

## ETEM Study of Oxygen Activity in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA) Cathode Materials at Various States of Charge

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Lithium ion batteries (LIBs) have been predominantly used in the consumer electronics and other power devices. The drive to use LIBs in the large-scale applications such as electric vehicles (EVs) and smart grids has spurred significant research activity, particularly concerning the cathode electrodes. The current cathode materials,  $\text{LiCoO}_2$  (~140 mAh/g) or  $\text{LiFePO}_4$  (~160 mAh/g), have relatively low energy densities, and can hardly match with the capacities of the next generation of anode materials (e.g. Si, ~4200 mAh/g). To improve upon this limitation, layered materials such as  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  (NCA) &  $\text{LiNi}_x\text{Mn}_{1-x-y}\text{Co}_y\text{O}_2$  (NCM) – which have discharge capacity ~200 mAh/g – have been actively pursued as potential replacements. However, these cathode materials suffer from rapid capacity fade and poor thermal instability, thus raising serious safety concerns. For example, these materials in a highly delithiated state (overcharged) can readily release oxygen at high temperature, and lead to complex phase transitions: layered (R-3m)  $\rightarrow$  disordered spinel (Fd-3m)  $\rightarrow$  rock-salt (Fm-3m). The released  $\text{O}_2$  can react with the flammable electrolyte, leading to thermal-runaway and catastrophic battery failure. Therefore, it is critical to understand the role that the oxygen release plays in the migration of transition metal (TM) cations (Ni, Co, & Mn) during the various phase transition processes. Environmental transmission electron microscopy (ETEM) provides a unique platform where individual nanoparticles can be investigated for any morphological, structural or chemical changes, under external stimuli, in real-time. Furthermore, the aberration-corrected ETEM with a differential pumping apparatus allows high spatial resolution of < 0.1 nm even in a high-pressure gas environment (e.g.,  $\text{O}_2$ ,  $\text{H}_2$ ) in the system. Here, we use *in-situ* ETEM to understand the role that oxygen plays in the rearrangement of the TM ions both at the surface & in the bulk of the NCA materials at elevated temperatures.

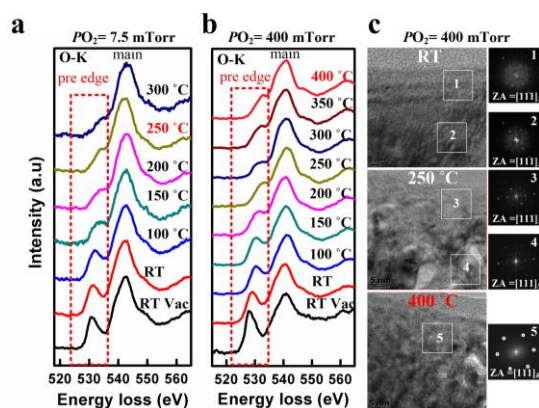
Previous *in-situ* TEM studies performed by Wu *et al* [1] demonstrated that both NCA and NCM exhibit a highly complex structure with a rhombohedral core, a spinel shell at the sub-surface region, and the rock-salt structure at the surface of the particles at elevated temperatures. Further heating of the particles inside the TEM showed the propagation of spinel and rock-salt phases, ultimately leading to the transformation of most particles into the rock-salt phase at 400 °C. Interestingly, upon charging (lithium extraction) of the overcharged particles, there was loss of oxygen at the surface of the particles [1-3]. The evolution of gases, such as  $\text{O}_2$  and  $\text{CO}_2$  has been attributed to the phase transitions that occur during thermal decomposition [3].

Here, we find that upon heating individual half-charged (50 % of lithium extracted electrochemically) NCA particles under low oxygen partial pressure ( $P_{\text{O}_2}$ ) ~ 7.5 mTorr, the pre-edge of the O-K edge EELS spectra shifts to a higher energy loss at 250 °C (Figure 1a). The pre-edge (~ 528-530 eV) depicts the transition of electrons from O 1s state to unoccupied O 2p states which hybridizes with the 3d state of TM (primarily Ni), while the main edge refers to the transition of electrons from the 1s state to hybridized O 2p and TM 4sp states. The fading and shifting of pre-edge towards higher energy loss occurs from the reduction of TM ions and creation of oxygen vacancies. In a vacuum environment, the

loss of the pre-edge has been reported to occur at temperature as low as 300 °C [2], which is roughly equivalent to our study at low  $PO_2$ . Upon heating the sample at a higher  $PO_2$  of  $\sim 400$  mTorr, the onset temperature for the release of lattice oxygen dramatically increases ( $\sim 400$  °C) (Figure 1b). The high resolution TEM (HRTEM) images and corresponding FFT patterns (Figure 1c) of the particle at  $PO_2 \sim 400$  mTorr show that most of the surface and near-surface regions have transformed to the spinel phase (FFTs 1 & 2) even at room temperature (RT). At 250 °C, the temperature at which the O-K pre-edge starts to fade, the surface of the particle appears roughened. The FFT patterns (3 & 4) suggest that surface and near-surface areas still remain as the spinel phase. However, at 400 °C, the O-K pre-edge shifts and becomes the shoulder of the main edge. The FFT (5) shows that the particle has transformed to the rock-salt phase. Thus, we find that the oxygen gas enrichment significantly delays the loss of lattice oxygen in the NCA particles & helps preserve the integrity of the NCA particles at higher temperatures. The fundamental understanding of the oxygen activity of NCA at various states of charge could facilitate the design & synthesis of better oxide electrodes for battery applications [4].

#### References:

- [1] Wu *et al*, Chem Mater. **23** (2011), 3953.  
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 [3] Bak *et al*, Chem. Mater., **25** (2013), 337.  
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**Figure 1.** Oxygen evolution & structural phase transition of half-charged ( $x = 0.5$ ) NCA particles upon heating in the ETEM at different  $PO_2$ . (a) O-K EELS intensity profile at  $PO_2 \sim 7.5$  mTorr. (b) O-K EELS intensity profile at  $PO_2 \sim 400$  mTorr. All spectra in (a) and (b) are normalized to the intensity of main edge. (c) HRTEM images obtained during  $PO_2 \sim 7.5$  mTorr at three different temperatures: RT, 250 °C and 400 °C. The numbered boxes in the images represent the areas from which the FFT patterns are extracted.