Invited Lecture

Bridging the Gap Between Disordered and Layered Li-Rich High-Capacity Cathodes

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'Disordered' rock salt (DRS) cathodes have attracted considerable attention because of their high first charge capacities with 'extra' contributions beyond the transition metal redox activity, and absence of unfavourable phase transformations during cycling. Here we investigate the structure and charge evolution of the several nanostructured Li-excess $Li_{1+x}Mn^{3+}_{1-3x}(Ti,Mn)^{4+}_{2x}O_2$ DRS with $0 \leq x \geq 1$ by multi-modal operando characterisations.

A comprehensive study of the structural and charge evolution points to a lattice densification with an effective loss of Li_2O, with the subsequent electrochemical activation of Li_2O as the main responsible mechanism for the 'extra' capacity.[1] Interestingly, and unlike previous studies, no capacity losses could be associated to the material's densification. On the other hand, a certain extent of the capacity fade in DRS can be linked to the in-situ formation of locally ordered layered nanodomains.[2] These nanodomains give rise to diffuse scattering peaks in the total scattering data that had previously been attributed to the formation of a second phase in other work.[3]

We combine total scattering and advanced spectroscopic methods at the Mn K-edge, namely High Energy Resolved Fluorescence Detected XANES and Emission (XES) Spectroscopies[4] including main and valence-to-core (V2C) transitions, performed operando for the first time [1]. The in-depth understanding of nanostructured DRS performance was facilitated by the combination of multiple operando datasets from different techniques and a new electrochemical cell design, which is compatible with all the X-ray techniques involved in the study [5]. In addition, operando multi-modal synchrotron investigations have been supported by improved structural refinement tools, to ultimately guide the development of better battery materials.[6] As an example, the lessons learnt in this study have been utilised to enhanced the first charge capacity of Li_2O:LiMnO DRS nanocomposites to up to 1157 mAh g^{-1} in a new class of prelithiation additives [7].

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