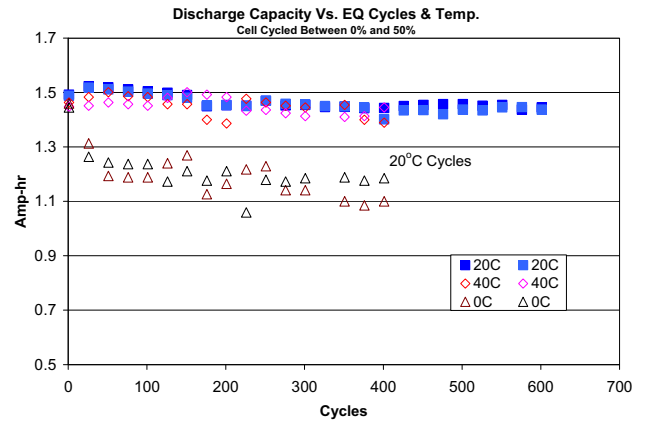


Figure 7. Discharge capacity as a function of cycles and temperature. Cells cycled at 1 Amp between 0% and 50% state-of-charge at 0°C, 20°C and 40°C.

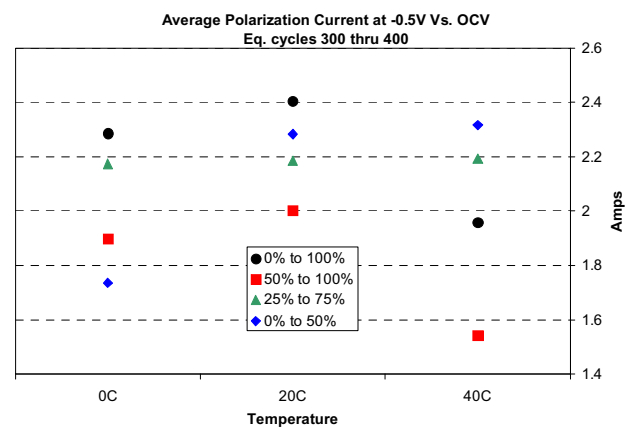


Figure 8. Polarization current as a function of maintained state of charge and Temperature. Sweep Voltammetry every 25th cycle from cycle 300 to 400. Cells cycled at 1 Amp, 20°C after 300 conditioning cycles at 0°C, 20°C and 40°C.

Figure 9 shows discharge capacity vs. cycles for 4S4P batteries undergoing asymmetric heating during cycling. This graph is representative of all of the configurations tested. Table 1 presents the reduced delivered capacity data.

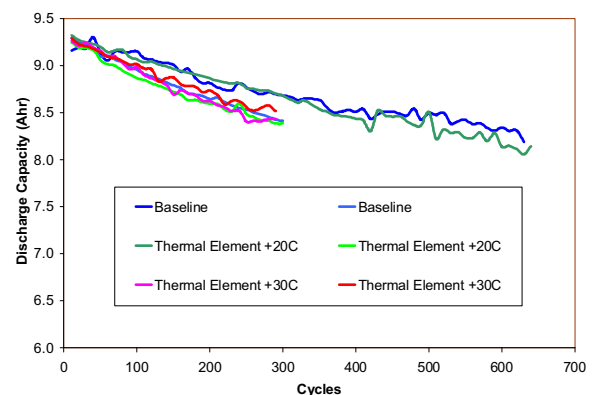


Figure 9: Discharge capacity vs. Cycles for 4S4P batteries undergoing asymmetric heating during cycling.