Aluminum Distribution in the Pristine NCA Cathode

Scientific Achievement
Assignment of the $^{27}$Al NMR shifts using insights from DFT and APT indicates a preference for lengthened Jahn-Teller Ni-O bonds to be orientated towards the Al in pristine LiNi$_{0.8}$Co$_{0.15}$Al$_{0.015}$O$_2$ (NCA).

Significance and Impact
Provides further insight into the role that Al plays in stabilizing the transition metal layer in doped-LiNiO$_2$.

Research Details
- $^{27}$Al and $^7$Li NMR were performed to investigate the Al distribution in NCA.
- NMR shift calculations combined with DFT structural calculations were used to assign the $^{27}$Al NMR shifts in a paramagnetic environment (near Ni$^{3+}$).
- Atom probe tomography was performed to confirm the homogenous distribution of cations in bulk NCA.

Findings: Al is homogenously distributed in the bulk NCA. NCA experiences a dynamic Jahn-Teller distortion. Although still a dynamic JT distortion, the lengthened JT Ni$^{3+}$-O bond is preferentially directed towards the Al atom. This preferential ordering of the lengthening of the JT Ni$^{3+}$-O bonds may lead to a stabilization of the metal layer.

N.M. Trease, et al. Chem. Matter. Accepted. DOI: 10.1021/acs.chemmater.6b02797

Work performed at Cambridge, ANL, UCSD, UCSB, Binghamton