

Learning the Electrochemistry of Degradation and Safety in Graphite Porous Electrodes for Lithium-ion Batteries

By
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Lithium-ion batteries have become the centerpiece of portable technology and electric transportation, as well as for grid stabilization for intermittent renewable sources. The varied applications involve varying requirements for safety, lifetime, and energy/power density. To optimally design these systems for each application, researchers have a very large design space. This requires extensive and costly experimentation or computationally heavy modeling.

Specifically, to design batteries with better lifetime and long-term capacity retention, relying on just experiments can take between weeks to months and thousands of cells to get any robust insights for process improvement. Data-driven and physics-based modeling, when done rigorously, can help inform experimentation, reducing time and cost requirements. However, modeling battery degradation is challenging as it not only is hard to visualize *in-operando*, but also affects cell performance at multiple scales - from single particle to porous electrode to the battery pack. Insights obtained from experimentation on a given scale to inform modeling, often performs poorly when it comes to prediction at other scales, limiting applicability.

This thesis is a small part of a collaboration between MIT, Stanford, Purdue and Toyota Research Institute to develop data-driven models for predicting battery performance and degradation, called the D3BATT: Data-Driven Design of Lithium-ion Batteries. We adopt a simultaneous 'bottom-up' (first principles) and 'top-down' (statistical analyses of experiments) approach to inform theory formulation at multiple scales. The thesis addresses the idea behind a multiscale 'bottom-up' approach to understanding battery degradation: *First*, we use experiments designed on simple systems to study the electrochemistry of key graphite degradation mechanisms such as solid-electrolyte interphase (SEI) growth and lithium plating at the single particle scale. This gives us robust kinetic and thermodynamic parameters that are invariant with scale. *Second*, we extend the single particle theory to the porous electrode scale to capture the effect of multi-particle interactions and macroscopic electrode and electrolyte properties. This is done using the Multiphase Porous Electrode Theory (MPET) software, developed in the Bazant Group at MIT. Third, by simulating various cycling protocols (such as slow and fast charging, full depth-of-discharge vs. shallow formation cycling and open-circuit storage), we can compare the predictions with that of data-driven models obtained from statistical analyses of cell data. This informs the porous electrode model of the key mechanisms relevant at the cell scale, and gives a reliable estimate of electrode-scale parameters that could not have been informed from single-particle models. As an example, we apply the informed porous electrode degradation model to battery formation cycling, and explain what makes a 'good' formation cycling protocol. This work can be applied to a multitude of cycling scenarios and battery chemistries to assist experimental design.

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