Atomic-resolution \textit{in-situ} TEM Studies of Lithium Electrochemistry in Co$_3$O$_4$-Carbon Nanotube Nanocomposite

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In typical charge and discharge cycling, electrodes may exhibit metastable phases with unusual ordering to repeatedly host and extract lithium-ion and electrons. This is a clear consequence of not enough time and/or energy available for such metastable phases to relax and transform into their equilibrium counterparts (1). Such metastable structures may exist only for a short duration, which makes it extremely difficult to measure or even identify them experimentally. Yet, they clearly play important roles in the battery figures of merit, such as cycling stability, voltage hysteresis, to capacity. The recent developments in \textit{in-situ} transmission electron microscopy (TEM) (2-6) has enabled us to observe de/lithiation processes at atomic resolution, identify metastable phases and monitor their continuous phase transformation, with the gradual addition of lithium-ions and electrons into the battery electrodes. Structural models of these metastable phases are derived from full DFT simulations, and seem to corroborate with high resolution phase contrast simulated images as compared to corresponding experimental ones.

Li-Co-O system represents one of the most important materials for lithium-ion battery with rich chemistry and structures, \textit{i.e.} LiCoO$_2$ has been used as intercalated cathode in the first commercialized battery by SONY, while Co$_3$O$_4$ and CoO are found to be high-capacity anode materials with conversion reaction: M$_x$O$_y$ + 2y Li$^+$ + 2y e$^-$ = xM$_0$ + yLi$_2$O.

Here, Co$_3$O$_4$ nanoparticles grown on highly conductive multi-wall carbon nanotubes (CNT) are employed as a model material system to study the structural evolutions with different amount of lithium inserted or reacted during electrochemical activation. The \textit{in-situ} electrochemical lithiation experiments were followed until cobalt oxide nanoparticles are completely reduced into Co nanoparticles along with the formation of Li$_2$O by conversion reaction and reverse de-lithiation until return back to cobalt oxide. When lithium-ions are introduced at lower rate, metastable lithium-inserted Li$_x$Co$_3$O$_4$ (x=1 to 5) crystalline phases are observed prior to formation of Co$_0$ and Li$_2$O clusters as the product of conversion reaction. At higher rate, lithium-ions can occupy any empty sites simultaneously that instantly break the Co$_3$O$_4$ spinel lattice bypassing the metastable crystalline phases. The amount of lithium-ions intake in a low rate is larger than that of the high rate, which provides insight on the charge/discharge rate and capacity relation. The presentation will cover intricacies of such metastable structures and the overall dynamics of electrochemical processes, as monitored by \textit{in-situ} TEM imaging, spectroscopy and diffraction.

References:
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Figure 1. Co$_3$O$_4$ nanoparticles on carbon nanotube (Co$_3$O$_4$/CNT) and their lithiation by in-situ TEM. (A) Low-magnification TEM image and (B) SEM images of Co$_3$O$_4$ nanocubes on CNT. (C) In-situ high resolution electron microscopy (HREM) image of lithiation of Co$_3$O$_4$/CNT showing decomposition of the Co$_3$O$_4$ nanocubes and illustration of experimental setting and phase transformation due to conversion reaction.

Figure 2. In-situ HREM of lithiation of a Co$_3$O$_4$ nanocube on CNT at a low lithiation rate. (A)-(G) upper row: time-resolved HREM images of the lithiation process with time labeled; low-row: structural models of lithium-inserted phases, from LiCo$_3$O$_4$ to Li$_8$Co$_3$O$_4$, calculated by DFT simulations. The structural model are oriented along the equivalent direction as the [121] of Co$_3$O$_4$. The simulated HREM images are inserted. The scale bar is 1 nm.