

ANALYSIS OF LITHIUM-ION BATTERY DEGRADATION DURING THERMAL AGING

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ABSTRACT

High power lithium-ion batteries are being developed for use in hybrid electric vehicles, as well as other applications, but performance has still been below requirements, particularly in the area of power fade. Sandia is participating in a study that seeks to identify the causes for degradation in lithium-ion cells so that material and design improvements can be accelerated. This study is being carried out on 18650-size hardware containing components representative of the high-power designs. Thermal aging produces a 20% decrease in pulse power capability and also reduces capacity. Complex ac impedance studies reveal that the interfacial impedance at the cathode is the major factor responsible for this decrease in power capability. Postmortem and chemical analysis of the cells has also been carried out after completion of the electrical tests. Although changes are seen in some components such as the electrolyte, there is no evidence for change in the bulk cathode structure or for transport of metallic species to other locations within the cell.

INTRODUCTION

Lithium-ion batteries have been a great commercial success for a variety of portable electronics applications due to their high cell voltage, attractive combination of energy and power, and good cycle life. Development of larger cells is now under way for stationary energy storage, space, and automotive applications. Each of these represents a more demanding situation in terms of safety requirements, environmental conditions, use profile, or some combination of the preceding factors. The electric vehicle (EV) and hybrid electric vehicle (HEV) applications, in particular, push known performance limits in all three areas. Sandia is collaborating on a study of the lithium-ion battery chemistry using 18650-size cells as a convenient test vehicle. The particular materials used in the cell are typical of the high-power lithium-ion chemistry being developed for use in HEVs. The major objective of this work is to determine the causes for power fade after these cells are exposed to elevated temperatures in life tests. A second objective is to develop diagnostic analysis methods that can be used to determine the causes for cell degradation. Another important goal is to characterize the thermal abuse tolerance of the cells and identify the mechanisms that are responsible for thermal runaway. This report will focus on results gathered for the life studies.

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EXPERIMENTAL

Li-ion cells were stored at 40, 50, 60, or 70°C for times of 2-8 weeks for the calendar and cycle life aging studies. Some cells were maintained at a single state-of-charge (SOC) (60 or 80%) for the calendar life tests, while others were cycled at a defined Δ SOC of 3, 6, or 9%. The high-power 18650 cell design investigated uses a mixed metal (Ni/Co) oxide cathode material, a graphitic carbon anode, and an ethylene carbonate (EC)/diethyl carbonate (DEC) electrolyte containing 1M LiPF_6 salt. AC impedance measurements were obtained with standard electrochemical equipment in both 2-electrode and 3-electrode configurations. A description of the lithium reference electrode construction has appeared elsewhere (1). Ion chromatography (IC) analyses for Li^+ were carried out using a conventional cation column, while the PF_6^- and F^- in the electrolyte were quantified with a Dionex Ion Pac AS-11 anion column. This analysis method for PF_6^- has not been previously reported. Metallic species in the electrolyte were analyzed by aspirating a sample diluted in 2.5% nitric acid directly into the instrumentation for inductively coupled plasma-mass spectrometry (ICP-MS). Solid electrode samples were dissolved by nitric acid digestion in high-pressure microwave vessels.

AC IMPEDANCE RESULTS

Complex AC impedance spectra of the high-power 18650 cells exhibit characteristics before aging as shown in Figure 1. An inductive tail associated with the spiral wound geometry is observed and the ohmic resistance averages 30 m Ω . Total cell impedance (100 mHz) is typically between 140 and 180 m Ω before aging, depending on the SOC. Nyquist plots show several superimposed interfacial loops to be the main contributors to the total impedance. Initially, the impedance is highest at low SOC due to the larger interfacial component. After thermal aging, the interfacial impedance is increased and, as shown in Figure 2, the total impedance becomes larger at high SOC if aging conditions are severe enough. Investigation of the total impedance at several states-of-charge shows that there is a minimum value at intermediate SOC, with somewhat higher values at high SOC (4.1 V) and much larger values at low SOC (3.1 V) (see Figure 3). Little change occurs in the low SOC impedance after aging, but significant increases are seen at high SOC. Three-electrode measurements reveal that the predominant contribution to the interfacial impedance comes from the cathode. After high-temperature aging, these cells typically show a 20-30% decreased power capability in standard PNGV electrical performance tests and capacity is also markedly reduced (2).

