Physics-Based Modeling Of Lithium Plating On Graphite Anode Of Commercial Lithium-Ion Batteries

Sina Navidi[1], Benjamin Nowacki[1], Aidan Lawlor[1], Jun Xu[2], Chao Hu[1]

[1]School of Mechanical, Aerospace, and Manufacturing Engineering, University of Connecticut, Storrs, CT, USA
[2]Department of Mechanical Engineering, University of Delaware, Newark, DE, USA

Abstract

Lithium plating on the graphite anode is a significant factor contributing to the degradation of cell capacity, initiation of internal short circuits, and escalation of thermal runaway in lithium-ion batteries. Non-intrusive detection methods for lithium plating are critical for the safe and reliable operation of lithium-ion batteries. This study presents a physics-based pseudo-two-dimensional (P2D) model that incorporates lithium plating and stripping reactions to describe the electrochemical behavior of commercial 18650 cylindrical cells with graphite and LiFePO4 (LFP) electrodes at high current rates and low temperatures. Simulations were performed using COMSOL MULTIPHYSICS 6.1, and the results were compared with experimental measurements obtained from a Neware CT-4000 series battery testing system. The voltage response and surface temperature of 48 commercial 18650 LFP cells at varying states of health (100% to 75% at an approximately 5% increment) and charge (100% to 0% at an approximately 5% increment) were collected. These results can inform the establishment of operational and design limits to mitigate capacity degradation and safety hazards inherent in these cells.

Figures used in the abstract

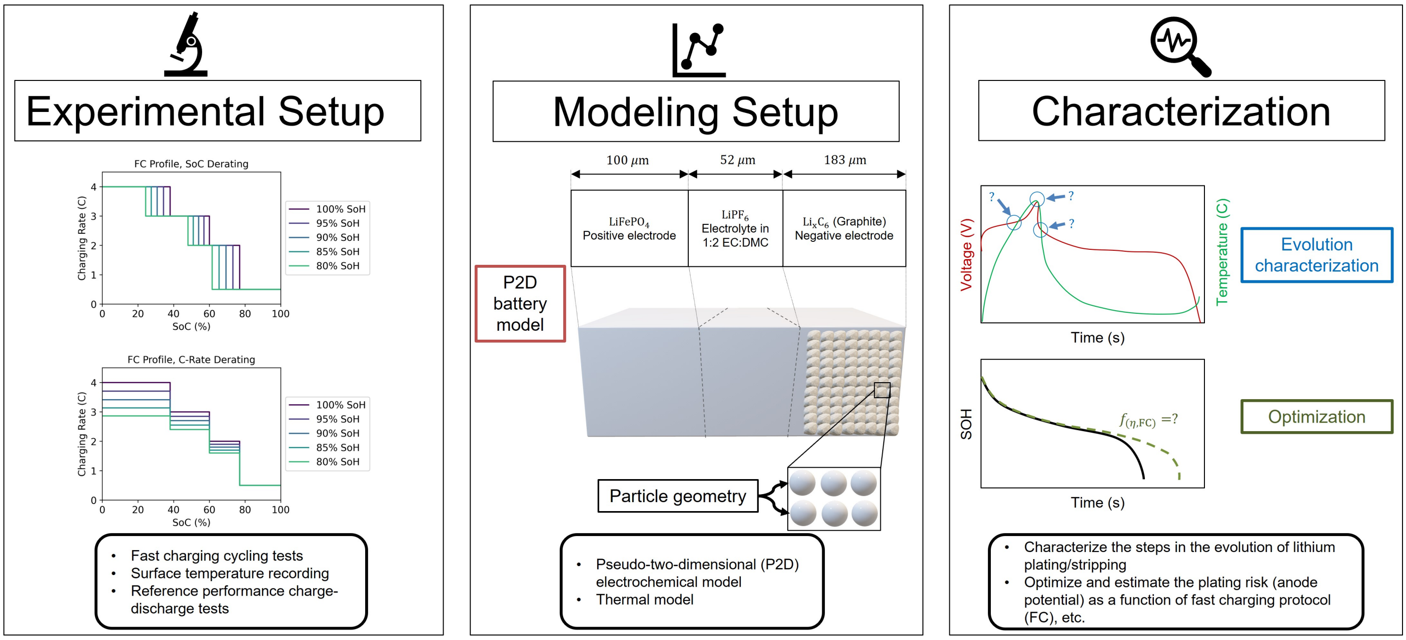
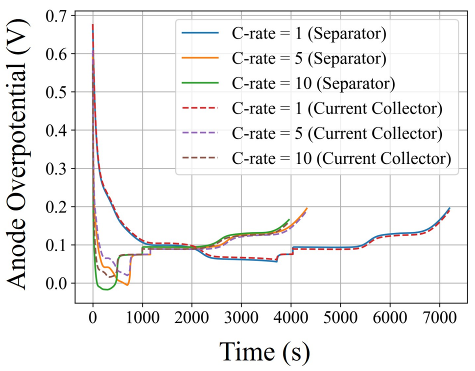


