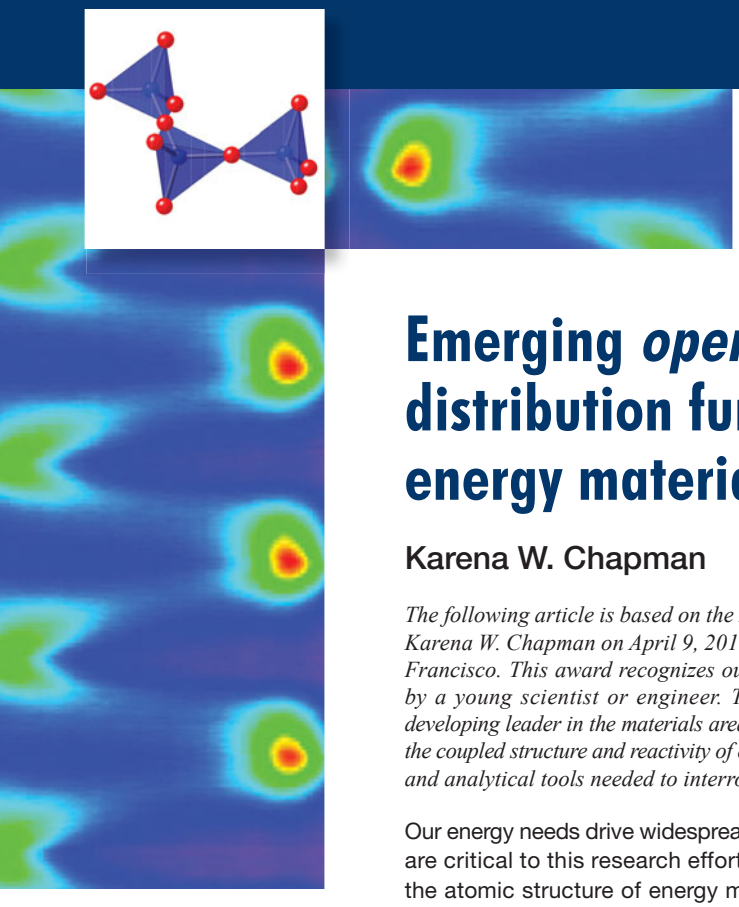


Emerging *operando* and x-ray pair distribution function methods for energy materials development

Karena W. Chapman

The following article is based on the MRS Outstanding Young Investigator Award Lecture presented by Karena W. Chapman on April 9, 2015, at the 2015 Materials Research Society Spring Meeting in San Francisco. This award recognizes outstanding, interdisciplinary scientific work in materials research by a young scientist or engineer. The award recipient must also show exceptional promise as a developing leader in the materials area. Chapman received the award "for contributions to understanding the coupled structure and reactivity of energy-relevant systems and for developing the incisive experimental and analytical tools needed to interrogate these complex materials systems."

Our energy needs drive widespread materials research. Advances in materials characterization are critical to this research effort. Using new characterization tools that allow us to probe the atomic structure of energy materials *in situ* as they operate, we can identify how their structure is linked to their functional properties and performance. These fundamental insights serve as a roadmap to enhance performance in the next generation of advanced materials. In the last decade, developments in synchrotron instrumentation have made the pair distribution function (PDF) method and *operando* x-ray studies more readily accessible tools capable of providing valuable insights into complex materials systems. Here, the emergence of the PDF method as a versatile structure characterization tool and the further enhancement of this method through developments in *operando* capabilities and multivariate data analytics are described. These advances in materials characterization are demonstrated by several highlighted studies focused on energy storage in batteries.

Emerging characterization capabilities and the energy frontier

Breakthroughs in functional materials and associated device performance can be driven by both advances in the materials themselves, or in the tools we use to probe and understand their function and limitations. New characterization capabilities can provide fresh insights for even familiar materials and problems to address fundamental questions relevant to materials development and device improvements. Innovations in materials characterization can be derived from entirely new experimental methodologies, from next-generation instruments with improved technical capabilities, from new measurement modalities, for example, enabled by *operando* sample environments, or from developments in data analysis. Advances in characterization have the potential to impact widespread areas of materials research, with functional materials enabling broad technologies from energy storage in lithium-ion batteries to selective capture of radiological gases within porous materials for safer nuclear energy.

Large scientific user facilities, such as synchrotron x-ray light sources, are centers of innovation in materials characterization. Synchrotron facilities support a diverse range of scattering, spectroscopic, and imaging-based characterization tools and instruments, with versatility in the experimental configuration supporting continued improvement and enhancements of instrument capabilities. The intense x-ray beams produced by synchrotrons allow large volumes of data to be efficiently collected in short periods of time, including fast time-resolved studies of materials dynamics.

Notably, when synchrotron x-rays are of high energy (with very short wavelengths, ~one-tenth that of most commercial x-ray scattering instruments), they can readily penetrate sample environments such as an operating battery device, to probe material function under real conditions, without perturbing

Karena W. Chapman, Argonne National Laboratory, USA; chapmank@aps.anl.gov
DOI: 10.1557/mrs.2016.26

© 2016 Materials Research Society

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

the system operation. High-energy x-rays such as these are also used for medical imaging, where x-rays penetrate the human body to reveal internal structures without damage to the patient. *Operando* experiments are increasingly being applied in battery research to capture dynamic reaction intermediates and explore kinetic effects.[1,2]

High-energy x-rays are critical to enabling x-ray pair distribution methods (PDF) methods (shown in **Figure 1**), because they provide access to the broad Q-range (the momentum transfer) that is needed for high-resolution, quantitative analysis. PDF methods have emerged as a versatile structure characterization tool capable of addressing traditionally challenging materials problems.[3] This cutting-edge method provides insight into otherwise intractable materials problems, but in combination with innovations in *operando* measurement capabilities, we can also gain a new understanding of functionality and failure. New insights into the structure and chemistry of complex materials, answers to long-standing mechanistic questions, and fundamental insights into emerging materials systems have been demonstrated. Here, several examples of the new insights that have been gained are described, including understanding the structural and chemical changes accompanying cycling in a promising new electrode material, identifying the fundamental mechanism underlying the high performance of a commercialized battery electrode, and exploring the nature of the charge-carrying species for novel electrolytes being explored for next-generation battery chemistries beyond Li-ion.

