

***In-Situ* TEM Electrochemical Processes in Conversion-Based Li-Ion Battery Electrodes**

K. Karki¹, G.G. Amatucci², M.S. Whittingham³, F. Wang¹

¹Brookhaven National Laboratory, Upton, USA

²Department of Materials Science & Engineering, Rutgers University, New Brunswick, USA

³Department of Chemistry and Materials, University of New York at Binghamton, Binghamton, USA

Intercalation-based cathode materials such as LiCoO_2 (~140 mAh/g) and LiFePO_4 (~160 mAh/g) are predominantly used in lithium-ion batteries because they provide exceptional cycling reversibility [1]. However, these materials have low capacity as they are limited to single electron charge transfer reaction, and thus are unlikely candidates for use in electric vehicles (EVs). Conversion compounds such as iron fluorides (FeF_2) are promising because of their high capacities (~570 mAh/g), 2-4 times higher than intercalation-based cathodes, by utilizing more than one Li ion per transition metals [2]. However, these materials suffer from issues such as slow kinetics, large cycling hysteresis (i.e. voltage gap between charge/discharge at certain charge-of-state), and insufficient charge reversibility preventing them from further commercial viability. We perform *in-situ* transmission electron microscopy (TEM) study to understand some of the key questions pertaining to conversion reaction mechanisms such as phase nucleation and evolution, electron and ion transport, reaction kinetics and reversibility during electrochemical charge and discharge.

In the previous study conducted using *in-situ* TEM, our group was able to track lithium transport and conversion in FeF_2 by exploiting the small diffusion length of the nanoscale particle size (10-20 nm in diameter) deposited on the conducting carbon TEM grid substrate [3,4]. We observed that the lithium conversion initiates locally on the surface, and propagates into the bulk resulting in the network of interconnected Fe nanoparticles (1-3 nm) mixed with amorphous LiF (insulator). This newly formed Fe nanoparticles network, along with three-phase (Fe/LiF/FeF_2) interface significantly improves the further conversion of FeF_2 deep inside the bulk, albeit at slower rate compared to the surface decomposition. However, it is still unclear about the mechanism of the formation of Fe nanocrystallites, and its role in the electron/charge transport as well as cycling hysteresis. It also remains to be seen if the lithium conversion reaction observed during the lithiation can be reversed back. Such a study on the reconversion (charge) reaction process, will provide new insights into the cycling hysteresis that plague most conversion electrodes, and may help to pave the way to develop high-energy conversion electrodes for lithium-ion batteries.

We study the FeF_2 model system by incorporating individual FeF_2 nanorods (NRs) using *in-situ* TEM open-cell technique. The open-cell technique utilizes solid electrolyte such as Li_2O , which is natively formed during the transfer of lithium metal counter electrode inside the TEM. The high transparency of open-cell electrodes in the TEM beam allows for observation of morphological/structural changes through high-resolution imaging in a real-time environment. The FeF_2 NRs are prepared using supercritical fluid (SCF) synthesis technique [5]. *In-situ* TEM lithiation of an individual FeF_2 NR (Figure 1) showed surprisingly comparable lithium reaction progression rate similar to nanoparticles demonstrated previously [4]. While bulk form of FeF_2 generally suffer their insulating characteristics, our *in-situ* TEM studies using optimized structures such as nanoparticles and nanorods demonstrate an improvement in the conversion reaction mechanism.

References

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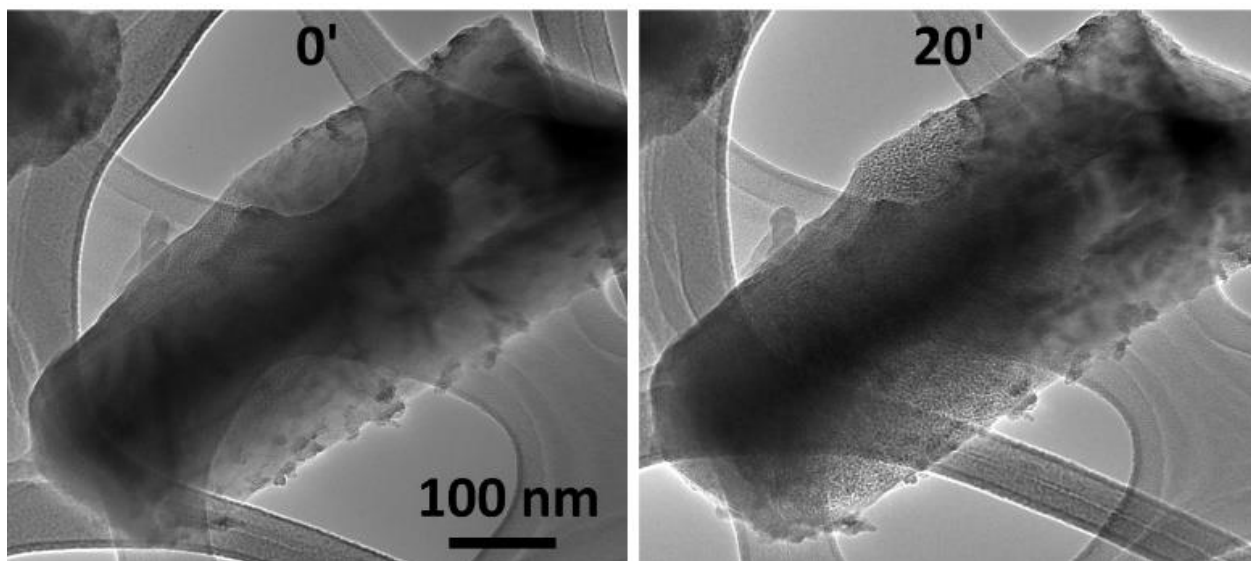


Figure 1: *In-situ* TEM images of a FeF₂ NR during lithiation. First image shows a pristine crystalline NRs. After applying a potential bias of -3V versus Li for 20 min, lithium ions progress through the NR, and reaction proceeds to presumably forming tiny Fe particles on the surface. Both figures have same scale bar.