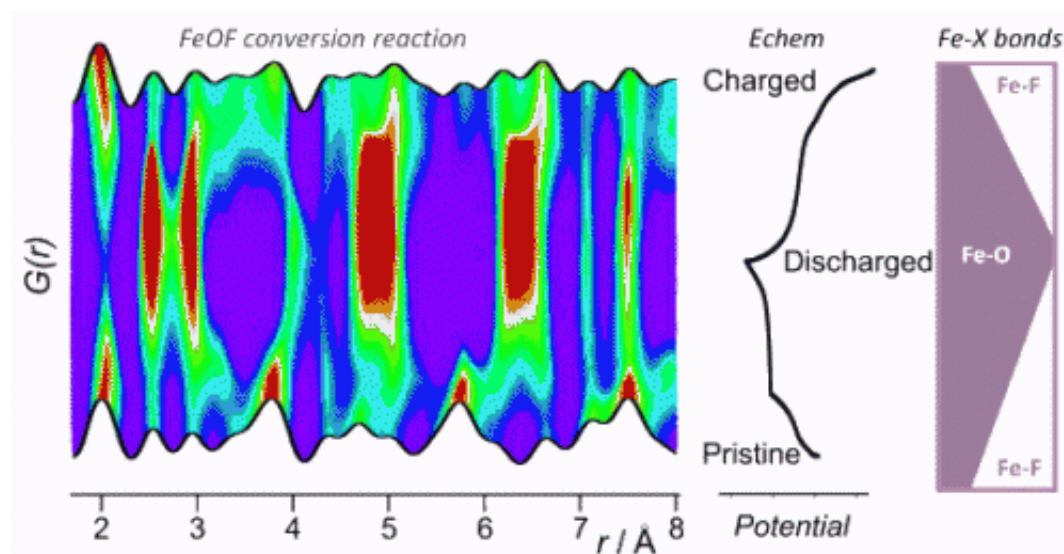


The superpower behind iron oxyfluoride battery electrodes

April 5 2013, by Vic Comello



Structural changes probed using operando PDF analysis indicates a partitioning of a FeOF-based electrode into fluorine- and oxygen-rich phases with different reactivity for each component.

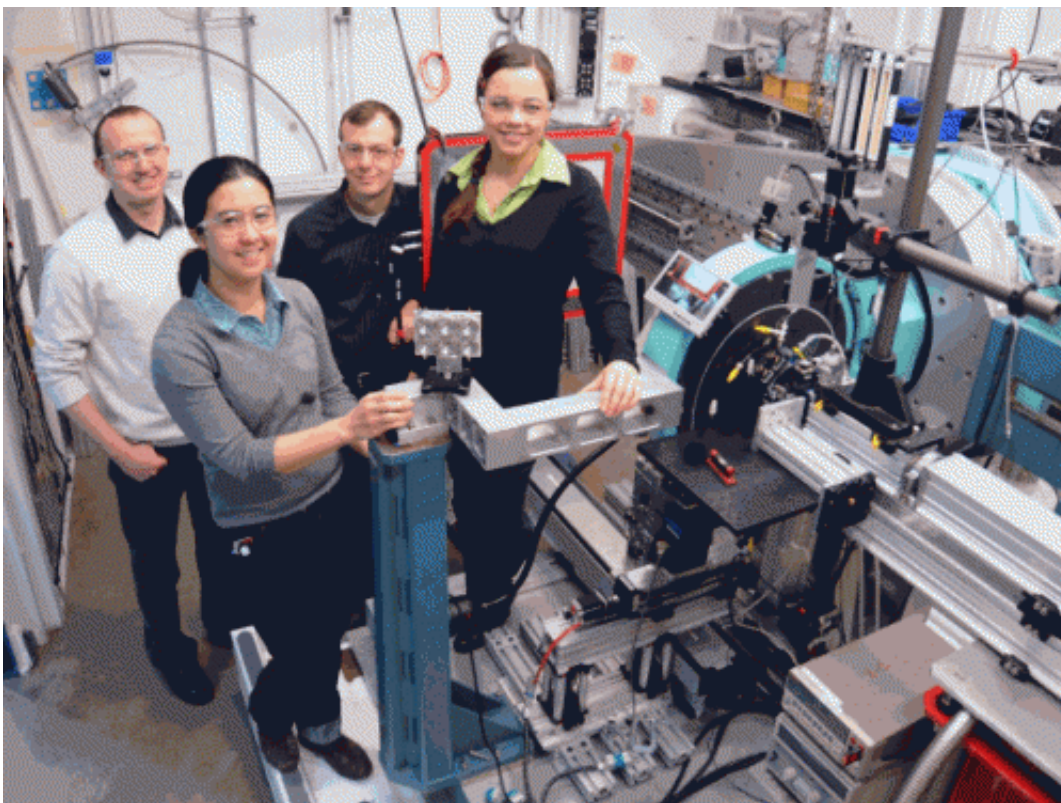
(Phys.org) —Innovative materials chemistries continue to drive advances in lithium-ion batteries-the state-of-the-art in rechargeable energy storage. While many different battery components contribute to their performance, the largest gains may be achieved through the development of new electrode materials that can power portable electronics longer and propel electronic vehicles farther. Electrodes based on so-called "conversion chemistry" have the potential to double energy storage capacities compared to electrodes in existing rechargeable batteries. This

