

A Capacity Fade Model for Li-ion Cells

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Introduction

Capacity fade of Li-ion cells is caused by various mechanisms, which depend on the electrode materials and also on the protocol adopted to charge the cell. This loss in capacity could be attributed to several factors namely unwanted side reactions that occur during overcharge, which causes electrolyte decomposition, passive film formation, active material dissolution and other phenomena.¹ The objective of this work is to develop a first principle model that would simulate the capacity fade in commercial Li-ion cells under normal cycling conditions. The model includes capacity loss arises from active material losses, rate capability and also resistance of the cell.

Capacity Fade Quantified:

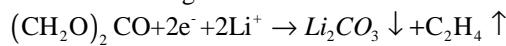
Initial performance data would be needed to check the validity of the model. Sony US18650S cells with a rated capacity of 1800 mAh were used for these studies. For cycling, the cell was charged at a constant current of 1 A until the potential reached 4.2 V. Subsequently the voltage was held constant at 4.2 V until the current drops to 50 mA. From the performance studies of the 18650 cells and the DPA analysis of fresh and cycled positive and negative electrodes, we could able to quantify the capacity loss with cycling based on three major losses namely loss of primary active material (Li^+), secondary active material ($\text{LiCoO}_2/\text{carbon}$) and rate capability losses^{2,3}.

Model Development:

Since most 18650 Li-ion cells are limited by negative electrode in terms of capacity, modeling the capacity fade with negative electrode alone under consideration would be sufficient. Loss of active material with continuous cycling could be attributed to continuous film formation over the surface of negative electrode.

During charging Li-ions will be intercalated into graphite, which causes an increase in volume of graphite particles. Hence the surface films on the edge planes, through which Li-ions are inserted into the graphite, are stretched and may be damaged during Li-ion insertion (due to the increase in the particle's volume), and thus the passivation is limited. This allows continuous small-scale reactions between the lithiated carbon and solution species, i.e., the breakdown and repair of the surface films that increase their thickness and hence the electrodes impedance upon cycling⁴.

There are several possible reaction schemes available in the literature for the reactions between the lithiated carbons and solution species. The nature of reaction depends upon the type of solvent mixture used in the battery electrolyte and the possible contaminants in the system that includes gases like CO_2 , O_2 and N_2 . The simplest reaction scheme to be considered for modeling capacity loss is the two-electron reduction of EC or PC followed by formation of Li_2CO_3 , which is the surface film over the surface of negative electrode.



Li-ion diffusion model has been used for capacity fade simulation and charge-discharge

characteristics. Based on the cycling data and the half-cell experiments, the parameters considered most significant for capacity losses are film resistance and SOC of the electrode material limited by capacity.

A semi-empirical correlation has been developed and presented earlier⁵ for explaining the variation of SOC with cycling that would account for the active material losses, and with film resistance and diffusion coefficient as fitting parameters, the drop in cell voltage and the rate capability losses could be simulated. Figure 1 presents the comparison of discharge performance obtained experimentally and based on simulation.

In this presentation we will be discussing the development of first principles model based on the side reaction assumed to explain the variation of SOC with cycling that accounts for the primary and secondary active material losses. Inclusion of rate capability loss and film resistance in the first principles model will also be discussed.

Acknowledgment

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References

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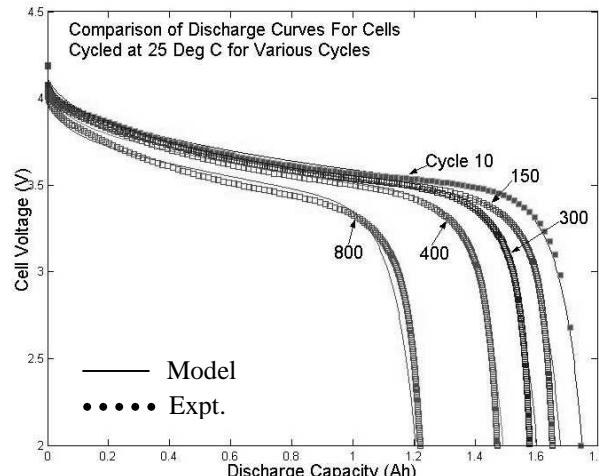


Fig. 1 Comparison of experimental and simulated discharge curves of Sony 18650 cells cycled at RT. The simulation is based on semi-empirical correlations developed for resistances and SOC of positive and negative electrodes based on Full cell and T-Cell studies.