Coat-doping strategies for stabilizing Ni-rich layered cathodes

Innes McClelland[1], Christopher Thomas[1], Jessie Isufaj[1] and Serena A. Cussen[1]

1 *School of Chemistry, University College Dublin, Belfield, Dublin 4, D04 V1W8, Ireland*

serena.cussen@ucd.ie

$LiNiO_2$-based cathodes offer high specific capacities for next-generation lithium-ion batteries, but their practical deployment is limited by structural and interfacial instabilities that emerge during electrochemical cycling. Oxygen loss, phase transitions, and surface reconstruction accelerate degradation in Ni-rich layered oxides, necessitating strategies that simultaneously stabilize bulk structure and surface chemistry.

Here, as part of the Horizon Europe INERRANT project, we develop robust Ni-rich single-crystal cathodes via integrated synthetic control and targeted structural modification. Optimized single-crystal synthesis enables a “coat-doping” strategy that addresses both bulk and surface degradation. Carefully selected cation substitutions stabilize the layered crystal structure while promoting the formation of a protective surface layer.

Through judicious cation and anion substitution, structural pillaring within the bulk is combined with enhanced surface stability, enabling the development of cathodes with improved cycling performance. There is also 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.

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.[1] 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.

[1] I. McClelland, S. G. Booth, N. N. Anthonisamy, L. A. Middlemiss, G. E. Perez, E. J. Cussen, P. J. Baker and S. A. Cussen, Chem. Mater. (2023). 35, 4149

The authors acknowledge funding from the European Union's Horizon Europe research and innovation programme under Grant Agreement No. 101147457 (INERRANT), and participation in Grant Agreement No. 101104022 (Battery 2030+ CSA3).