PDF analysis: A broadly insightful and versatile characterization tool

In the last decade, PDF analysis of high-energy x-ray scattering data has grown to become a valuable tool to probe the local atomic structure of materials.[3,4] It provides a wide range of local structural information with crystallographic resolution for broad classes of materials. This includes materials on the nanoscale or in amorphous, liquid, or gaseous phases, for which conventional Bragg structural analysis fails. In principle, one can measure the PDF of any sample, provided that it is not a single crystal.

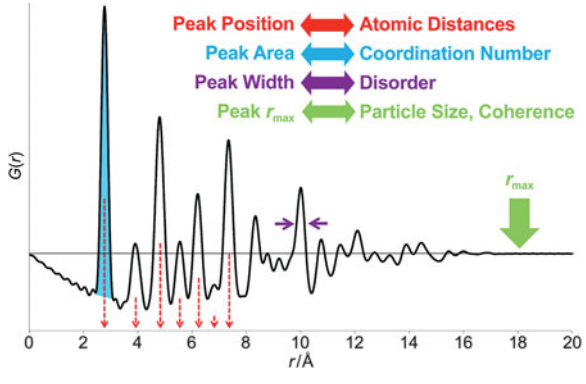


Figure 1. A pair distribution function, $G(r)$, derived from high-energy x-ray total scattering, provides real-space structure information independent of structure modeling. Note: r, interatomic distance.

Structural information in the PDF is available as a weighted histogram of all atom–atom distances within a material. It is a function in real space, where peaks indicate an increased probability of finding atoms at a particular distance r, the characteristic interatomic distance or bond length. The coordination number is related to the area of a peak. The peak width provides insight into the distribution of similar distances (i.e., disorder). The highest distance at which peaks are observed is related to the size of a particle or coherent domain. In addition to insights being derived directly from the features in the PDF, structure models can also be refined against the data; in addition, the data can be used to benchmark computational simulations.[5]

The PDF is derived from a scattering measurement, specifically, a specialized powder diffraction measurement. It is the Fourier transform of the total structure factor that is related to the coherent part of the scattering intensity from an x-ray or neutron-scattering measurement. The analysis, alternatively referred to as total-scattering analysis, utilizes both Bragg and diffuse contributions to the scattering, following correction of the measured data for background and inelastic scattering contributions.

That a PDF is related to the experimental total-scattering data via a Fourier transformation gives rise to several practical challenges that until recently, had limited the application of x-ray PDF in materials characterization.[4] First, the resolution of the PDF is ultimately limited by the finite range of scattering data measured and used for the Fourier transform. A high-resolution PDF, suitable for quantitative analysis, requires the scattering be collected over a wide range, ideally to $Q > \sim 20$ Å^{-1}, where $Q = 4\pi \sin(\theta)/\lambda$ is inversely related to the d-spacing (interplanar spacing) and the x-ray wavelength (λ); 2θ is the diffraction angle. Typical laboratory-based diffraction instruments (equipped with a Cu-Kα x-ray generator) only routinely collect scattering data to $Q \sim 6$–8 Å^{-1}. For many years, access to a wide Q-range limited x-ray PDF analysis. Second, any sample environment must provide access to wide scattering angles and Q-range. Scattering from the sample environment itself must by highly reproducible and ideally low, such that the background scattering can be independently measured and subtracted from the sample scattering data.

While the formalism behind the PDF methodology was established ~90 years ago (not long after the foundation of crystallography), until recently, the experimental challenge in collecting data to high values of Q prevented widespread application of the methodology. With limited data quality and access, PDF was, for the most part, a specialized tool used by experts. Further applications were focused on static studies of relatively simple material compositions.

It is only in the last 10 years that increased access to high-quality data has transformed the PDF methodology into a

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

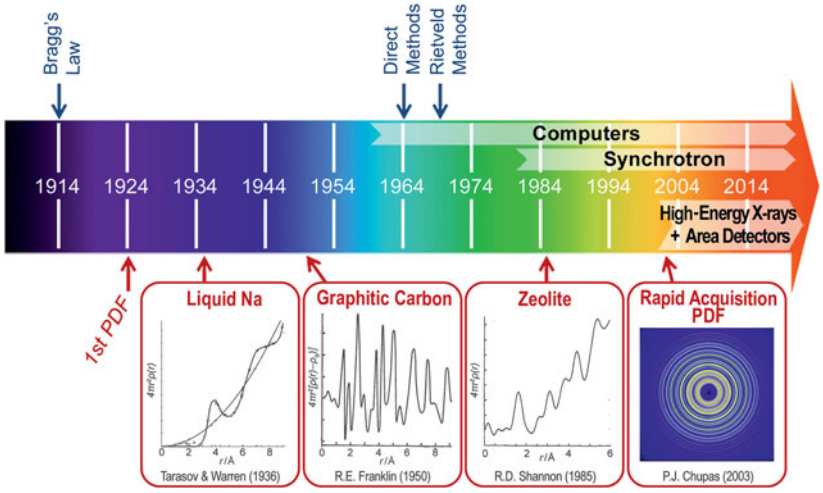


Figure 2. A brief history of pair distribution function (PDF) measurements. Gains have been made through the advent of computers to perform the Fourier transformation, synchrotron sources of intense x-ray beams, and, most recently, the combination of high-energy x-rays from large third-generation synchrotron sources with large-area detectors.[9,19–22] Note: r, interatomic distance; ρ_0, average number density; $\rho(r)$, r dependence of the number density; PDF $G(r) = 4\pi r[\rho(r) - \rho_0]$.

useful and broadly applicable tool for materials research (see **Figure 2**). This paradigm shift resulted from a new approach to how x-ray scattering data for PDF analysis are measured. In the past, a point-counting detector was scanned through the required Q-range that required up to 12 hours to accumulate sufficient statistics. Today, the wide Q-range required for an individual PDF is collected simultaneously in a single-detector exposure of a second or less.[1,2] The wide Q-range is accessed by combining high-energy x-rays with a large-area detector placed close to the sample in a transmission geometry, as shown in **Figure 3**. High-energy (i.e., short wavelength, λ) x-rays compress the scattering data into a small angular range, while placing the large detector close to the sample means that a large angular range intersects the detector. The Advanced Photon Source, the synchrotron storage ring located at Argonne National Laboratory, is one of the world's brightest sources of high-energy x-rays and home to the first dedicated x-ray PDF instrument in the world.

