Operando X-ray based Diagnostics in Energy Storage

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How Did we get Here?

IBM Almaden
…, batteries

SLAC
…, batteries

Ca 2002
• Length and Time Scales
  - Diagnostic Tools Development
• **LiS**: spectroscopic imaging of cathode, electrolyte, anode
• SEI composition and formation
  - **Si(100) model electrodes** – high resolution thickness
  - **Li metal anodes** – composition and mapping
• Summary
Operando Characterization: many size scales

- observe and evaluate batteries during operation
- *operando*, real time & realistic conditions
- many size scales – electrode -> particles -> atomic

Energy Storage Landscape at SSRL

**Model Systems**
- Electrolyte layering
- Li ion diffusion
- SEI @ Si single crystal
- Reactions at epitaxial thin film electrodes
- Chemical imaging SEI

**Operational Half Cells**
- LiS chemical imaging
- Ge & Si anode imaging
- Li-excess oxides
- Li/solid-electrolyte interface

**Commercial Cells**
- Failure modes in 18650 cells
- Validation of BMS
Operando Methodology

Operando Battery Cell – follow structural & morphological changes:
• *In situ*, in real time (slow: mins -> hours)
• X-ray “transparent” cell

Electrochemistry in coin cells vs. pouch cells

[1C charge for 0.4Li extraction - 1C discharge to 2.0 V (fully discharge)] x 2 cycles

LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$

1C = 278 mA g$^{-1}$

CR2032@lab

Pouch cell@11-3

Jihyun Hong

Chris Takacs
Outline

• Length and Time Scales
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• **LiS:** spectroscopic imaging of cathode, electrolyte, anode
• SEI composition and formation
  ➢ **Si(100) model electrodes** – high resolution thickness
  ➢ **Li metal anodes** – composition and mapping
Objectives – mapping Sulfur speciation in LiS

- **Goal**: understand mechanisms of operation and failure
- **Approach**: obtain a spatially-resolved picture of sulfur species during operation

- **X-ray absorption spectroscopy**:  
  - sulfur species at different states of charge  
  - Spatially resolve sulfur distribution across the electrolyte and electrodes

\[ S_8 + 16Li \rightarrow 8Li_2S \]
**Operando Cell Design & Chemistry**

- **Electrolyte**: 1 M LiClO$_4$ + 0.2 M LiNO$_3$ in 1:1 DOL:DME
- **Cathode**: 64 wt% Sulfur + 26 wt% carbon nanotubes/Super P carbon + 10 wt% poly(ethylene oxide)/bis(trifluoromethane)sulfonimide (PEO$_{10}$LiTFSI)
- **Anode**: Li foil
- **Separator**: Glass microfiber
- “tender” X-ray microprobe
  - 5 µm spot size
  - He environment
Multi-Energy Mapping of X-ray Absorption Near-Edge Structure (XANES)

![Graph showing normalized absorption vs. energy (eV)]

- $S_x^2$ at 2470.3 eV
- $S_8$ at 2472.6 eV
- $Li_2S$ at 2477.5 eV
- $SO_4^{2-}$ at 2480.6 eV
- “total sulfur” at 2500 eV

*Sulfur atom environment*

<table>
<thead>
<tr>
<th>Sulfide/Polysulfide</th>
<th>2/-1-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfoxide</td>
<td>2+</td>
</tr>
<tr>
<td>Sulfone, Sulfite</td>
<td>4+</td>
</tr>
<tr>
<td>Sulfate</td>
<td>6+</td>
</tr>
</tbody>
</table>

Operando Cell  Electrochemistry & Mapping Time Points

Charge/Discharge Current = 0.38 mA/cm² (nominal C/20)

Total cycling time = 24 h
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Total cycling time = 24 h
Polysulfide Maps – 2470.35 eV

- PS increases w/ discharge, decreases w/charge
  - PS area expands → some PS conversion is irreversible
- Discontinuities → changes faster than time resolution
Elemental Sulfur Maps – 2472.6 eV

- Sulfur intensity decreases with discharge, increases with charge
- Changes throughout electrode
- Discontinuities -> structural changes throughout the electrode & then recovered on charge
Sulfate/Sulfonimide Maps (LiTFSI) – 2480.6 eV

- LiTFSI does not change significantly until charge intensity changes.
- Intensity changes -> binder participates in electrochemical processes.
Electrode structure dramatically changed
PS intensity decreased but area remains expanded → shuttle?
Sulfur & LiTFSI structure compromised → connect to capacity loss
Summary – mapping Sulfur speciation in LiS

Summary

- Changes in sulfur speciation & location
- Evolution of the sulfur structure at the interface & within the electrode with cycling time

Future Directions

- New operando cell design
- Focus on electrolyte/electrode interface
- Quantitatively analyze maps for sulfur species concentrations
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Solid Electrolyte Interphase (SEI) on Si

- Reaction layer formed with electrolyte
- Loss of Li; Columbic inefficiency
- Complicated and not well understood

