

## X-RAY DIFFRACTION

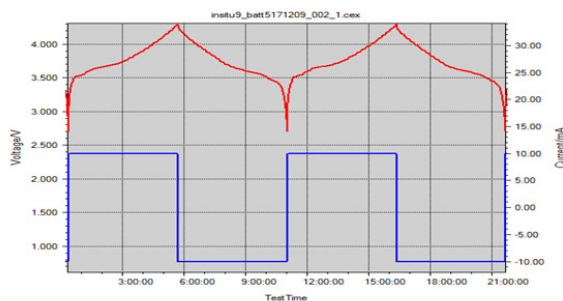
# In Operando XRD of Battery Pouch Cells

Characterization of an NMC pouch cell with the EIGER2 R 500K

Pouch cells have become an industry standard battery design due to their efficient shape and lightweight construction. In operando measurements allow simultaneous monitoring of the cathode and anode for cycling effects which influence energy storage performance. This lab report describes in operando characterization of an NMC pouch cell using XRD with the D8 ADVANCE equipped with Mo radiation and the EIGER2 R 500K detector.

The pouch cell used in this experiment was made of a single NMC ( $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ ) layer (67  $\mu\text{m}$ ) coated on Al foil (15  $\mu\text{m}$ ), a separator (40  $\mu\text{m}$ ), and graphite (82  $\mu\text{m}$ ) coated on Cu foil (9  $\mu\text{m}$ ). The electrodes were immersed in a  $\text{LiPF}_6$  electrolyte solution, and packed in a polymer-Al composite bag.

The pouch cell was positioned in the center of the diffractometer, held by two clamps. The total thickness of the pouch cell was about 920  $\mu\text{m}$ . Mo radiation rather than the more common Cu radiation was used for the transmission measurements to reduce the effects of X-ray absorption by the pouch cell. The thick Si sensor of the EIGER2 R 500K is well suited for wavelengths ranging from Cr to Mo, producing high signal while reducing the background by minimizing the effects of charge sharing.



**Figure 1**

Charge/discharge profile showing the evolution of the cell voltage (red) with applied current (blue)

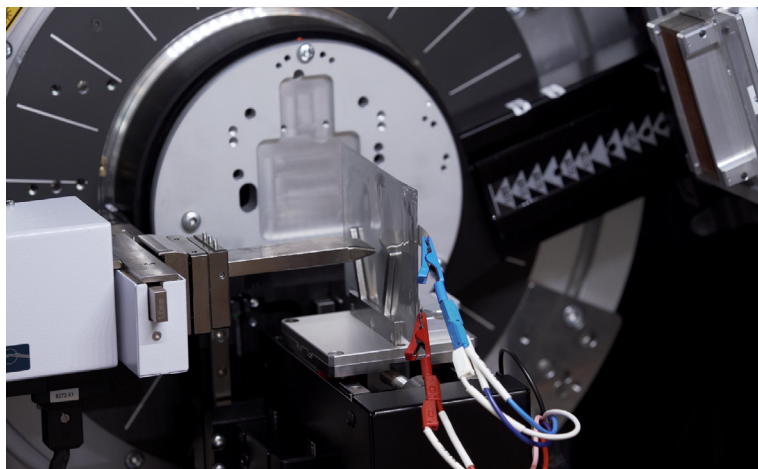
Two charge/discharge cycles were done at C/5 rate (5 hr charge, 5 hr discharge), leading to a total cycling time of 20 hours. The pouch cell was charged at constant current, the charge/discharge profile is shown in figure 1.

Diffraction data were collected during charge/discharge cycling. For this particular experiment, diffraction patterns were collected in transmission geometry from 7-32° 2 $\theta$ . This angular range was covered in a single shot with the EIGER2 R 500K detector. This allows for fast data collection with only 3 min per diffraction pattern, resulting in 400 diffraction patterns collected over the 20 hr experiment. The fine time slicing provides detailed insight on the structural changes happening during the cycling process. The excellent data quality and high intensity of the individual diffraction patterns suggest that data collection time could be reduced below 1 minute.

