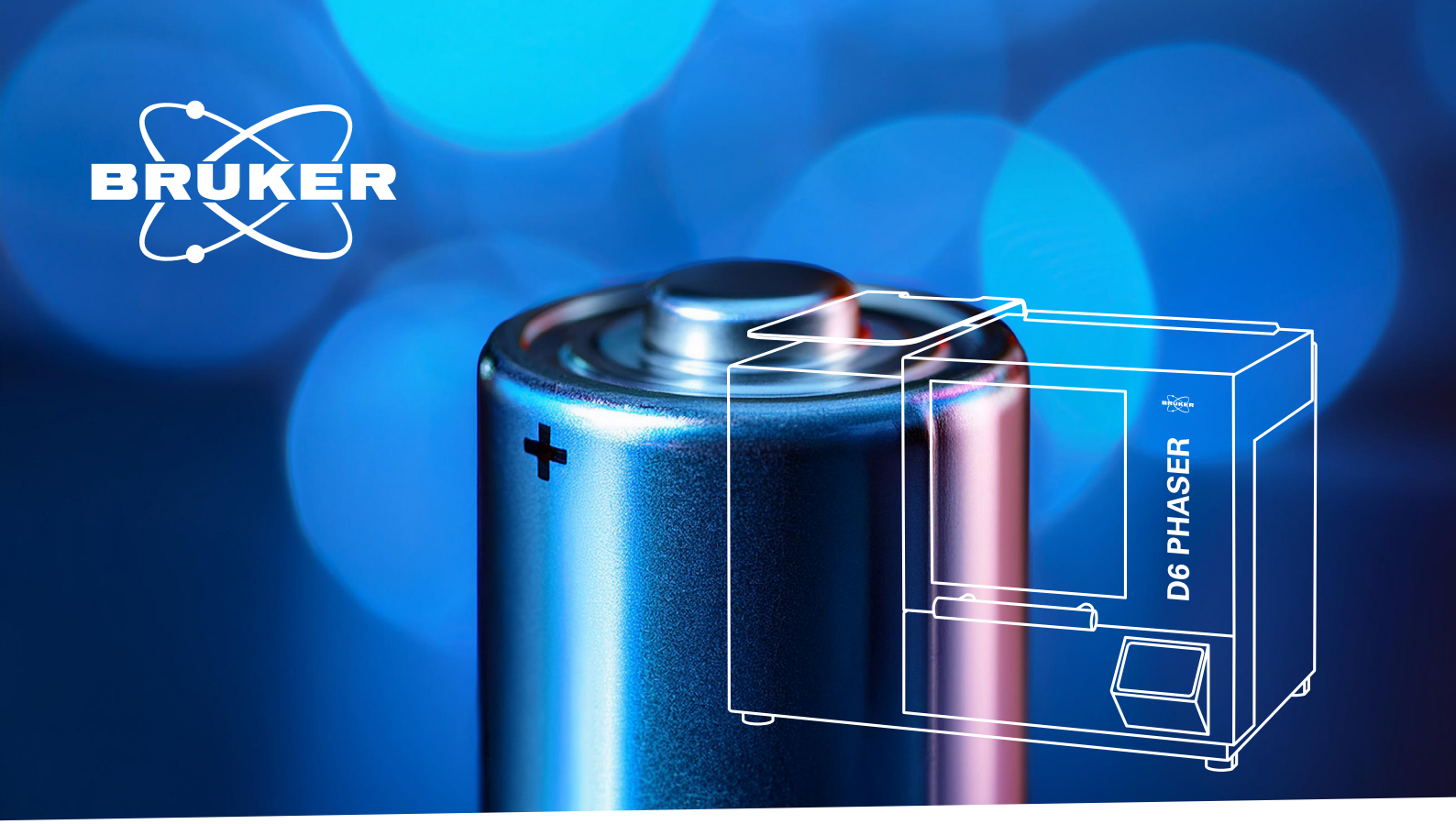

X-RAY DIFFRACTION

D6 PHASER – Operando XRD on a Benchtop

Application Report 49

Operando X-ray diffraction plays a crucial role in advancing our understanding of energy storage systems, aiming to enhance the efficiency and durability of batteries by providing valuable insights into dynamic processes such as phase transitions, lattice parameter variations, and other crystallographic transformations within the electrodes. In this report, we present the capabilities of the D6 PHASER for operando XRD analysis on a Li-ion battery pouch cell.

The pouch cell used in this experiment consisted of a single 139 µm thick layer of NMC622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) coated on Al foil (15 µm), a separator (20 µm), and a graphite layer (46 µm) coated on Cu foil (10 µm), all packed in a polymer-Al composite bag.

The total thickness of the pouch cell was about 500 µm. Typically for diffraction experiments on pouch cells, shorter wavelength X-ray sources like a Mo tube that produce harder radiation are preferred to reduce the effects of X-ray absorption and to penetrate through the entire cell. However, for relatively thin pouch cells like this, a Cu source can also provide excellent results.

