

Using In-Situ Methods to Characterize Phase Changes in Charged Lithium Nickel Cobalt Aluminum Oxide Cathode Materials

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Lithium ion batteries find ubiquitous use in mobile devices such as smartphones, tablets and laptops, and are being increasingly considered for use in both transportation and Smart Grid applications. In all of these applications, there is a demand for higher capacity, faster charging rate and improved safety. In particular, lithium nickel cobalt aluminum oxide cathode materials ($\text{Li}_x\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_3$ – “NCA”) are seeing increasing use in demanding energy storage applications due to their high energy storage capacity. However, these materials can experience undesirable thermal runaway in real life applications, leading to catastrophic failures.

In this presentation, I will review our work investigating the atomic scale changes that occur in NCA, including during thermal excursions. These studies will mostly focus on the use of in-situ transmission electron microscopy (TEM) but will include information gleaned from complementary probes such as in-situ x-ray diffraction and x-ray absorption. We have used these approaches to understand how the surface structure changes as a function of state of charge, with the extent of change being a strong function of the extent of lithium extraction.[1]. Thereafter we will describe how thermal excursions can lead to bulk oxygen loss from the structure, how this oxygen loss is correlated with the movement of the transition metal ions, and how these movements lead to a series of structural changes from the spinel structure to the ‘disordered spinel’ structure to the rock-salt structure on the surface of the particles.[2] Environmental TEM also allows use to explore how we can tune the surface activity, leading to the suppression of both oxygen loss and the initiation of the phase transitions.[3]

References:

[1] S. Hwang, S. M. Kim, S.-M. Bak, B.-W. Cho, K. Y. Chung, J. Y. Lee, W. Chang and E. A. Stach, *ACS Appl. Mater. & Inter.* **6**, 15140-15147 (2014).

[2] S. Hwang, W. Chang, S. M. Kim, D. Su, D. H. Kim, J. Y. Lee, K. Y. Chung and E. A. Stach, *Chem. Mater.*, **26**, 1084-1092 (2014).

[3] Khim Karki, Yiqing Huang, Sooyeon Hwang, Andrew D. Gamalski, M. Stanley Whittingham, Guangwen Zhou, and Eric A. Stach, *ACS Appl. Mater. Interfaces*, **8**, 27762-27771, 2016.

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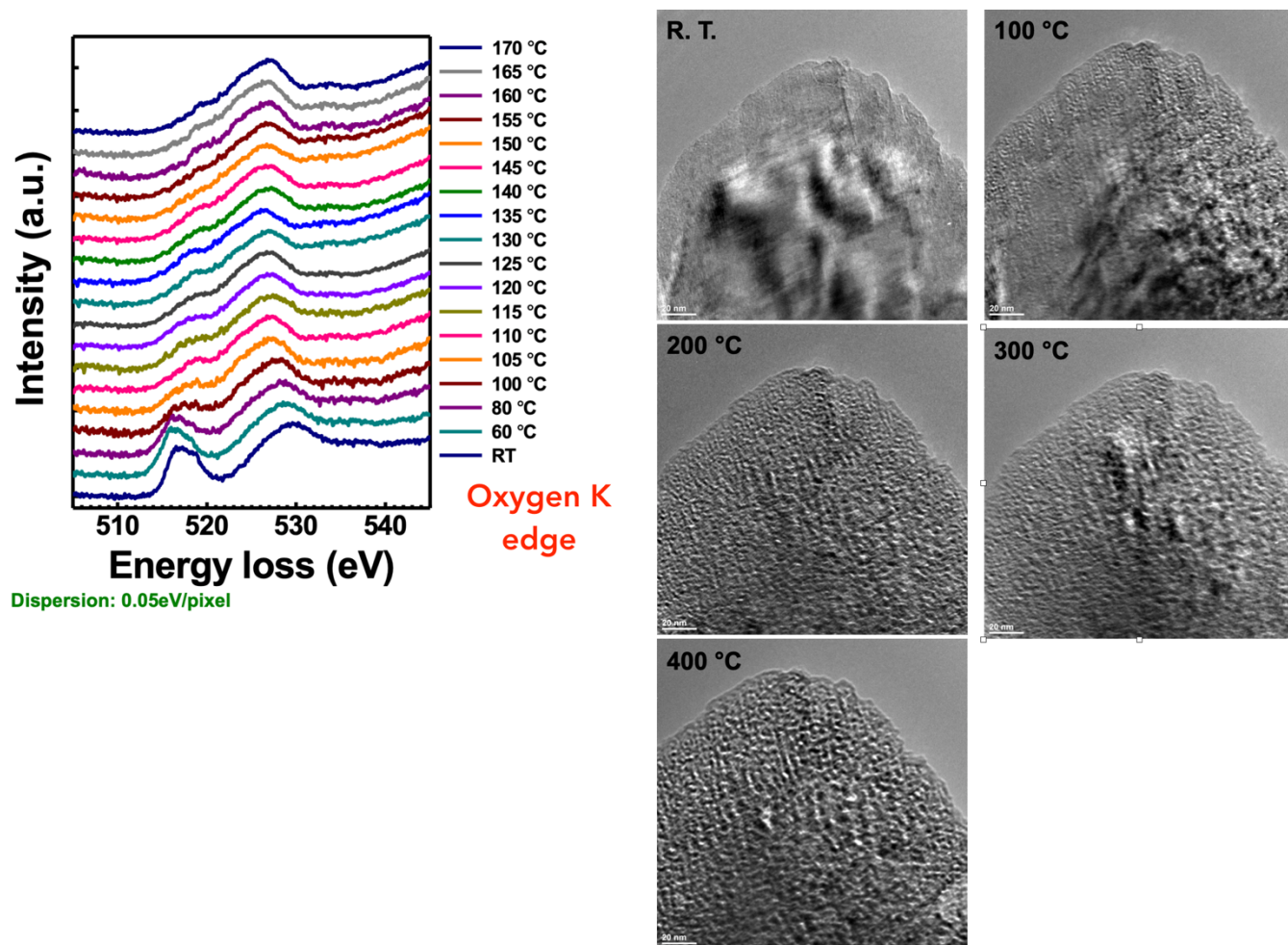


Figure 1. Changes in $\text{Li}_{0.8}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_3$ nanoparticles during thermal excursions. The electron energy loss spectra show changes in the near edge features associated with the changes in the oxidation state of the transition metals. The images on the right show the extensive changes that occur in the sample during the thermal excursions.