

## In-situ (S)TEM Investigation of Phase Transformation Mechanism in the Ni-rich Cathodes During Cycling

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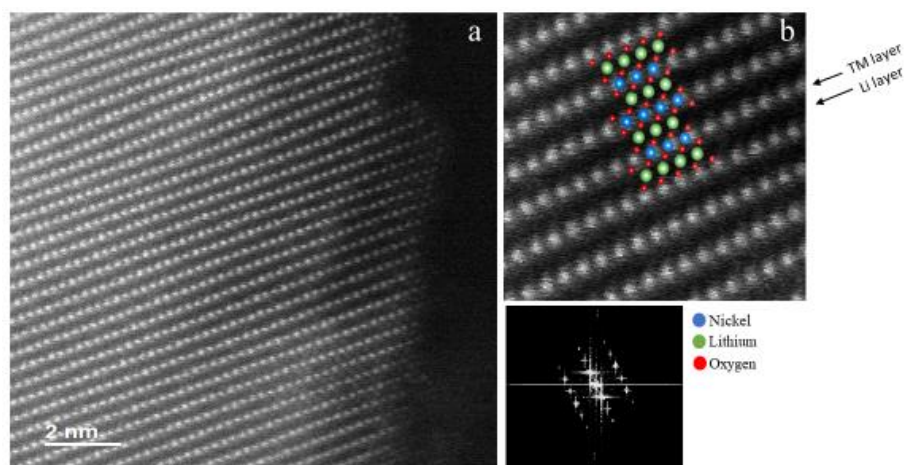
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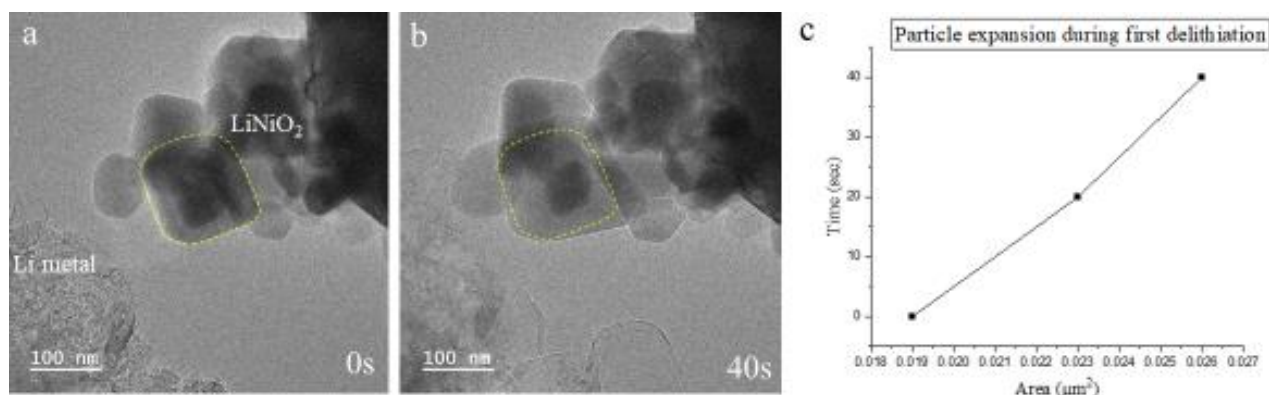
Lithium ion batteries have become one of the most important energy storage batteries for both industrial and household applications such as electric vehicles, portable electronics [1]. One of the most promising lithium containing cathode are  $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$  ( $x \geq 0.5$ ) (NMC),  $\text{LiNi}_x\text{Co}_y\text{Al}_{1-x-y}\text{O}_2$  ( $x \geq 0.5$ ) (NCA),  $\text{LiCoO}_2$  (LCO) and  $\text{LiMn}_2\text{O}_4$  (LMO). However, both LCO and NCA show fast capacity fade, and high cost due to the high content of cobalt [1]. LMO results in poor cycling performance due to undesirable structural changes [3]. High Ni content NMCs ( $x \geq 0.8$ ) show high power capability, but their structure tends to degrade during cycling [4]. Layered  $\text{LiNiO}_2$  is one of the most promising cathode active materials (CAM), due to its higher capacity than LCO and NCA [3]. Nevertheless, it suffers from structural changes during (de)lithiation, high surface reactivity and severe oxygen evolution during cycling, raising the need for further investigation [5].

During cycling we can identify three distinct stages where, the layered O3 stacking sequence is reduced from trigonal structure with rhombohedral symmetry  $R\bar{3}m$  to monoclinic  $C2/m$ , then into a layered mixture of O3 and O1 (H2-H3) stacking and further to a spinel phase ( $Fm\bar{3}m$ ) [6, 7]. Among all phases, the H2 to H3 transformation results in poor structural stability especially while operating at high voltages [7]. In situ electron microscopy techniques such as scanning electron microscopy (STEM) allows for high temporal and spatial recognition of real-time structural changes of LNO cathode during cycling and precise identification of  $\text{Li}^+$  diffusion within LNO layers [7, 8].

In this work we focus on investigating dynamics of the degradation mechanism of LNO cathodes with starting structure of the O3 stacking sequence, which is the most dominant structure before further delithiation. An example can be seen in **Figure 1** where the layered structure of pristine LNO with approximately 5 to 10 atomic layers of cation mixing layer shows an open channel available for effective  $\text{Li}^+$  diffusion. The structural and compositional changes of the  $\text{LiNiO}_2$  have been studied with application of constant potential of 4.3 V. Figure 2 illustrates series of the first delithiation cycle achieved by *in situ* TEM. An expansion of 36.8% is demonstrated when the particle was charged for 40 seconds versus Li metal source as the anode. This expansion is a result of the increase in the c lattice parameters causing phase transition from H1 to monoclinic, then into H2 and H3 (which is referred as a collapse of the layered structure). Further studies will focus on comparing the simulated and experimental steps of phase reconstruction mechanisms from layered to spinel during the degradation process of Li and oxygen loss in the LNO cathode during cycling [2, 9].



**Figure 1:** (a) DF-STEM images of pristine layered  $\text{LiNiO}_2$ . (b) DF STEM of the O3 lattice stacking sequence with a space group of  $R\bar{3}m$ . The arrows indicate the Li layer and the transition metal layer ( $\text{NiO}_2$ ).



**Figure 2:** *In-situ* TEM images of the LNO cathode before (a) and after (b) cycling at 4.3V. a) shows the initial stage of the delithiation at 0s and b) 40 seconds during the delithiation process. c) a diagram of the LNO cathode expansion as a function of time during delithiation, showing 36.8% expansion.

#### References:

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