

The effect of crystal structure, chemical composition, and binder on the full-cell performance of high voltage spinel positive electrodes for lithium-ion batteries

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The $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LNMO) spinel has attracted great interest as a promising cathode material in lithium ion batteries due to its low cost, high power performance and high operating voltage ($\sim 4.8\text{V}$). However, the LNMO system presents several challenges related to its synthesis and structural properties. These include the presence of impurity phases and the fact that LNMO has both an ordered and disordered phase, which arises from the arrangement Ni and Mn in the spinel structure, both of which are strongly dependent on synthesis conditions and can impact the electrochemical performance of the material. In addition, LNMO has a propensity for manganese to dissolve from the electrode into the electrolyte, particularly at elevated temperatures, resulting in severe degradation in cycling performance. Here we will discuss several strategies to mitigate the dissolution of Mn and improve the full cell cycling behavior of LNMO-based cells.

Firstly, in an attempt to better understand the correlation between the ratio of order-to-disorder in LNMO and its electrochemical performance, a detailed structural study was undertaken which includes neutron diffraction, transmission electron microscopy (TEM), and XRD in combination with extensive electrochemical testing. The results show that LNMO samples formed integrated nano-domains between Ni/Mn ordered and disordered phases after annealing at 700°C . In addition, the ratio of ordered-to-disordered phases varied from the surface to the bulk in a particle. For example, Fig. 1 shows a high resolution (TEM) image and the corresponding selected area electron diffraction (SAED) pattern processed to contain only contributions from ordered Ni/Mn regions. The non-uniformity of the distribution of ordering indicates the existence of ordered and disordered nano-domains. The impact of the degree of disorder and the presence of impurity phases on cycling performance and the possible correlation to the extent of Mn dissolution will be discussed.

Secondly, the effects of several strategies to modify the SEI to improve full-cell performance, which involves electrode and electrolyte modification, will be highlighted. Despite the good performance of LNMO/Li half-cells, the LNMO/MCMB full-cell suffered from poor capacity retention during cycling, especially at elevated temperatures, see Fig. 2. The capacity fading of the LNMO/MCMB can be explained by the impact of Mn dissolution, and active Li^+ loss in the full-cell system through continuous SEI formation (electrolyte reduction) prompted by reduced Mn which is present on top of the graphite surface [1]. To improve the full-cell performance, advanced binders and Ti-substituted spinel material (LNMTO) [2] were employed. Their performance improvement mechanisms will be presented in relation to

Mn dissolution and the oxidative decomposition of electrolytes at high voltages and temperatures.

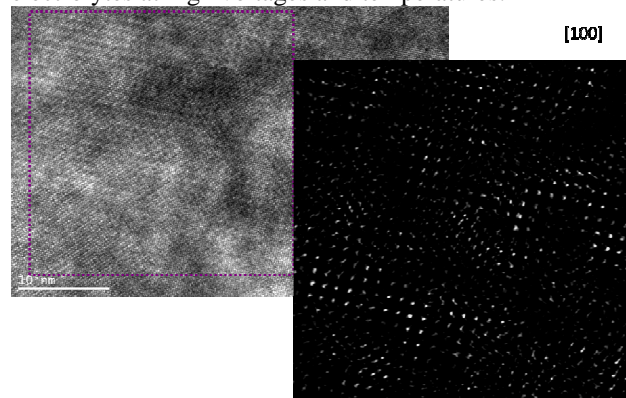


Figure 1. High resolution TEM image and corresponding SAED diffraction pattern processed to reflect only Ni/Mn ordering.

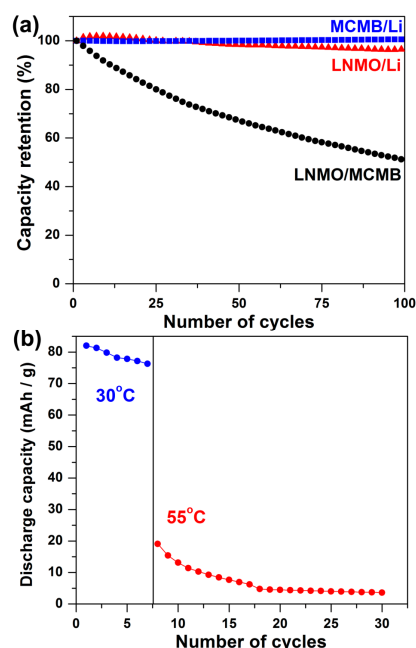


Figure 2. (a) Comparison of cycle lives of LNMO/Li, MCMB/Li, and LNMO/MCMB cells at 30°C . (b) Cycle life of LNMO/MCMB full-cell upon changing temperature from 30 to 55°C after 7 cycles.

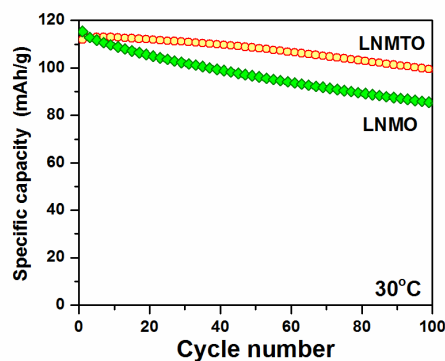


Figure 3. (a) Comparison of cycle lives of LNMO/graphite and LNMTO/graphite full-cells at 30°C . (b) Cycle life of LNMO/MCMB full-cell upon changing temperature from 30 to 55°C after 7 cycles.

References

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- [2] J.-H. Kim, S.-T. Myung, C. S. Yoon, and Y.-K. Sun, *J. Electrochem. Soc.*, **151** (11), A1911-A1918 (2004).