# In-situ Studies of Electrochemical Energy Storage at the APS

## X-Ray Science Division (XSD)

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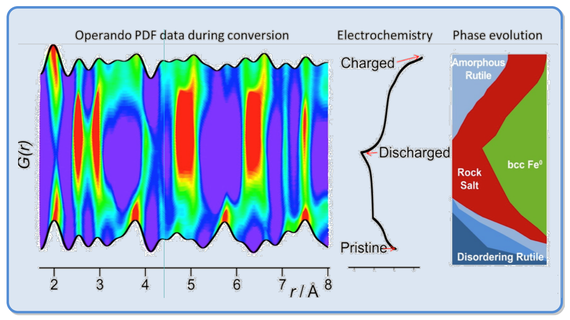
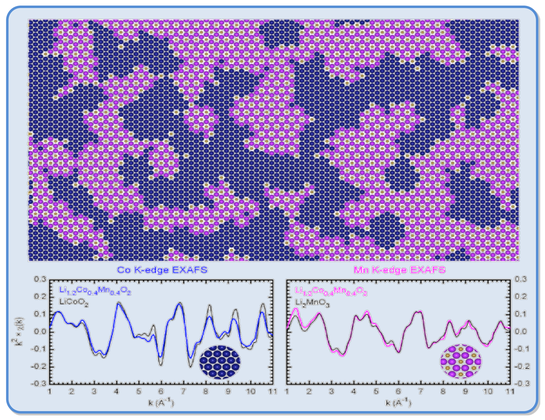
### In-Situ Structural Characterization Tools for Energy Storage at the Advanced Photon Source (APS)

The development of new technologies for electrical energy storage is a critical to our national energy infrastructure spanning grid-based applications (for continuous wind and solar energy), electric vehicles for transportation and personal electronic devices. Operation of these electrical energy storage devices is governed by phenomena that span multiple length and time scales. Incisive characterization tools are essential to advance our fundamental understanding of these phenomena and how they impact performance. Gaps exist in our understanding of charge transfer, mass transport, and structural changes that impedes the rational optimization of capacity, charge rate, lifetime, and safety. The X-ray Science Division utilizes the unique characteristics of the Advanced Photon Source to penetrate the complex multicomponent device architectures to resolve their function in both time and space, to develop fast time-resolved measurements that match the timescales of processes relevant to chemical energy storage from charge transfer (fs-ps), to ions hopping on and off surfaces (ps), to diffusion (ms), to structural transitions and grain fracturing (s-min), to cell failure (hr-year).

### Local Structure (PDF & XAS)

Increasingly complex materials such as Fe conversion electrodes are promising candidates for new battery electrodes that provide the best compromise between capacity and stability. This work by APS researchers *(Wiaderek et.al.)* uses Pair Distribution Function (PDF) analysis of in-operando X-ray scattering to probe the average Fe-O/F bond distances to study how phases and chemical composition evolve during the electrochemical reaction. The resulting map of phase evolution reveals the mechanisms responsible for improved electrochemical performance



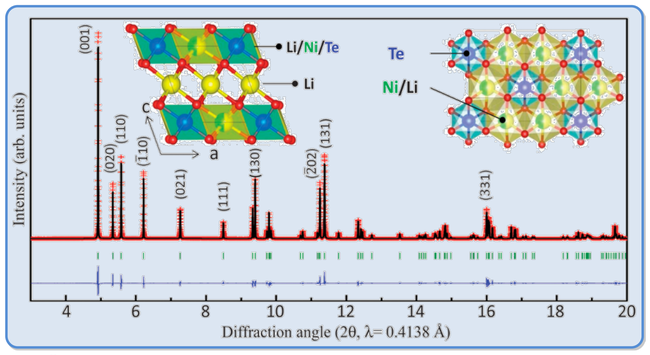

Li-ion based materials are critical to recent advances in batteries for vehicular applications, but new breakthroughs are needed to further scale up this energy storage technology. Using X-ray core-shell absorption spectroscopy (XAS) methods, researchers at the APS can capture the intricate details of the electronic structure as well as the element specific local structure of Li-ion based systems. *(Bareno et.al.)* This insight is key to understanding structure-property correlations and developing new novel materials with high capacities and stable crystal structures.

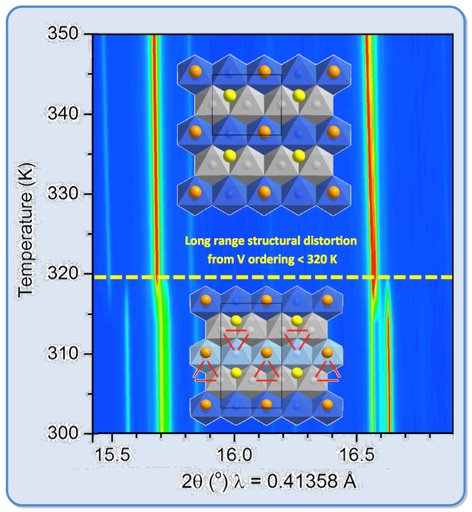
#### References

Bareno, Balasubramanain and Abraham et al., Chem. Mater. 23 (8), 2039 (2011)
Wiaderek, Borkiewicz, Castillo-Martínez, Robert, Pereira, Amatucci, Grey, Chupas, Chapman. J. Am. Chem. Soc. 4070-4078 (2013)

### Extended Structure (Powder Diffraction)

The connection between structure and property functionality also depends critically on long-range chemical order. At the APS, powder diffraction is used to understand the crystallography of new energy materials. Analysis of high resolution powder diffraction revealed how ~2 Li ions per unit cell move within the $Li_4NiTeO_6$ structure during cycling *(Sathiya et.al.)*. This could release/uptake twice the charge of a traditional $Li_2MO_3$ battery material. Beyond Li, researchers are using in-situ powder diffraction at the APS to explore $NaVO_x$ based materials *(Guignard et.al.)* for future battery technologies.