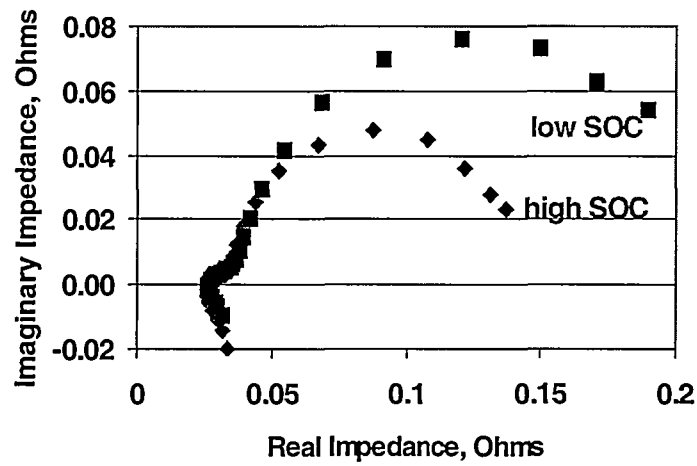


Figure 1. Nyquist Plot of EIS data for an Unaged Lithium-Ion Cell.

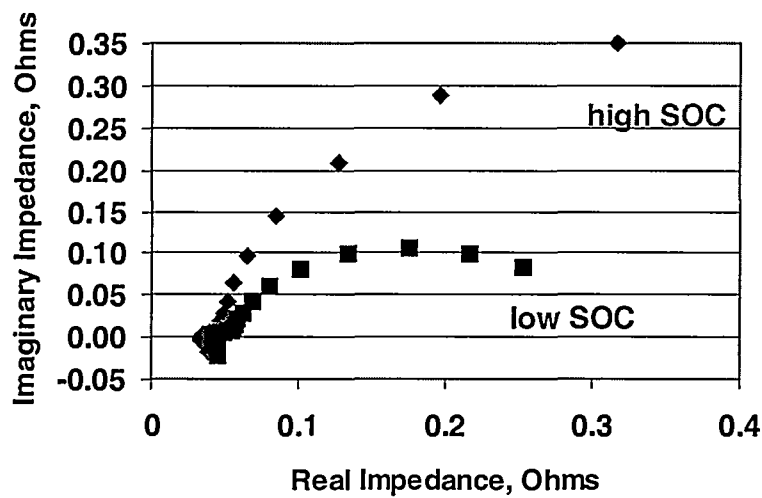


Figure 2. Nyquist Plot of EIS Data for a Lithium-Ion Cell Heated at 70°C for 8 Weeks.

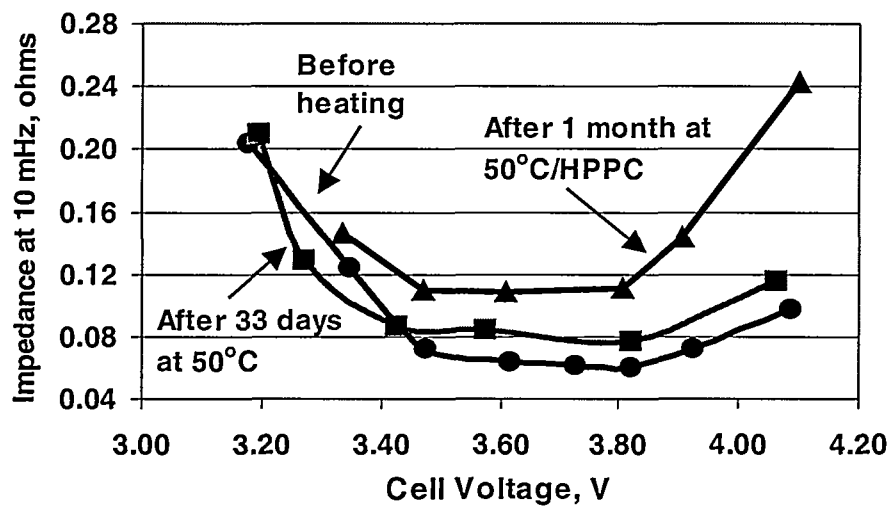


Figure 3. Low Frequency Impedance versus Lithium-Ion Cell Voltage.

