

Tracking Ionic Transport and Electrochemical Dynamics in Battery Electrodes Using *in situ* TEM-EELS

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The design and development of safe, high energy electrodes for next-generation batteries, requires better understanding how electrode function by *real time* tracking of electrochemical dynamics in active constituent, *i.e.* individual particles, and the collective electrochemical behavior of particles assembled in an electrode. Due to the inherent heterogeneity of the electrodes, this type of characterization requires developing new tools and techniques for measurements at a range of relevant length scales. Most of the available *in-situ* techniques, such as those based on hard X-ray scattering, are suited for bulk measurement at electrode level, but very often have no adequate spatial resolution to probe local structural changes in single particles or interfaces. High-resolution transmission electron microscopy (TEM) imaging and energy-loss spectroscopy (EELS), capable of exceptional spatial resolution [1], has been unsuitable for *in-situ* studies until very recently, when *in-situ* electrochemical cells were developed for operation inside the transmission electron microscope. In the last several years, *in-situ* TEM has been widely applied for studying electrochemical reactions in different electrode systems and at scales spanning from a single particle to composite electrodes [2-4].

Figure 1a shows one type of electrochemical cell specialized for studying lithium reactions in nanoparticles being loaded onto carbon-coated TEM grids [4]. The carbon film, being used as the support of nanoparticles, also provides the pathway for electronic and ionic transport. The counter electrode, lithium metal coated with natively formed surface lithium oxynitride (acting as electrolyte), is attached to a piezo-driven biasing probe that is built into the TEM–STM sample stage. The cell design is simple while widely applicable for studying electrochemical reactions in various anode and cathode materials. The special design of the electrodes, only consisting of thin carbon film and single layer of nanoparticles, allows the use of the low energy-lying Li K-edge EELS spectrum as a lithium probe, to identify Li species through fine-structure fingerprinting technique (Fig. 1b)[1], and to track the evolution of chemical states of Li during electrochemical reactions [4].

The developed electrochemical cell was recently utilized for studying lithium transport and electrochemical dynamics in single FeF₂ particles and thin films (Figure 2). The results from the real time observation provided the 1st experimental evidences showing that lithium moves fast across the surface of the FeF₂ nanoparticles, but penetrates into the bulk of FeF₂ particles at a much slower rate, taking a few minutes for a 10-nm particle, because of the insulating nature of FeF₂. Diffusion of Li into the bulk is prohibited, and so the reaction front propagates, layer-by-layer, into the bulk, during which iron percolating network is formed to provide electronic transport pathway [4, 5]. With these *in-situ* TEM studies, we were able to identify the rate-limiting factors of electrochemical reactions in conversion-type electrodes, and use knowledge to design new mixed -cation cathodes, in which a 2nd cation was introduced to improve the local electronic and ionic transport properties and thereby reduce the cycling hysteresis [6]. Very recently we developed a liquid-type electrochemical cell from a flow liquid platform (designed by Hummingbird Scientific) [7], and utilized it to investigate the electrode-electrolyte interactions in the liquid electrolyte through correlative *in-situ* TEM-EELS and synchrotron X-ray measurements. The versatility of *in-situ* TEM technique for studying ionic transport and electrochemical dynamics in battery electrodes will be discussed along with our recent results on several conversion and intercalation cathode materials [8].

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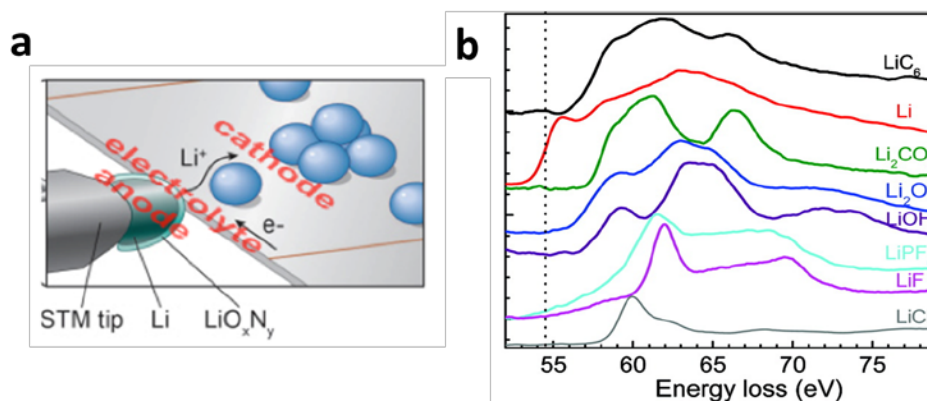


Figure 1. (a) Schematic illustration of *in-situ* electrochemical cells for operation in the transmission electron microscope, (b) experimentally measured Li K-edge EELS spectra for a series of lithium compounds, which may be used as fingerprints for differentiating different lithium species.

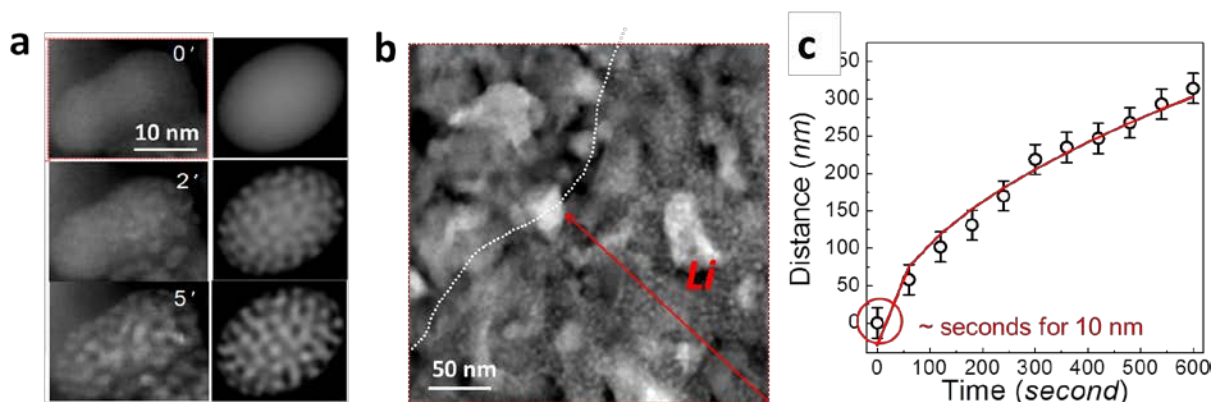


Figure 2. Tracking lithium transport and reaction in FeF₂ by *in-situ* STEM: (a) selected annual dark field scanning TEM (ADF-STEM) images of one single nanoparticle in comparison to the phase-field simulation (on the right), (b) ADF-STEM image of FeF₂ film showing the movement of the reaction front across the area, as indicated by the white dashed lines, (c) moving distance of the reaction front versus time, indicating ~100x higher speed of lithium diffusion along the surface than that in the bulk.