

# Abstract

The increasing need for energy storage devices dedicated to the electrification of vehicles, results in the expanding market for rechargeable batteries. The most promising rechargeable battery system is lithium-ion batteries (LIBs) which is the highest energy-density battery system for practical applications. Among various electrode materials for LIBs, cation-disordered rocksalt (DRS) oxides are emerging new chemistry because the reversible capacity reaches  $300 \text{ mA h g}^{-1}$  with both cationic/anionic redox. However, irreversible oxygen loss causes gradual capacity fading on continuous cycles. Therefore, capacity retention as electrode materials is currently unacceptable for practical battery applications. In this thesis, three solutions are discussed to overcome these problems.

Firstly, the influence of chemical compositions on electrode performance is systematically compared, and the optimization of reversible capacities originating from cationic/anionic redox is targeted in a Nb-Mn binary system. In this research, the particle size reduction process was also conducted to  $\text{Li}_{1.1}\text{Nb}_{0.1}\text{Mn}_{0.8}\text{O}_2$  to improve the electrode kinetics, coupled with highly concentrated electrolyte to avoid the side reaction on charged positive electrode materials with electrolyte.

Another strategy is conducted on  $\text{Li}_{1.15}\text{Nb}_{0.15}\text{Mn}_{0.7}\text{O}_2$ , and the stabilization of anionic redox is targeted through the formation of chemical bonds with a higher covalent nature. For this purpose, 7 mol%  $\text{Li}_3\text{PO}_4$  was integrated into  $\text{Li}_{1.15}\text{Nb}_{0.15}\text{Mn}_{0.7}\text{O}_2$  with DRS structure by high energy ball milling process. The  $\text{Li}_3\text{PO}_4$  integrated sample shows much better capacity retention. The Raman spectra study and STEM/EDX measurement prove the successful integration of  $\text{Li}_3\text{PO}_4$  into DRS  $\text{Li}_{1.15}\text{Nb}_{0.15}\text{Mn}_{0.7}\text{O}_2$ .

Lastly, to deepen the current understanding of factors affecting anionic redox reversibility, new Li-excess oxides with Nb and Co ions are synthesized. The detailed

study on a  $\text{Li}_3\text{NbO}_4\text{-CoO}$  binary system reveals that anionic redox is partially reversible process and less stable when compared with  $\text{NiO}$  binary system.

Based on these studies, important scientific progresses on stabilization of electrode performance with cationic/anionic redox are discussed in detail.

This thesis is structured as follows:

Chapter 1 is a general introduction. The technological development of LIBs is described and summarized, including working mechanisms of LIBs and the classification of positive electrode materials with different crystal structures. The advantage of structural stability of DRS structure is also described. Moreover, the modification processes on Li-excess materials with DRS structure are summarized, and the research purposes of this thesis are expounded.

Chapter 2 discusses the factors affecting electrode reversibility of Li-excess cation-disordered rocksalt oxides with Mn ions. Research starts from a binary system of  $x \text{Li}_3\text{NbO}_4 - (1 - x) \text{LiMnO}_2$  with DRS structure. Samples with different chemical compositions are synthesized through a calcination process. However, oxides with micrometer-sized particles show limited reversible capacity as positive electrode materials for LIBs. To overcome the slow Li ion migration within particles for DRS oxides, the particles are treated with different mechanical milling times and speeds to reduce particle sizes. Shorter Li ion migration paths and better electronic conductivity effectively improve the electrode kinetics of oxides with DRS structure. The sample with the maximum Mn content shows the best capacity retention due to less utilization of anionic redox. Besides, the use of highly concentrated electrolyte effectively improves electrode reversibility because of the better stability of electrolyte for anionic redox, leading to superior cycle stability.

In Chapter 3, to further improve the electrode reversibility,  $\text{Li}_3\text{PO}_4$ , which has highly covalent P-O bonds, is integrated into  $\text{Li}_{1.15}\text{Nb}_{0.15}\text{Mn}_{0.7}\text{O}_2$  with DRS structure

through by high-energy mechanical milling. The successful integration of  $\text{Li}_3\text{PO}_4$  is evidenced by Raman spectroscopy and STEM/EDX measurement. P ions are located at tetrahedral sites, the strong covalent P-O bonds can partially avoid excessive anionic redox. Therefore, the sample integrated with  $\text{Li}_3\text{PO}_4$  shows superior electrode performance, including capacity retention and rate capability. Additionally, better thermal stability is achieved through  $\text{Li}_3\text{PO}_4$  integration. From these results, factors affecting electrode reversibility related to anionic redox stability with Mn ions are discussed in detail.

Chapter 4 describes the anionic redox reversibility in  $x \text{Li}_3\text{NbO}_4 - (1 - x) \text{CoO}$  binary system, and partially reversible anionic redox is concluded due to the stabilization of ligand holes associated with the presence of Co ions. Reaction mechanisms in this binary system are systematically studied combined with theoretical study. Structural evolution in Li cells is studied by *in-situ* XRD study, and obvious and irreversible phase degradation is evidenced. Nevertheless, *ex-situ* XAS study reveals that partially reversible ligand hole formation is achieved, suggesting that the presence of Co ions partially stabilizes anionic redox in oxides with DRS structure.

Chapter 5 is the conclusions of this thesis.

Chapter 6 is acknowledgments.