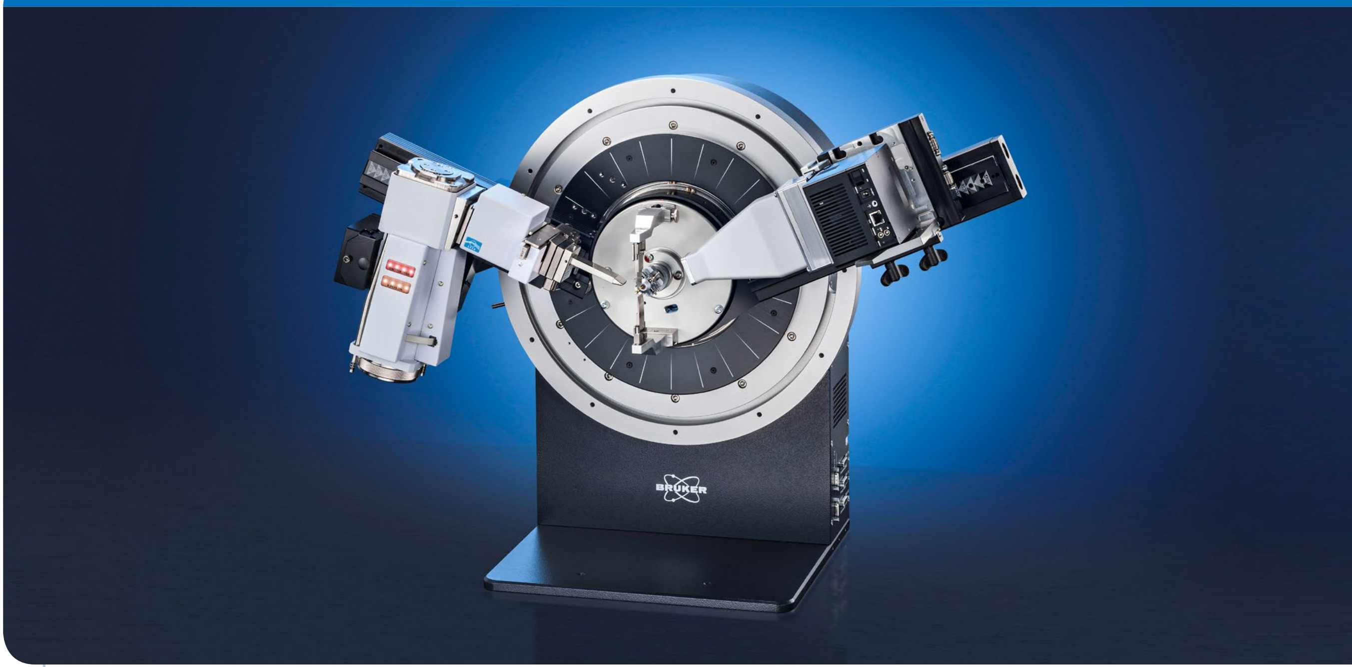

Lab Report XRD 90

PDF Analysis with D8 ADVANCE

- Rietveld and PDF refinements using Ag radiation and EIGER2 R 500K detector

This labreport describes a Pair Distribution Function (PDF) measurement of $LiFePO_4$ powder to investigate structural disorder using a D8 ADVANCE multipurpose diffractometer.

$LiFePO_4$ (LFP) is widely used as cathode material in commercial Li-ion batteries for its good cycling properties and excellent safety characteristics.

New synthesis routes are constantly developed to reduce the battery cost, and also to tune the structural properties since they are known to affect the electrochemical properties of LFP.

Combined PDF and Rietveld refinements are an effective tool to study local defects and help guide more effective synthesis routes.

The EIGER2's large active area of 2,978 mm^2 and the flexible sample to detector distance enables capturing a large portion of the diffracted signal simultaneously, substantially improving sensitivity for PDF measurements. For this measurement, the EIGER2 was placed at a distance of 118 mm from the sample, which equates to 36° 2θ of coverage. Data were collected on LFP powder in a capillary in 1D scanning mode between 2 – 152° 2θ (Q = 0.4 – 21.7 $Å^{-1}$) using a variable counting time strategy (VCT). An empty capillary was also measured and subtracted as background.

Table 1. D8 ADVANCE configuration
Ag radiation (0.56 Å - 22.2 keV)
Focusing Goebel mirror, 1 mm exit slit, 4° primary Soller collimator
0.7 mm Kapton capillary
4° panoramic Soller collimator, EIGER2 R 500K detector in 2θ-optimized mode at 118 mm sample to detector distance
Variable counting time scan from 2 – 152° 2θ 8 h total measurement time

