High Energy X-ray Applications: PDF and *in-operando* Studies with the EIGER2 R 500K Detector

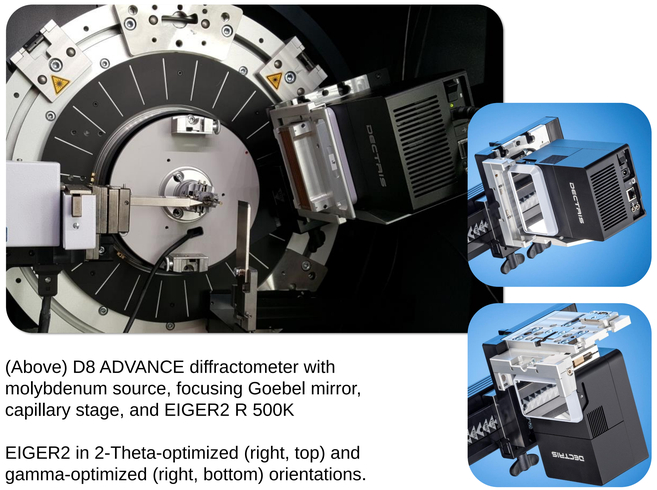
Nathan Henderson, Brian Jones, Ning Yang, Michael Evans
Bruker AXS, Madison, Wisconsin, US
Contact: Nathan.Henderson@Bruker.com

69th Annual Conference on Applications of X-ray Analysis (Denver X-ray Conference)

Laboratory-scale diffraction and scattering experiments can benefit from hard radiation types (e.g., Mo and Ag) when analyzing dense materials in transmission. This includes Debye-Scherrer geometries employing glass or polymer capillaries as well as flat plate geometries in applications such as battery pouch cells. Relative to more commonly used wavelengths like Cu, the use of higher energy X-rays results in increased beam penetration, larger sampling volumes, and access to higher Q–which has implications for PDF studies.

Data collection extends beyond the choice of X-ray tube, of course. As is frequently the case with thoughtful experimental design, it is important to consider the quality and efficiency of the experiment in total. This includes aspects like counting statistics, angular coverage of the detector, and minimization of background contributions.

Here, we highlight several case studies using high energy X-rays, including Pair Distribution Function (PDF) analysis and *in operando* characterization of battery cells during charge and discharge cycles. A key component in these experiments is the EIGER2 R 500K detector, which has a large asymmetric active area that can be quickly switched between 2-Theta- and gamma-optimized orientations (for 1D and 2D experiments, respectively). The large angular coverage enables rapid data collection for high temporal granularity during *in operando* studies and exceptional signal-to-noise in PDF experiments. The detector distance can also be rapidly switched without the need for tedious recalibration, allowing for collection of high-intensity (towards PDF studies) and high-resolution (towards Rietveld work) datasets as needed.



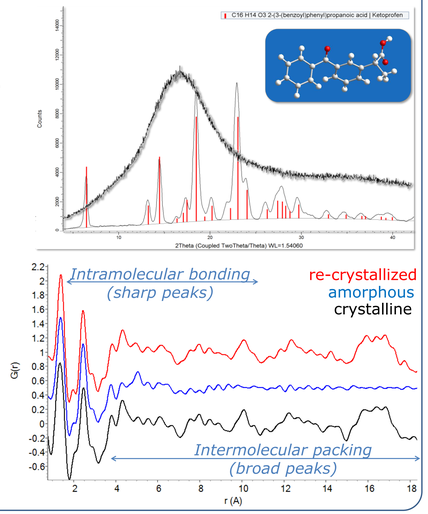
(Above) D8 ADVANCE diffractometer with molybdenum source, focusing Goebel mirror, capillary stage, and EIGER2 R 500K

EIGER2 in 2-Theta-optimized (right, top) and gamma-optimized (right, bottom) orientations.

PDF of Amorphous/Crystalline Small Molecule APIs

Specimens of ketoprofen were prepared from crystalline and amorphous (melt-quenched) batches and analyzed in capillary transmission geometry for 1 hour. Diffraction data (right, top) demonstrate classic behavior for crystalline (peaks observed) and amorphous (broad scatter) phases.

