Soft X-ray Scanning Transmission Microscopes (STXMs) at the ALS

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Transmission X-ray Microscope – best tool for soft x-ray spectroscopy

\[ I = I_0 e^{-\rho \mu d} \]

Can be measured at the same way as the \( I \)

Spectra from line scan

Spectra from 150 individual images (stack analysis)

Fig. 3.6 Point spectra of multiple regions of Dow#355 sample, recorded simultaneously. (left) location of points. (right) spectra derived from point signals and hole signal (out of image range) recorded at same
Scanning Transmission Soft X-ray Microscopy

![Diagram of Scanning Transmission Soft X-ray Microscopy](image)
Soft X-ray Spectromicroscopy summary

Soft X-ray spectroscopy has high chemical sensitivity. Combined with a microscope, it provides high chemical sensitivity on a nanoscale. Spectroscopy can be done easier because one can measure $I_0$ at the same time as the absorption.

Current x-ray microscope spatial resolution:
- 10 nm for imaging
- 50 nm for spectroscopy

Ways to improve resolution:
- Improvement of the zone plates - technical limitation
- Laue lenses - difficult to make for soft X-rays
- Combination of the scanning transmission microscope and scanning probe microscope for modification of the X-ray beam shape
- Ptychography (combination of transmission scanning microscope with diffraction) - demonstrated resolution:
  - 2 nm for imaging
  - 5 nm for spectroscopy
Zone plates and working distance

Beam size $d = 1.22 \times \Delta R$

<table>
<thead>
<tr>
<th>$\Delta R$ [nm]</th>
<th>D [µm]</th>
<th>Working distance</th>
<th>Focal length [mm]</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>at 300 eV</td>
<td>300 eV</td>
</tr>
<tr>
<td>45</td>
<td>240</td>
<td>700</td>
<td>2810</td>
</tr>
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<td>25</td>
<td>240</td>
<td>350</td>
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X-ray fluorescence in STXM

Tracking Lithiation in Real Time in Real Battery

Particle-by-particle intercalation pathway

In-Situ STXM environmental cell #2

450°C, 2 bar

Creemer, J. F. et al., Ultramicroscopy 108, 993–998
In situ catalytic reactions

Chemical contour maps of a region of a catalyst particle during the different stages of reaction. A: Before treatment at RT in 1 bar He. B: After 2h in H2 at 350°C. C: After 4h in CO/H2 at 250°C. The corresponding regions of the O K-edge (e, g, i) and Fe L2,3-edge spectra (d, f, h) are indicated in the figures. Dotted lines indicate the linear combination fits, with the bars representing the contribution of the different phases to the spectra.

Frenel zone plate with a central stop beam profile

Focused X-ray beam has a complex beam shape. Up to 50% of the total X-ray intensity is in the area outside the “nominal” beam size.
Ptychography

Sample is scanned in the plane of focused, coherent X-ray beam with steps smaller than the beam size. At each step, a diffraction pattern is recorded. Amplitude and phase shift images of the sample are reconstructed with much higher resolution than the beam size.
The Spatial Resolution of Soft X-ray Microscopy

< 2 nm

2.8 nm lines

Line profiles
2 nm edge

Ptychography at ALS bl 11.0.2
Ptychography

Ptychography – 6 nm resolution for chemical mapping

State-of-Charging Mapping via STXM

Chemical mapping from 3 energy

Chemical mapping from a stack

500 nm
51.3 % SoC

200nm
EELS studies

Characterization of Fly Ash Using STXM

Production of cement is responsible for about 8% of global CO2 emission. If byproduct (fly ash) could be used then the overall negative aspects will be reduced.

**Figure 1**: STXM images of Class F fly ash for Al K-edge taken at (a) 1550 eV; (b) 1570 eV; (c) image map of samples by taking a contrast between (a) and (b); (d) image map of the smaller area shown as a white rectangular region in (c) for spectral analysis.

