## Application Note XRD 608

# D8 ADVANCE

● In Operando Characterization of Lithium Batteries using XRD

Since their commercial introduction beginning of the '90ties, small-size lithium-ion batteries have found wide-spread use in consumer electronics due to their high specific energy and energy density. Recently lithium-ion batteries have also started replacing nickel-metal hydride batteries in hybrid and electric vehicles. These automotive applications require large-size batteries with high energy density and superb cycle life time.

In particular the cathode material has a major impact on the battery capacity. Therefore improving batteries for automotive and power grid applications is very much focused on researching cathode materials and their characteristics, in particular under in operando conditions.

The current application note describes in operando characterization of lithium-based cathode materials using XRD with the D8 ADVANCE.

Innovation with Integrity

XRD

Fig. 1: Battery cell basic design

The battery cell used for the in operando study was developed by the Laboratoire de Réactivité et de Chimie des Solides at the Université de Picardie Jules Verne (Amiens, France), and is exclusively commercialized by Bruker AXS. This user friendly, Swagelock-type battery cell is used by numerous other research groups worldwide and has proven to work efficiently. The basic design is shown in Fig. 1. The positive electrode, the separator (soaked with electrolyte) and the negative electrode are stacked layer by layer in between a Be window and a stainless steel plunger. Further technical details are described by J.B. Leriche et al. in the Journal of The Electrochemical Society 157 (5) A606-A610 (2010). The battery cell fits straight to the rotating sample holder of the D8 ADVANCE diffractometer. Besides for lithium-based electrode materials, the battery cell can also be used for in operando characterization of sodium-based electrode materials.

For the current experiment, the battery cell was prepared in a glove box using $Li^+Fe^{2+}PO_4$ (LFP) as positive electrode material. 15 charge/discharge cycles were run at C/2,5 rate using a potentiostat SP-50 from BioLogic (Claix, France).

Because structural changes occur during cycling it is of utmost importance to collect several diffraction patterns while charging/discharging. The D8 ADVANCE features Dynamic Beam Optimization (DBO), which enables collection of highest quality data over a large angular range in shortest measurement time.

For this particular experiment diffraction patterns were collected from 16°(2θ) up to 38°(2θ) in only 5 minutes. This time slicing results in about 30 diffraction patterns collected during charge and discharge respectively, about 900 diffraction patterns in total in 75 hours.

Upon charging $Li^+$ ions transfer from the positive electrode to the negative electrode. As a consequence LFP is reduced to the Li-free phase ($Fe^{3+}PO_4$, FP). Upon discharging the opposite reaction occurs.

Fig. 2 shows a qualitative phase analysis on a diffraction pattern taken in the course of the charge cycle. Both LFP and FP phases are easily identified.
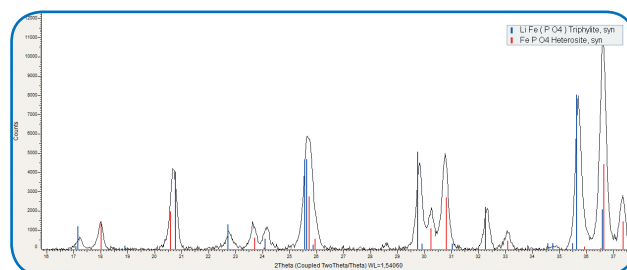