Experiment	Start Time	Duration	Operation	Applied	Unit	Start	End	Status
Charge 1	08:00:00	5:00	Charge	25.00	[A]	08:00:00	08:05:00	Success
Discharge 1	08:05:00	5:00	Discharge	-10.00	[A]	08:05:00	08:10:00	Success
Charge 2	08:10:00	5:00	Charge	25.00	[A]	08:10:00	08:15:00	Success
Discharge 2	08:15:00	5:00	Discharge	-10.00	[A]	08:15:00	08:20:00	Success

**Figure 2**

Experiment planning table view in DIFFRAC.WIZARD



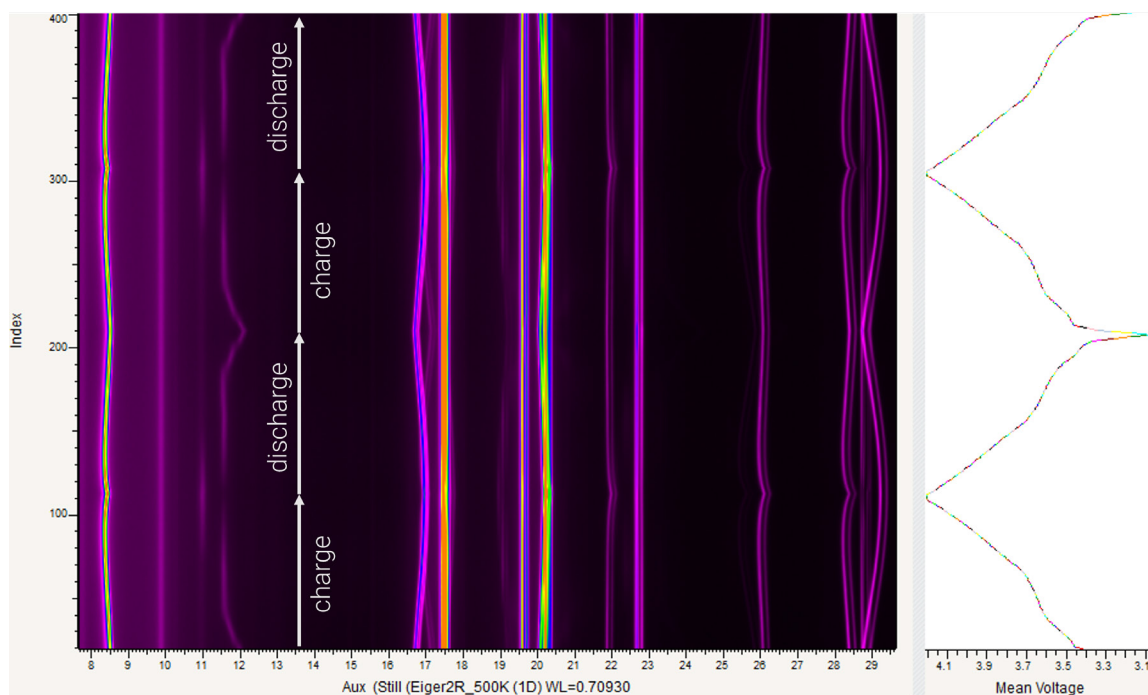
**Figure 3**

Set-up of the D8 ADVANCE used for the in-operando charge/discharge experiments

During charging Li<sup>+</sup> ions migrate from the positive electrode to the negative electrode, where they intercalate in the graphite layers. This process is reversed upon discharge.

