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Electrochemical Impedance Spectroscopic Analysis of Lithium-ion Battery Aging Mechanisms

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Introduction

Lithium-ion battery (LiB) technology has successfully made the transition from powering small portable electronic devices to large scale hybrid (HEV) and pure electric vehicles (EV). While the short life cycles of ~2 to 3 years for portable electronic devices has not imposed a severe cycle life demand on LiBs, automotive applications require both a long calendar life and cycle life in order to meet the severe demands of automotive use.[1] These demanding automotive requirements have caused battery manufacturers to develop battery life-time performance models based on realistic load cycling, temperature cycling, storage, and abuse conditions in order to meet the new cycle-life targets.

Estimation of battery lifetime requires a deep understanding of the LiB aging mechanisms. Performance loss in LiBs over calendar and cycle life can be broadly attributed to two different causes: i) capacity (energy) fade, and ii) power fade. Capacity fade arises due to the loss of active materials and/or the loss of active (cycleable) Li content.[2] On the other hand, power fade primarily occurs due to the increase in electrode impedance (solid electrolyte interface (SEI), inter-particle contact, current collector corrosion, etc.). Such performance losses could arise either under various storage conditions (self-discharge) and/or various drive cycle conditions.

Performance loss in LiBs under various storage and cycling conditions is a complicated phenomena which requires a range of complementary analytical techniques (such as electrochemical, microscopic and spectroscopic) in order to identify both the aging mechanism and the source of degradation.[1] Electrochemical Impedance Spectroscopy (EIS) provides a unique characterization tool to investigate and discern inter-dependent aging processes occurring at various time scales under both in situ and non-destructive fashion.[1,2,3,4]

In this work, we employ a combination of various electrochemical and impedance spectroscopic techniques to investigate the aging mechanisms of LiB and propose strategies to mitigate the performance losses.

Materials and Methods

Coin cells were fabricated using various combinations of anode (graphite, Si) and cathode ($LiNi_xCo_yMn_{1-x-y}O_2$) active materials. Electrolyte solutions were prepared using 1 M $LiPF_6$ dissolved in organic solvents (EC, DEC, FEC). Polypropylene membrane was used as separator. For half-cells, Li-metal counter electrode was used. In addition, 3-electrode cells incorporating Li-metal reference electrode were used to study half cell polarization behavior. After coin cell assembly, two formation cycles were carried out at C/10-rate.

Results and Discussions

Typical short-term cycle-life testing (for graphite/$LiNi_xCo_yMn_{1-x-y}O_2$) was carried out with 1C-rate charging to 4.2 V, followed by a taper charge at 4.2 V for 1 hour and a 1C-rate discharge to 3.0 V. EIS measurements were carried out from 200 kHz to 10 mHz before and after cycle-life testing with a 10 mV amplitude on cells at 50 % state-of-charge (SOC). As shown in Figure 1 (inset), over a period of 50 cycles at 1C-rate, a marginal loss in capacity of about 3% is observed. Preliminary EIS investigations of this 50 cycle durability test revealed a combined increase in electrolyte resistance and cathode reaction resistance. (Figure 1) Long-term life-cycle testing experiments are currently being carried out to understand the aging mechanism under various life-cycle testing conditions. Carefully designed experiments involving the use of a lithium reference electrode are also being performed to assign the source of degradation to the anode and/or cathode electrodes.

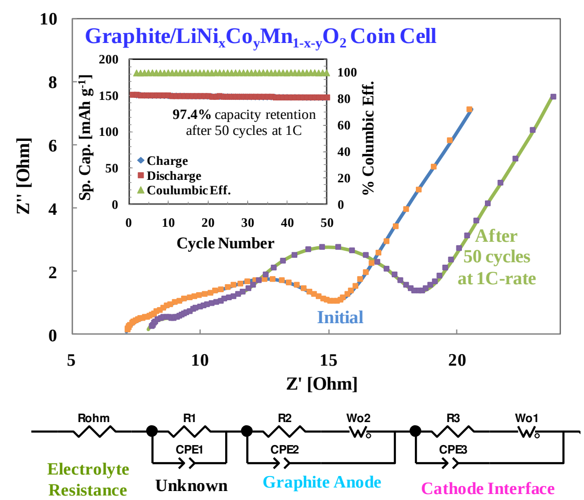

Figure 1: (Top) Plots showing the impedance spectra of Graphite/ $LiNi_xCo_yMn_{1-x-y}O_2$ cell before and after 50 cycles. Inset shows the capacity retention behavior during the short 50 cycle test. (Bottom) Electrochemical equivalent circuit model utilized for the interpretation and fitting of the experimental EIS spectra.

References

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