

## Evolution of Local Structural Ordering and Chemical Distribution upon Delithiation of a Rock Salt-Structured $\text{Li}_{1.3}\text{Ta}_{0.3}\text{Mn}_{0.4}\text{O}_2$ Cathode

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Abstract: Lithium - rich disordered rock - salt oxides have attracted great interest owing to their promising performance as Li - ion battery cathodes. While experimental and theoretical efforts are critical in advancing this class of materials, a fundamental understanding of key property changes upon Li extraction is largely missing. In the present study, single - crystal synthesis of a new disordered rock - salt cathode material,  $\text{Li}_{1.3}\text{Ta}_{0.3}\text{Mn}_{0.4}\text{O}_2$  (LTMO), and its use as a model compound to investigate Li concentration - driven evolution of local cationic ordering, charge compensation, and chemical distribution are reported. Through the combined use of 2D and 3D X - ray nanotomography, it is shown that Li removal accompanied by oxygen oxidation is correlated with the development of morphological defects such as particle cracking. Chemical heterogeneity, quantified by subparticle level distribution of Mn valence state, is minimal during Mn redox, which drastically increases upon the formation of cracks during oxygen redox. Density functional theory and bond valence sum mismatch calculations reveal the presence of local short - range ordering in the pristine oxide, which gradually disappears along with the extraction of Li. The study suggests that with cycling the transformation into true cation-disordered state can be expected, which likely impacts the voltage profile and obtainable energy density of the oxide cathodes.