

## Insight into the Structural Changes of High-Voltage Spinel during the Lithium Intercalation

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Due to its high energy density, excellent rate capability and outstanding cycling stability, the high-voltage spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is considered as one of the most attractive cathode materials for lithium ion batteries aiming at hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs). The remarkable performances of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  based electrodes are attributed to the unique crystal structure of spinel, which provides three-dimensional channels for fast Li-ion diffusion within the framework of spinel.

From the view of crystal structure, only tetrahedral sites (8a) are involved for lithium intercalation/de-intercalation in spinel structure as the  $x$  in  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is less than 1. Several researchers have reported that, as  $x$  is beyond 1, 16c octahedral sites are involved for further lithium intercalation/de-intercalation, which always take place with the cut-off voltage lower than 3 V. Furthermore, the work done by Ariyoshi and co-workers indicated that the composition of spinel could reach to  $\text{Li}_{2.5}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  with discharge voltage lowering to 1.2 V. In fact, the composition of spinel could reach to  $\text{Li}_3\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$  if all 8a and 16c sites are occupied by lithium. The question is that whether all 16c and 8a could be occupied or not, as well as the stability of the structure with fully occupied 16c and 8a sites. In addition, the possibility of occupying the rest tetrahedral sites (48f) is also worth of being considered. In this work, we put as much as 4 lithium ions into  $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . The structure change and electrochemical performance will be investigated.

Fig. 1 shows the x-ray diffraction (XRD) patterns of pristine powders and electrodes discharged to different states. Obviously, the crystal structure transforms from cubic to tetragonal as the cut-off potential was lowered gradually from 4.95 V to above 2 V (vs.  $\text{Li}/\text{Li}^+$ ). However, a new phase appears as the cut-off voltage below 1 V and is characterized to be rock-salt phase with Fm-3m symmetry. Further microstructure analysis on the discharged electrodes through electron microscopes demonstrates that there is significant misfit of co-existed phases, leading to the large stresses, which was finally released through the initiation of fractures in the particles.

After undergoing the excessive lithium intercalation, the structure of electrode could be reformed back to the original cubic spinel structure, at least most-like the original structure, at the end of the following charge process. In addition, the reformed electrode could deliver 13% more capacity than that from conventional high-voltage spinel based electrodes, and demonstrated highly electrochemical stability with 89% capacity retention being preserved after more than 40 cycles.

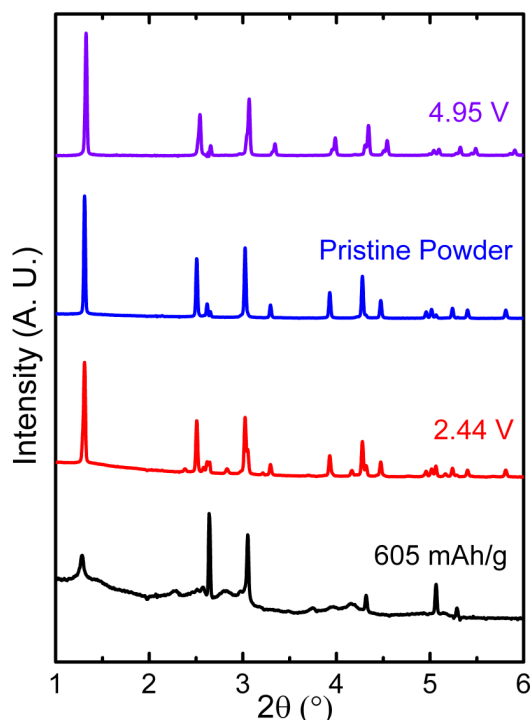


Figure 1. The XRD patterns of pristine sample and electrodes with being discharged to different states. Except the pristine sample, all electrodes were first charged to 4.95 V followed by being discharged to different states. The locations at which the discharge processes were stopped for XRD examination are shown in the figure. The XRD data was collected at 11-ID-C beamline at Advance Photon Sources (APS) at Argonne National Laboratory with wavelength ( $\lambda$ ) of 0.108 Å.

### Acknowledgement

Support from David Howell and Peter Faguy of the U.S. Department of Energy's Office of Vehicle Technologies Program is gratefully acknowledged. We'd like to thank Dr. Chikai Lin, Dr. Zonghai Chen, and Dr. Yang Ren for XRD data collection. The valuable discussion with Dr. Michael Thackeray is also acknowledged.