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Spectroscopy and Microscopy to Unravel the Advantages of Ti Substitution in $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ Cathode Materials

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Abstract

NMC materials, such as $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$, represent a widely investigated Li-ion battery cathode family due to their high capacity, high operating voltage and slow reaction with electrolytes. Electrochemical performance of these materials could be further improved by the substitution of Co with foreign elements (i.e., substitution), along with additional advantage of reducing cost. Previously, we have studied the effects of substitution of Co with Fe, Al and Ti in NMC materials.¹⁻⁴ Specifically, within a limited range of solid solution (Ti < 4%), Ti substitution increased the practical discharge capacity by ~ 15% and provided better capacity retention during electrochemical cycling relative to the pristine $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ materials between voltage limits of 4.7–2.0 V.⁴

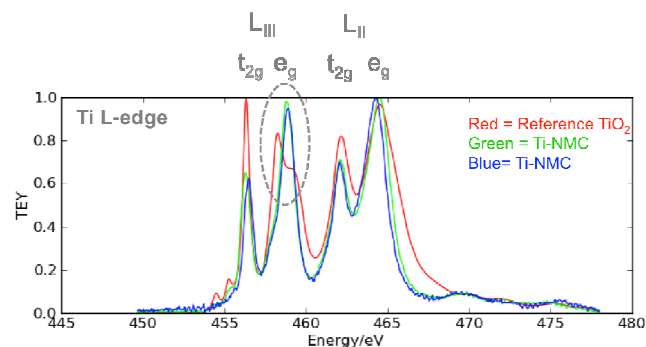


Figure 1. Ti L-edge XAS to illustrate the successful substitution of Ti in the NMC lattice.

Herein, we continued our previous studies with expanded materials synthesis and comprehensive understanding of Ti-substituted NMC materials using soft X-ray absorption spectroscopy, synchrotron X-ray diffraction and STEM-EELS. The characterization was performed for electrode materials before and after electrochemical cycling. For example, Ti L-edge XAS in **Figure 1** clearly demonstrates the incorporation of Ti in the NMC lattice according to the absence of e_g splitting in L_{III} edge. Structural evolution (e.g., valence state, crystal structure) was identified and scheme to explain electrochemical behavior was successfully drawn. The present study demonstrates the relationship between materials synthesis, electrochemical performance and

structural variations, which will further benefit our future design of substituted NMC materials.

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