Real-time Observation of Electrochemical Sodiation of \( \text{Co}_3\text{O}_4/\text{CNTs} \) by \textit{in-situ} Transmission Electron Microscopy

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In recent years \textit{in-situ} transmission electron microscopy (TEM) has become a unique and effective technique in revealing the underlying mechanisms and fundamental science of charge and ion transport, such as in lithium-ion batteries (LIBs) [1-7] and sodium-ion batteries (NIBs) [8-11] as well as potassium-ion batteries (KIBs) [11]. Such \textit{in-situ} or so-called in-operando observations enable direct monitoring of the microstructural evolution during the electrochemical reaction process. Sodium ion battery as inexpensive and reliable energy storage setup attracts more and more researchers’ attention. In this work, the electrochemically driven sodiation process and microstructural evolution of \( \text{Co}_3\text{O}_4/\text{carbon nanotube} \) nanocomposites are directly visualized in real-space and investigated close to atomic resolution by \textit{in-situ} TEM under applied electrical bias.

Uniform \( \text{Co}_3\text{O}_4 \) nanocubes with a regular cuboidal shape and size of ~5 nm anchored on the surface of carbon nanotube were synthesized by a simple hydrothermal method [12]. Carbon nanotube can act as both, the substrate to support active materials (\( \text{Co}_3\text{O}_4 \) nanoparticles) and a good conductor of ions and electrons. Upon the first sodiation reaction as shown in Fig.1, sodium ions firstly diffuse along the surface of carbon nanotube and then get inserted into \( \text{Co}_3\text{O}_4 \) crystalline lattice leading to a collapse of the \( \text{Co}_3\text{O}_4 \) crystalline lattice and formation of Na-Co-O amorphous clusters, a process which is reminiscent of solid amorphization reaction. \textit{In situ} diffraction patterns indicate that the amorphous phase then gradually transforms into a composite of Na\(_2\)O and Co phase with continuous Na\(^+\) insertion in the sodiation process. There is about two-fold volume expansion of one nanotube after full sodiation, which is smaller than that in lithiation of \( \text{Co}_3\text{O}_4 \). Both discharging rate and reaction depth of sodiation reaction are much lower than that of lithiation due to larger ionic size of Na\(^+\). Thus, the sodiation dynamics is quite different from that of lithiation.

In summary, we have observed the electrochemical reaction and microstructure evolution of \( \text{Co}_3\text{O}_4/\text{CNTs} \) nanocomposites during sodiation process, confirming that some of the 3\textit{d} transition metal oxides have potential as electrode materials in sodium ion batteries [13, 14]. These observations may help understand the sodiation mechanism and aid in designing new advanced electrodes for high-performance NIB battery in the future.

Reference:

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Figure 1. (a)-(l) The typical morphological evolution of one $\text{Co}_3\text{O}_4$ nanocube on the edge of CNT during sodiation process. Regular cube (a) has gradually changed to a smoothly expanded oval shape (l) (indicated by the red ovals in (a) and (l)), with the (111) crystalline lattice of $\text{Co}_3\text{O}_4$ disappearing from the surface in the sodiation process. The (111) lattice finges of $\text{Co}_3\text{O}_4$ are shown by the yellow arrowheads.