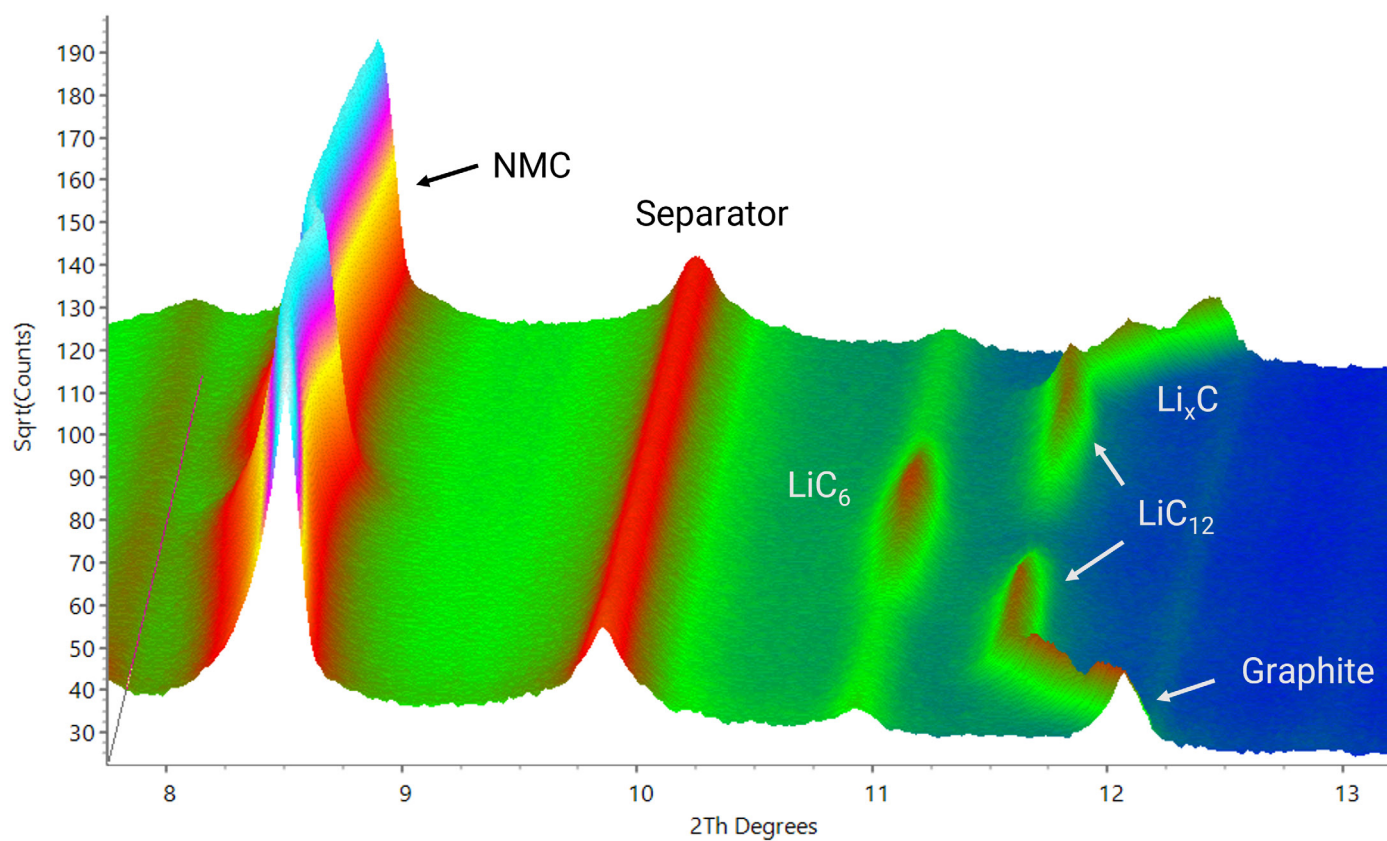
The iso-intensity plot in figure 4 shows the changes in phase composition during the two charge/discharge cycles. In the side view on the right, additional parameters like the mean voltage can be plotted together with the diffraction data, making it easier to identify new species or transition points. Figure 5 shows a waterfall plot of all scans between 8 and 13° 2 $\theta$ . As Li<sup>+</sup> ions migrate to the anode during charging, different lithium carbide phases are formed, which is clearly seen in the peaks between 11 and 12° 2 $\theta$ . At the same time, the (003) peak of NMC shifts to lower angle, indicating an increase in the distance between the layers of metal-oxygen atoms.

Beyond this qualitative information, more details can be extracted from a Rietveld refinement. A typical in-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[1]. This kind of complex sample model can be easily setup in DIFFRAC.TOPAS.