The behavior of the impedance during aging was examined in more detail for several of the cells that were measured at either 2 week or 4 week intervals during the experiments. Reference performance test data collected at the end of each aging interval included capacity, pulse power, and complex impedance. Since the impedance change is most significant at high SOC, interfacial impedance and ohmic resistance values were compared at this condition. Figure 4 shows these results for three different aging temperatures. It is apparent that there is very little change in the ohmic crossing point at any of the conditions studied. The largest step increase in the interfacial impedance occurs after the first aging interval at 40 or 70°C and thereafter it nearly levels off. At 50°C, the interfacial impedance continues to increase for at least 8 weeks. The total increase is largest at the highest temperature, as expected. Both charge transfer and surface film resistances are represented in the interfacial impedance measurements and at this point we have not attempted to distinguish them experimentally. Three-electrode measurements show two loops for each electrode, although those for the negative electrode are substantially smaller than the ones for the positive. The high frequency loops are invariant with SOC, while the lowest frequency loop changes significantly in size during charge and discharge. This type of behavior has been interpreted in the literature for a $\text{Li}_{1-x}\text{CoO}_2$ electrode as indicating that the low frequency loop is due to charge transfer (3). Although this seems to be a reasonable assumption in the present situation, experiments are planned to definitively assign the largest interfacial impedance loop to either charge transfer or film resistance for this mixed Ni/Co oxide cathode.

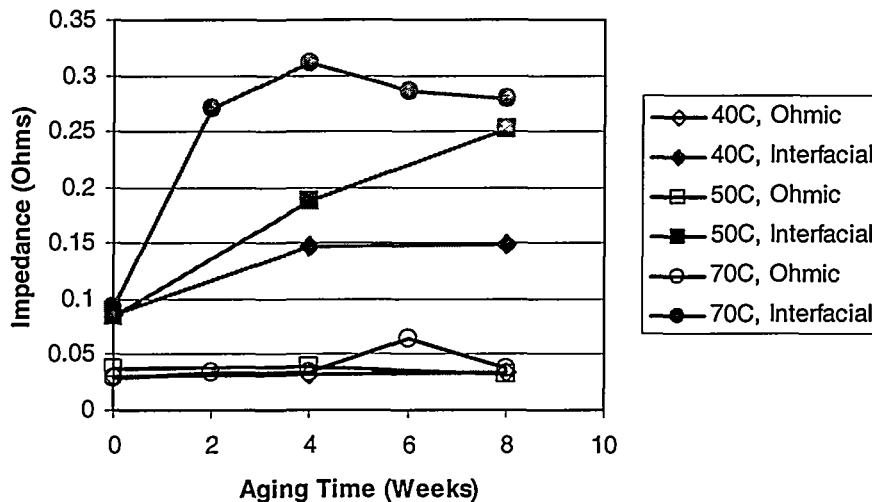


Figure 4. Changes in Interfacial Impedance and Ohmic Resistance after Aging at Different Times and Temperatures.

POSTMORTEM AND COMPONENT ANALYSIS

Samples of electrolyte and electrode materials have been recovered during cell postmortems and analyzed to identify which of the various possible cell degradation mechanisms are present. Specific mechanisms that were looked for are electrolyte decomposition and reaction, cathode and current collector dissolution, and shifts in the

lithium inventory within the cell. Contributions of these mechanisms to the observed changes in cell performance have been assessed.

Electrolyte Recovery and Analysis

A complete analysis of the electrolyte composition has been made possible at Sandia by development of a specialized ion chromatography (IC) method for PF_6^- and F^- . The instrumental response for PF_6^- has been shown to be linear over a wide range of concentrations. Sensitivity for F^- by this method is also good with a detection limit of as little as 6.6 mM in the undiluted electrolyte. Li^+ was measured by a standard IC technique, thus allowing the $\text{Li}^+/\text{PF}_6^-$ ratio to be checked. Gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) analyses were also done on the organic solvents revealing the presence of reaction products. Samples of electrolyte from whole cells generally show elevated concentrations of LiPF_6 and depletion of EC and DEC.

Electrolyte samples were recovered from a number of Gen1 life test cells by centrifuging. Cells stored at 40, 50, and 70°C, cycled and uncycled, were sampled, as well as two control cells that had not been heated or cycled. Figure 5 shows the IC results. The Li^+ and PF_6^- concentrations were nearly the same, as expected, but in most cases the salt concentration was considerably above the nominal 1M at which the cell was built. The only significant discrepancy between the Li^+ and PF_6^- results is for one of the 70°C samples, but the highest overall salt concentrations occurred in 40°C samples. Small amounts of fluoride were detected in most samples (17-89 ppm), but there was no consistent trend with the aging conditions, suggesting that the high LiPF_6 concentrations are most likely due to reaction of the electrolyte solvents with other materials within the cell. This is supported by low peak area responses for both EC and DEC on the GC compared to an unaged sample of bulk electrolyte.