There is a homogeneous oxidation and coordination state of Al as shown in Al K-edge NEXAFS spectra with heterogeneity in its spatial distribution. Si and Al are spatially correlated at nanometer scale in which high concentrations of Si and Al were concurrently and consistently observed within the 30 nm resolution. However, Fe distribution did not show any specific correlation to Al and Si and mostly oxidized form of Fe based on Fe LII,III-edge NEXAFS spectra. Unlike Al and Fe where no variation in chemical oxidation and coordination was observed, Si showed spatial inter- and intraparticle variations in polymerization.
STXM studies of Li batteries

Li ions from the liquid electrolyte insert into solid host particles in the electrode. Nanoscale intraparticle electrochemical inhomogeneities in phase and in composition are responsible for mechanical strain and fracture which decrease the reversibility of the reaction. Moreover, these nonuniformities make it difficult to correlate current-voltage measurements to microscopic ion insertion mechanisms but quantifying nonuniform nanoscale reaction kinetics and the underlying material composition at the solid-liquid interface holds the key to improving device performance.

A gold standard material for investigating ion insertion reactions is Li$_x$FePO$_4$ (0<X<1), which separates into two phases at equilibrium. Recent studies using in situ X-ray diffraction observed a continuous distribution of lattice constants at high rates of (de)lithiation. Precise quantification of the Li composition (X) is difficult because the lattice constant change convolves information from both Li composition and mechanical strain. Whereas heterogeneous current distributions between particles have been studied, there exists little understanding of how compositional nonuniformities evolve within individual particles.

In Li$_x$FePO$_4$, an insertion reaction changes X as well as the valence of Fe. Thus, tracking the spatial and temporal evolution of the Fe oxidation state reveals both the composition and the nanoscale insertion rate. Scanning electrochemical microscopy provides quantitative current/voltage measurement but is insensitive to the Li composition. Redox-sensitive liquid microscopy techniques such as transmission hard X-ray microscopy, fluorescence soft X-ray microscopy and transmission electron microscopy (TEM) have been employed to track Li transport with single-particle sensitivity in insertion electrodes. However, tracking the spatial evolution of lithiation within the same particles under multiple electrochemical conditions in liquid has not been realized due to insufficient spatial/temporal resolution, high beam-induced damage, and/or low absorption contrast.

Here comes STXM
Operando Study of $\text{Li}_x\text{FePO}_4$

Frames from operando charging and discharging

Fig. 2. Representative operando frames of Li insertion and extraction. (A) Operando Li composition frames of a single particle over multiple lithiation and delithiation cycles. The hue represents the Li composition (green, x = 0; red, x = 1). (B and C) Representative frames of different particles taken at various lithiation and delithiation rates, respectively. (D) Ex situ frames of Li composition for relaxed particles, showing the equilibrium distribution of Li within particles. Because the particle loading on the electrode is low, each acquired image typically contains a single particle, and this figure assembles multiple images together. Numbers below each frame indicate the time in minutes (white) and the C rate (yellow; see supplementary text for calculation protocol). t = 0 is defined as the starting time of the (de)lithiation cycle.
Determining the Li composition at each pixel: The composition is determined by solving the following matrix equation, consistent with previous work (20):

\[
\begin{bmatrix}
S_{706} \\
S_{713}
\end{bmatrix} = \begin{bmatrix}
LFP_{706} & FP_{706} \\
LFP_{713} & FP_{713}
\end{bmatrix} \begin{bmatrix}
\alpha \\
\beta
\end{bmatrix}
\]

(S2)

Here, \(S_{707}\) and \(S_{712}\) are the optical densities of each pixel at 706 and 713 eV, minus the OD at 703 eV. \(a\) and \(b\) represent the LiFePO\(_4\) and FePO\(_4\) statefractions. To solve the Li composition (X in Li\(_x\)FePO\(_4\)) we used the following equation:

\[
X = \frac{a}{a + b}
\]