**Figure 4**

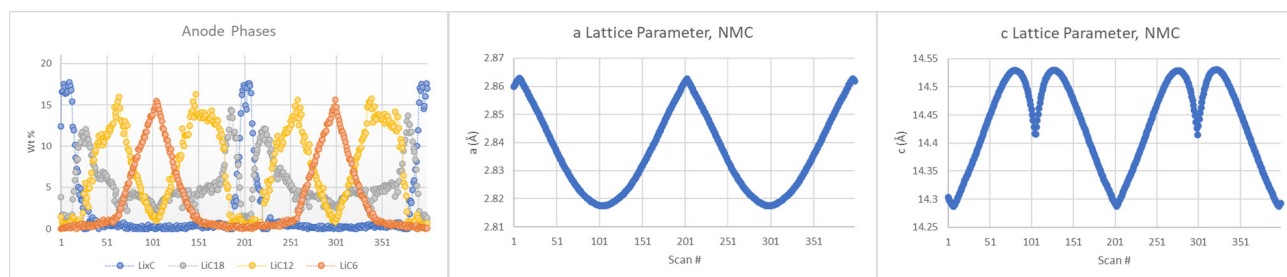
Iso-intensity plot of the two charge/discharge cycles with DIFFRAC.EVA, including mean voltage information in the side view



**Figure 5**

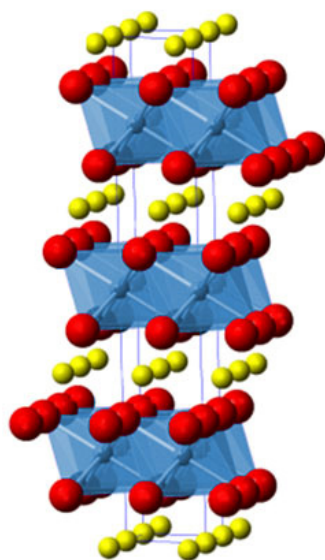
Waterfall display of the low-angle region of a single charge/discharge cycle, including phase identification





**Figure 6**  
Evolution of the different lithium carbide phases present in the anode (left), and the lattice parameters of NMC (middle, right) as a function of state of charge

The left image in figure 6 shows the evolution of lithium carbide phases present in the anode during the cycling process. As  $\text{Li}^+$  intercalates into the graphite layers during charging, the interlayer spacing begins to expand and a  $\text{Li}_x\text{C}$  phase starts to form, followed by  $\text{LiC}_{18}$ , then  $\text{LiC}_{12}$ , and finally a Li-rich  $\text{LiC}_6$  phase. Once fully charged, the anode consists almost completely of  $\text{LiC}_6$ .



**Figure 7**  
Layered structure of NMC; Li (yellow),  $\text{O}^{2-}$  (red), M (blue)

The other two images in figure 6 illustrate the interesting behavior of the NMC structure during cycling. The a-lattice parameter decreases during charge, as intuitively expected since Li transfers from NMC to graphite. The c-lattice parameter shows a strong initial increase during charge, followed by a decrease just before reaching its maximum capacity. This behavior is linked to the layered structure of NMC. Figure 7 shows that the metal atoms (Ni, Mn and Co) are arranged in layers of  $\text{MO}_6$  octahedra stacked along the c-axis with Li atoms in-between. During charge, Li leaves the structure leading to strong O–O electrostatic repulsion. As a consequence, the c-lattice parameter expands. The then following reduction of the c-axis at higher charge levels (at > 4V) can possibly be linked to a charge transfer from oxygen to the transition metals, which would reduce again the O–O electrostatic repulsion. At the same time, the transition metal oxidation state increases, reducing the radii of the metal ions and resulting in a stronger M–O attraction. This primarily affects the  $\text{MO}_6$  layers in the ab-plane and explains the decrease of the a-lattice parameter.

This lab report demonstrates that a wealth of structural information can be obtained from in operando studies on battery materials using a D8 ADVANCE diffractometer equipped with Mo radiation and the EIGER2 R 500K detector. Efficient data collection strategies allow for fine time slicing, providing detailed insight on the structural changes happening during the cycling process.

## References

- [1] Rowles, M.R. & Buckley, C.E. (2017), J. Appl. Cryst.50, 240-251

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