Tuning high energy density cathodes for electrochemical energy storage

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Layered Ni-rich oxides as cathode active materials offer the promise of high energy densities in Li-ion batteries, where quasi-spherical secondary assemblies are composed of smaller primary particles. However, the deleterious effects of secondary assembly cracking and the associated chain of degradation reactions that can occur with surrounding electrolyte significantly impinge upon capacity performance and retention. There is a strong morphology-structure-property interplay at work here stemming from synthesis conditions, which have profound effects on the primary grain assembly, orientation and void formation within the secondary structure. In this talk, I will discuss our latest work on controlling the precipitation and growth of Ni-rich cathode particles, where alignment of primary particles can fine-tune Li+ transport modes. Single-particle nanoindentation studies reveal directionally-dependent mechanical strength, complemented by X-ray computed tomography which elucidates grain boundary weakening and severe intergranular cracking exacerbated by void formation. These insights are validated by electrochemical cycling data. We show that cathode active material performance and lifetime can be optimised through design principles based on tailoring the orientation of primary particles within energy dense secondary assemblies. These insights therefore limit void formation and subsequent degradation in Ni-rich cathode active materials. I will also discuss a new operando muon spectroscopy (μSR) method which can be applied to investigate how local Å-length scale diffusion and internal field properties change in cathodes as a function of state-of-charge, which we have recently demonstrated for Ni-rich cathodes. Our design of a new Battery Analysis by Muon (BAM) cell allows monitoring of diffusional properties with highly correlated structural changes in the unit cell during operating conditions.