- Nucleation: SEI formation at the beginning of initial discharge
- Composition:
  - Inhomogeneous; varies with electrolyte
  - two separate layers - an inorganic inner layer & covering layer of organics
- Thickness:
  - Varies with electrolyte and Si surface
  - SEI thickness - 2 and 170 nm
X-ray Reflectivity (XRR): surface-sensitive technique to characterize surfaces, thin films and multilayers.

\[ \theta_i = \theta_r = \theta \]

\[ q_z = k_r - k_i = \frac{4\pi}{\lambda} \sin \theta \]

\[ R(q_z) = \frac{I(\theta)}{I_0} \]

In-situ XRR measured at 12 keV, SSRL BL 2-1
In-situ Cell

in-situ electrochemistry cell for XRR experiments:

1. Li foil electrode
2. Si wafer electrode
3. Screw (also acts as current collector)
4. PEEK frame
5. Gasket
6. Kapton window
7. Stainless Steel Frame

Cao, Toney et al., NanoLetters, 16, 7394–7401 2016
Experimental Methods

- **Half Cell configuration:**
  - Working electrode: n-type Si wafer, resistivity = 0.001-0.005 Ω·cm, Cu film evaporated on back
  - Counter electrode: Li metal
  - Electrolyte: 1 M LiPF₆ in ethylene carbonate (EC) & dimethyl carbonate (DMC) (1:1 by wt)

- **Galvanostatic cycling**

- **in-situ XRR data on:**
  - (100) oriented Si: 25, 50 and 100 μA/cm²
  - Si orientations (100), (110) & (111) at 50 μA/cm²
  - 3- 5 minutes per XRR scan

**first cycle lithiation of Si (100), current density = 25 μA/cm².**

About C/4: discharge in 4 hours

Cao, et al., NanoLetters, 16, 7394–7401 2016
Lithiation process: 1. $E_{\text{we}} \approx 0.6V$

1. $E_{\text{we}} \approx 0.6V$: SEI starts to grow
Lithiation process: 2. Ewe < 0.6V to the initial plateau

1. Ewe ≈ 0.6V: SEI starts to grow
2. Ewe < 0.6V to plateau:
   - Lithiation of oxide -> Li-silicate & Li$_x$Si
   - Li$^+$ diffusion into bulk Si

\[ \frac{Z}{2}SiO_2 + yLi^+ + ye^- \rightarrow Li_ySiO_z + \left(\frac{Z}{2} - 1\right)Si \]

\[ \left(\frac{Z}{2} - 1\right)(Si + xLi^+ + xe^-) \rightarrow \left(\frac{Z}{2} - 1\right)Li_xSi \]
In-situ XRR data on Si (100), 25 μA/cm², first lithiation process

Cao, et al., NanoLetters, 16, 7394–7401 2016
SEI layer properties

**SEI – inner part**
- thickness increases: 10 Å -> 80 Å
- electron density starts high, decreases to ≈0.42 e/Å³.

**Graphs and Diagrams**
- **Thickness (D)** vs. charge (µAh/cm²)
- **Density (ρ)** vs. charge (µAh/cm²)
- **Roughness (σ)** vs. charge (µAh/cm²)
- **Electrolyte, SEI, Lithiated Si (LiₓSi), Dense Si, Si** layers with `LiₓSi` roughness vs. charge (µAh/cm²)
- **Energy (Eave)** vs. charge (µAh/cm²)
Evolution of the SEI with discharge/charge

Dependence of SEI on cycle:
- Variation in $\rho_{\text{SEI}} \cdot D_{\text{SEI}}$ and $D_{\text{SEI}}$ - periodic
- increases during lithiation & decreases during delithiation.
- “breathing” behavior - similar to neutron reflectivity – organic part of SEI

Li Metal Anodes

- High capacity anode material – large volume changes
- Plating issues: dendrite formation, uneven plating, dead Li
- Potentials outside of the electrolyte stability window -> **Solid-Electrolyte Interphase (SEI) layer**
Coin Cell Cycling for XAS

- X-ray Absorption Spectroscopy
- C, F, O, N edges

Coin cells cycled at 0.5 mA/cm\(^2\) following conditioning cycle at 0.2 mA/cm\(^2\)
- Initially a Li plating of 5 mAh/cm\(^2\) with subsequent half cycles of 3 mAh/cm\(^2\)
- Cells disassembled in glovebox
- Cu electrode removed for analysis
C K-edge

- organic (i.e. $\text{ROCO}_2\text{Li}$) and inorganic (i.e. $\text{Li}_2\text{CO}_3$) carbon containing compounds
- No systematic evolution in half cycles.
Ex-situ X-ray Absorption Spectroscopy: identification of SEI components

- SEI components develop over time,
- differ after stripping and plating cycles, either due to redox of existing SEI or half cycle dependent decomposition of electrolyte components
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www-ssrl.slac.stanford.edu/toneygroup/