

Capacity Fade Studies of Li-ion Cells Cycled at Different Temperatures

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Introduction

There has been a tremendous interest in using Lithium-ion batteries to power several devices in consumer electronics. With their high capacity and energy density, these batteries are ideally suited to satisfy the high power demands of several devices. One of the problems associated with the performance of Li-ion batteries is capacity fade with cycling. Capacity decay is caused by various mechanisms, which depend on the electrode materials and also on the protocol adopted to charge the cell. Capacity fade in Lithium-ion cells can be attributed to unwanted side reactions that occur during overcharge, which cause electrolyte decomposition, passive film formation, active material dissolution and other phenomena¹.

Moreover for safe use of Li-ion cells in portable electronics, it becomes critical to study battery performance at elevated temperatures up to 60°C². Elevated temperature can accelerate the degradation of battery materials, which causes a decline in capacity and premature cell death. Our capacity fade studies on spinel based Li-ion cells showed us the influence of the charging protocol on capacity fade³. Objectives of this study were to find the capacity fade mechanisms of Li-ion cells cycled at elevated temperatures and to compare the capacity fade among them using direct current.

Experimental

Sony US18650S cells with a rated capacity of 1800 mAh were used for these studies. For cycling studies, the cell was charged at a constant current of 1 A until the potential reached 4.2 V. Subsequently the voltage was held constant at 4.2 V until the current drops to 50 mA. The cells were cycled under four different temperatures namely 25, 45, 50 and 55°C.

Charge-discharge studies were carried out in the potential range of 2.0–4.2 V. Solartron SI 1255 HF Frequency Response Analyzer (FRA) and Potentiostat /Galvanostat Model 273A were used for the electrochemical characterization of Sony US18650S cells. For the impedance measurements the cells were left on open circuit for 1 hour for the potential to get stabilized. The cell was stable during the experiments and its voltage changed less than 1 mV. EIS measurements were done on the cells at both charged and discharged states. The impedance data generally covered a frequency range of 0.002 to 5000 Hz. A sinusoidal AC voltage signal varying by +/- 5mV was applied.

The following studies were done to understand the processes occurring at individual electrodes of the cell. The can of cycled Sony US18650S cells was carefully opened at fully discharged state in a glove box filled with ultra pure argon. Next, pellet electrodes were made from the positive and negative electrodes of Sony US18650S cell and were used as working electrodes in the T-cell. Pure lithium metal was used as the counter and reference electrode. 1 M LiPF₆ was used as the electrolyte in a 1:1 mixture of ethylene carbonate (EC), and di-methyl carbonate (DMC). EIS studies were done on the T-cells to understand the influence of the positive

and negative electrode on the total impedance of the cell. Impedance was measured at both charged and discharged states. The frequencies of the AC signal ranged from 10 kHz to 5 mHz. XRD and EDAX measurements were also done on the cycled electrode materials.

Results and Discussion

Capacity fade of Sony 18650 cells studied when cycled at different temperatures. It was found that capacity fade of the lithium ion cells increases with increase in temperature. Fig. 1 gives a comparison of the discharge curves for the cells cycled at different temperatures. The rate capability of the cells continues to decrease with cycling and this decrease in rate capability can be attributed to increased resistance at both electrodes. Impedance measurements for both full and half-cells show an overall increase in the cell resistance with cycling and temperature. Cyclic voltammetric studies reveal the decrease in the magnitude of peak currents and vanishing of the lithium intercalation and de-intercalation peaks with cycling. Charge-discharge studies on individual pellet electrodes show a reduced tendency for lithiation for both LiCoO₂ and carbon. XRD studies of the positive electrode up to 300 cycles shows a decrease in the lithium stoichiometry with cycling. Thus, capacity fade in Sony Li-ion cells is attributed to oxidation of cathode (LiCoO₂) during overcharge. Both primary (Li⁺) and secondary active material (LiCoO₂) is lost during charging. The higher capacity fade for the cell cycled at 55°C can be due to repeated film formation over the surface of anode, which results in increased rate of lithium.

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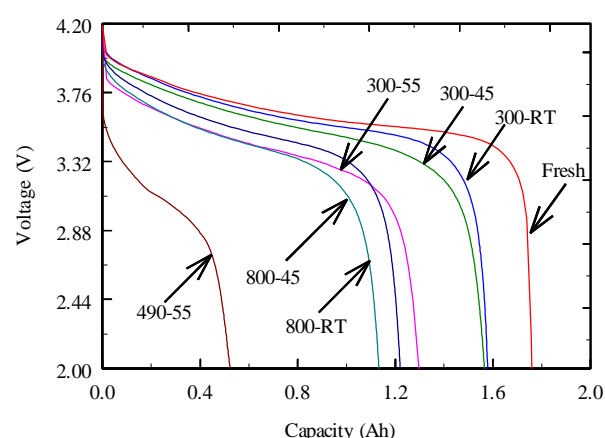


Fig. 1 Discharge curves of Sony 18650 cells cycled at RT and 45°C for 800 cycles and 55°C for 490 cycles.