Expanded access to high-quality, quantitative PDF data has changed the types of materials, experiments, and questions that can be answered. Accessibility to data provides new opportunities—more data means more ways to approach a question. It is no longer necessary to extract all possible information from a single precious data set. Multiple data sets, collected for a series of materials or for a single material system under different conditions, can be leveraged to gain new insights, including model-independent structural parameters derived directly from the PDF. This has opened the door to studying more complex systems. We can now characterize more complex heterogeneous materials, recover chemical sensitivity, undertake detailed *in situ* or *operando* studies, and use direct insights from real-space features in the PDFs to address questions relevant to energy storage and conversion, nucleation and growth, sorption and separations, and catalysis and reactivity.

The characterization challenge in energy storage and PDF

The potential impact of advances in characterization is exemplified in the challenge in developing next-generation batteries, electrodes, and electrolyte systems that provide increased efficiency, improved effectiveness, and greater safety at reduced expense. Today's batteries only attain 25% of their theoretical energy-storage capacity. Understanding the processes that govern operation and limit performance in battery materials is an important step toward closing the gap between what is theoretically possible and what can be achieved in practice. However, as batteries are complex, multicomponent devices, understanding their operation and limitations is a substantial, multifaceted characterization challenge. Reactions and transport processes that govern device performance involve coupled changes in structure, chemistry, and electronic states spanning multiple length and time scales: From ion insertion and cation-ordering phenomena on the atomic scale,[6] to strain and reaction propagation across individual electrode particles that lead to fracturing,[7] to transport limitations across the full composite electrode architecture.[8]

Nanomaterials are associated with many strategies being pursued to enhance battery performance. These include increasing energy-storage capacities, accelerating charging and discharging, and extending long-term cycling stabilities. In Li-intercalation-based battery electrodes, where up to a single Li-ion is reversibly inserted into a metal compound structure without transforming the structure ($MX + Li^+ + e^- \leftrightarrow LiMX$,

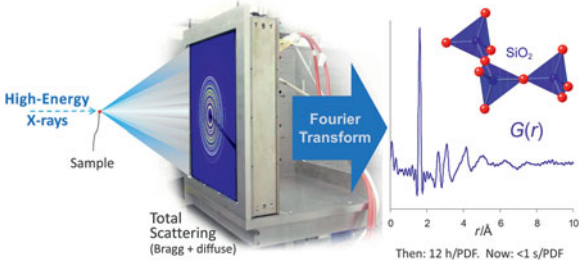


Figure 3. Modern x-ray pair distribution function (PDF) measurements use a transmission geometry setup, where high-energy x-rays compress a wide Q-range into a small angular range that is intersected by a large-area detector placed close to the sample. This configuration has reduced data acquisition times from ~half-day to less than one second per PDF. The PDF data shown here, along with the accompanying schematic structure, are for amorphous SiO_2 with Si shown in blue and oxygen in red. Note: Q, momentum transfer; $G(r)$, PDF; r, interatomic distance.

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

where M is a metal cation and X is the counteranion), nanoscale materials can support improved rate capabilities. In developing conversion-based electrodes that are being explored as a possible route to increase energy-storage capacities beyond 1 electron per metal center by reacting several electrons per metal center to reduce a metal compound to the metallic state ($M^{z+}X + nLi^+ + ne^- \leftrightarrow M^0 + Li_nX$), the associated structural rearrangements break the electrode material up into nanoparticles.[3] While the original electrode material assembled into the battery may have large particle sizes, these are reduced to nanoparticles during the initial conversion reaction.

Understanding the structure of nanomaterials is a characterization challenge that complicates our understanding of their reactivity in battery electrodes. For nanoparticles, Bragg diffraction peaks are severely broadened, such that traditional crystallography provides limited insight into their atomic structure. For example, while the position of broad diffraction peaks of ~10° wide may be sufficient to confirm that metallic iron with a body-centered-cubic structure forms by fully reducing an iron-containing electrode, it offers few insights as to why one iron-based electrode might deliver better rate capabilities or improved reversibility compared to a related iron-based electrode. Identifying the reaction mechanisms and, ultimately, the origin of the performance differences in related iron-conversion electrodes can only be understood by probing how the local atomic structure and chemistry evolve during electrochemical cycling, for example, using *operando* PDF methods.

The local structure information from PDF analysis can decouple chemical, structural, and electronic changes using a single *operando* measurement by probing the electrode during active electrochemical cycling, as shown in **Figure 4**. In a study of a mixed-anion iron oxyfluoride system, *operando* PDF helped provide insights into why the mixed-anion oxyfluoride delivered better performance as an Fe-conversion electrode than the related fluoride and oxide phases.[4] The iron oxyfluoride conversion electrodes exhibit good rate capability and reversibility, with complete recovery of the initial discharge capacity following charging.

These observations stimulate a number of questions: If the full capacity is recovered, does this necessarily mean that the original structure is regenerated? How does the structure evolve during discharge and charge? How does the anion O/F chemistry evolve and influence the reaction? By optimizing structure models to fit the PDF data and by model-independent evaluation of the local bond lengths and peak areas, these questions can be resolved.

