

## Comparison of Modeling Prediction with Experimental Cycle Life Data

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### Introduction

A first principles based charge-discharge model was developed to simulate the cycle life behavior of Li-ion batteries. The model is based on the loss of active lithium ions due to solvent reduction reaction and the rise on the anode film resistance. The effect of parameters such as exchange current density, depth of discharge (DOD), end of charge voltage (EOCV), the film resistance and the overvoltage of the parasitic reaction were studied quantitatively. The model controls the required DOD by controlling the discharge time and estimates the end of discharge voltages as a function of cycle number. The simulations of both the cycling and the capacity check are performed using the same program. [1-10]

### Experimental

Pouch li-ion batteries were tested as received. The positive material is composed of 91% C-022  $\text{Li}_x\text{CoO}_2$ , 4% KS-6 Graphite, 2% Super P + 3% Polyvinylidene Fluoride (PVdF) coated on aluminum foil and the negative material is composed of 91.5% MCMB 2528, 0.5% Super-P, 8% PVdF coated on copper foil. The designed negative to positive capacity ratio is 1.1. Each pouch is filled with 1M  $\text{LiPF}_6$  / EC: PC: EMC: DEC (30%:5%:35%:30%).

Data used for comparison are for the battery cycled at 35 °C, charge rate (CR) of 1.67 A, end of charge voltage (EOCV) of 4.0 V, and depth of depth (DOD) of 40%. CC-CV charging protocol was used to charge the battery to 4.0 V and the current control value during CV charging stage was set to be 50 mA.

Capacity was checked on monthly basis. The battery was initially discharged using discharge current of 0.835 A to 3.0 V. Next, the battery was charged by applying a conventional CC-CV protocol (0.334 A to 4.2 V with a cut-off current of 50 mA). The fully charged battery was discharged for second time to 3.0 V. The discharge capacity estimated in the second discharge process was used for capacity fade analysis.

### Model Development

Starting from the assumption that liquid phase potential can be neglected and the electrode region could be treated as a whole under low/mild charge/discharge condition, the averaged local reaction current density can be obtained over the entire superficial area of the electrode region. Side reaction is assumed to be the electrochemical reaction between ethylene carbonate (EC) and lithium ions in the electrolyte phase. The side reaction takes place whenever the overpotential in the Tafel equation is cathodic. To estimate the capacity or the discharge performance at a specified cycle number, the diffusion equations in the solid phase were first solved to obtain the value of the concentration of lithium at the solid/electrolyte interface. Next, this value was substituted into the BV equation in order to solve for the potential in the solid phase of the positive and negative electrode. During the CV charging process, a trial and error method was used to solve for the continuous decay of the current.

The loss of the active lithium ions and the rise in

the surface film on MCMB negative electrode were estimated using Tafel Eq., The dimensionless initial lithium concentration and the surface film resistance of the MCMB negative electrode were modified at the beginning of every discharge-charge cycle.

Fig. 1 presents the comparison of voltage profile between modeling prediction and experimental data curve after 1124 cycles as described above.

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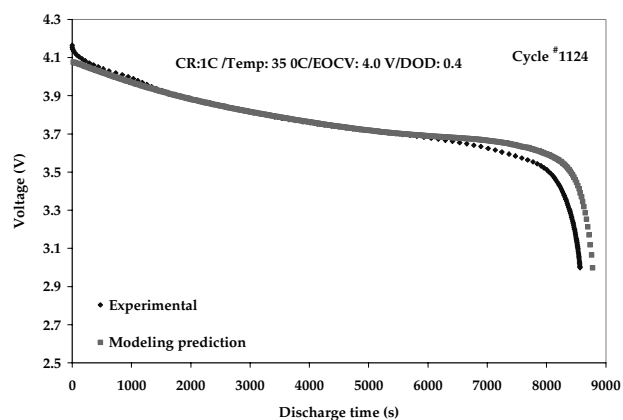


Figure 1. Voltage profile after 1124 cycles.