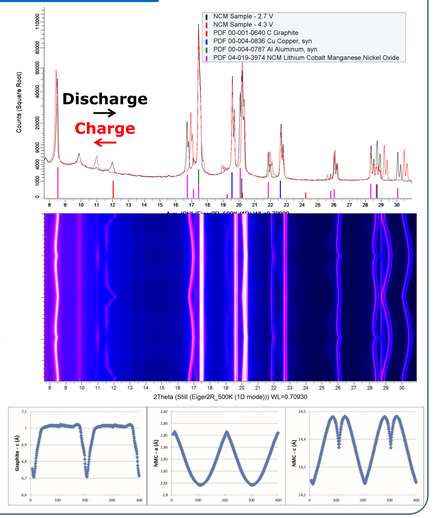
PDF data (right, bottom) for crystalline, amorphous, and re-crystallized specimens are overlaid with a slight y-offset for viewing clarity. Two distinct regions are observed: sharper peaks at low *r* values that are governed by well-defined intramolecular covalent bond distances and broader peaks at higher *r* values arising from intermolecular distances that are less strictly defined (van der Waals interactions). In the amorphous PDF, there is a loss of observed signal beyond 10 Å, which corresponds to the loss of long-range ordering in the glassy state.



in operando Diffraction of Li-Ion Batteries

A pouch cell was prepared using a single layer of NMC (Li[Ni,Mn,Co]O_2) as the cathode material. The pouch cell was analyzed in transmission geometry with Mo radiation. Single 1D frames (7-32 degrees 2-Theta) were taken every 3 minutes, with 400 scans collected during the experiment, which covered two full charge and discharge cycles over 20 h.

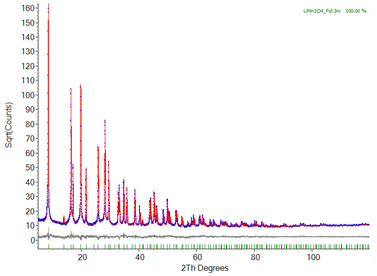
Two selected scans for fully charged and discharged states are shown to the right (top). Despite the rapid data collection speed, exceptional signal-to-noise is obtained due to the detector performance and active area. An iso-intensity plot of all 400 scans (right, middle) describes the expansion and contraction of the NMC and graphite (anode) lattices during cycling as well as the formation of Li/C phases resulting from Li intercalation. Lattice parameters (right, bottom) were refined in batch using DIFFRAC.TOPAS.



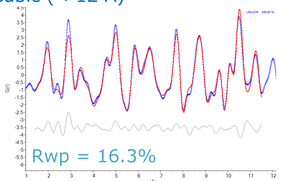
Joint PDF/Bragg Refinement of $LiMn_2O_4$

A sample of $LiMn_2O_4$ (LMO) was analyzed in capillary transmission geometry over a wide scanning range (75 min total scan time). Rietveld refinement data are shown to the right. The y-axis is plotted in square root counts to emphasize the quality of fit.

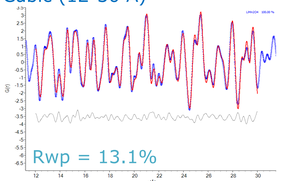
At room temperature, LMO adopts a cubic structure with average Mn valence of 3.5+ and equivalent Mn-O bond lengths. At low temperatures, LMO adopts an orthorhombic structure due to Mn^{3+}/Mn^{4+} ordering. PDF data and refinements are shown below for both cubic and orthorhombic structures at both short and intermediate distances. At r = 12-30 Å, both models fit well. For r < 12 Å, however, the orthorhombic model is a noticeably better fit, suggesting some degree of ordering at short distances.

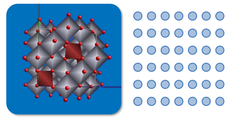


Cubic (< 12 Å)

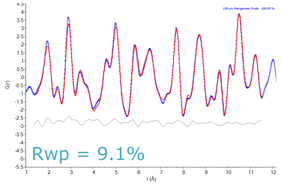


Cubic (12-30 Å)

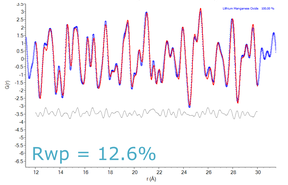


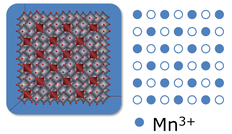


Orthorhombic (< 12 Å)



Orthorhombic (12-30 Å)





Summary

- The EIGER2 is a versatile detector that supports high-end diffraction experiments like PDF analysis and *in operando* studies
- PDF data for amorphous and crystalline small molecule APIs demonstrate similar data at short distances but distinct behavior at longer distances due to loss of ordering in the glassy phase
- Time-resolved studies of energy storage materials are supported by rapid collection of large numbers of diffractograms and batch refinement of lattice parameters in DIFFRAC.TOPAS
- Joint PDF and Rietveld refinements allow for studies of both average, long-range structure and local order/disorder

X-ray Diffraction