For iron oxyfluoride conversion electrodes, *operando* PDF data, collected at fine intervals during the initial discharge and subsequent charge, show smooth variations in the local structural features and bonds as the electrode transforms from the original iron oxyfluoride to metallic iron.[9] Structure models can be fit to the data in a real-space analogue to Rietveld refinement (i.e., the PDF calculated for a structural model is refined against the experimental data using a least-squares minimization) at each point during the reaction to evaluate how the structure and phases evolve. This shows that the electrode structure initially transforms to metallic iron via an intermediate phase (in this case, a rock-salt-type phase). Despite achieving the same capacity upon charging as the original discharge, however, charging does not regenerate the original single-phase electrode. Instead, the charged electrode is a two-phase nanocomposite—this is the "real" electrode material responsible for the reversible energy storage.[9]

Distinguishing the role of the O and F atom chemistries in the mixed-anion oxyfluoride is a more subtle challenge. O and F anions have similar x-ray scattering factors and hence similar contributions to the x-ray scattering and the PDF data. While neutrons often provide scattering-contrast elements with similar x-ray scattering factors, O and F are a pathological pairing that are poorly distinguished by both x-rays and neutrons. However, the different anion chemistries are also distinguished by different coordination-bond characteristics and bond lengths for a given Fe^{n+} oxidation state and coordination number. Deriving the bond lengths, oxidation state, and coordination numbers from the positions and intensities of the Fe–O/F and Fe–Fe peaks in the PDF and applying a bond–valence analysis allowed the changing distribution of the oxo- and fluoroanions to be quantified. This shows that the nanocomposite electrode in the recharged electrode responsible for the reversible energy storage contains anion partitioning with oxide-rich and fluoride-rich component phases. This suggests that the performance advantages associated with the oxyfluoride may be achieved by forming a nanoscale composite of pure oxides and fluorides that opens the door to a broader range of mixed oxide–fluoride electrode systems.[4]

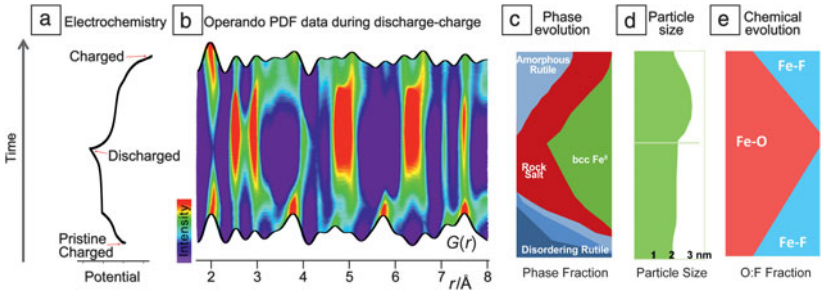


Figure 4. Applied during cycling, pair distribution function (PDF) analysis can decouple chemical, structural, and electronic changes within a single experiment. During (a) the electrochemical lithiation (discharge) and delithiation (charge) processes, (b) a series of PDF data can be obtained at fine reaction intervals (0.1 Li steps here). Structural models can be fitted to the data to show how (c) the phases and (d) particle size evolve during the reaction, or (e) the changes in the Fe-O and Fe-F features can be evaluated to show how the chemistry changes. Reprinted with permission from Reference 9. © 2013 American Chemical Society. Note: *G*(*r*), PDF; *r*, interatomic distance.

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

Challenges and advantages of *operando* studies

The ability to probe a reaction *in situ*, for example, within the charging and discharging electrochemical cell, is critical to deriving important insights and understanding. In the case of iron oxyfluoride, continuously probing a single sample and eliminating variability that arises from studying different electrodes recovered from different cycling states was critical to separating the reactions of the O and F anions. However, developing sample environments that enable *operando* characterization without compromising either the x-ray measurement itself or the electrochemical performance is non-trivial. An x-ray-enabled *operando* electrochemical cell must provide access to appropriate scattering angles and must have acceptable x-ray transmission and scattering properties.

Straightforward and widely utilized *operando* electrochemical cell concepts that replace part of the stainless-steel casing of a standard electrochemical coin cell with a ubiquitous x-ray transparent window such as a polyimide film often suffer from deficiencies in the electrochemical performance.[5] Because the window surface has different electrical conductivity and mechanical stiffness compared to the rest of the stainless-steel cell, the region of the electrode in contact with the x-ray window can exhibit vastly different (delayed) reactivity relative to the rest of the electrochemical cell and the electrochemical potential recorded for the whole cell. Notably, the region with the greatest deficiency in electrochemical performance occurs in precisely the region being probed by an x-ray experiment (i.e., under the x-ray window), where localized delays of the reaction of up to 20% have been documented (see **Figure 5**).[5] The x-rays are seeing an extreme state within the cell that deviates systematically from the average reaction state.

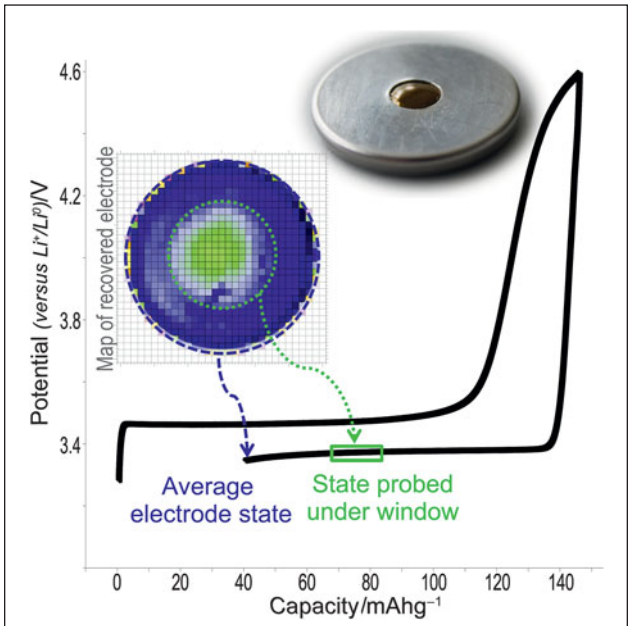


Figure 5. In nonoptimized *operando* cell designs, the cell can impact the sample state observed experimentally, leading to misleading results. (Upper right inset) A photograph of a widely used operando electrochemical cell where part of the stainless-steel casing of a standard electrochemical coin cell is replaced with an x-ray transparent polyimide window. (Left inset) A map of the charge state for an electrode cycled within this type of operando cell is also inset. The region of the electrode under this flexible, nonconductive window (outlined in green) is at a less advanced state of charge, as indicated on the electrochemical potential curve. Reprinted with permission from Reference 23. © 2015 American Chemical Society.

