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Tracking lithium transport and reactions in nanoparticles by *in situ* TEM-EELS

Feng Wang,[1] Hui-Chia Yu,[2] Min-Hua Chen,[2] Lijun Wu,[1] Nathalie Pereira,[3] Katsuyo Thornton,[2] Anton Van Der Ven,[2] Yimei Zhu,[1] Glenn G. Amatucci[3], and Jason Graetz[1]
[1]Brookhaven National Laboratory, Upton, NY 11973
[2]Department of Materials Science and Engineering, Michigan University, Ann Arbor, MI 48109
[3]Department of Materials Science and Engineering, Rutgers University, North Brunswick, NJ 08902

In order to design safe, high-energy electrodes with long-cycle life, we need a better understanding how electrode materials function by *real-time* tracking of lithium transport and electrochemical reaction in a working electrode, ideally at the level of single particles. This type of characterization requires high sensitivity to Li and other constituents at relevant spatial and temporary resolution. High-resolution transmission electron microscopy (TEM) imaging and energy-loss spectroscopy (EELS), have been shown powerful for probing Li with sub-nm spatial resolution [1]. However TEM-EELS has been mostly used in *ex situ* measurements, providing limited information on phase nucleation and propagation, which is critically important for identifying pathways for lithium and electron transport, and the reaction kinetics of the electrode.

Recently we have developed a novel *in situ* TEM-EELS approach to track electrochemical reactions of individual nanoparticles in real time and used it to study the lithium conversion reaction in individual FeF_2 particles. The *in-situ* measurements enable us, for the first time, to reveal the *real time* conversion of FeF_2 into tiny Fe and LiF particles (Fig.1)[2]. The reaction appears to start from surface as indicated by the formation of sub-nm Fe particles in the near-surface region of the particles. While in the fully lithiated sample, 1-3 nm Fe particles are formed within the domains of the parent FeF_2 particles. The structural and chemical changes were also monitored with *in situ* EELS, coupled with TEM images and diffraction patterns acquired from a same area.

The experimental results were combined with *first principles* calculations and *Monte Carlo* simulations to gain insight on reaction pathways and kinetics of the conversion reactions. The versatility of this new *in-situ* TEM-EELS technique for studies of various nanoparticular electrodes will be discussed along with our recent results on FeF_2 and other electrodes.

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References

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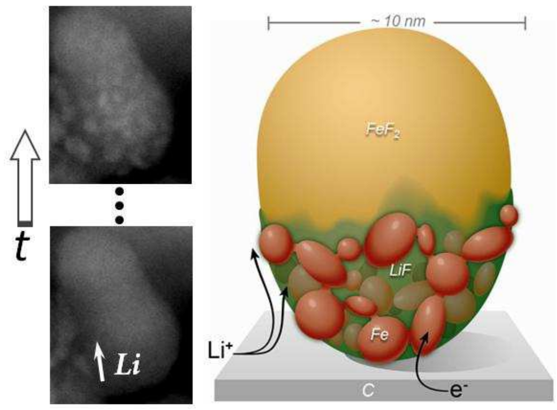

Fig. 1. Selected scanning TEM (STEM) images of one single FeF_2 nanoparticle in the initial and final states from the in-situ TEM measurements (left), and schematic illustration of the propagation of the reaction front through a single FeF_2 particle via a "layer-by-layer' process and possible pathway for electron and lithium transport (right).