

Accelerating Next Generation Battery Development through the Application of Cross-Correlative *In-Situ* Microscopy

Adam Kammers¹, Daan Hein Alsem¹, Jongwoo Lim², Yiyang Li², William Chueh², and Norman J Salmon¹

¹ Hummingbird Scientific, Lacey, WA, USA.

² Stanford University, Department of Materials Science and Engineering, Stanford, CA, USA.

TEM liquid cell microscopy allows electrochemical reactions in battery materials to be studied dynamically at the nano-scale. These experiments permit relationships between battery performance and the structure and chemical composition of the cell to be established, which is critical to the development of next generation batteries. Recent *in-situ* TEM works have demonstrated solid electrolyte interface growth during intercalation of lithium into natural graphite [1] and gold [2] from Li-ion electrolytes. Additional studies have built nanobatteries from Si nanowires to study degradation mechanisms during use [3]. This information has provided new insight into the dynamics of battery cycling and degradation at the nanoscale.

Recently, researchers have begun to look outside of the TEM and have been carrying out cross-correlative experiments in multiple imaging systems to allow links between the nanoscale behavior and the meso- and bulk scale to be made. Some of the imaging tools utilized are X-ray microscopy, scanning electron microscopy, and light microscopy. The recent development of a liquid cell which is transferrable between these imaging systems encourages the cross-correlative approach and is already being utilized to yield new information.

The liquid cell used in this work consists of two microfabricated chips with electron transparent SiN viewing windows and a (patented) sealing mechanism. The cell is contained within a fully serviceable tip that can be transferred between imaging systems as shown in figure 1. By imaging the experiments with an X-ray microscopy, links can be made between nano-, meso-, and bulk scale phenomena. X-ray makes this possible through the application of probes including x-ray diffraction, x-ray absorption spectroscopy, and scanning transmission x-ray microscopy (STXM). SEM imaging allows for rapid probing of electrolytes and cell geometries and allows for microscale characterization over a larger field of view than what is possible in the TEM. Observations in a Raman microscope provide researchers with the Raman spectra from a large area of the electrode. This allows composition maps to be created that show the evolution of the electrode in space and time.

Presently, a cross correlative approach utilizing Raman, TEM, and X-ray microscopy is being utilized to achieve a better understanding of the ion insertion and extraction mechanisms in battery electrodes and the effects of cycling on the electrode material. Here we present details on the cross correlative tools and techniques used in this research into next generation battery materials. Initial results from the application of this approach to the study of lithiation of lithium iron phosphate particles will be discussed. Through this cross correlative approach, state of charge mapping can be linked to the microstructure of the particles as demonstrated in figure 2. The results demonstrate the usefulness of cross-correlative liquid cell microscopy in the characterization of future battery cathode materials.

References:

- [1] R.R. Unocic *et al*, *Microscopy and Microanalysis* 20 (2014), p. 1029-1037.
- [2] R.L. Sacci *et al*, *Chemical Communications* 50 (2014), p. 2104-2107.
- [3] M. Gu *et al*, *Nano Lett.* 13:12 (2013) p. 6106–6112.

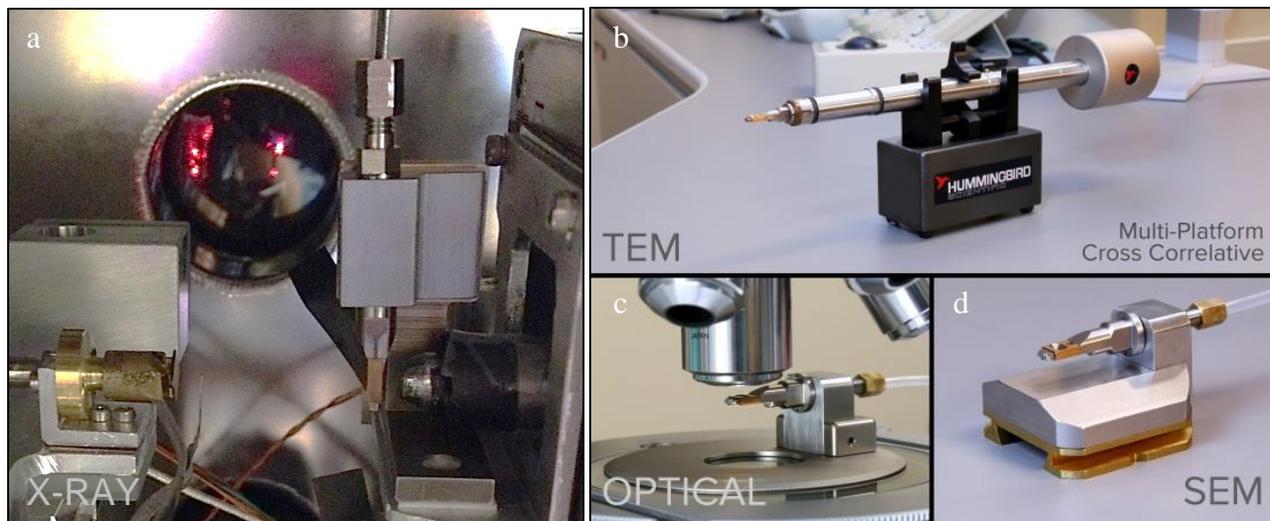


Figure 1. Cross correlative platforms for imaging electrochemistry experiments in (a) LBNL Beamline 11.0.2, (b) a JEOL TEM, (c) an optical (or Raman) microscope, and (d) a JEOL SEM.

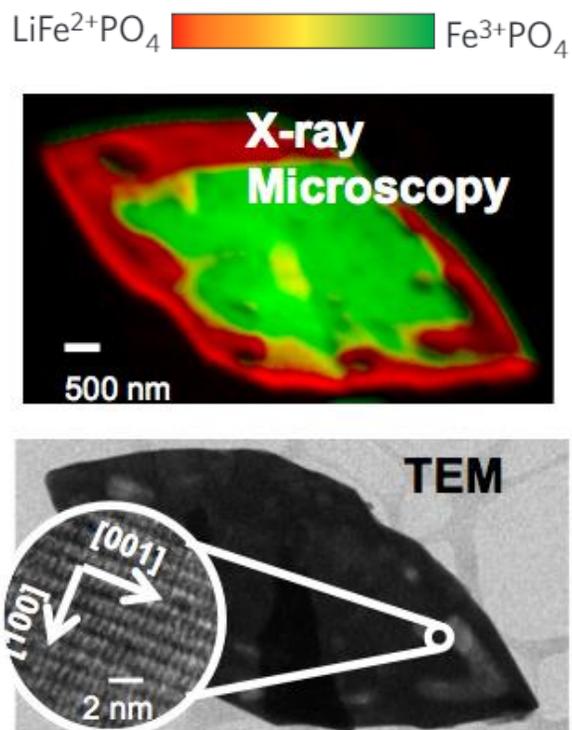


Figure 2. A single lithium iron phosphate particle showing (top) a snapshot state of charge map during cycling in the LBNL STXM beamline 11.0.2 and (bottom) an atomic resolution TEM image of particle.