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Investigation of Elevated Temperature Aging Effects on Lithium-Ion Cells

Rudolph G. Jungst, Ganesan Nagasubramanian, and David Ingersoll

Lithium Battery R&D Department 1521

MS-0613, Sandia National Laboratories

P.O. Box 5800, Albuquerque, NM 87185-0613

Phone: (505) 844-1103, fax: (505) 844-6972, email: rgjungs@sandia.gov

Abstract

Electrical and chemical measurements have been made on 18650-size lithium-ion cells that have been exposed to calendar and cycle life aging at temperatures up to 70°C. Aging times ranged from 2 weeks at the highest temperature to several months under more moderate conditions. After aging, the impedance behavior of the cells was reversed from that found originally, with lower impedance at low state of charge and the total impedance was significantly increased. Investigations using a reference electrode showed that these changes are primarily due to the behavior of the cathode. Measurements of cell impedance as a function of cell voltage reveal a pronounced minimum in the total impedance at approximately 40 - 50% state-of-charge (SOC). Chemical analysis data are presented to support the SOC assignments for aged and unaged cells. Electrochemical impedance spectroscopy (EIS) data have been recorded at several intermediate states of charge to construct the impedance vs. open circuit voltage curve for the cell. This information has not previously been available for the $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ cathode material. Structural and chemical analysis information obtained from cell components removed during postmortems will also be discussed in order to reveal the true state of charge of the cathode and to develop a more complete lithium inventory for the cell.

Introduction

Lithium-ion batteries are considered the power source of choice for a number of applications due to their attractive energy and power density. However, questions remain regarding the ability of lithium-ion cells to survive elevated temperatures without performance degradation and their safety

during thermal abuse. We have been investigating the performance of commercial lithium-ion cells for several years, and recently have begun to study the electrical behavior and thermal abuse tolerance of 18650-size high power lithium-ion cells that have been subjected to calendar and cycle life aging at temperatures of up to 70°C. These particular cells contain a graphitic carbon anode, a $\text{LiNi}_{0.85}\text{Co}_{0.15}\text{O}_2$ mixed metal oxide cathode, and an ethylene carbonate (EC)/diethyl carbonate (DEC)/ LiPF_6 electrolyte. There are no built-in safety features such as a positive temperature coefficient (PTC) device that would obscure the effect of temperature on cell performance.

Experimental

Standard electrochemical equipment was used for the impedance measurements. The cell impedance was measured in both 2 and 3-electrode configurations. We performed the 3-electrode impedance measurements to more accurately locate the source of impedance increases and to correctly assign the two loops typically seen in the Nyquist plots to the two electrodes. The 18650 cell was opened in a glove box for 3-electrode measurements to accommodate the Li reference electrode in the mandrel hole that runs along the length of the cell at the center [1]. The reference electrode assembly consists of a thin platinum wire fused at one end to a ~ 1 mm diameter glass tube. The other end of the platinum wire protrudes from the opposite end of the glass tubing for electrical contact. The fused end of the glass tubing was made flat by polishing to form a smaller area platinum disc electrode and lithium metal was cold-welded to the flat platinum electrode to complete the reference electrode assembly. The cell with the reference electrode was kept in a plastic beaker to which an appropriate electrolyte was added.

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Chemical analysis of the lithium content of electrodes was done by inductively coupled plasma – mass spectrometry (ICP-MS).

Impedance Measurements

Impedance, a non-destructive technique, has been applied very successfully to monitor changes due to corrosion/degradation of active components in power systems [2]. However, few papers are published on the full cell impedance behavior of the 18650 lithium-ion cells. A typical Nyquist plot of the cell impedance shows an inductive tail at high frequency followed by two loops at lower frequencies (see Figure 1). The inductive tail has been observed by others for Li-MoS₂ cells [3] and in that case has been attributed to the jellyroll and/or porous electrode design. The inductive tail in the case of 18650 cells is also likely due to a similar design feature. None of the publications except one [4] has assigned which loop corresponds to which electrode. Ozawa [4], from his 2-electrode impedance data, has assigned the larger loop at low frequencies in the Nyquist plot to the anode and the smaller loop to the left of the larger loop to the cathode. He has supported these assignments with the observations from two related impedance measurements on half-cells. We have shown that the larger loop is correctly assigned to the cathode.

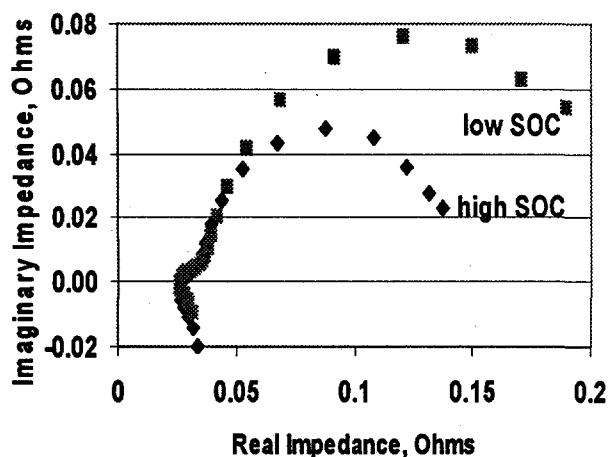


Figure 1. Nyquist plot showing impedance of an unaged high power 18650 Li-ion cell at high and low SOC.

