Modeling degradation of Nickel-rich cathodes induced by phase transition

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Introduction

High energy density has enabled layered nickel manganese cobalt oxides (e.g., NMC811) as promising cathode materials of lithium ion batteries. However, their layered structures are prone to irreversible phase transitions to disordered spinel and rock-salt structures, leading to capacity fade. We quantify the degradation with loss of active material (LAM), loss of lithium inventory (LLI), and resistance increase within a particle degradation model [1] and reveal how the degradation leads to cell-level capacity loss.
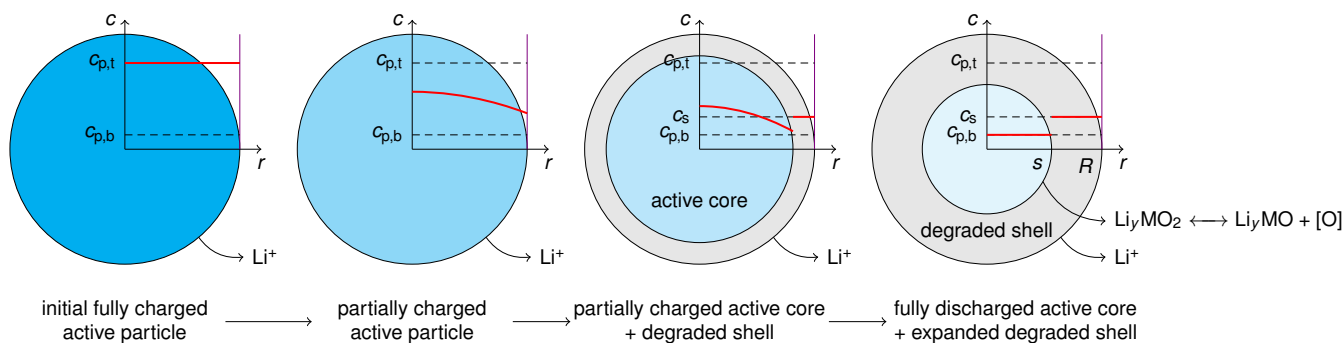

Fig. 1. Degradation of a positive electrode particle with moving phase boundary during delithiation. Quantities $c_{p,t}$, $c_{p,b}$, and c_s are the active core concentrations at 100% SoC, at 0% SoC, and fixed concentration trapped in the degraded shell. Oxygen gas is released by chemical reaction at the phase boundary and diffuses out through the shell.

Particle degradation model

▷ We solve equations for lithium diffusion in the core and oxygen diffusion in the shell.
▷ The degraded shell denotes LAM, contributes to LLI due to trapped lithium c_s, and increases resistance.

results are obtained by implementing particle degradation model into the DFN model framework in PyBaMM [2].
Fig. 3 shows the difference between the first and last cycles of a cyclic test, where capacity fade is evident from the shrinking SoC range.
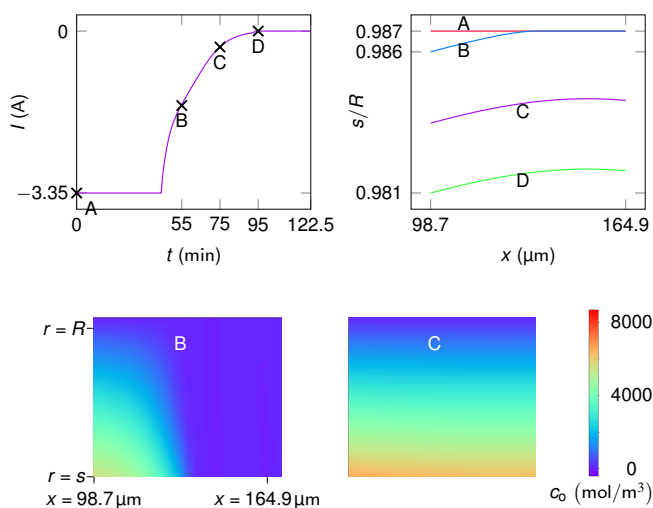

Fig. 2. Phase boundary location s/R variation in electrode thickness direction indicates degradation heterogeneity. The increase of oxygen concentration c_o at the separator side at time B is because phase transition starts earlier there.

Fig. 3. Effects of LAM, LLI, and shell layer resistance on stoichiometry drift in cyclic aging.

Conclusions

▷ LAM reduces capacity by terminating discharging earlier.
▷ LLI in terms of cyclable lithium, rather than total lithium, impacts the cell performance.

Results and discussion

We first present the degradation heterogeneity across the electrode under 1C constant current charging followed by voltage control and a half-hour rest, as shown in Fig. 2. The
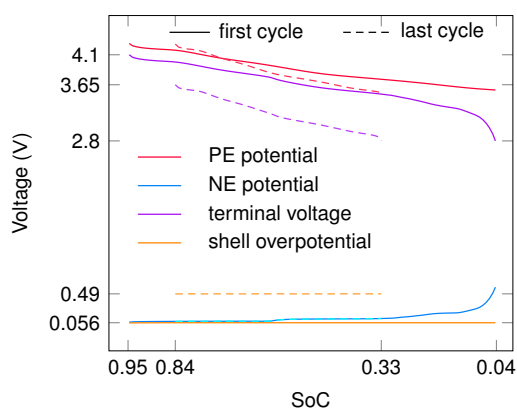
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