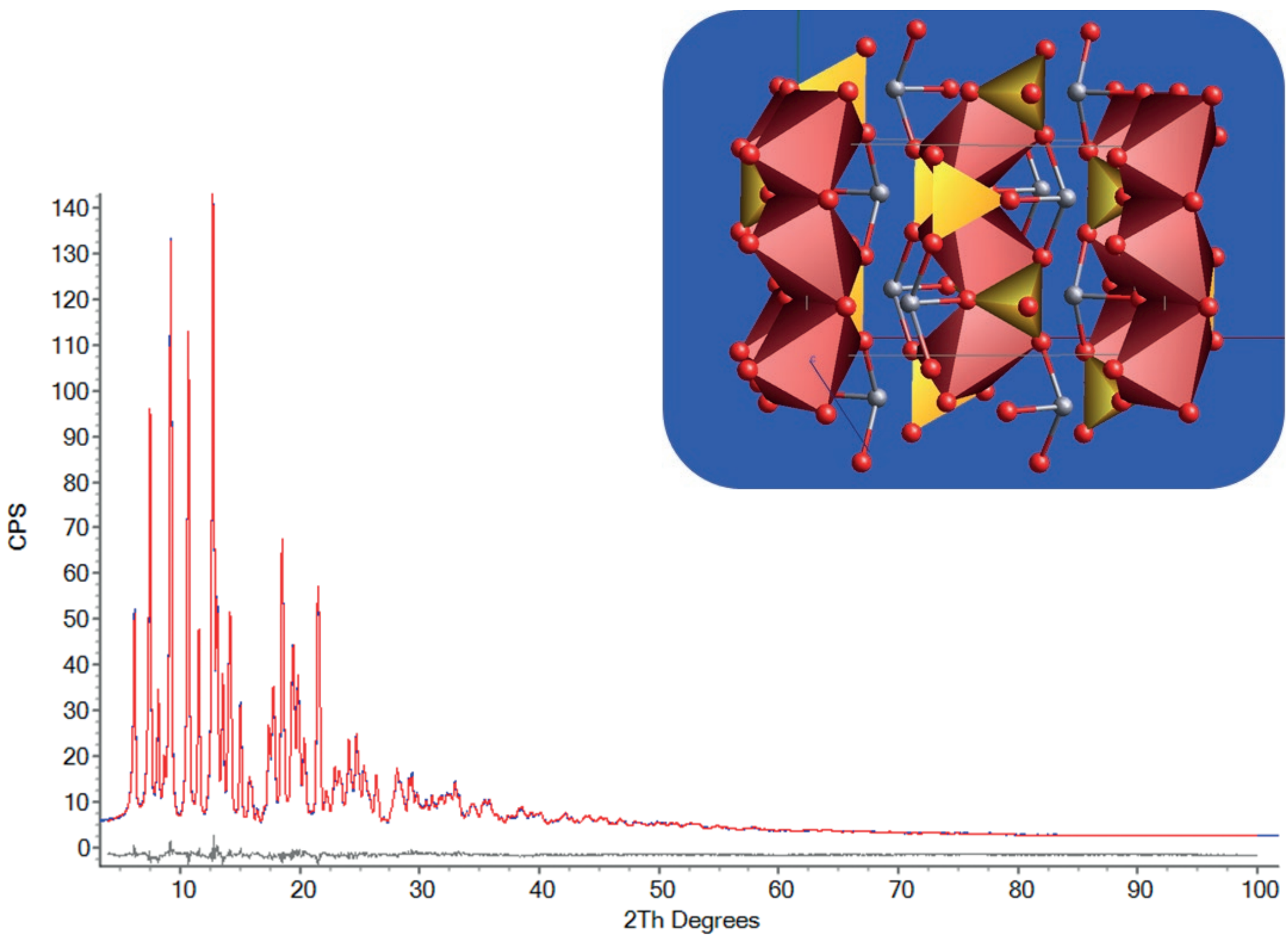

Figure 1: Rietveld structure refinement of LFP with DIFFRAC.TOPAS.

The PDF was created from the raw data using the program PDFgetX3 [1]. The data collection strategy was planned using the WIZARD plugin of DIFFRAC.MEASUREMENT. Rietveld and PDF structure refinements were done using DIFFRAC.TOPAS V6.

The Rietveld structure refinement fit to the raw data is shown in Figure 1. The olivine-type average structure can be described in space group Pnma, and consists of PO_4 tetrahedra with Fe and Li atoms 6-fold coordinated by O atoms. Selected structural parameters are listed in Table 1.

Alternatively, examining the PDF data can give deeper insight about the local structure, and how it may deviate from the average structure [2]. Figure 2 (top) shows the small box refinement fit to the PDF data using the average structure as a model. Disorder can be introduced to the model by using a larger unit cell or by lowering the symmetry. Figure 2 (bottom) shows the PDF fit after lowering the symmetry to $P2_1$, a subgroup of Pnma. Beta was fixed to 90° to keep the unit cell edges orthogonal and Li atom positions were also fixed due to their low scattering power, but all other

