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Impedance studies on Li-ion cathodes

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Abstract

This paper describes our 2- and 3-electrode impedance results of metal oxide cathodes. These results were extracted from impedance data on 18650 Li-ion cells. The impedance results indicate that the ohmic resistance of the cell is very nearly constant with state-of-charge (SOC) and temperature. For example, the ohmic resistance of 18650 Li-ion cells is around 60 mΩ for different SOCs (4.1V to 3.0V) and temperatures from 35°C to -20°C. However, the interfacial impedance shows a modest increase with SOC and a huge increase of between 10 and 100 times with decreasing temperature. For example, in the temperature regime (35°C down to -20°C) the overall cell impedance has increased from nearly 200 mΩ to 8000 mΩ. Most of the increase in cell impedance comes from the metal oxide cathode/electrolyte interface.

Introduction

Li-ion batteries have generated widespread interest as batteries of choice for a number of applications, because of their attractive energy and power densities. Although the electrical performance of the Li-ion cells at room temperature is very respectable that at sub-ambient temperatures is very limited. This limitation has been attributed to the increase in cell impedance at sub-ambient temperatures. The impedance increase severely restricts the power output of the cells at sub-ambient temperatures.

We have studied the impedance characteristics of commercial 18650 cells at different temperatures from 35°C down to -20°C. A-C impedance measurements seem to indicate that the ohmic resistance of the cells increases only marginally at sub-ambient temperatures. This ohmic resistance includes electrolyte resistance, electrodes bulk resistance, current collector and tab resistances. Most of the increase in cell impedance comes from the electrode electrolyte interfacial impedance. We at Sandia National Laboratories and others have shown that in Li-ion cells the increase in impedance comes mostly from the cathode electrolyte interface and not from the anode electrolyte interface [1]. The next question then is, "where exactly the increase in cathode impedance comes from?" Whether it comes from the interfacial impedance (including charge- transfer resistance and the resistance of the Solid-Electrolyte- Interphase) or the diffusional impedance inside cathode matrix. To answer these questions, we are currently investigating impedance characteristics Li-ion cells containing $LiCoO_2$ and $Li_1Ni_{0.85}Co_{0.15}O_2$ as the cathode at different temperatures and states-of-charge. A thorough understanding of the source of the cathode impedance should help offer

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solution(s) for improving the power performance and cycle life of Li-ion cells.

Experimental

Standard Electrochemical equipment was used to make impedance and other electrochemical measurements [2]. The cell impedance was measured both in a 2-electrode and 3-electrode configuration. We performed the 3-electrode (the third electrode being a Li reference electrode) impedance measurements to locate more accurately the source of the impedance increase especially at lower temperatures and to correctly assign the two loops in the NyQuist plots to the two electrodes (anode and cathode). The cell configuration was modified to accommodate the Li reference electrode in the mandrel hole that runs along the length of the cell at the center. Both the bottom and the top of the cell were carefully cut-open in a glove box with a Dremel tool and subsequently tabs were attached to the anode and cathode for electrical contacts. After the cell was opened at both ends, it was never exposed to air, to prevent degradation of the cell components by reacting with oxygen and water vapor. A Li reference electrode made beforehand was introduced in to the cell through the mandrel hole. The reference electrode assembly consists of a thin platinum wire and a ~ 1 mm diameter glass tube. The platinum wire is fused at one end to the glass tubing. The other end of the platinum wire sticks out 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 platinum disc electrode of tiny area and lithium metal was cold-welded to the flat platinum electrode. This completes the reference electrode assembly. The cell with the reference electrode was kept in a plastic beaker to which Sony type electrolyte {Ethylene Carbonate, Propylene Carbonate and Diethyl Carbonate (1:1:2 v/v) containing 1M $LiPF_6$} was added for impedance studies. This assembly was then put in a "Kerr Jar" for easy handling. The initial operational checks (for internal shorts, open circuit voltage etc.) were done in a glove box. The impedance measurements were carried out at different temperatures and cell temperatures during measurements were controlled with a Tenney Jr. temperature chamber (benchtop model, Union, New Jersey).

Results and Discussion

<u>Electrode Impedance Studies</u>

Before opening cells for the 3-electrode studies, 2-electrode impedance measurements were made at different temperatures. In Figure 1 are shown NyQuist plots at different temperatures from 35°C to 0°C.

