

***In-Situ* Liquid Cell TEM Studies of Electrochemical reactions in Lithium-ion Batteries**

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Lithium-ion batteries (LIBs) are the preferred energy storage devices for portable electronics and electric vehicles due to the long cycle life and high energy density [1]. The development of new electrodes for next-generation batteries requires better understanding how electrodes function by real-time tracking the electrochemical reactions in individual particles and the collective behavior of particles assembled in an electrode. Various available characterization methods, such as *in-situ* X-ray techniques, are powerful for *real time* tracking charge/discharge dynamics of electrodes in liquid electrochemical system, but with limited spatial resolution. Recently the development of *in-situ* TEM techniques enables *real time* observation of structural and chemical evolutions of electrodes during battery operation at high spatial and temporal resolution [2]. However, due to the use of an open-cell configuration in these platforms, solid or ionic liquid electrolyte needs to be used for compatibility with high vacuum in the TEM column. In order to study the lithium reaction with electrodes in liquid electrolyte as generally used in LIBs, we developed a liquid electrochemical cell with thin membrane windows to seal the liquid electrolyte, allowing for both TEM and X-ray measurements with the sample in liquid environments. Here, we present our recent results from the development and application of the liquid electrochemical cells for *in-situ* TEM studies of lithium transport and reaction in individual particles upon lithiation and delithiation.

For electrochemistry experiments, the electrochemical capabilities were developed inside a liquid cell TEM holder (designed by Hummingbird Scientific)[3], as shown in Figure 1a and b. This holder uses micro-fluidic techniques and two micro-fabricated chips each having an electron transparent SiN viewing windows (Figure 1c), and uses a sealing mechanism in which the chips can be secured on the tip of the holder and sealed from vacuum in the TEM column by means of a mechanical sealing mechanism using miniature O-rings and a simple yet reliable clamping solution. The micro-fabricated chips possess three electrodes with different metal options with electrical biasing capabilities. The active electrode material can be attached to metal on-chip leads – those are only exposed to the electrolyte in the TEM viewing area of the cell.

By using the liquid cell we performed *in-situ* studies of electrochemical reactions in single particles of two model systems, LiFePO₄ and FeF₂. They are the most extensively studied cathodes due to their intriguing phase transition behaviors, which are still under intense debate [2, 4]. For the *in-situ* measurements, a standard liquid electrolyte (*e.g.* 1M LiPF₆ salt in ethylene carbonate and dimethyl carbonate) is sealed within the thin membranes (50 nm or below) of the top and the bottom chips. Figure 2 shows the typical morphology of FeF₂ nanoparticles, with a plate-like shape of about a few micrometers long but only several tens of nanometers thick. Good contrast of nanoplates in the liquid electrolyte was obtained by bright-field TEM imaging. The orientation of those nanoplates in the liquid electrolyte was also determined by electron diffraction. They are mostly oriented along {001} or {110} directions, allowing us to study the orientation-dependent chemical and structural evolution in single-

crystalline FeF_2 particles during lithiation and delithiation, in a combination of TEM imaging, diffraction and valence electron energy-loss spectroscopy [5]. Results from *in-situ* TEM studies of the lithium transport and electrochemical dynamics, as well as the complex reactions at the electrode-electrolyte interfaces in individual FeF_2 and LiFePO_4 nanoparticles, will be discussed [6].

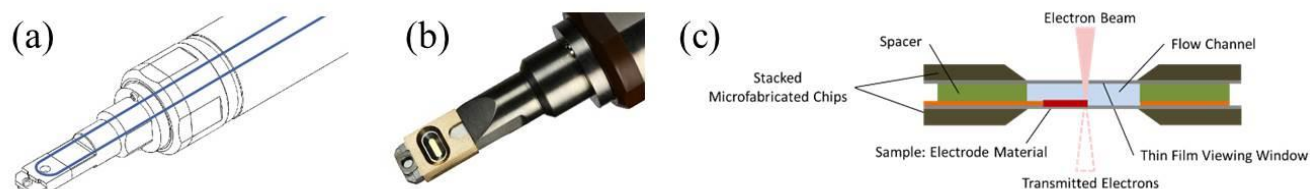


Figure 1. (a) Liquid flow path in liquid TEM flow holder, (b) *in-situ* TEM liquid holder tip, (c) cross-section of the liquid-electrochemical cell.

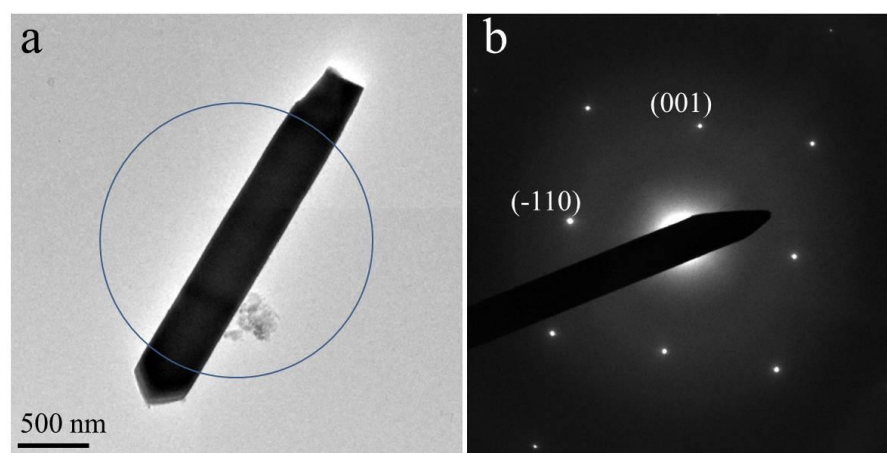


Figure 2. (a) Bright-field TEM image of a single FeF_2 nanoplate in the presence of liquid electrolyte, (b) a diffraction pattern recorded from the region masked by blue circle of FeF_2 nanoplate in (a), indicating the [110] zone axis.

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