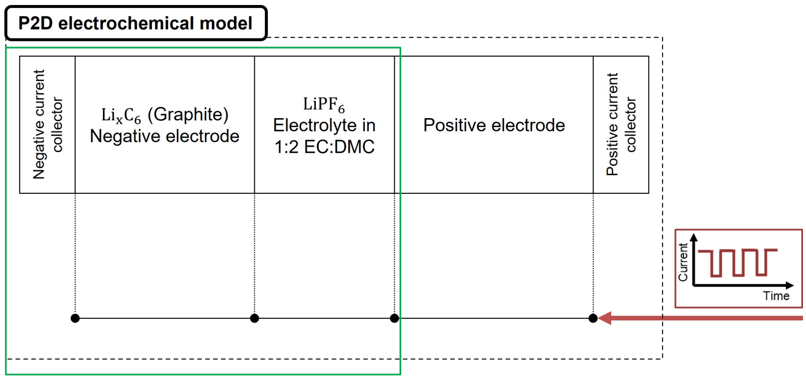
Figure 1 : Graphical abstract

Process	Reaction	Current (A/m^2)	Kinetics Equations
Intercalation	$\mathrm{Li}_x\mathrm{C}_6 + \Delta x\ \mathrm{Li}^+ + \mathrm{e}^- \rightarrow \mathrm{Li}_{x+\Delta x}\mathrm{C}_6$	j_1	$j_1 = i_{0,1}.\left[\exp\left(\frac{\alpha_{a,1}F\eta_1}{RT}\right) - \exp\left(\frac{\alpha_{c,1}F\eta_1}{RT}\right)\right]$ • $i_{0,1} = k_1.c_e^{\alpha_{a,1}}(c_{s,max} - c_{s,surf})^{\alpha_{a,1}} c_{s,surf}^{\alpha_{c,1}}$ • $\eta_1 = \phi_s - \phi_e - U - FjR_{SEI}$ • $U = U_{ref}(x) - (T - T_{ref})\left(\frac{dU}{dT}\right)$ • $R_{SEI} = (\delta_{SEI,0} + \Delta\delta_{SEI})/\sigma_{SEI}$
Plating	$\mathrm{Li}^+ + \mathrm{e}^- \rightarrow z_1\mathrm{Li}_{rev}^{(s)} + z_2\mathrm{Li}_{dead}^{(s)} + z_3\mathrm{SEI}$	j_2	$j_2 = i_{0,2}.\left[\exp\left(\frac{\alpha_{a,2}F\eta_{Li}}{RT}\right) - \exp\left(\frac{\alpha_{c,2}F\eta_{Li}}{RT}\right)\right], \eta_{Li} < 0$ • $i_{0,2} = k_2.c_e^{\alpha_{a,2}}$ • $\eta_{Li} = \phi_s - \phi_e - U_{Li} - FjR_{SEI}$
Stripping	$\mathrm{Li}_{rev}^{(s)} \rightarrow \mathrm{Li}^+ + \mathrm{e}^-$	j_3	$j_3 = i_{0,2}.\left[\exp\left(\frac{\alpha_{a,2}F\eta_{Li}}{RT}\right) - \exp\left(\frac{\alpha_{c,2}F\eta_{Li}}{RT}\right)\right].\left(\frac{\beta.n_{Li,rev}}{1+\beta.n_{Li,rev}}\right)$, $\eta_{Li} > 0, n_{Li,rev} > 0$

Figure 2 : Modeling overview for the kinetics of the main reactions



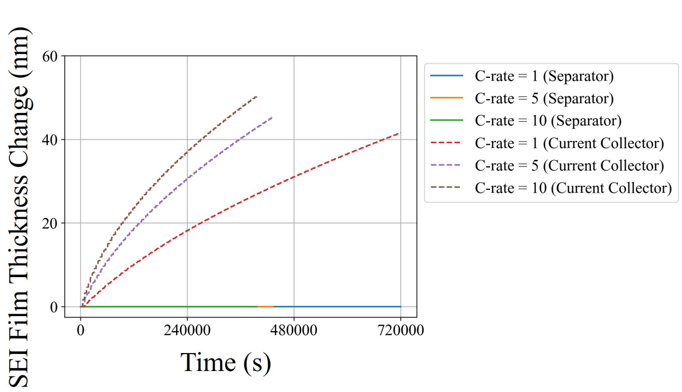
- C-rate sweep at a constant temperature of 298 K
- Two locations (current collector and separator)
- Results for one charge and discharge cycle until hitting the cutoff conditions



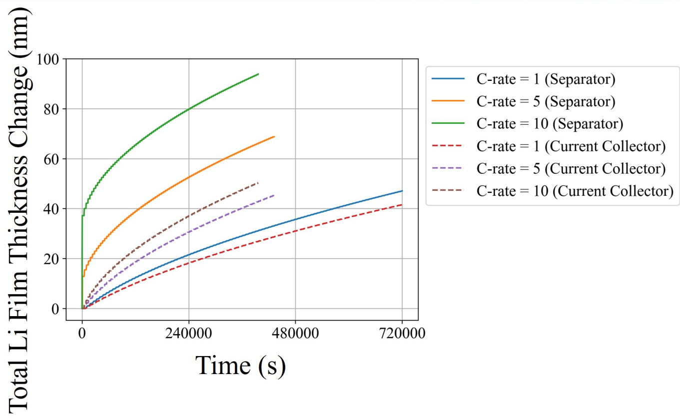
The Lithium insertion reaction rate (local current density) is expressed by the Butler-Volmer equation:

$$i_{loc} = i_0\left\{\exp\left(\frac{(1-\alpha)F}{RT}\eta\right) - \exp\left(\frac{-\alpha F}{RT}\eta\right)\right\}$$

Figure 3 : Preliminary results - graphite anode overpotential



- SEI film thickness for 100 cycles
- C-rate sweep at a constant temperature of 298 K
- Two locations (current collector and separator)



- Total film thickness of deposited lithium for 100 cycles
- C-rate sweep at a constant temperature of 298 K
- Two locations (current collector and separator)

Figure 4 : Preliminary results - deposited lithium film thickness