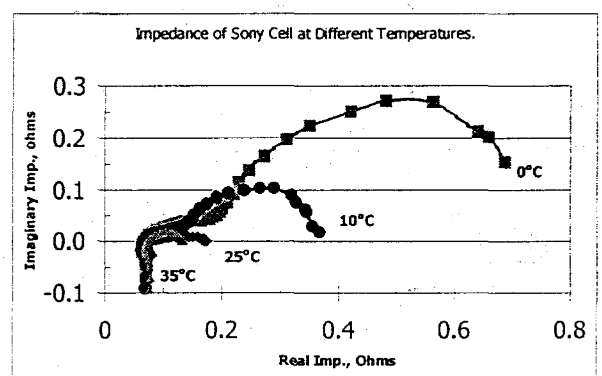

Figure 1. NyQuist Plot for a Sony 18650 Li-ion cell at Different Temperatures from 35°C to 0°C.

These plots indicate that the ohmic resistance of the cell remains almost constant, while the total cell impedance (low frequency x-axis intercept) increases significantly. Similar results have been reported by Anderman *et al.* [3].

Further these plots show that the interfacial resistance is much higher than the ohmic resistance. Although the 2-electrode measurement indicates that the interfacial impedance dominates the cell impedance, especially at lower temperatures, it doesn't tell us whether it is the anode or the cathode electrode/electrolyte impedance that is responsible for the increase. To identify which electrode is the cause for the impedance increase, we carried out 3-electrode impedance studies. In Figures 2 and 3 are given NyQuist plots for the anode, cathode and the full cell impedance of the opened cell (measured in 2-electrode mode) at 0°C and -20°C, respectively.

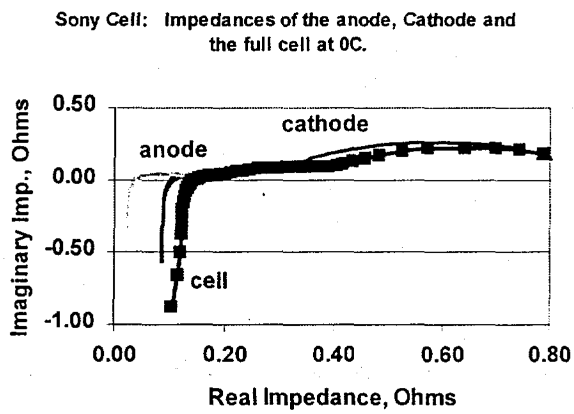

Figure 2. Sony cell. NyQuist Plots for anode, cathode and the full cell at 0°C.

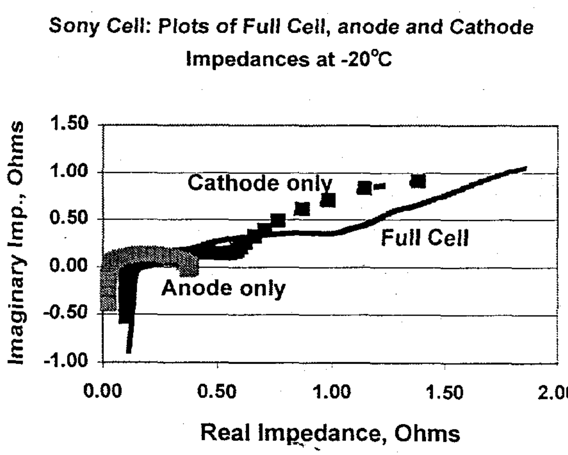

Figure 3. Sony cell. NyQuist Plots for anode, cathode and the full cell at -20°C.

The plots clearly show that the impedance of the anode/electrolyte interface is lower than the cathode/electrolyte interface which dominates the overall cell impedance. Further, both electrodes contribute to both loops, with the cathode contributing the most to the second loop. In Figure 4 are compared the sum of the anode and cathode impedances and the 2-electrode impedance (from Figure 2) at 0°C.