Fig. 2: Qualitative phase analysis with DIFFRAC.EVA of diffraction pattern (background-subtracted) collected during the charging process. LFP and FP are easily identified.
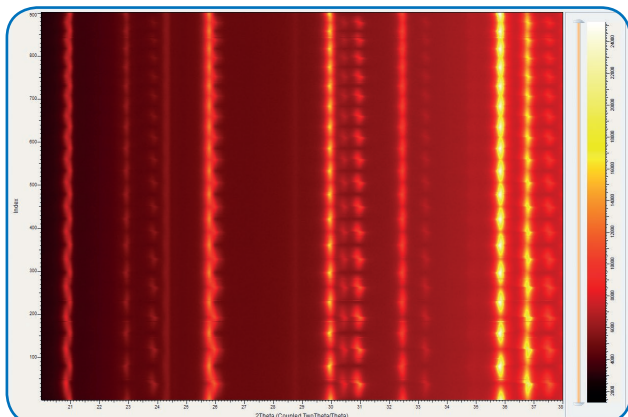
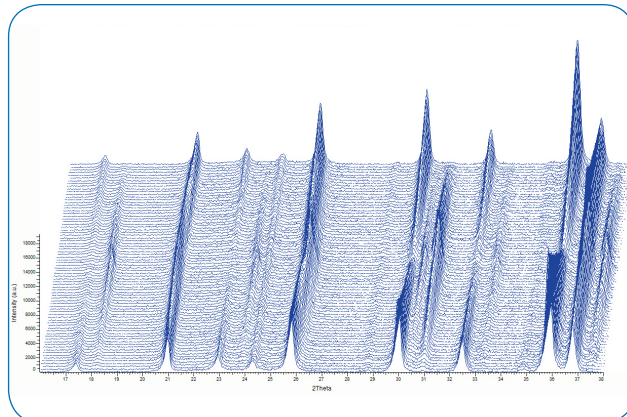Fig. 3a: Iso-intensity plot of the 15 charge/discharge cycles with DIFFRAC.EVA.



Fig. 3b: Waterfall plot of the first charge/discharge cycle with DIFFRAC.EVA.

The iso-intensity plot in Fig. 3a nicely demonstrates that the phase composition changes upon cycling, the waterfall plot in Fig. 3b shows this more in detail for the first charge-discharge cycle.

Fig. 4 shows a zoomed view on the LFP(200) and FP(200) reflections during charge. As expected for this rather slow charge rate the LFP(200) gradually diminishes and the FP(200) gradually increases, indicative of a first-order phase transition.

Beyond this qualitative information, also quantitative and (micro)structural information can be extracted from a Rietveld refinement. This was done in an automated way on all diffraction patterns using DIFFRAC.TOPAS

in batch modus. A typical in operando experiment will consist of several hundreds or even thousands charge/ discharge cycles, hence automated batch mode evaluation is essential to efficiently analyze the large number of diffraction patterns.

Fig. 5 shows a Rietveld refinement of a typical diffraction pattern. Rietveld refinement enables quantification of the respective crystalline phases, as well as obtaining structural information such as the lattice parameters, and microstructural information such as crystallite size parameters.
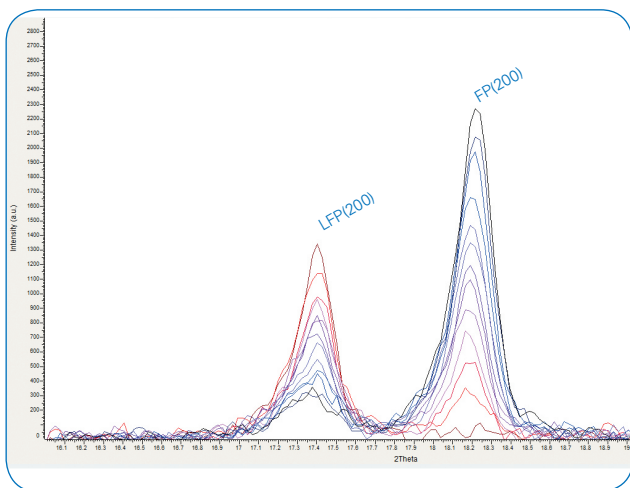


Fig. 4: Zoomed view on the LFP (200) and FP(200) reflections during the first charge cycle. For clarity only every third diffraction pattern is shown.
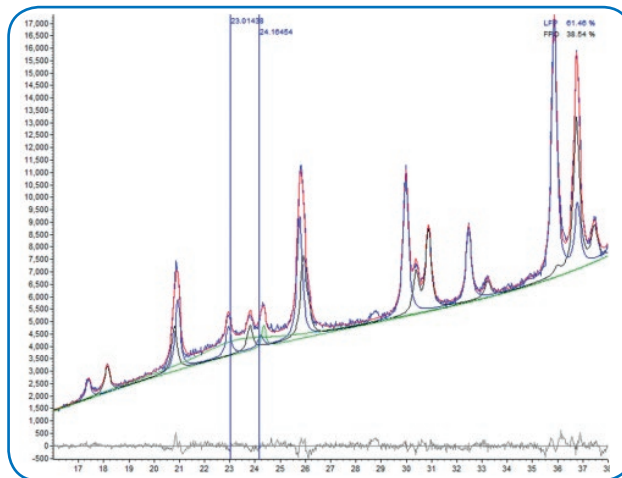


