Probing Structure-Property Relationship of Energy Storage Materials Using Ex Situ and In Situ Dynamic Microscopy and Spectroscopy with High Spatial and Fast Temporal Resolution

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Purpose

- Establish structure-property relationship of energy storage materials and its correlation with charge and ion transport
- Search for a general guiding principle for accelerated discovery of new materials for high-density and high-power energy application
- Develop capabilities that drive chemical imaging and spectroscopic analysis of materials under ex situ and in situ conditions with high-spatial and fast-temporal resolution

Expected Outcomes

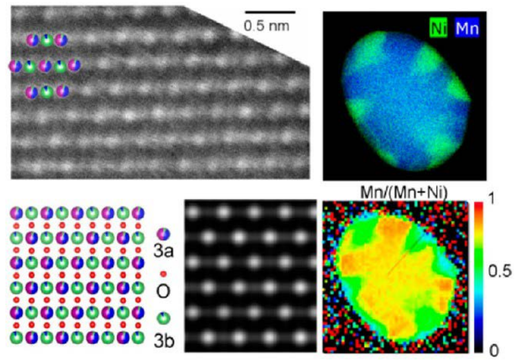
- Scientific understanding of the mechanisms responsible for capacity fading and power—new energy storage materials development
- Fundamental electrochemistry (e.g., reversibility) of Li-S and Li-air battery materials
- Fundamental insights relating structure-property relationship of energy materials with lattice dynamics and electronic structure

Key Successes

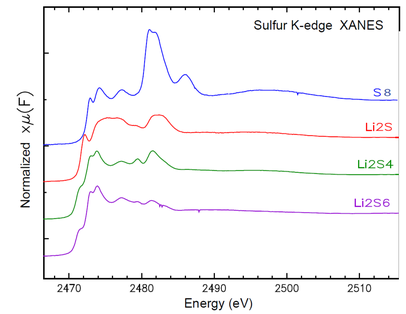
- Initiated fundamental concept for in situ atomic-level structure and chemical imaging
- Vitalized field of in situ imaging of structure and chemistry of energy storage materials
- Paved critical path for chemical imaging of energy material, including characterization tasks of Joint Center for Energy Storage Research (JCESR)

Research Accomplishments

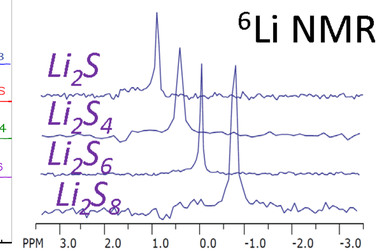
Atomic-level structure and chemistry of electrode materials for Li-ion battery



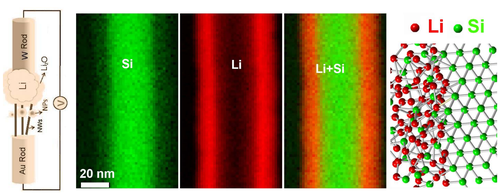
Scanning transmission electron microscopy-high-angle annular dark field (STEM-HAADF) images and energy dispersive spectrometry (EDS) maps revealing nanoscale chemical inhomogeneity in $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (Gu M et al. 2013. *ACS Nano* 7: 760-767)



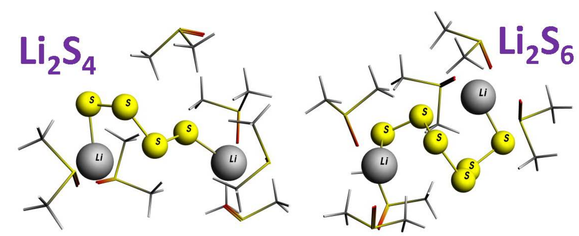
X-ray absorption near edge structure (XANES) of S with different polysulfide



Nuclear magnetic resonance (NMR) spectra of ^6Li with different polysulfide



Electron energy loss spectroscopy (EELS) mapping reveals chemical evolution of Si anode materials (Wang C et al., under review)



- Multiple lithium polysulfide (Li_2S_n, $1 \leq n \leq 8$) formation under battery cycling conditions
- XANES, NMR, and computational studies of solvation, solubility, and diffusivity of polysulfide in polar electrolyte molecules
- Knowledge gained will significantly advance the ability to design optimal electrolyte for high-energy-density Li-S battery technology

- Combining in situ TEM, STEM-EELS, and computational calculation to determine structural and chemical information of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ and phase transformation
- Scientific understanding of the bottleneck in charge/discharge rate and voltage fading of Li-ion battery

References and outcomes

- Gu M et al. 2013. *ACS Nano* 7:760-767
- McDowell MT et al. 2013. *Nano Letters* 13:758-764
- Genc A et al. 2013. *Ultramicroscopy* 131:24-32
- Gu M et al. 2013. *Chemistry of Materials* 25:2319-2236
- Gu M et al. 2012. *ACS Nano* 6:8439-8447
- Gu M et al. 2012. *Nano Letters* 12:5186-5191

Next Steps

Scientific research

- Develop liquid cell-based electrochemical station
- Integrate scanning transmission X-ray microscopy (STXM) and XRT ability with ex situ, in situ TEM, STEM, and dynamic TEM (DTEM) to image hierarchical nanostructures in Li-S and Li-air battery system
- Tackle the dynamics of solid electrolyte interface layer, its formation, structure, chemical composition
- Obtain DTEM images and diffraction for in situ electrochemical cell with fast temporal resolution

Programmatic development

- JCESR
- Batteries for Advanced Transportation Technologies (BATT) funding to probe battery failure mechanism
- BES proposal on atomic-level imaging of energy materials
- BES white paper on ionic transport in solid