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Investigating Phase Equilibrium during Synthesis of LNMO via Comprehensive Neutron and X-ray Diffraction Study

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$LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) emerges as a highly promising material for positive electrodes in Li-ion batteries (LIBs), owing to its elevated operating voltage (4.8 V vs Li^+/Li) attributed to the $Ni^{4+}/Ni^{3+}/Ni^{2+}$ redox couples, crucial for development LIBs¹.

LNMO crystallizes with different extents of Ni/Mn ordering; in the fully ordered phase ($P4_332$ space group), Ni and Mn ions occupy $4a$ and $12d$ octahedral sites respectively, whereas in the fully disordered phase ($Fd\bar{3}m$ space group), they share the same $16d$ site. Elevated temperatures ($>750^\circ\text{C}$), required to obtain the disordered phase, induce oxygen loss, forming rock salt-based impurities and reducing $Mn(IV)$ to $Mn(III)$.

The degree of Ni/Mn ordering significantly impacts LNMO's performance; disordered LNMO demonstrates enhanced performance at high C-rates and improved cycling stability compared to ordered LNMO^{2,3}. Additionally, disordered Mn-rich LNMO ($Ni/Mn = 22/78$) can be prepared without oxygen deficiency, leading to superior electrochemical performance⁴. This unexpected finding motivates a systematic exploration of the Ni/Mn ratio's effect on LNMO's phase equilibrium and electrochemical behavior. In this investigation, *ex situ* and *in situ* Neutron and Synchrotron X-ray powder diffraction under air and oxygen atmospheres were conducted to monitor the Ni/Mn ordering process during LNMO synthesis with varying initial Ni/Mn ratios (25/75 for stoichiometric LNMO and 23/77 for Mn-rich LNMO).

Our results demonstrate that oxygen release disrupts the Ni/Mn ordering process for both Ni/Mn ratios, indicating that fully disordered LNMO cannot be achieved without rock salt-based impurities. Moreover, our data suggest that the extent of Ni/Mn ordering in LNMO is governed primarily by the concentration of $Mn(III)$ in LNMO's crystal structure, which can be controlled by adjusting the Ni/Mn ratio and partial oxygen pressure during synthesis. In addition, Mn-rich LNMO samples exhibit superior discharge capacity, C-rate capability, and capacity retention, indicating an important role of Mn excess in enhancing the electrochemical performance of LNMO⁵.

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References

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