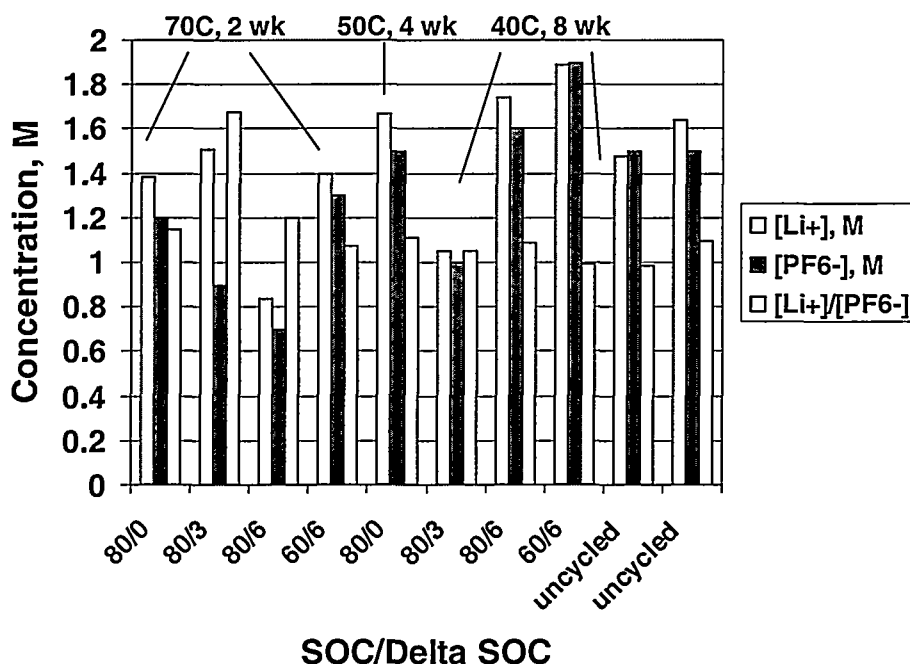


Figure 5. Li^+ and PF_6^- Concentrations in Electrolyte Sampled from Aged Li-Ion Cells.

Cell Disassembly

Two slightly different procedures were used for cell disassembly depending on the tests to be done. In both cases, the first step taken was to cut off the top of the cell just below the crimp seal using a Dremel tool. The power leads to the positive electrode were then cut using a nonconductive ceramic scissors. For 3-electrode work, it is only necessary to provide an access for additional electrolyte through the bottom of the cell. If the electrolyte had been previously sampled from the cell, the existing hole punched in the bottom was used directly and power leads then spot-welded on for the measurement. If the cell had not yet been punched, a hole was ground part way around the bottom with the Dremel. For cells undergoing a complete tear down, a carbide slitting saw was used next to completely remove the cell bottom and to cut a slit up the side of the cell case. The case was then partially pried open and the cell roll removed and unrolled. The electrodes were cut into 2-inch pieces using the ceramic scissors again. Electrode samples for ICP-MS analysis were also punched out in a dry room with a ½-inch diameter steel punch. Selected samples were washed with reagent grade DEC prior to analysis.

In aged cells, active material was observed adhering to the separator in some cases after the cell roll was pulled apart. This was equally prevalent for the positive and negative electrodes. Delamination more commonly appeared on the exterior rather than the interior side of the cell winding and more of it was also seen in the interior of the roll near to the mandrel hole where the radius of curvature is greater. The cathode tended to leave a stain on the separator after aging, but it is not known whether this is due to chemical reaction or simply physical impregnation of particles in the polypropylene.

Cathode and Current Collector Dissolution

Inductively coupled plasma – mass spectrometry (ICP-MS) analysis was done for both electrode and electrolyte samples to measure the types and amounts of metallic species present. Trace metal concentrations were measured to assess the migration of current collector and cathode material within the cell. Rinsing of the samples with DEC prior to analysis had no effect on the trace metal results. Metal concentrations for a cathode and an anode from a cell heated 2 weeks at 70°C are shown in Figure 6. Most of the metals found are present at less than 100 ppm. The species of particular interest are aluminum, nickel, and cobalt in the anode and copper in the cathode. The only one of these that is present at levels of any significance is copper at 252 ppm. Iron arises as an impurity in lithium. Comparison with samples stored at lower temperatures shows no trend to indicate that copper concentration is proportional to aging temperature. In fact, the trace metal concentrations were all comparable or lower in a cathode sample from a cell heated for 56 days at 60°C. Consistent with these findings, the concentrations of current collector metals in 10 different samples of electrolyte were all below 2 ppm except for one showing 3.4 ppm aluminum. Nickel ranged from 0.4 to 8.3 ppm and cobalt was less than 0.1 ppm in most electrolyte samples. The overall conclusion of this part of the study is that little migration of current collector material (Al, Cu) or cathode metal oxide constituents seems to be occurring at relatively short aging times regardless of temperature.

