Exploring the composition space of disordered rocksalt battery cathode materials

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The discovery of new sustainable battery materials is vital for the green transition. Larger capacities are required to store the intermittent electricity produced from renewable energy sources and the current reliance on scarce metals like cobalt and nickel causes environmental and geopolitical challenges. Our research focuses on the search for new cathode materials for lithium and sodium ion batteries, specifically within the class of disordered rocksalts, i.e. $LiMO_2$ and $LiMO_{2-x}F_x$ where M is generally some mixture of transition metals. The conventional layered cathodes rely heavily on transition metals such as cobalt and nickel that suppress cation disorder and stabilise the layered structure, as many other transition metals diffuse too readily and disrupt the layered ordering. In contrast, DRX structures do not need to maintain long-range cation order, which allows for a much wider compositional space.

The DRX structure is composed of a cubic-close packed lattice of oxygen with lithium or sodium and transition metals distributed in the octahedral holes. Due to electrostatic repulsion between lithium and highly charged transition metals, lithium conduction preferably occurs via tetrahedral holes surrounded by only [LiO_6] octahedra – the so-called Li_4-diffusion pathway. The network of Li_4 pathways is crucial for the electrochemical performance of the cathode, however due to the disordered nature of the structure, it is difficult to characterise experimentally. Furthermore, the wide compositional space is unreasonably large to interrogate through experimental trial-and-error. Hence, we explore this space using cluster expansions: a computational tool trained on DFT structures used to predict large supercells of a given composition.

We span compositions across mixtures of sustainable transition metals (e.g. titanium, iron, manganese etc.) and compute various metrics from the produced big box structures. For each composition, we can retrieve the proportion of Li4 sites, predict diffuse scatter in reciprocal space planes and determine short-range order parameters like Warren-Cowley parameters or structure factors. One metric missing from the literature is a measurement of the morphology of the percolating network. Two networks with the same Li_4 count can give rise to completely different battery performance due to differences in the shape and connectivity of the network. Here, we describe our metric for describing and comparing these features.

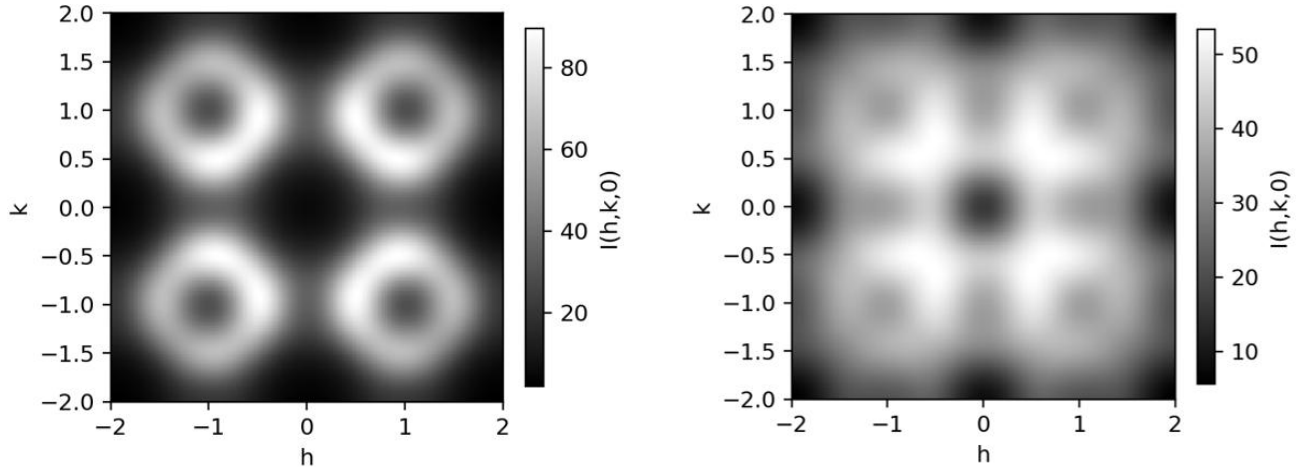


Figure 1. *Predicted transition from octahedral- to cube-type short-range order in $xLiMnO_2$ - (1-x)LiF solid solutions.*