Abstract

Lithium-rich layered oxides (LRLOs) are promising cathode materials for next-generation high-energy lithium-ion batteries (LIBs). Their commercial implementation, however, is limited by voltage fade and capacity loss arising from progressive layered-to-spinel/rocksalt phase transformation during cycling. These structural changes are triggered by oxygen redox activity and associated transition-metal (TM) migration, whose reversibility is strongly influenced by crystallographic defects intrinsic to LRLOs. Therefore, the rational control of defect chemistry during synthesis is essential for stabilizing oxygen redox, while suppressing irreversible phase evolution. This thesis explores the effect of synthesis-driven defect chemistry on oxygen redox and cation migration in LRLOs during cycling, and further evaluates targeted dopant substitution as a strategy to enhance structural stability. Complementary structural, spectroscopic, and electrochemical techniques are combined to correlate precursor chemistry, stacking disorder, oxygen-vacancy incorporation, dopant site occupancy, and redox mechanisms with phase stability. The research presented in this thesis is divided into two studies: the first study investigates LRLOs synthesized by sol–gel routes employing chelating agents of contrasting strength. All samples adopt a faulted $R\bar{3}m$ layered framework on average, yet local structural variations emerge from precursor chemistry: the weaker chelating agent promotes oxygen-vacancy incorporation at high temperature, which later migrate into the bulk during cycling, expand the lattice, suppresses TM migration, and lead to improved electrochemical performance. The second study investigates Zn substitution as a means of regulating oxygen redox and cation migration. Moderate Zn incorporation yields the most favorable balance between capacity retention and structural durability. Electrochemical analysis indicates that dopant effectiveness depends on lattice site occupancy, with possible dual-site occupancy, Li-site and TM-site, stabilizing the oxygen sublattice while preserving Li-ion transport pathways.

Keywords: Li-ion batteries, Li-rich layered oxides, oxygen vacancies, stacking faults, sol-gel synthesis, chelating agents, advanced structural characterization.