

Lawrence Berkeley National Laboratory

Energy Storage & Distributed Resources

Title

Spectroscopy and Microscopy to Unravel the Advantages of Ti Substitution in
LiNi_{0.4}Mn_{0.4}Co_{0.2}O₂ Cathode Materials

Permalink

<https://escholarship.org/uc/item/8xm1r39x>

Author

Lin, Feng

Publication Date

2013-10-14

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

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

Feng Lin,^{1,*} Isaac Markus,^{1,2} Dennis Nordlund,³ Tsu-Chien Weng,³ Mark Asta,² Marca Doeffl^{1,*}

1. Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
2. Materials Science and Engineering, University of California, Berkeley, CA 94720
3. Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025

* Feng Lin: flin@lbl.gov

* Marca Doeffl: mmdoeffl@lbl.gov

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 ($\text{Ti} < 4\%$), Ti substitution increased the practical discharge capacity by $\sim 15\%$ 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

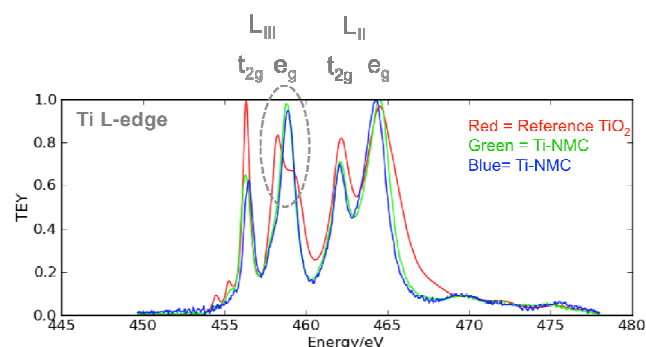


Figure 1. Ti L-edge XAS to illustrate the successful substitution of Ti in the NMC lattice.

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.

References

- [1] J. Wilcox, S. Patoux, and M. Doeff, *J. Electrochem. Soc.*, 156, A192 (2009).
- [2] J. D. Wilcox, E. E. Rodriguez, and M. M. Doeff, *J. Electrochem. Soc.*, 156, A1011 (2009).
- [3] K. C. Kam and M. M. Doeff, *J. Mater. Chem.*, 21, 9991, (2011).
- [4] K. C. Kam, A. Mehta, J. T. Heron and M. M. Doeff, *J. Electrochem. Soc.*, 159, A1383 (2012).

Acknowledgement

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231 under the Batteries for Advanced Transportation Technologies (BATT) Program. Portions of this research were carried out at the Stanford Synchrotron Radiation Lightsource, a Directorate of SLAC National Accelerator Laboratory and an Office of Science User Facility operated for the U.S. Department of Energy Office of Science by Stanford University.