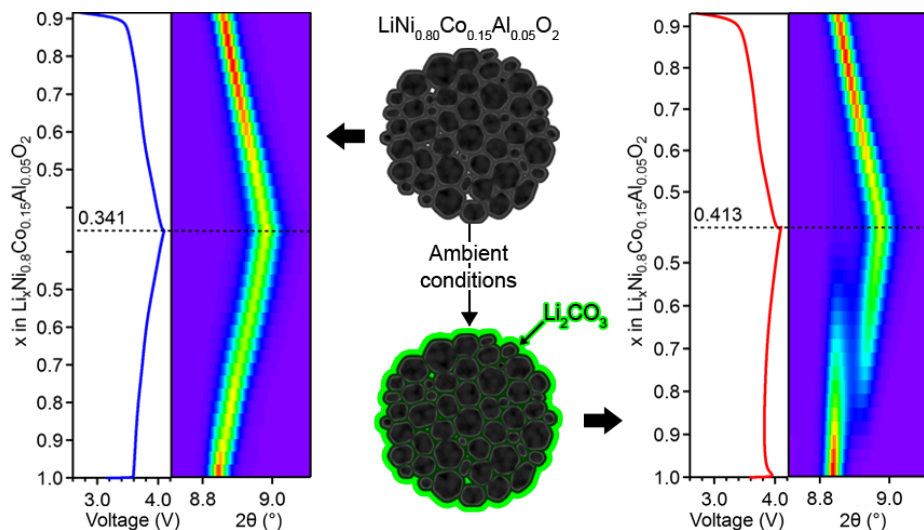


Reaction Heterogeneity in Li-ion Electrodes Induced by Surface Coatings



Adventitious surface layers that form on cathodes when exposed to air qualitatively changes the reaction observed in the bulk – often interpreted as the mechanism.

A two-phase delithiation mechanism previously reported for the 1st charge of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) is not intrinsic to the electrode material but is an artifact of a Li_2CO_3 surface layer. Formed upon exposure to air, the Li_2CO_3 layer blocks the electrochemical reactions but is progressively eroded during the 1st charge. The resulting bimodal distribution of Li composition was mistakenly interpreted as a two-phase mechanism in earlier studies.

Reference:

Grenier, A.; Liu, H.; Wiaderek, K. M.; Lebens-Higgins, Z. W.; Borkiewicz, O. J.; Piper, L. F. J.; Chupas, P. J.; Chapman, K. W. Reaction Heterogeneity in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ Induced by Surface Layer. *Chem. Mater.* **2017**, DOI: 10.1021/acs.chemmater.7b02236

Work was performed at Argonne National Laboratory and Binghamton University.

Scientific Achievement

By identifying (and controlling for) factors that impact how (de)lithiation proceeds in Li-ion electrodes, we identify their intrinsic behavior, providing a valuable experimental benchmark for computational studies.

Significance and Impact

This shows how reactions observed in Li-ion batteries can be influenced by surface layers, that may be only a minor component of the electrode. It resolves longstanding discrepancies in the mechanism reported for these widely investigated systems.

Research Details

- During air exposure, Li_2CO_3 progressively forms on the surface of NCA particles due to reaction with atmospheric CO_2 .
- The surface layer impedes transport and electrochemical reactions, creating a bimodal distribution of Li composition between near-inactive NCA particles coated by the Li_2CO_3 layer, and active NCA particles in which Li_2CO_3 has eroded.
- For pristine NCA, this heterogeneity is eliminated. The intrinsic behavior for NCA involves a solid-solution.