Degradation of lithium ion batteries employing graphite negatives and nickel−cobalt−manganese oxide + spinel manganese oxide positives: Part 1, aging mechanisms and life estimation

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HIGHLIGHTS

- We report on cycling-induced capacity fade in NCM + LMO/graphite Li-ion cells.
- Capacity loss is strongly affected by the rate, temperature, and depth of discharge.
- Lithium loss outpaces loss of active negative and positive electrode materials. .
- Calendar loss follows a square root of time relationship.
- Cycle loss is approximately linear as a function of charge throughput.

ARTICLE INFO

ABSTRACT

We examine the aging and degradation of graphite/composite metal oxide cells. Non-destructive electrochemical methods were used to monitor the capacity loss, voltage drop, resistance increase, lithium loss, and active material loss during the life testing. The cycle life results indicated that the capacity loss was strongly impacted by the rate, temperature, and depth of discharge (DOD). Lithium loss and active electrode material loss were studied by the differential voltage method; we find that lithium loss outpaces active material loss. A semi-empirical life model was established to account for both calendar-life loss and cycle-life loss. For the calendar-life equation, we adopt a square root of time relation to account for the diffusion limited capacity loss, and an Arrhenius correlation is used to capture the influence of temperature. For the cycle life, the dependence on rate is exponential while that for time (or charge throughput) is linear.

1. Introduction

Lithium ion batteries are now used in the automotive, commercial aircraft, and space industries. For vehicular applications, understanding battery life performance is important; not knowing a battery's useful life increases business risks and warranty costs. There have been extensive efforts focused on the development of battery life models to predict capacity fade in lithium ion batteries [1–12]. Different capacity fade models have been established based on the proposed aging mechanisms such as parasitic side reactions [7,8,13], SEI formation [11], and resistance increase [2,14]. However, experimental data are needed to understand the capacity fade and validate the aging mechanisms. Very often, a significant amount of testing is needed to develop a reliable model to account for multiple factors effecting battery life. Very few groups have attempted to develop a life prediction model using a large experimental data set. Bloom and Wright et al. [15–17], presented the testing and life modeling of lithium ion batteries with Ni-based lithium insertion cathodes including $LiNi_{0.8}Co_{0.2}O_2$ and $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$. Recently, we established cycle-life models of a graphite/LiFePO$_4$ battery using a large cycle-test matrix [18]. These results have demonstrated the importance of using large test matrixes to evaluate and validate the life modeling of lithium ion batteries.

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Manganese-based lithium ion batteries have been considered as a viable candidate for large scale energy storage systems such as vehicular applications. In particular, $[LiNi_{1/3}Co_{1/3}Mn_{1/3} + LiMn_2O_4]$ composite cathode electrodes promise a good balance of both energy density and power density [19–22]. $LiNi_{1/3}Co_{1/3}Mn_{1/3}$ provides very good energy storage capacity at 180 mAh g^{-1}, while $LiMn_2O_4$ offers excellent rate capabilities. However, capacity fade

behavior and life modeling for this battery has not been well established. Recently, Dubarry et al. [23,24], presented an insightful aging analysis of lithium ion battery comprising $[LiNi_{1/3}Co_{1/3}Mn_{1/3} + LiMn_2O_4]$ composite cathode using incremental capacity technique for the cell cycled at 2 C rate. In another report, Gering et al. [25], investigated the aging behavior of the same targeted chemistry cycled under specific vehicle duty cycle protocols. In this report, we further evaluate the aging mechanisms of a $LiNi_{1/3}Co_{1/3}Mn_{1/3} + LiMn_2O_4$ composite cathode cell under a wide range of temperatures, rates, and depth of discharge (DOD). The results agree with prior reports indicating that capacity fade is mainly caused by the loss of active lithium inventory.

This report focuses on understanding the aging mechanisms and developing a semi-empirical life model to account for both calendar life loss and cycle life loss using data collected from a large cycle-test matrix. Through the capacity data trend analysis and differential voltage analysis of the discharge profiles, we identify the aging behaviors of lithium ion batteries with $LiNi_{1/3}Co_{1/3}Mn_{1/3} + LiMn_2O_4$ composite cathode chemistry. We determine that there are two degradation mechanisms contributing to the lithium loss: 1) high rates at low temperature triggers accelerated lithium loss, perhaps due to excessive SEI formation of cycle-induced cracks on graphite particles, and 2) high temperatures cause accelerated calendar life loss, likely due to chemical side reactions that consume lithium.

Fig. 1. Test matrix for accelerated cycle life study. Two cells were tested at each condition. Colored highlights represents the selected test conditions: four temperatures (10 °C, 22 °C, 34 °C, 46 °C) five discharge currents (0.5 C, 2 C, 3.5 C, 5 C, 6.5 C) and five discharge depths (10%, 30%, 50%, 70%, 90%). Lines shown here are for the guidance of the data trend, not from model fit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
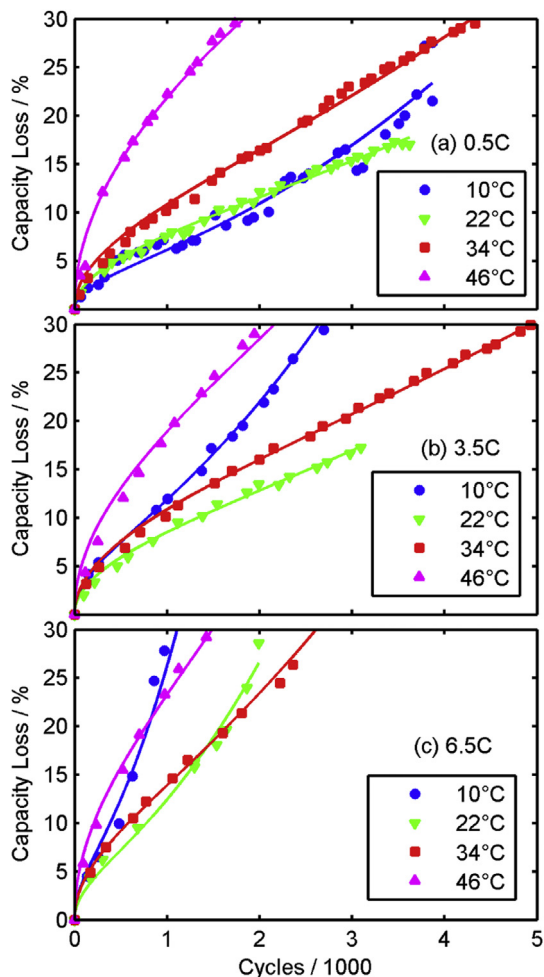

Fig. 2. Capacity loss at four temperatures (10 °C, 22 °C, 34 °C, 46 °C). The panels each correspond to a single rate (0.5 C, 3.5 C, 6.5 C, respectively). The depth of discharge is 50% for all data points in the figure. The x-axis scale is thousands of cycles. Lines shown here are for the guidance of the data trend, not from model fit.