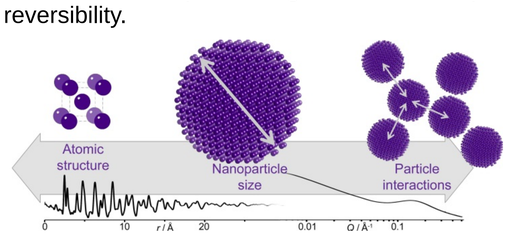

Expedited structural understanding of newly discovered materials is critical to current research on energy storage systems. This is facilitated by a successful rapid access mail-in service for high resolution powder diffraction measurements offered by the APS.

#### References

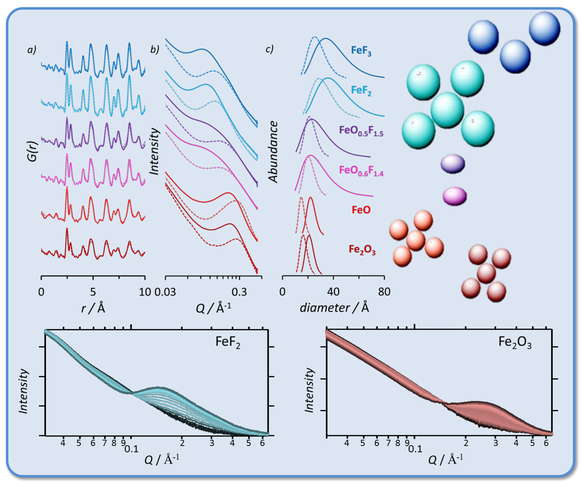
Sathiya, Tarascon et. al., Li4NiTeO6 as a positive electrode for Li-ion batteries. Chem. Commun. 11376-11378 (2013)
Guignard, Suchomel, Delmas et al. Vanadium Clustering/Declustering in P2–Na1/2VO2 Layered Oxide. Chem Mater, 26, 1538–1548 (2014)

### Mesoscale Structure (SAXS)

Batteries are intricate multicomponent devices in which the mesoscale structure and chemistry of different components, and of their interactions, drives functionality and performance. For example, nanostructuring of the composite electrodes provides bi-continuous electrically and ionicly conductive paths essential to electron/ion transport, while excessive nanoparticle growth can impair reversibility.




In this example *(Wiaderek et.al.)* complementary small angle X-ray scattering (SAXS) and pair distribution function (PDF) data revealed that anion chemistry of the initial electrode governs mesoscale structure of Fe nanoparticles during



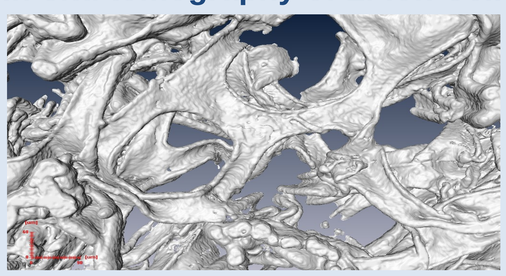

electrochemical conversion by influencing defect formation, annealing, atomic mobility, and particle growth rates. In F-rich environment, Fe atoms have enhanced mobility, leading to more facile annealing and particle growth. In an oxygen-rich environment, more defects are formed and defect annealing occurs in preference to growth.

#### References

Wiaderek, Borkiewicz, Pereira, Ilavsky, Amatucci, Chupas, Chapman. "Mesoscale effects in electrochemical conversion of iron-based electrodes" (Submitted, 2014)

### X-ray Imaging, Tomography, and Microspectroscopy

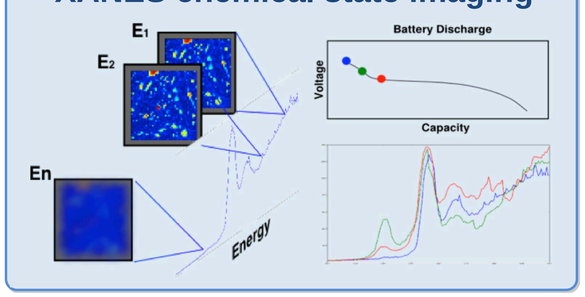
#### In-situ tomography of Li-ion Cell



During the electrochemical cycle of battery cells, APS researchers exploit in-situ X-ray Absorption Near Edge Structure (XANES) to construct spatially resolved maps of the sulfur electronic state in a cathode *(Vogt et.al.)*. This data is analyzed to produce maps of the chemical speciation in the cathode as a function of charge and discharge. These detailed maps provide insight into common limitations of Li-S batteries such as short cycling lifetime and capacity fading and help to guide development of new energy storage materials.

Synchrotron microtomography at the APS can be used to understand the in-situ 3D structure of microporous composite Cu:Sn electrodes. This allows researchers to track changes in the topological structure of the electrode and calculate the surface/volume ratio evolution throughout cycling *(Xiao et.al.)*. Such information is not only helpful for improving the engineering of the 3D microporous composite anodes but it also offers critical insights into the structure-activity relationships of high-capacity porous materials within operating electrochemical energy storage devices.

#### XANES chemical state imaging




#### References

Xiao et.al., J. Mater. Res., Vol. 28, p 2444 (2013)
Vogt et.al., Microscopy and Microanalysis, pp 1614-1615 (2012)

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