Results and Discussion

Full frequency a-c EIS recorded prior to the high temperature soaking show a total impedance of about 0.14 ohms at low charge (3.1 V) and 0.12 ohms at full charge (4.1 V) on average. An example Nyquist plot is shown in Figure 1. This behavior is considered normal and has been observed by us before with commercial lithium-ion cells from other sources. Following as little as two weeks of high temperature aging, in conjunction with pulsing or cycling, the impedance behavior of the cells as a function of SOC was found to be the reverse of what was originally observed. A cell stored open circuit at 60°C for 56 days showed a total impedance of 0.17 ohms at low SOC and 0.28 ohms at full charge. Nyquist plots for an aged cell at high and low SOC are shown in Figure 2. Assignment of the EIS features to a particular cell component has been completed through the 3-electrode studies, which show that the cathode is mainly responsible for the increased impedance.

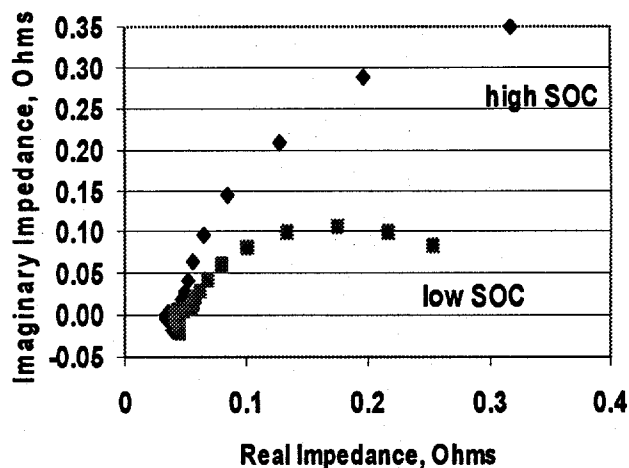


Figure 2. Nyquist plot showing impedance of a high power 18650 Li-ion cell after heating at 70°C for 8 weeks.

EIS data have also been recorded at several intermediate states of charge to construct the impedance vs. open circuit voltage curve for the cell. This information has not previously been available for cells containing the LiNi_{0.85}Co_{0.15}O₂ cathode material. Figure 3 shows low frequency (10mHz) impedance data for a Li-ion cell at

various temperatures and voltages. These low frequency impedance values mainly reflect the contribution of the interfacial loop. Furthermore, 3-electrode measurements show that the cathode interfacial impedance is dominant. A pronounced minimum in the low frequency impedance is observed near 3.6 V (40% SOC) at all temperatures. The width of the SOC window showing the most favorable impedance also becomes noticeably smaller at -10°C , which has implications for degraded power performance of this cell design.

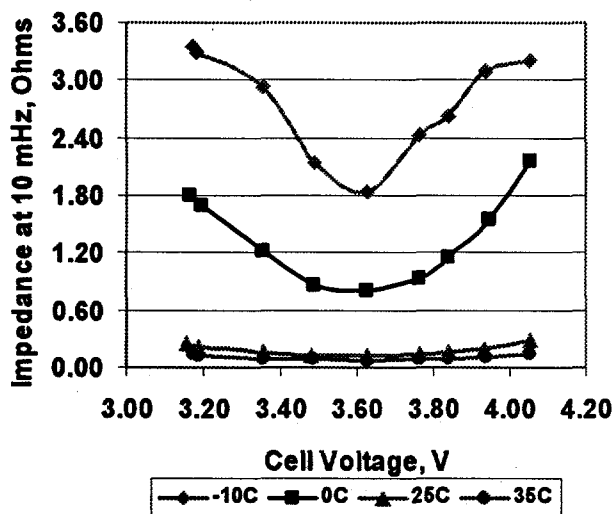


Figure 3. Low frequency impedance of a high power 18650 Li-ion cell at different voltages and temperatures.

This parabolic shape for the cathode total impedance versus cell voltage has not been observed for the LiCoO_2 material. Choi, et al. [5] carried out half-cell impedance measurements on both LiNiO_2 and LiCoO_2 electrodes and found a continuous increase in total impedance with increasing lithium content for LiCoO_2 . The impedance behavior of the mixed metal oxide cathode studied here is more similar to pure LiNiO_2 , which shows a shallow minimum.