To eliminate localized delays in the electrochemical reaction, an optimized design of the *operando* electrochemical cell that ensures uniform electrical conductivity and mechanical stability of the entire electrochemical cell, particularly across the x-ray window, is necessary.[5,6] We have developed such an *operando* electrochemical cell (see **Figure 6**) at Argonne's Advanced Photon Source that is compatible with a broad range of synchrotron-based x-ray characterization tools and is not limited to PDF analysis, powder diffraction, small-angle x-ray scattering, and x-ray absorption spectroscopies.[6,7] This cell has been used to demonstrate a rate dependence of the reaction mechanism and intermediate phases in olivine electrodes,[1,10] to probe how metallic nanoparticles form and aggregate in iron conversion electrodes,[11] to monitor the V oxidation state change in VO_2,[12] and to probe the reaction mechanism of nanoscale systems (e.g., RuO_2, FeOF, CuF_2).[13,14]

Beyond improved experimental efficiency, data consistency, and sensitivity, developing an optimized *operando* electrochemical cell

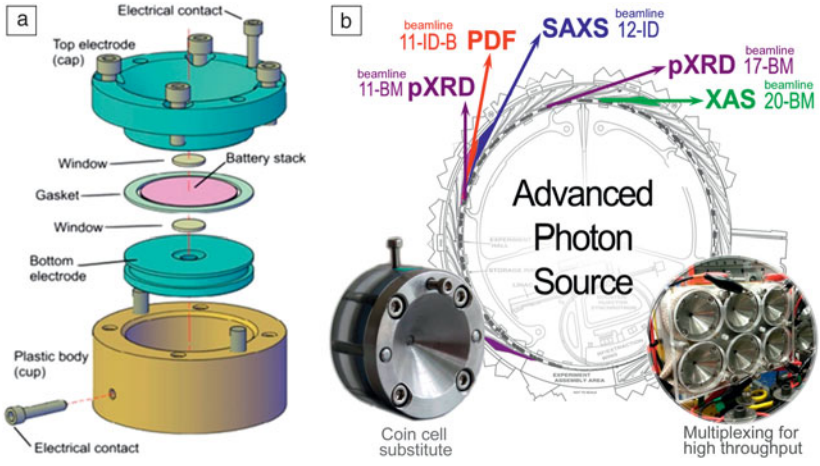


Figure 6. (a) The AMPIX (Argonne National Laboratory's multipurpose in situ x-ray) electrochemical cell developed at Argonne's Advanced Photon Source delivers uncompromised electrochemical performance. Because it is optimized for the pair distribution function (PDF), the cell can be characterized by a variety of other x-ray tools and multimodal studies: (b) powder x-ray diffraction (pXRD) at beamlines (instruments) 11-BM and 17-BM, small-angle x-ray scattering (SAXS) at beamline 12-ID, and x-ray absorption spectroscopy (XAS) at beamline 20-BM. Note that the dedicated PDF instrument is 11-ID-B. Reprinted with permission from Reference 24. © 2012 International Union of Crystallography.

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

opens new opportunities for reliable *operando* studies to directly probe the reaction mechanisms, to correlate features in the electrochemical potential curves with changes observed in the structure and scattering, to identify dynamic phenomena and intermediates, and to explore reaction kinetics and rate-dependent effects.

Operando experiments to explore dynamic phenomena

Dynamic phenomena, such as reaction kinetics and rate-dependent mechanisms, can only be probed experimentally through *operando* measurements within a reliable *operando* cell. Such rate-dependent studies can be critical to identifying the mechanisms that allow fast charging and discharging in certain electrode systems. Fast rate capabilities equates to higher-power delivery that can be desirable in power tools or during acceleration of an electric vehicle.

Lithium iron phosphate ($LiFePO_4$) is the archetypical high rate capability battery electrode material that finds applications in power tools and electric vehicles. Despite widespread experimental and computational studies exploring the reaction mechanisms in this system, the high rate capability observed for $LiFePO_4$ has been the subject of a long-standing paradox.[8] The observed fast rate capability was inconsistent with apparent reaction mechanisms. However, due to limitations in the experimental characterization, the reaction mechanism during fast rate cycling had not been probed directly. The Li composition phase diagram for $LiFePO_4$ indicates that lithium ions should insert and be removed via a two-phase reaction mechanism. Studies of the electrode recovered from the different states, or during slow rate experiments that were feasible, support the two-phase reaction mechanism where only different proportions of either the fully lithiated or the fully delithiated electrode states. However, two-phase reactions are inherently rate-limited, in conflict with the observed fast rate capability.

By combining an optimized *operando* electrochemical cell, free from localized delays in the electrochemical reaction, with the fast-time resolved data-acquisition capability possible for synchrotron area-detector scattering measurements, it became possible to drive and probe the electrochemical reaction at the fast rates needed to directly explore mechanisms associated with fast rate cycling. The direct probing revealed an intermediate reaction product—a solid solution. This intermediate phase was found to be metastable—when the electrochemistry was paused at an intermediary point during the cycling, the intermediate relaxed to either the fully charged or discharged state. The metastable intermediate could be identified as a solid-solution phase, with variable lattice dimensions between those of the charged and discharged states. Reactions via solid-solution mechanisms are not subject to the same rate limitations as two-phase mechanisms. The metastable solid-solution intermediate that could only be captured through fast rate *operando* measurements accounts for the exceptional rate capability of $LiFePO_4$ and resolves the long-standing paradox between the apparent mechanism and the observed rate capability (see **Figure 7**).