Fig. 5: Rietveld refinement with DIFFRAC.TOPAS. Note that the increase in the background is due to the fact that data have been collected using a variable divergence slit to keep a constant 12 mm footprint. This significantly improves counting statistics at high 2Theta angles without over-illuminating the sample at low 2Theta angles. Unlike traditional Rietveld refinement programs requiring fixed divergence slit data, DIFFRAC.TOPAS can correctly handle both fixed and variable divergence slit data. The hump in the background observed about 23-24°($2\theta$) comes from the amorphous glass fiber separator material.

The quantitative phase amount as obtained from the Rietveld refinement (Fig. 6) is plotted for the first charge-discharge cycle. The data indicate that upon charging there is a conversion from LFP to FP, which is completly reversible upon discharging.

$Li^+$ extraction and insertion also has an effect on the crystal structure of the respective phases and clearly follows the charge/discharge cycle. Fig. 7 shows the evolution of the c-lattice parameter during cycling.

Also the crystallite size changes upon cycling. The effect is rather small for LFP, but the FP crystallite size decreases significantly upon approaching full discharge (Fig. 8).

This application note demonstrates that a wealth of information can be obtained from in operando studies on battery materials using a home-lab diffractometer.
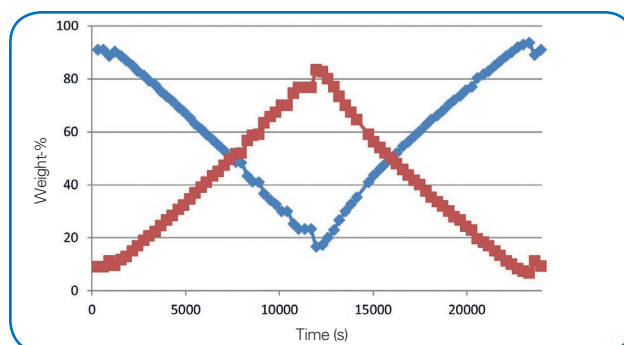
### Acknowledgement

Fig. 6: Quantitative phase analysis results for the first charge-discharge cycle, derived from Rietveld refinement with DIFFRAC.TOPAS, LFP (blue) and FP (red)
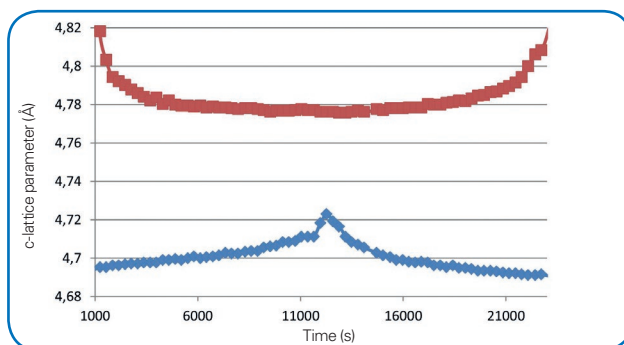


Fig. 7: Evolution of the c-lattice parameter for the first charge-discharge cycle, LFP (blue) and FP (red). Results close to full discharge have not been taken into account since FP is almost not present.
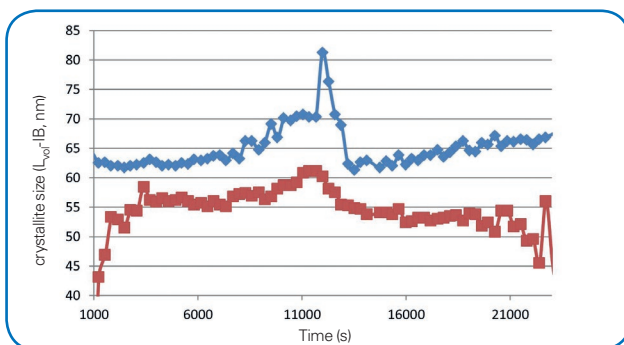


Fig. 8: Evolution of the crystallite size for the first charge-discharge cycle, LFP (blue) and FP (red). Results close to full discharge have not been taken into account since FP is almost not present.

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