The parabolic nature of the cell impedance versus cell voltage dependence raises the possibility that the reversed trend in impedance after aging could be due to the change in the shape of the impedance

curve after heating. Alternatively, a shift in the cycling window with respect to cathode lithium content could have occurred due to loss of active lithium. This may happen due to changes in the cathode structure or accumulation of significant amounts of lithium in solid electrolyte interphase (SEI) layers.

In order to investigate the first possibility, low frequency impedance values at various voltages were compared for cells before and after aging. Figures 4 and 5 show the results for cells heated at 50°C and 70°C , respectively. The 50°C cell shows only a minor amount of increase, although the

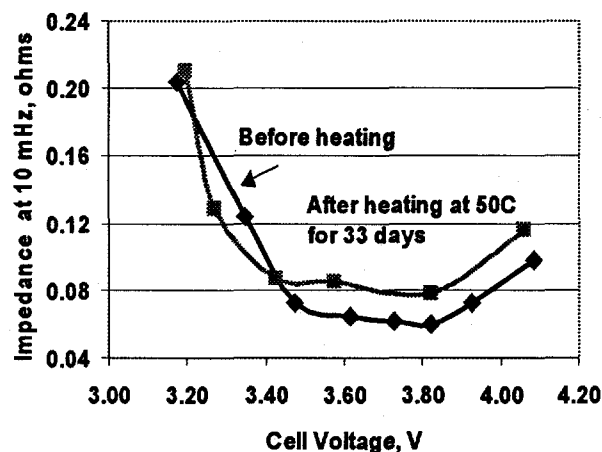


Figure 4. Low frequency impedance of a high power Li-ion cell at 25°C before and after heating at 50°C .

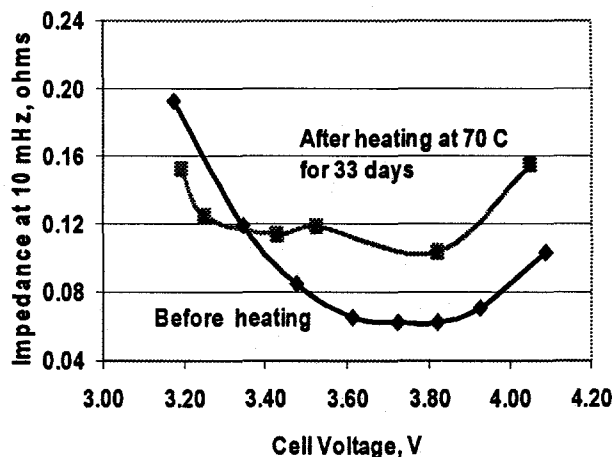


Figure 5. Low frequency impedance of a high power Li-ion cell at 25°C before and after heating at 70°C .

greatest change is in the high voltage region, in agreement with the trend observed overall in the impedance results. A larger shift can be seen for the 70°C cell, where the high SOC impedance has indeed increased enough to slightly exceed the low SOC value after 33 days of heating. It appears that the impedance curves do shift after high temperature aging. Whether this change is promoted by cycling the cells while they are exposed to high temperature is still under investigation.

The second mechanism for a crossover of the high and low SOC impedance values is a shift in the cycling window relative to cathode lithium content. In order to determine whether more lithium is retained in the SEI layers with time, cells were postmortemed and samples of anode and cathode materials removed for analysis. The weight % of lithium in the cathode was determined and compared to that for the unaged cell to see whether a significant shift in the cycling SOC window for the cathode could be detected. Results are shown in Table 1. Very little difference in lithium content

Table 1. Cathode Composition for Aged Li-ion Cells

Opened Cell Voltage	Aging Conditions	Cathode Li Content, Li _x	Estimated Li _x of Unaged Cell at Same SOC
3.48	60°C, 56 day	0.73	0.75
3.28	60°C, 4 wk	0.82	0.81
3.42	70°C, 2 wk	0.78	0.77

was found compared to the values expected for an unaged cell at the same SOC. This shows that the aged cells are not cycling over a shifted SOC window and the impedance trends must be due to changes in the impedance versus cell voltage curve as described above. Since the impedance increase results mainly from growth in the interfacial impedance loop assigned to the cathode, the interfacial properties of the cathode are changing as it ages.

Conclusions

A reversal has been observed in the low frequency impedance behavior of aged 18650-size Li-ion cells containing a LiNi_{0.85}Co_{0.15}O₂ mixed metal oxide cathode. The impedance at low SOC is higher for unaged cells, but after heating, the impedance at high SOC was found to be larger. Measurements of cell impedance were carried out on cells at various open circuit voltages, showing a pronounced minimum in low frequency impedance at 3.6 – 3.8 V for cells aged at high temperature. Larger increases in the high SOC impedance values are observed after exposure to higher temperatures. Chemical analysis of the lithium content of cathodes from aged cells shows little difference from that expected for unaged cells. Therefore the SOC window during cycling has not changed significantly and the impedance behavior can be attributed to changes in the interfacial properties of the cathode material as it ages.

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