Multivariate data analyses to resolve physically inseparable components

The functioning of complex devices such as batteries relies on the reactions and interactions of many different components, however, decoupling the role of an individual component and its impact on performance can be challenging. Some components, such as the charge-carrying anionic and cationic species of the electrolyte, can never be physically isolated and characterized separately, motivating a need for selective probes. In the case of PDF analysis, where the measurement is sensitive to all atom–atom correlations within the sample, the methodology itself is not intrinsically element-or chemical-specific. However, the new efficiency, with which a large series of PDF data can be measured, opens new opportunities to recover chemically specific insights analytically by applying multivariate data analyses, such as principal component analysis.[9] Principal component analysis allows a large, complex series of data to be visualized in terms of a smaller number of variables by transforming the series of data into an orthogonal basis set. The original data is expressed as a linear combination of new orthogonal components.[15]

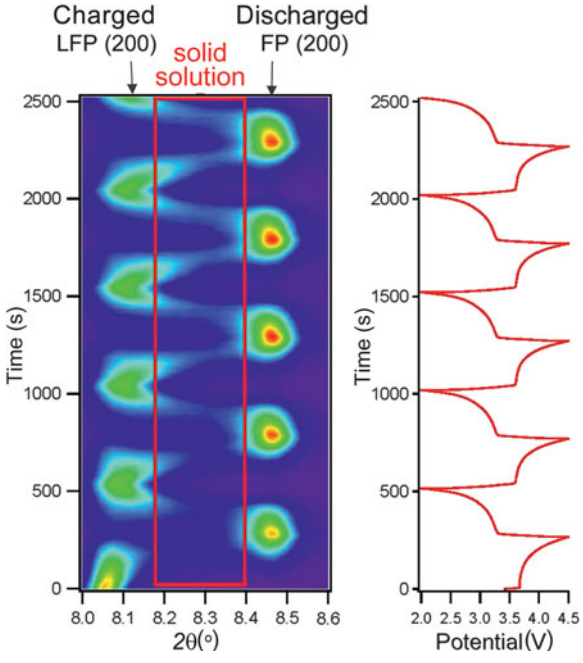


Figure 7. Operando measurements are needed to capture short-lived metastable intermediates involved in the activation of a different mechanism for $LiFePO_4$ during fast rate cycling. When the lithiation and delithation are driven at fast rates, the electrode not only transforms directly between the LFP and FP phases that have distinct contributions to the x-ray diffraction data; instead, the reaction proceeds via an intermediate with variable Li composition (i.e., a solid solution), which is evident in the diffraction data at 2θ between the LFP and FP states (highlighted in the red box). While a two-phase reaction (i.e., LFP to FP) is kinetically limited, a solid-solution mechanism can allow for much higher cycling rates. Reprinted with permission from Reference 1. © 2014 AAAS. Note: 2θ, diffraction angle; LFP, $LiFePO_4$; FP, $FePO_4$.

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

In an electrolyte, the structure and speciation of the charge-carrying species governs critical parameters such as the kinetics and energetics for ion mobility, and desolvation and reaction at the electrode. Understanding these properties is critical to the development of novel electrolytes and will be needed to enable new battery chemistries, beyond Li-ion, such as high-capacity multivalent Mg-ion batteries.

PDF is well suited to probe to the local atom–atom distances that define the solvation structure of the charge-carrying species within the electrolyte. However, the contribution from the cation-solvation structure and the anion-solvation structures overlap in the measured PDF data. Interpreting the data and assigning different features to specific atom–atom pairs can be challenging. Resolving these overlapping contributions can be considered an underdetermined problem with more unknown variables than data. Accordingly, it should be possible to resolve these overlapping contributions by collecting more data and applying appropriate data analytics.

With high throughput now possible for PDF measurements, large systematic series of different sample compositions can be efficiently collected (see **Figure 8**). By looking at a series with a common anion and solvent, but with different cationic species, including the Mg electrolyte of interest, the contributions common to all solutions (i.e., associated with the common anion solvation structure) can be isolated through application of principal component analysis.[10] The solvation structures of the individual cations can, therefore, also be recovered by a differential approach that involves subtracting the PDF of the common species from the total PDF for each solution. This application of multivariate analysis is an expansion on an established differential approach to recovering chemically sensitive PDF data by separately measuring a reference PDF for an individual component and subtracting it from the data;[11] however, in this case, the reference PDF is determined analytically from the principal component analysis instead of being measured directly.

Summary

Developing new *operando* experimental tools, multimodal measurements, and analytical approaches push the boundaries of materials characterization to provide new insights into long-standing materials problems. Innovations and improvements can derive from all parts of experimental characterization from improved technical capabilities to new ways of applying a methodology involving *operando*, time-resolved, or spatially resolved measurements or analyzing the resulting data. These developments are critical to enabling new science. While the initial effort to develop these capabilities can be substantial, the payoffs are broad. Although the examples discussed here focus on energy storage and battery development, new characterization capabilities can have a widespread impact spanning broad areas of chemical and materials sciences, including identifying the active catalytic sites in heterogeneous catalysts or in materials discovery, to identify the earliest atomic aggregates that lead to nucleation of different phases.

For x-ray PDF methods, we are no longer limited by access to high-quality data. Development of new *operando* capabilities are equally important in allowing new scientific questions to be answered. High-energy x-ray PDF analysis can provide a detailed understanding of functional materials, especially when applied *in situ*. We can evaluate structural parameters from the real-space data directly. Highly consistent data provides greater precision and opportunities for new types of data analysis. With major upgrades planned for experimental user facilities such as the Advanced Photon Source at Argonne National Laboratory in the USA,[16] the Diamond Light Source[17] in the UK, the European Synchrotron Radiation Facility,[18] and the construction of new dedicated PDF instruments, the future is bright.

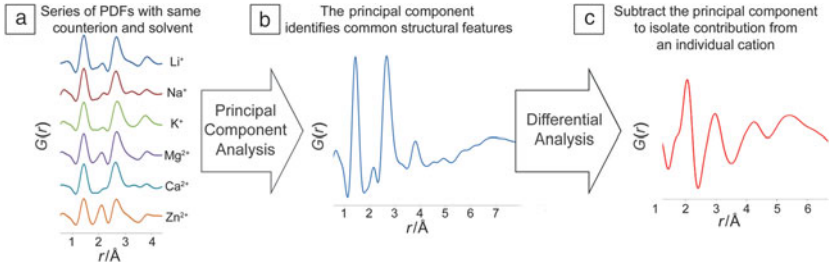


Figure 8. (a) By obtaining data for a compositional series of solutions, (b) the contribution from the common chemical species can be isolated and, accordingly, (c) the atom–atom correlations unique to the cation-solvation structures can be separated. Reprinted with permission from Reference 25. © 2015 International Union of Crystallography. Reprinted with permission from Reference 26. © 2014 Royal Society of Chemistry. Note: *r*, interatomic distance; *G*(*r*), PDF; PDF, pair distribution function.