higher energy storage capacity is achieved because each metal atom can react with several electrons in conversion systems, compared to the single electron limit of conventional electrodes. Although these new materials initially deliver higher capacities, their capacities often diminish with repeated charging and discharging. Nevertheless, unusually good long-term performances, with consistently high capacities, have been found with mixed-anion systems such as oxyfluorides. Although they combine the favorable performance characteristics of simple oxides and fluorides, the electrochemical reactions giving rise to the improved performance of these more complex materials remain a mystery.

A team of scientists utilized the high-energy x-rays available at the U.S. Department of Energy Office of Science's Advanced Photon Source (APS) at Argonne to investigate the fundamental basis for the performance advantage offered by mixed-anion iron oxyfluoride (FeOF) conversion electrodes, over electrodes made of simple oxide or fluoride phases. This research represents the first-of-a-kind application of operando pair distribution function (PDF) methods (that probe the structure of battery electrodes in situ while they are being cycled) to study [electrochemical reactions](#) in batteries. The PDF measurements provided exceptionally precise insight into the atom-atom bond distances, the proportion of each type of atom-atom bond, and how these evolve over dozens of points during the electrochemical reaction. This represents significant milestones in both understanding electrochemical reactions in battery electrodes and in the experimental tools available to investigate such reactions.

The scientists from Argonne National Laboratory, in collaboration with researchers at the University of Cambridge, Stony Brook University, Rutgers University, and CIC Energigune carried out their studies at X-ray Science Division (XSD) beamline 11-ID-B at the APS. A notable result was that the evolution of oxygen (O) and fluorine (F) species could

be separated despite their nearly identical contributions to the x-ray measurements. These element-specific insights were recovered based on the distinct chemical bonding characteristics of these anions, with the bond lengths and coordination numbers within the electrodes being specified with high precision by the PDF data.



Members of the research team and journal article co-authors in the 11-ID-B research station. Left to right: XSD postdoc Olaf Borkiewicz, Argonne chemists Karena Chapman and Peter Chupas, and XSD postdoc Kamila Wiaderek. Borkiewicz and Wiaderek are working with Chapman and Chupas in the XSD Structural Science Group. Next to Chapman's hand is a multicell holder with six AMPIX electrochemical cells.

The PDF study (in combination with solid-state nuclear magnetic

resonance spectroscopy) enabled the elucidation of a complex nanoscale transformation mechanism and provided new insights into the functionality of FeOF. Several critical insights emerged from the work that will impact the design of new battery materials:

- There is a preferential reaction of the fluoride component during both discharge and charge.
- The active electrode does not consist of the single-phase oxyfluoride of the pristine uncycled electrode, but rather contains multiple electrochemically active phases—an O-rich rock salt phase and a F-rich rutile phase (see the figure).
- Competition between electrochemical reactions involving the rock salt and rutile components in the active electrode and frustration in O/F ordering within these phases may favor the nanosized composite electrode structure that contributes to enhanced cyclability.

These results have important implications for producing other mixed-anion systems, suggesting a possible cost- and time-saving shortcut to achieving exemplary electrochemical performance. There may be no need to go to the trouble of preparing a single-phase oxyfluoride, because simply mixing an oxide with a fluoride could yield similar performance improvements, which is an entirely unexplored route for the development of new battery materials. This is particularly important in systems where oxyfluoride phases are not known (such as nickel).

The operando x-ray PDF studies were made possible by a newly developed electrochemical cell that is compatible with PDF measurements and a broad range of other x-ray scattering and spectroscopic methods. Argonne's Multi-Purpose In-situ X-ray (AMPIX) electrochemical cell provides reliable electrochemical cycling without compromising the x-ray measurement. The suitability of the AMPIX cell

for a broad range of synchrotron-based x-ray scattering and spectroscopic measurements has been demonstrated with studies at eight APS beamlines to date. Compatible techniques include PDF analysis, high-resolution powder diffraction, small-angle scattering, and x-ray absorption spectroscopy. These techniques probe a broad range of electronic, structural, and morphological features relevant to battery materials.

The AMPIX cell enables experiments providing greater insight into the complex processes that occur in operating batteries by allowing the electrochemical reactions to be probed at fine reaction intervals with greater consistency (within the charge-discharge cycle and between different methodologies) with the potential for new time-dependent kinetic studies or studies of transient species.

More information: Wiaderek, K. et al. Comprehensive Insights into the Structural and Chemical Changes in Mixed Anion FeOF Electrodes by Using Operando PDF and NMR Spectroscopy, *J. Am. Chem. Soc.* 135(10), 4070 (March 13, 2013). [DOI:10.1021/ja400229v](https://doi.org/10.1021/ja400229v)

Provided by Argonne National Laboratory

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