Two charge/discharge cycles were performed at a C/10 rate (10 h charge, 10 h discharge, 40 h total), controlled by a SP-50 potentiostat from BioLogic. The potentiostat is fully integrated into DIFFRAC.SUITE, meaning the entire experiment can be planned and controlled in DIFFRAC.WIZARD. Diffraction patterns between 15 – 62° 2θ were continuously collected during cycling.

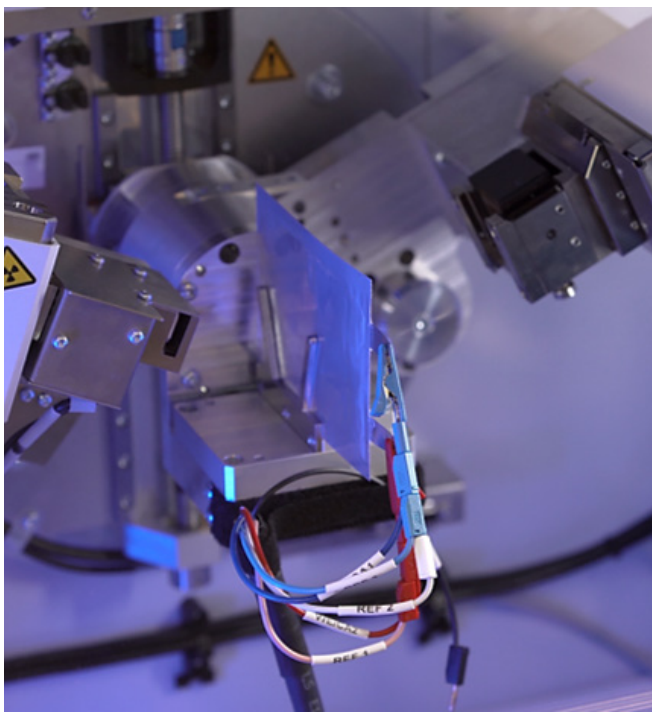

Figure 1
A pouch cell mounted in the D6 PHASER.

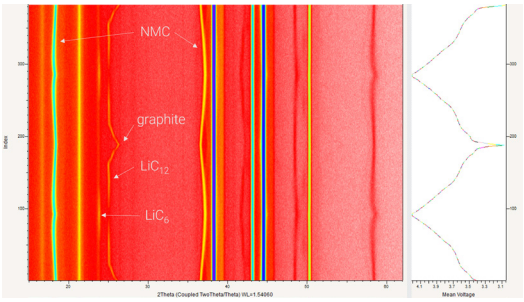

Figure 2
2D iso-intensity plot of all diffraction patterns, including the mean voltage for each scan.

Thanks to the high-power generator (1200 W) and compact size of the D6 PHASER, high quality diffraction data could be obtained in just 6 min, resulting in nearly 400 patterns over the duration of the experiment. The large number of datasets provides detailed insights into the structural changes occurring during the cycling process. Figure 2 shows a 2D iso-intensity plot of all the diffraction patterns, along with the mean voltage for each scan, allowing for easy correlation of structural changes or new species formation with electrochemical parameters.

More detailed information, like lattice parameters, phase quantities, and crystallite size, can be extracted from a Rietveld refinement. A typical operando experiment consists of several hundred or even thousands of datasets. In this example, the nearly 400 datasets were analyzed in just a few seconds using DIFFRAC.TOPAS. An additional challenge to analyzing pouch cells with XRD is the sandwich layer design of the cell itself. Each phase has a different thickness, absorption coefficient, and is at a different spatial position within the cell, meaning corrections for peak positions, intensities, and profiles must be included for an accurate structural evaluation. This kind of complex sample model can be easily setup in DIFFRAC.TOPAS.

Figure 3 summarizes the results of the Rietveld refinement of all 384 scans, including the evolution of the lattice parameters for NMC and the phase changes occurring in the anode.

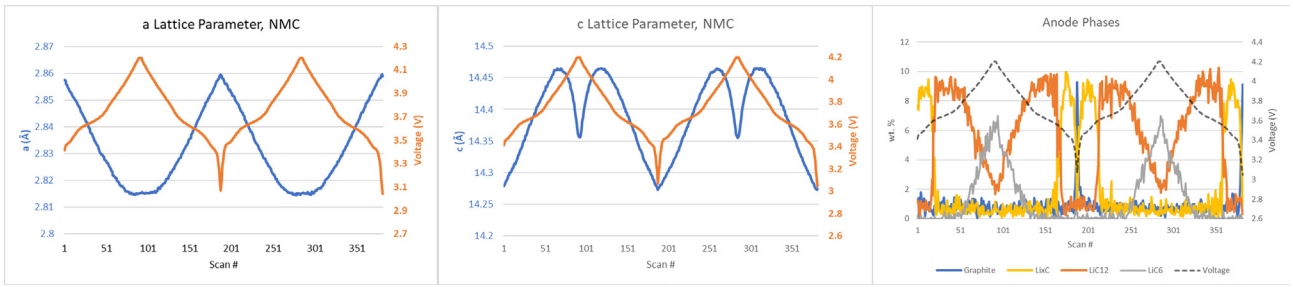

Figure 3
Evolution of the lattice parameters of NMC (left, middle) and quantification results of the anode phases (right) as a function of state of charge, plotted with the mean voltage.

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