Acknowledgments

Contributions from P. Chupas, K. Wiaderek, O. Borkiewicz, S. Lapidus, B. Shyam, C. Kurtz, and collaborations with H. Liu, F. Strobridge, E. Castillo-Martinez, R. Robert, and C. Grey (University of Cambridge), N. Periera, G. Amatucci (Rutgers University), N. Rajput, and K. Persson (Lawrence Berkley National Laboratory) are gratefully acknowledged. Work done at Argonne and use of the Advanced Photon Source, an Office of Science User Facility operated for the US Department of Energy Office of Science by Argonne National Laboratory, were supported by the US Department of Energy under Contract No. DE-AC02–06CH11357. Work was supported as part of NECCES, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0001294 and DE-SC0012583, and as part of the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the US Department of Energy, Office of Science, Basic Energy Sciences.

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

References

1. H. Liu, F.C. Strobridge, O.J. Borkiewicz, K.M. Wiaderek, K.W. Chapman, P.J. Chupas, C.P. Grey, *Science* **344** (6191) (2014), doi: 10.1126/science.1252817.
2. X. Zhang, M. van Hulzen, D.P. Singh, A. Brownrigg, J.P. Wright, N.H. van Dijk, M. Wagemaker, *Nano Lett.* **14** (5), 2279 (2014).
3. T. Egami, S.J.L. Billinge, *Underneath the Bragg Peaks Structural Analysis of Complex Materials* (Pergamon, Oxford, 2012).
4. P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey, S.J.L. Billinge, *J. Appl. Crystallogr.* **36**, 1342 (2003).
5. K.W. Chapman, P.J. Chupas, in *In-Situ Characterization of Heterogeneous Catalysts*, J.A. Rodriguez, J.C. Hanson, P.J. Chupas, Eds. (Wiley, Hoboken, NJ, 2013), pp. 147–168.
6. J. Bréger, N. Dupré, P.J. Chupas, P.L. Lee, T. Proffen, J.B. Parise, C.P. Grey, *J. Am. Chem. Soc.* **127** (20) 7529 (2005).
7. A. Ulvestad, A. Singer, H.-M. Cho, J.N. Clark, R. Harder, J. Maser, Y.S. Meng, O.G. Shpyrko, *Nano Lett.* **14** (9), 5123 (2014).
8. F.C. Strobridge, B. Orvananos, M. Croft, H.-C. Yu, R. Robert, H. Liu, Z. Zhong, T. Connolley, M. Drakopoulos, K. Thornton, C.P. Grey, *Chem. Mater.* **27** (7), 2374 (2015).
9. K.M. Wiaderek, O.J. Borkiewicz, E. Castillo-Martinez, R. Robert, N. Pereira, G.G. Amatucci, C.P. Grey, P.J. Chupas, K.W. Chapman, *J. Am. Chem. Soc.* **135** (10), 4070 (2013).
10. F.C. Strobridge, R.J. Clement, M. Leskes, D.S. Middlemiss, O.J. Borkiewicz, K.M. Wiaderek, K.W. Chapman, P.J. Chupas, C.P. Grey, *Chem. Mater.* **26** (21), 6193 (2014).
11. K.M. Wiaderek, O.J. Borkiewicz, N. Pereira, J. Ilavsky, G.G. Amatucci, P.J. Chupas, K.W. Chapman, *J. Am. Chem. Soc.* **136** (17), 6211 (2014).
12. T.E. Ashton, D.H. Borras, A. Iadecola, K.M. Wiaderek, P.J. Chupas, K.W. Chapman, S.A. Corr, *Acta Crystallogr. B Struct. Cryst. Eng. Mater.* **71** (6), 722 (2015).
13. Y.Y. Hu, Z.G. Liu, K.W. Nam, O.J. Borkiewicz, J. Cheng, X. Hua, M.T. Dunstan, X.Q. Yu, K.M. Wiaderek, L.S. Du, K.W. Chapman, P.J. Chupas, X.Q. Yang, C.P. Grey, *Nat. Mater.* **12** (12), 1130 (2013).
14. X. Hua, R. Robert, L.S. Du, K.M. Wiaderek, M. Leskes, K.W. Chapman, P.J. Chupas, C.P. Grey, *J. Phys. Chem. C* **118** (28), 15169 (2014).
15. I.T. Joliffe, *Principal Component Analysis* (Springer-Verlag, New York, 2002).
16. www1.aps.anl.gov.
17. www.diamond.ac.uk.
18. www.esrf.eu.
19. L.P. Tarasov, B.E. Warren, *J. Chem. Phys.* **4**, 236 (1936).
20. C. Kittel, *Introduction to Solid State Physics* (Wiley, 2004).
21. R.E. Franklin, *Acta Crystallogr.* **3** (2), 107 (1950).
22. R.D. Shannon, K.H. Gardner, R.H. Staley, G. Bergeret, P. Gallezot, A. Auroux, *J. Phys. Chem.* **89** (22), 4778 (1985).
23. O.J. Borkiewicz, K.M. Wiaderek, P.J. Chupas, K.W. Chapman, *J. Phys. Chem. Lett.* **6** (11), 2081 (2015).
24. O.J. Borkiewicz, B. Shyam, K.M. Wiaderek, C. Kurtz, P.J. Chupas, K.W. Chapman, *J. Appl. Crystallogr.* **45** (6), 1261 (2012).
25. K.W. Chapman, S.H. Lapidus, P.J. Chupas, *J. Appl. Crystallogr.* **48** (6), 1619 (2015), http://dx.doi.org/10.1107/S1600576715016532.
26. S.H. Lapidus, N.N. Rajput, X. Qu, K.W. Chapman, K.A. Persson, P.J. Chupas, *Phys. Chem. Chem. Phys.* **16** (40), 21941 (2014). □



