

Nanostructure Transformation as A Signature of Oxygen Redox in Li-Rich Cathodes

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Lithium-rich transition metal oxide cathodes are of intense current interest as higher capacity alternatives to the stoichiometric layered cathodes currently used in today's automotive applications. These Li-rich cathodes store extra energy through extensive high-voltage oxygen oxidation. The mechanism by which the changes in oxygen redox chemistry is accommodated by the cathode remains actively debated, particularly in terms of the structure changes. How does the change in O chemistry impact the structure and dynamics of the transition metal and lithium cations? Without understanding how oxygen oxidation is accommodated by the cathode structure, and how this is linked to performance limitations, we cannot design strategies to mitigate limitations and displace current automotive electrodes or develop new robust electrode chemistries that access additional O-based redox capacity. Using operando and complementary ex situ X-ray scattering studies (XRD and SAXS) we explore the dynamic restructuring of transition metal cathodes that occurs during cycling. Focusing on lithium-rich nickel manganese cobalt oxide (LRNMC) cathodes, we identify nanopores within the cathode as a structural consequence of O oxidation using small-angle X-ray scattering (SAXS) and operando X-ray diffraction (XRD). A feature observed in the small angle scattering region suggest the formation of nanopores, which first appear during O oxidation, and is partially reversible. This feature is not present in traditional cathode materials, including stoichiometric NMC and lithium nickel cobalt aluminum oxide (NCA), but appears to be common to other Li-rich systems. Coarsening of residual pores with extended cycling can be linked to performance degradation.