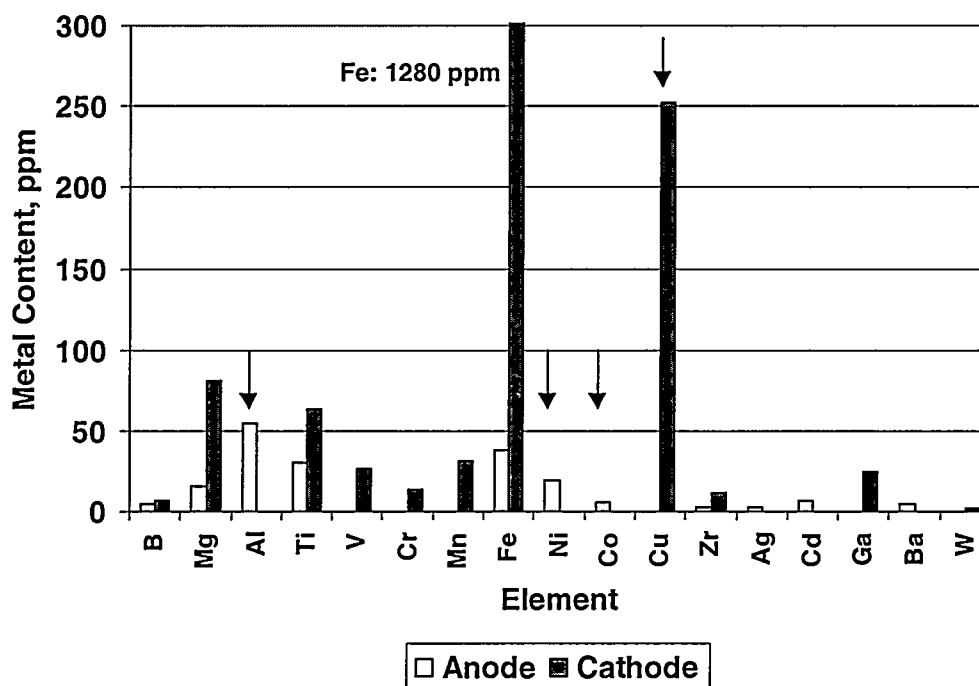


Figure 6. Trace Metals Content of Electrodes from a Lithium-Ion Cell Heated at 70°C for 2 Weeks.

Lithium Inventory

The lithium content of the anodes and cathodes was also determined in the same ICP-MS measurements. Several aged cells were opened at slightly different SOC's and the measured lithium values compared to those expected for unaged cells. Table 1 shows a comparison of the measured lithium content of the cathode with the amount expected for three cells based on their open circuit voltage when opened. The values agree closely for the three cells that were analyzed, although this test cannot distinguish whether all the lithium is capable of being cycled. X-ray diffraction measurements were made to confirm whether any new phases were present in the positive active material and none were found. The close agreement in all cases, shows that the thermal aging performed here has not caused a shift of lithium to the anode solid electrolyte interphase (SEI) layer. This method cannot distinguish lithium in the cathode SEI layer. Another implication is that the cathode SOC window during cycling has not shifted dramatically.

Table 1. Cathode Lithium Content for Aged Lithium-Ion Cells

Cell Voltage When Opened, V	Aging Conditions	Cathode Lithium Content, Li _x	Estimated Cathode Li _x for an Unaged Cell at the Same SOC
3.48	60°C, 56 days	0.73	0.75
3.28	60°C, 4 weeks	0.82	0.81
3.42	70°C, 2 weeks	0.78	0.77

SUMMARY AND CONCLUSIONS

Measurements of impedance and chemical analyses of materials have been carried out for 18650 lithium-ion cells heated at temperatures from 40 to 70°C for various lengths of time. Other studies on these cells have shown a degraded power capability after exposure to the same thermal aging conditions. EIS experiments reveal that the total impedance is significantly increased after aging and that most of the change occurs in the cathode interfacial impedance. The ohmic resistance of the cell is largely unaffected. Assignment of the interfacial impedance change to charge transfer resistance is reasonable by analogy, but this has not been confirmed experimentally. Chemical analyses show that the salt concentration in the electrolyte is elevated, probably due to reactions of the organic solvents. No changes in bulk electrode properties have been observed. ICP-MS measurements of metallic species in the system do not show any migration of current collector or positive electrode material within the cell after short periods of high temperature aging. Aging also appears to have no effect on the distribution of lithium within the cell at this stage. Further studies of the cathode interfacial properties are in progress.

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