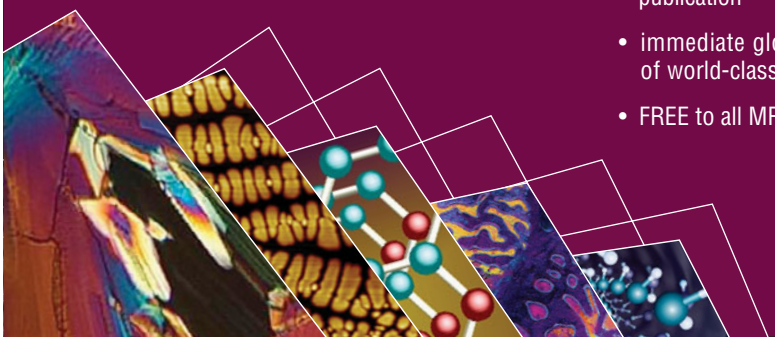
Karena W. Chapman is a chemist within the X-ray Science Division at Argonne National Laboratory (ANL). She received her BSc and PhD degrees in chemistry from The University of Sydney, Australia. Her research exploits PDF analysis of high-energy x-ray scattering data and other complementary methods to probe the atomic and nanoscale structure of crystalline, nano-, and amorphous materials that are beyond the limits of conventional crystallography. Chapman leads the dedicated PDF instrument, 11-ID-B, at ANL's Advanced Photon Source and is co-editor for the *Journal of Applied Crystallography*. She joined ANL in 2005 as the Arthur Holly Compton Postdoctoral Scholar, becoming a staff scientist in 2009. Chapman can be reached by email at chapmank@aps.anl.gov.

MRS Advances

A new peer-reviewed online-only journal

Inaugural Content Now Available!
mrs.org/mrs-advances

- devoted to publishing new and emerging materials science, particularly rapid reports of work in progress
- designed to reflect the way materials researchers work, write, publish and share their results
- editorial leadership ensures rapid peer review and speed of publication
- immediate global distribution alongside the MRS portfolio of world-class, peer-reviewed publications
- FREE to all MRS members



MRS MATERIALS RESEARCH SOCIETY® CAMBRIDGE UNIVERSITY PRESS

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

J.A. Woollam Co.

MRS Booth 107

Ellipsometry Solutions[sm] for your Thin Film Characterization.



J.A. Woollam Co. has the world's widest variety of **Spectroscopic Ellipsometers** with **8** different models to non-destructively characterize thin film thickness and optical constants. After **29** years, over **15,000** samples characterized in our lab, and over **150** patents – we are the Ellipsometry Experts.

Ellipsometry Solutions



alpha-SE®

Designed for low cost and ease-of-use, the alpha-SE is perfect for routine measurements of thin film thickness and refractive index. Compact base with three manually-selectable angles of incidence and a spectral range which includes 180 wavelengths from 380-900nm.



IR-VASE®

The IR-VASE is the first and only spectroscopic ellipsometer to combine the chemical sensitivity of FTIR spectroscopy with thin films sensitivity of spectroscopic ellipsometry. Spectral range includes 1.7 to 30 microns (333 to 5900 wavenumbers).



RC2®

The RC2 design builds on 25 years of experience. It combines the best features of previous models with innovative new technology: dual rotating compensators, achromatic compensator design, advanced light source, and next generation spectrometer design.



VASE®

The VASE is our most accurate and versatile research ellipsometer for all types of materials: semiconductors, dielectrics, organics, metals, multi-layers, and more. Now available with the widest spectral range from ultraviolet to infrared.

www.jawoollam.com • 402.477.7501 • 645 M Street, Lincoln, Nebraska USA

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press

Strange Matter. Green Earth.

Experience the Power of Materials for a Sustainable World—The Stuff That Matters

Strange Matter Green Earth is a new pioneering educational venture brought to you by the Materials Research Society—an international traveling science exhibition that will enable millions of people across the globe to discover ways in which advances in materials can lead to a more sustainable future.

A network of science educators, science center professionals and materials researchers from three continents—North America, South America and Europe—will collaborate to create interactive exhibit experiences and dynamic community programs that will emphasize materials, from the mundane to the mysterious, and how they profoundly influence the quality of our lives and the planet.

Building on the incredible success of the MRS traveling exhibition Strange Matter, now in its second decade of touring, Strange Matter Green Earth aims to empower the world's citizens to make sustainable choices in their own lives and communities.

Companhia Brasileira de Metalurgia e Mineração Sponsors Strange Matter Green Earth

MRS is proud to announce CBMM—the world's premier supplier of niobium and niobium technology—as the first sponsor of Strange Matter Green Earth. CBMM is recognized globally for environmental, community and technological leadership through a sustainable mission to transform a natural resource into solutions to build a better world.

Sponsorship opportunities are still available.

Contact **Richard A. Souza,** Manager, Education & Outreach,
at 724-779-2734 | souza@mrs.org.

International Collaborators



Museum of Science Boston
Science Museum of Minnesota
Museum of Life and Science
Red de Popularización de la Ciência y la Tecnología en América Latina y el Caribe
U.S. Department of Commerce - National Institute of Standards and Technology
Museo Nazionale della Scienza e della Tecnologia Leonardo da Vinci
Materials Science and Engineering Expert Committee (MatSEEC)
Instituto de Fisica Gleb Wataghin Universidade Estadual de Campinas
Sociedad Mexicana para la Divulgación de la Ciência y la Técnica
Association of Science and Technology Centers
Fundação de Amparo à Pesquisa do Estao de São Paulo
Fraunhofer Institute for Mechanics of Materials Freiburg
Consejo Mexiquense de Ciências y Tecnologia
Dirección General de Divulgación de la Ciência, UNAM
University of Illinois Urbana–Champaign
Materials Research Society
Centro de Investigación en Energía, UNAM
Los Alamos National Laboratory
Princeton University PCCM
Sociedad Mexicana de Materiales
Fraunhofer Brussels
Materials Research Institute, UNAM
Maloka Centro Interactivo
Sociedade Brasileira de Materiais
Royal Ontario Museum
Arizona State University
Museo Exploratorio de Ciências
Duke University Triangle MRSEC
University of Minnesota MRSEC
Science Museum Universum
University of Milan
Italian Institute of Technology
Academia de Ciências de Morelos
Science Center NEMO
Lehigh University
University of Massachusetts
Bangor University
University of Virginia
Ontario Science Centre

www.mrs.org/strange-matter-green-earth

https://doi.org/10.1557/mrs.2016.26 Published online by Cambridge University Press