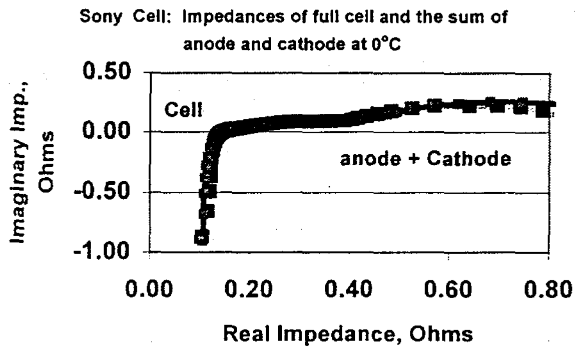

Figure 4. Sony cell. NyQuist Plots for the full cell and for the sum of the anode and cathode impedances at 0°C.

In **Figure 5** are shown similar NyQuist plots at -20°C.

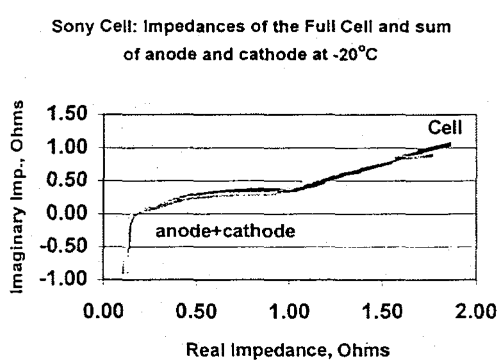

Figure 5. Sony cell. NyQuist plots for the full cell and for the sum of the anode and cathode impedances at -20°C.

The impedances obtained from the 2-electrode measurement and the sum of the anode and cathode (obtained from the 3-electrode measurements) are comparable which provides an internal check for the correctness of the measurement. Our 3-electrode impedance data very clearly indicate that:

1) both anode and cathode contribute to the two loops and
2) cell impedance comes mostly from the cathode/electrolyte interface and not from the anode/electrolyte interface.

This observation still, however, doesn't tell us where exactly impedance in the cathode comes from. Whether it comes from the interfacial resistance or from the diffusion of Li^+ inside the cathode lattice. To answer these questions we have evaluated impedance characteristics of the 18650 Li-ion cells with $LiNi_{0.85}Co_{0.15}O_2$ as cathode at different temperatures as a function of depth-of-discharge. In Figure 6 shows NyQuist plots for the cell at four temperatures at 3.18V OCV. The figures in clock-wise direction (starting from the upper left) represent impedance plots at 35°C, 25°C, 0°C and -10°C for the cell. At 35°C the diffusional line is larger than at 25°C and at 0°C and -10°C there is no evidence of a diffusional line.

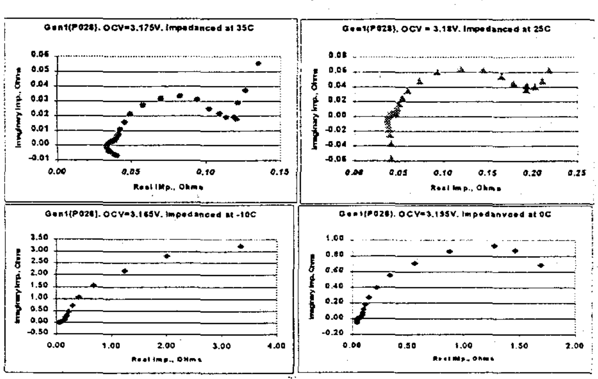

Figure 6. Progressive disappearance of diffusional impedance and increase in interfacial impedance going from 35°C to -10°C.

However, over this temperature regime, the interfacial resistance has increased by over an order of magnitude and dominates the cell impedance.

Conclusions

2- and 3-electrode impedance measurements were made on 18650 Li-ion cells at different temperatures ranging from 35°C to -20°C. Although the ohmic resistance remains almost constant, the total cell resistance increases by nearly 2 orders of magnitude at sub-ambient temperatures. The increase in cell impedance comes mostly from the cathode/electrolyte interface as shown by our 3-electrode study. Further, our impedance studies with $LiNi_{0.85}Co_{0.15}O_2$ cathode suggest that the charge transfer resistance dominates the cell impedance at lower temperatures.

Acknowledgments

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References

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3. Fan, G. Nagarajan, R. M. Spotnitz, and M. Anderman *in Lithium Batteries* , **PV 98-16,** p. 512, The Electrochemical Society Proceedings Series, Pennington, NJ (1999).