Experiment Brief

Gatan Imaging Filter & DENSsolutions Wildfire Holder

Title

Observing the effects of oxygen activity on NCA battery electrodes via *in-situ* EELS

Gatan instrument used

Gatan imaging filter and DENSsolutions Wildfire heating holder.

Background

Lithium ion batteries are already used in many consumer electronics, but significant research is being devoted to increasing the capacity of these batteries. One of the promising cathode materials being currently pursued is $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). This material suffers from thermal instability, especially when overcharged or overheated, leading to oxygen loss from the surface of cathode particles. This, in turn, can produce new phases which lower the capacity of the battery. The loss of oxygen from the structure of an individual NCA particle can be monitored locally using electron energy loss spectroscopy (EELS) in the transmission electron microsope (TEM), to determine the effect of ambient oxygen on the structural oxygen loss.

Materials and Methods

A DENSsolutions Wildfire heating holder was used within an aberration corrected environmental TEM (AC-ETEM) to achieve an elevated temperature in gas environments of O_2, He, and H_2. TEM-EELS was performed using a Gatan Imaging Filter to measure the O K-edge at around 525 eV as a function of temperature and gas environment, as seen in Figure 1. Individual NCA particles change structure due to oxygen loss based uon the temperature and environment applied, and the degree of oxygen loss as a function of temperature in each environment was determined from EELS data. The oxygen pre-peak and main- peak arise from transitions to different oxygen-metal hybridized orbitals so the change in the pre-peak intesnsity and/or the energy difference between the pre-peak and main-peak can thus be correlated with the oxidation state of the transition metal ions.

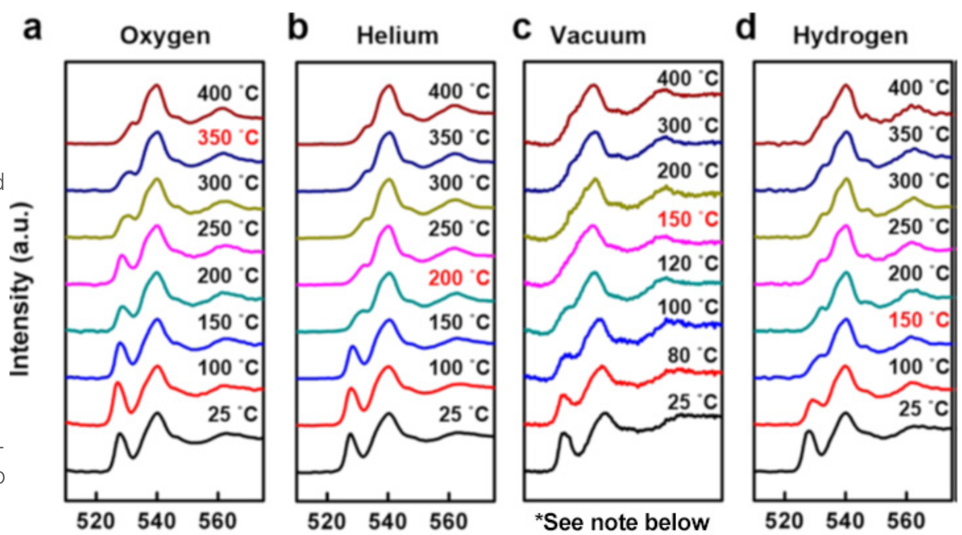

Figure 1. Series of *in-situ* EELS spectra showing oxygen loss. The intensity of the oxygen pre-peak around 527 eV was significantly decreased as the temperature was raised above 100 °C in vacuum and in H_2. A He environment suppressed this slightly, while O_2 gas suppressed the loss of oxygen from the structure significantly so that much higher temperatures were required to achieve the same level of oxygen loss. Karki, K., Huang, Y., Hwang, S., Gamalski, A. D., Whittingham, M. S., Zhou, G., Stach, E. A., 2016. ACS Applied Materials & Intefaces 8, 27762–27771 doi:10.1021/acsami.6b09585 *This data originally appeared in reference 15 of the cited article.

Summary

In-situ EELS at elevated temperatures in varied gas environments was used to measure oxygen loss from individual NCA particles. TEM images (not shown), revealed that the structure of the particles had changed from the original layered structure to spinel or rock-salt phases. The measurement of oxygen loss from EELS spectra revealed that maintaining an O_2 environment around the particles delayed the onset temperature for oxygen loss to 350 °C. This illustrates the fundamental mechanisms responsible for NCA degradation and points toward possible strategies for enhancing the performance of future cathode materials.

Credit(s)

Special thanks to Khim Karki, NECCES, BNL; Yiqing Huang, NECCES; Sooyeon Hwang, BNL; Andrew D. Gamalski, BNL; M. Stanley Whittingham, NECCES; Guangwen Zhou, NECCES; Eric A. Stach, BNL.

Gatan, Inc. is the world's leading manufacturer of instrumentation and software used to enhance and extend electron microscopes—from specimen preparation and manipulation to imaging and analysis.

The Center for Functional Nanomaterials at Brookhaven National Laboratory The Center for Functional Nanomaterials (CFN) explores the unique properties of materials and processes at the nanoscale. The CFN is a user-oriented research center whose mission is to be an open facility for the nanoscience research community and advance the science of nanomaterials that address the nation's energy challenges.

EB-in-situ_EELS-CA-FL2-NOV20