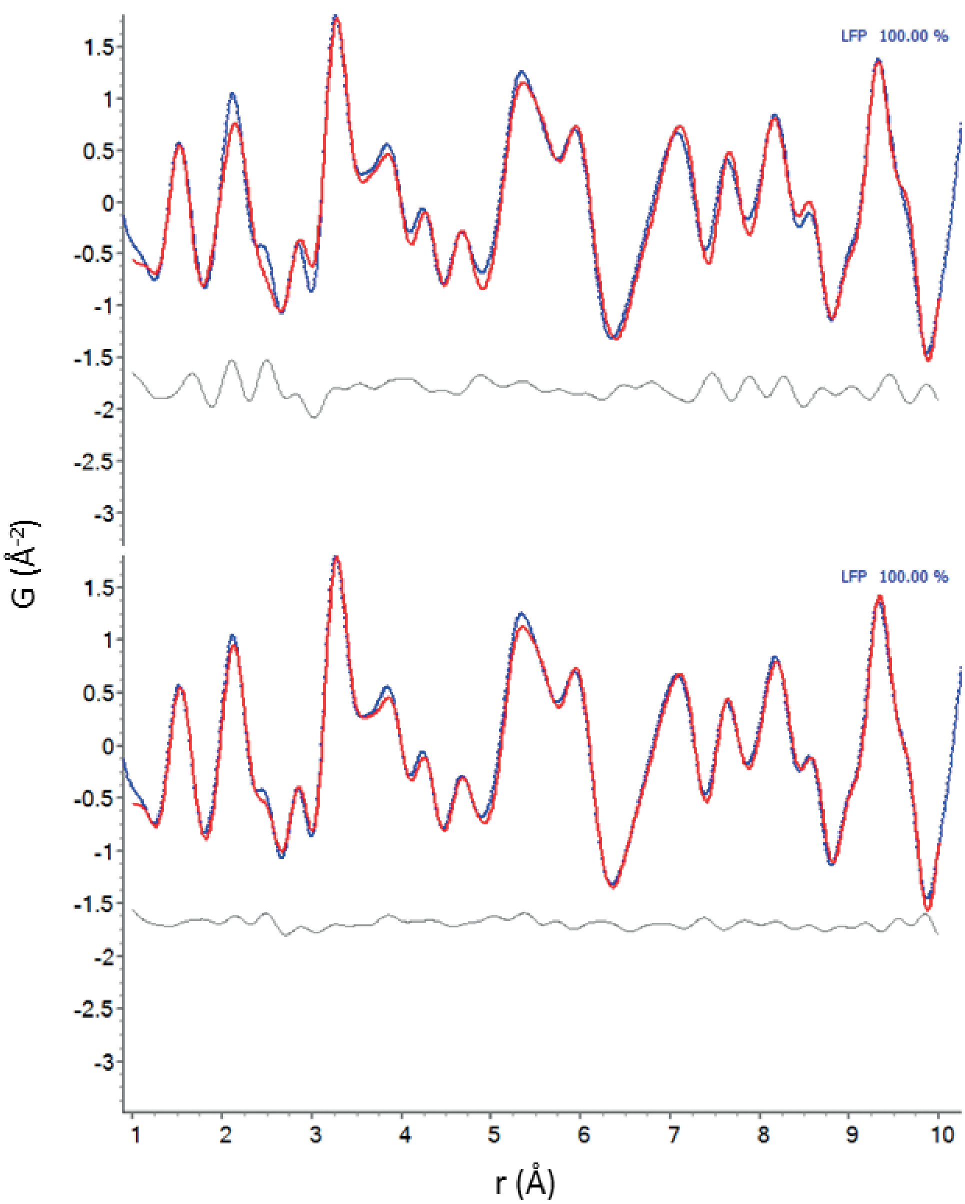

Figure 2: Structure refinements to the PDF data for $LiFePO_4$ using the average structure model (top) and the disordered model (bottom).

atomic coordinates were refined. The resulting fit is considerably better than the Rietveld model (R_{wp} = 6.9 % vs. 14.1 %). While the improvement in R_{wp} is not surprising as there are more refineable parameters, the refined structure remains chemically reasonable and similar to Rietveld model (Table 2).

The D8 ADVANCE with silver radiation and EIGER2 R 500K detector, supported with DIFFRAC.TOPAS represents an ideal solution for PDF investigations in the home laboratory.

	Rietveld (Pnma)	PDF ($P2_1$)
a, Å	10.3168(2)	10.343(3)
b, Å	6.0008(1)	5.999(2)
c, Å	4.6918(1)	4.6825(9)
Li–O, Å	2.086(1) – 2.193(1)	1.87(2) – 2.42(1)
Fe–O, Å	2.049(1) – 2.247(1)	2.03(4) – 2.39(2)
P–O, Å	1.537(2) – 1.574(1)	1.42(4) – 1.68(3)

Table 2: Selected structural parameters from Rietveld and PDF refinements.

Small box PDF refinement

PDF refinement is a new feature available in DIFFRAC.TOPAS V6. A small box PDF refinement is similar to Rietveld structure refinement in that one utilizes a unit cell to describe the structure, but focuses on a different length scale. The flexible macro language combined with ultra-fast speed and stability means that structural models can be quickly and reliably tested. Many PDF-specific macros have been written and are included in the software release.

References

[1] P. Juhás and T. Davis, C. L. Farrow, S. J. L. Billinge, J. Appl. Cryst. 46, 560-566 (2013)

[2] M. Bini et al. RSC Adv. 2, 250-258 (2012)

Bruker AXS GmbH

info.baxs@bruker.com

www.bruker.com

Worldwide offices

bruker.com/baxs-offices

Online information

bruker.com/xrd