

# Pushing the Limit of Layered Transition Metal Oxide Cathodes for High-Energy Density Rechargeable Li Ion Batteries

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Lithium-ion batteries (LIBs) have become a dominant power source for portable electronic devices and electric vehicles (EVs) and are the most promising energy-storage medium for smart power grids that use renewable energy sources.<sup>[1]</sup> Nickel rich  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  layered cathode materials ( $x > 0.6$ ) are of interest because they can provide very high specific capacity without pushing charging potentials to levels that oxidize the electrolyte solutions. However, these Ni-enrichment strategies suffer from structural instability and subsequent capacity fading. In particular, abrupt anisotropic volume change stemming from multi-phase transition leads to develop the microcracks formation which propagated to the surface providing channels for electrolyte penetration and subsequent degradation of the exposed internal surfaces.<sup>[2]</sup>

To simultaneously address the inherent limitations of capacity and safety, it is necessary to balance the physico-chemical role of each transition metal in a new microstructure design. An ideal approach is the gradient Ni-rich  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  layered cathode material designed by maximizing the Ni content in the inner part of the particle and the Mn content near the particle surface.<sup>[3]</sup> This cathode material can deliver high capacity from the Ni-rich inner part and providing outstanding thermal properties from the Mn-rich outer surface. The enhanced cycling and chemical stability (relative to conventional Ni-rich NCM cathodes) were also attributed to the strong crystallographic texture, the unique particle morphology, and the highly correlated particle orientation.

Alternatively, we investigated that tungsten (W) doped nickel rich  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  layered cathode materials remarkably improves their electrochemical and structural stability. The partial phase transition from layered phase to rock salt phase on particle surface buffers abrupt anisotropic volume change and protects active material from detrimental reactions with electrolyte. Through the advanced TEM techniques (HR-TEM and ASTAR analysis), segregation between rocksalt  $\text{Fm}\bar{3}\text{m}$  phase and a bulk  $\text{R}\bar{3}\text{m}$  phase on W-doped particle surface was clearly observed. This tungsten doped layered  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  cathode materials drastically improve their electrochemical behavior, impedance features and thermal stability compared to the un-doped nickel rich  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  layered cathodes.

## References:

- [1] S.-T. Myung, F. Maglia, K.-J. Park, C. S. Yoon, P. Lamp, S.-J. Kim, Y.-K. Sun, *ACE Energy Lett.* 2017, 2, 196-223.
- [2] H.-H. Ryu, K.-J. Park, C. S. Yoon, Y.-K. Sun, *Chem. Mater.* DOI: 10.1021/acs.chemmater.7b05269.
- [3] C. S. Yoon, K.-J. Park, U.-H. Kim, K. H. Kang, H.-H. Ryu, Y.-K. Sun, *Chem. Mater.* 2017, 29, 10436-10445.