

## In-situ TEM Investigation on Reaction Mechanisms of Conversion Electrode Materials for Batteries

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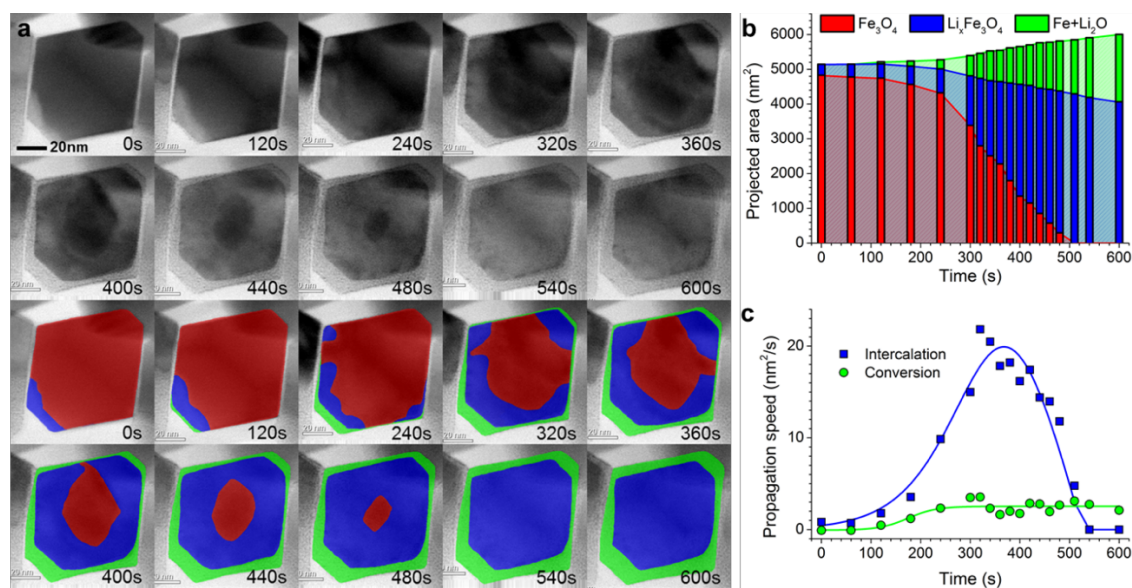
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Lithium ion batteries (LIBs) have dominated portable electronics and are penetrating the markets of electric vehicles. Current electrode materials have specific capacities ranged only from 140 to 200 mAh g<sup>-1</sup> for cathode and about 370 mAh g<sup>-1</sup> for anode, which limit their energy densities. Alternatively, conversion compounds are regarded as a kind of high-energy density electrode materials for secondary ion batteries. However, these compounds suffer a severe voltage hysteresis and a poor cycling stability. These problems have been believed to be intrinsic nature of the conversion reaction chemistry, and the hope of using conversion reaction materials in the next-generation lithium batteries waned. As electrochemical properties are highly dependent on how these complicated reactions proceed, *in situ* investigation of the reaction pathways is of importance to understand their intrinsic reaction nature.

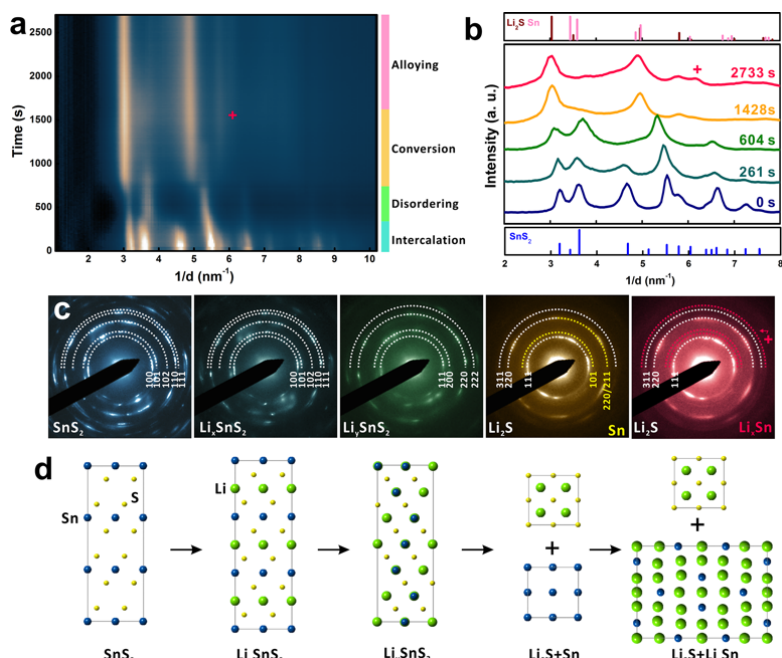
In this talk, I would review the research frontier of the *in situ* transmission electron microscopy (TEM) study on the dynamic reaction behavior of conversion metallic compounds, e.g. oxides, fluorides and sulfides, especially on the works using the dry-cell approach in my group [1-8]. Real-time structural evolutions induced by lithium ion's insertion are reflected from in-situ electron diffraction, and thus, from the appearance and disappearance of peaks, we could distinguish reaction steps and possible intermediate phases. On the other hand, *in situ* TEM or scanning-TEM imaging can help us to understand the phase evolution in real space. In past years, we developed a strain sensitive-STEM imaging approach to visualize the phase boundary movement induced by Li ions' insertion in Fe<sub>3</sub>O<sub>4</sub>, Co<sub>3</sub>O<sub>4</sub> and SnS<sub>2</sub>. Using in-situ TEM techniques, we investigated the phase evolutions and intermediate phases at non-equilibrium states in conversion compounds during discharging. With the help of X-ray characterizations and DFT calculations, we corroborated information from real-time TEM observation with the performances. Our results may provide new insights into designing conversion-type electrode materials for applications [9].

### References:

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**Figure 1.** *In situ* observation of two-step phase transformation during lithiation process [3]. (a) BF-STEM image series showing phase evolution upon lithiation. The overlaid false colors indicate different phases: pristine Fe<sub>3</sub>O<sub>4</sub> (red), Li-inserted Li<sub>x</sub>Fe<sub>3</sub>O<sub>4</sub> (blue), and Fe+Li<sub>2</sub>O composition after conversion (green). (b) Projected areas of the three phases as a function of time. (c) Propagation speed of intercalation and conversion as a function of time.



**Figure 2.** *In situ* selected area electron diffraction patterns of SnS<sub>2</sub> during lithiation [6]. (a) Electron diffraction intensity profile as a function of reaction time during in situ lithiation of SnS<sub>2</sub>. + denotes the evolution of Li-Sn alloy phase. (b) Radial intensity profiles of diffraction patterns at certain time. (c) Diffraction patterns corresponds to intensity profiles at (b). (d) Atomic models representing phase evolution during lithiation.