(S3)
Identification of domains in Li composition

Fig. 3. Identification of domains in Li composition. (A) Line cuts of Li composition ($x$) of the same particles under different cycling conditions. The same pixels in a particle were sampled. (B) Line cuts of the relaxed, phase-separated particles. (C) The fast domains, outlined in blue, do not substantially grow in size. (D) Current density quantification reveals regions of higher insertion kinetics, calculated from delithiation. The same fast domains are present in both charge and discharge. (E) The uniformity coefficient increases with cycling rate and is consistently higher for lithiation than for delithiation. This was calculated from the standard deviation of $x$ in each frame of a particle, where higher standard deviation indicates lower uniformity (see fig. S14). A coefficient of 0 indicates a binary distribution in the phase separation limit, whereas a coefficient of 1 indicates the uniform solid-solution limit. The value in parentheses indicates the number of particles analyzed under that condition. (F) Scheme of the insertion pathway as a function of the lithiation rate.
3D localization in Li$_x$FePO$_4$

Figure 4| Representative three dimensional (3D) chemical phase distribution of individual particle. a,d,g, Front (left) and backside (right) views of isosurface of three chemical components. Cross-sectional views along the thickness direction (b, e, h) and along the large face (c, f, i), respectively. The cross-section planes are indicated as magenta and cyan colored boxes in 3D isosurface plots. The red, green, and blue indicate LFP-rich, mixed, and FP-rich voxels, respectively. The positions of each particle are noted as (I), (II), and (III) in Fig. 3a for (a), (d) and (g), respectively.
Spatial heterogeneities in reaction rates account for the compositionally nonuniform solid-solution domains during (de)lithiation of LixFePO4, and that the skewed current density to composition relationship amplifies reaction heterogeneities during delithiation but suppresses them during lithiation, consistent with theoretical predictions. These results highlight the crucial role of surface reaction rate in lithiation, with implications for electrode engineering and battery management. Higher rates of lithiation suppress compositional nonuniformities within particles and minimize mechanical stress, and have been shown to improve cyclability. However, the same statement is not true for delithiation, where reaction heterogeneities manifest as compositional nonuniformities.
Tantalum oxide memristors are frontrunners for next generation memory technology due to their promise of long endurance, long retention, and low power. Recent efforts to uncover the nanophysics behind resistance switching in tantalum oxide and several related materials suggest local conductive channel formation by oxygen ion migration as the mechanism of operation.
Spectro-pychography of a PEM-FC cathode

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GOALS: 
(1) explore spatial resolution improvements using ptychography 
(2) determine if F 1s signal in cathode (ionomer) can be measured using ptychography

EXPERIMENTAL: AFCC sample A (from fall 2010) used. Microtomed sections were made in Aug 2011.

RESULTS:

CONCLUSION: F-mapping CAN be done with ptychography with not much more damage than regular STXM
Cement – Calcium Silicate Hydrate

Fig. 1. STXM and soft X-ray ptychographic image of 17 d hydrated C₃S. (a) single image taken at 1840 eV, (b) image contrast map (Ca), (c) image contrast map (O), (d) image contrast map (Si) (C: core and Op: outer product C–S–H), (e) RGB overlay maps using SVD based on the NEXAFS spectra obtained from the Op C–S–H and core area marked in (c) (Op: outer product C–S–H and CH: Ca(OH)₂), (f) ptychographic image, and (g) O K edge NEXAFS spectra from the selected area in (c).
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Conclusions

- Strong side of using soft X-rays – chemical information – spectroscopy on < 100 nm scale, especially good for C, N, O
- Relatively low radiation damage
- In-situ measurements
  - Many different environmental cells are used
  - In STXM – temperature 450 °C and 2 bar pressure
  - Working electrochemical cell
  - Working batteries (using fluorescence yield)
- Ptychography – a new method allowing to use zone plates with much larger working distances. Much better spatial resolution (demonstrated 2 nm – potentially diffraction limited, C 4 nm, Mg 1 nm).