ALS SCIENCE HIGHLIGHT

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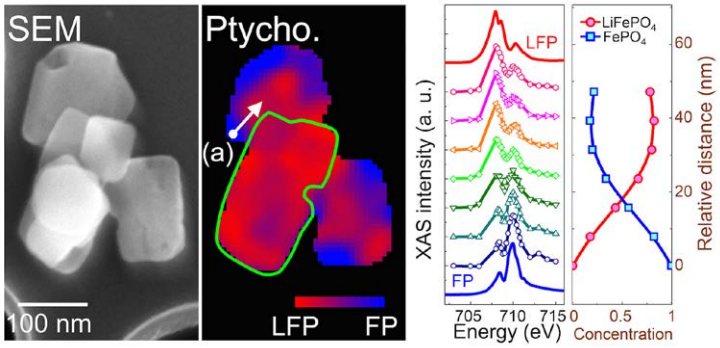
# X-Ray Microscopy Reveals How Crystal Mechanics Drive Battery Performance

Rechargeable lithium-ion batteries power most portable electronics and are becoming more widely used in large-scale applications like electric vehicles. Scientists have long observed that lithium iron phosphate nanoparticles are one of the best performing battery electrode materials, able to repeatedly charge and discharge in an extremely reversible manner, but the precise mechanism responsible for their performance has remained unclear. By using a powerful suite of imaging tools, a team of scientists at the ALS, the University of Illinois at Chicago (UIC), and the NorthEast Center for Chemical Energy Storage has revealed a relationship between the chemical processes that drive a battery's operation and the mechanical degradation of the electrode material. Their findings show that small crystal size is key to maintaining mechanical stability upon cycling, and establish soft x-ray ptychography as an essential tool for studying chemical states in nanoparticles.

Batteries operate through the movement of charged particles between two electrode materials. In the case of lithium-ion batteries, the electrodes are typically made of graphite for the anode and a compound like lithium iron phosphate ($LiFePO_4$) for the cathode. As the battery charges, lithium ions and electrons move from the $LiFePO_4$ to the graphite—a process called delithiation. The process must reverse during discharge to ensure long battery life. As the battery discharges and recharges, the electrodes' crystal lattices expand and shrink in response to the gain and loss of ions, creating strain in the structure that fatigues, and ultimately fractures, the material. To determine precisely how the evolution of composition and microstructure varies with crystal size and shape requires spatial and chemical resolution at the nanoscale.




**Morphology (left) and chemical phase maps from ptychographic images (center) of partially delithiated $LiFePO_4$. Fe $L_3$ x-ray absorption spectra (right) were collected along the paths defined by white arrow. Chemical concentration profiles of $LiPO_4$ (LFP) and $FePO_4$ (FP), obtained by linear-combination fits of the spectra, and their relative positions are presented in the adjacent panel.**

Ptychography uses a combination of multiple coherent diffraction measurements to construct 2D or 3D spatial maps with high resolution and chemical sensitivity. Because of the sensitivity of soft x-rays to electronic states, they can be used in ptychography to image chemical phase transformations and the resulting mechanical consequences. The ability to map these changes at the required nanoscale resolution without damaging the sample material is a capability unique to the ALS.

After synthesizing and partially delithiating $LiFePO_4$ crystals of different sizes, ALS and UIC researchers used soft

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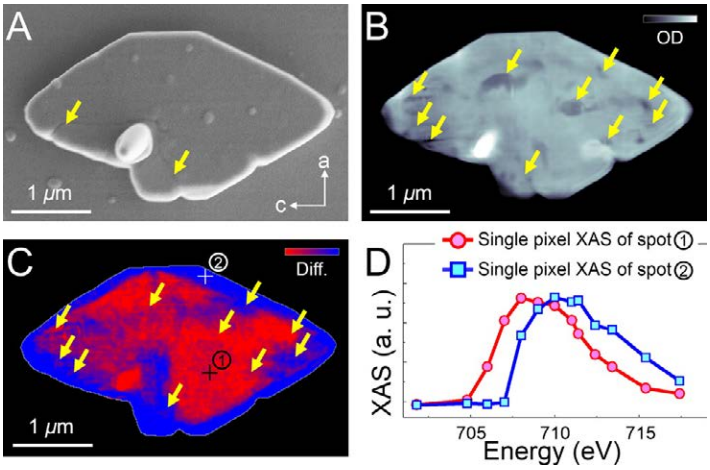
## Taking Ptychography to a New Dimension

The ability to use soft x-rays to create high-resolution chemical maps of nanomaterials is not only important for understanding battery cathode materials like $LiFePO_4$—it opens up possibilities for improving other nanomaterials, as well. These might include nanocatalysts designed to more quickly and efficiently drive chemical reactions, or magnetic nanostructures that could make computers faster.

Before exploring additional types of materials, ALS scientists David Shapiro and Young-Sang Yu of the Experimental Systems Group microscopy team are taking their 3D ptychography capabilities to the next level—4D! By adopting computed tomographic (CT) methods—the same technology used for medical scans of your body—the researchers can expand from one chemical phase dimension (e.g., represented by color) plus two spatial dimensions (i.e. length and width), to include an additional spatial dimension (i.e. depth), ultimately creating a 4D map of chemical information at a resolution of 10 nm.

What would a 4D map look like? The images included here show multiple crystals stacked on top of one another. The overlap makes it hard to distinguish which chemical information comes from which crystal. Examining the third spatial dimension and combining it with the other data creates a complete picture of a complex material's composition. To appreciate the final chemical map, just don your 3D glasses or look at a holographic projection.




**(A) Scanning electron microscopy image and (B) optical density (OD) map obtained by ptychographic microscopy of a micron-sized, partially delithiated crystal. The darker areas in the crystals (indicated by yellow arrows) indicate regions of lower density, which occur as expected near surface cracks but are also present due to internal defects (cracks and voids). (C) Difference map between ptychographic microscopy images collected at 708 and 710 eV. The red and blue areas indicate the highest content of $LiFePO_4$ and $FePO_4$, respectively. Defect positions, which are confirmed by the OD map in (B), are also identified by yellow arrows. (D) Selected single pixel x-ray absorption spectra (XAS) from spots 1 and 2 in C, which, though saturated owing to sample thickness, clearly indicate the presence of two chemical components.**

x-ray ptychographic microscopy, combined with x-ray absorption spectroscopy and electron microscopy, to map chemical and structural changes in the micro- and nanocrystals during the delithiation process. Ptychography measurements were recorded with the STXM instruments at ALS Beamlines 11.0.2 and 5.3.2.1.

The results showed that all sizes of partially delithiated crystals contained two phases—the original $LiFePO_4$ and its delithiated state, $FePO_4$. The high resolution of the imaging technique also allowed the team to see the location of undesirable cracks in the crystal structure that can degrade the material's performance as an electrode. They found that the defects tended to be located along the interface where the two phases meet, which is also where the crystal structure experiences the most strain as lattices of different sizes attempt to match up. More significantly, the team found that the larger microcrystals were severely fractured, whereas the nanocrystals had no mechanical damage, which is consistent with the prediction that the number of potential defects in a crystal decreases significantly with a reduction in its size.

The findings indicate that mechanics are a principal driver in the outstanding electrode performance of $LiFePO_4$ nanoparticles. They also demonstrate the importance of carefully controlling morphological and chemical characteristics of electrode materials in next-generation electrical energy storage systems, which will help achieve theoretical limits of energy density and battery lifetime.