Comparison of Co₃O₄ and CoO Nanoparticles as Anodes for Lithium-ion Batteries

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The development of portable electronic devices demands improvements in rechargeable batteries that will lead to high energy and power density, low cost and long cycle life. Among of the available kinds of batteries, lithium-ion batteries have attracted extensive attention because of their high energy density. Because the graphite anodes conventionally used in commercial lithium-ion batteries have a limited specific capacity (372mAh g⁻¹), other anode materials are being investigated, e.g. transition metal oxides which have much higher specific capacity. Cobalt based oxide materials have attracted significant attention due to their high theoretical capacity (890mAh g⁻¹) and good capacity retention[1,2]. While the electrochemical performance of Co₃O₄ and CoO has been widely studied, the reaction mechanisms that occur during lithiation in these materials remain unclear. Early studies suggested that the lithiation of Co₃O₄ is a two-step reaction (first proceeding by intercalation then by conversion), other studies have shown that decomposition occurs at the initiation of the process [3]. Because Co₃O₄ and CoO have both different cycling performance and different crystal structures, an understanding of their reaction mechanisms and kinetics and the relation of these to their structures is of fundamental interest.

Here, we report investigation of the lithiation process of Co_3O_4 and CoO nanoparticles using aberration-corrected transmission electron microscopy (TEM) techniques. We have studied samples that have been cycled in coin cells, and correlated these with real time studies using an in-situ electrochemical dry cell approach (Figure 1a). As shown in the scanning TEM (STEM) images of Figures 1b and c, we observed different lithium induced changes in the structure of Co_3O_4 and CoO respectively. In Figure 1b, from left to right, significant contrast changes occur in Co_3O_4 at the beginning of lithiation, with the formation of fine-sized nanoparticles during further lithiation. In contrast, only fine-sized nanoparticles form during the lithiation of CoO (Figure 1c).

Electron diffraction patterns (Figure 2) allow us to track the phase transitions that occur during lithiation directly. As shown in Figure 2a, an intermediate rock-salt phase (LiCoO₂) is generated when Li⁺ ions first enter the structure, and the system decomposes into metallic Co and the anti-fluorite structure Li₂O during further lithiation. In contrast, CoO is reduced to metallic Co and Li₂O directly (Figure 2b). We found that during lithiation, the irreversible incorporation of Li⁺ pushed the Co²⁺ ions that were present in the 8a site to neighboring 16c sites during the initial insertion into the spinel Co₃O₄ structure. At the same time, Co²⁺ ions at the 16d sites maintain the general framework along with oxygen expansion, which corresponds to the intermediate phase (LiCoO₂). With further lithiation, the Co²⁺ ions originally present at the 16d sites had been removed from these sites, leading to the formation of the anti-fluorite Li₂O structure. In the case of CoO (which has the rock-salt structure), the incorporation of Li⁺ pushed the Co²⁺ ions out of all of the tetrahedral sites. Electron energy-loss spectroscopy (EELS) and high resolution TEM (not shown) confirmed these results in the *ex situ* cycled samples. Understanding the difference in the reaction mechanisms between Co₃O₄ and CoO provides needed insight into the differences observed in their performance [4].

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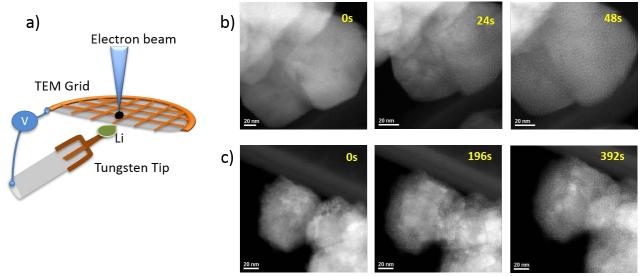


Figure 1. (a) Schematic illustration of in-situ TEM dry cell. Time sequence of STEM images showing the structural evolution of (b)Co₃O₄ and (c) CoO during in-situ lithiation.

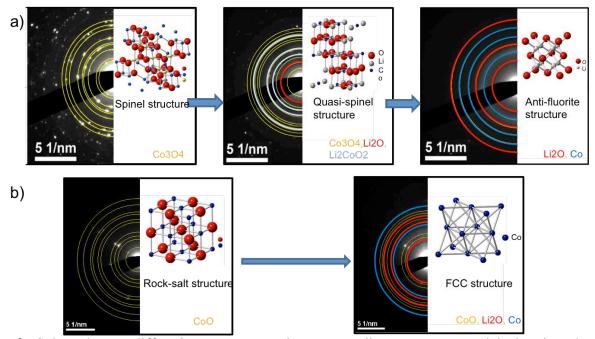


Figure 2. Selected area diffraction patterns and corresponding structure model showing the phase evolution of (a) Co_3O_4 and (b) CoO.