IN SITU AND *OPERANDO* CHARACTERIZATION OF **BATTERY MATERIALS USING X-RAYS**

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INTRODUCTION

X-ray diffraction, scattering and imaging are powerful tools for the study of battery materials [1, 2].
We describe here X-ray methods which allows the researcher to combine multiple X-ray techniques to obtain a wealth of information about new materials used in battery applications.

By using X-ray diffraction (XRD) it is possible to identify the different crystallographic phases, and with the Rietveld method [3] it is possible to refine the crystallographic structures of the different materials and quantify the amount of each phase in the bulk material.

It is also possible to perform *in situ* and *operando* XRD measurement of the complete batteries. This can be done either in reflection geometry or in transmission geometry [4-6]. In order to perform the measurements in transmission geometry, more penetrating radiation is required, e.g. Mo or Ag X-ray anodes. A newly developed Malvern Panalytical X-ray detector (GaliPIX^{3D}) allows for shorter measurement time and/or better data quality thanks to the higher efficiency of the CdTe sensor material [7].

In addition, the short-range structure of crystalline, nano-crystalline and amorphous materials can be studied with the Pair Distribution Function method (PDF), based on a total scattering approach. Also for this technique, hard X-ray radiation (Mo or Ag) is required.

Imaging is also a very useful technique, enabling detailed view of the interior structure of the battery in a non-destructive way.

All X-ray scattering and imaging experiments can be performed on a single X-ray instruments, such as a Malvern Panalytical Empyrean multipurpose diffractometer.

A. X-RAY TECHNIQUES ON LABORATORY SYSTEMS FOR BATTERIES

Below a non-exhaustive list of applications which are possible on a laboratory system is reported:

- Phase identification
- Phase quantification
- Lattice parameters refinement
- Structural behavior *in situ* and *operando*
- Pair Distribution Function analysis
- Nanoparticle size analysis (SAXS)
- Non-ambient experiments
- Imaging (radiography/CT)

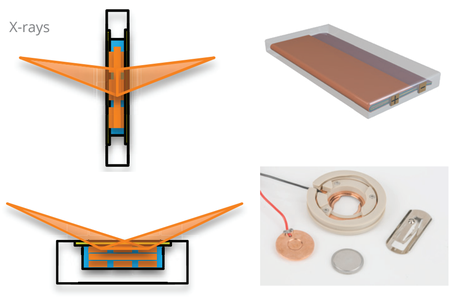
Different solutions are available for XRD studies of batteries:

Transmission geometry:

- Gives the full picture, on pouch cells or prismatic batteries
- Hard radiation tubes and optics
- Efficient detectors for hard radiation (i.e. GaliPIX^{3D})
- Customizable sample holders to fit sample shape and size

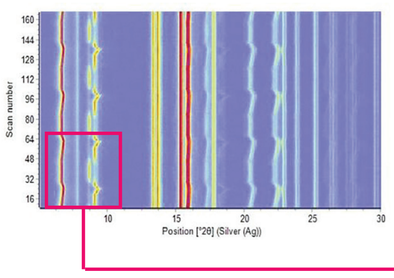
Reflection geometry:

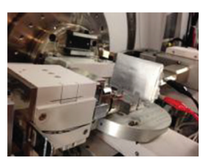
- Sample holders for coin cell with electrical contacts
- Electrochemical sample stages integration
- Customizable solutions

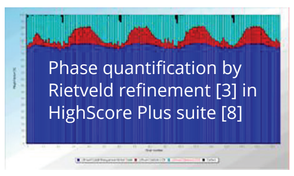


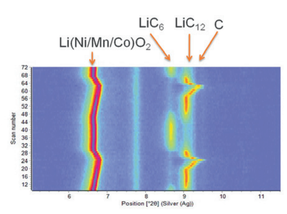
B. *IN SITU* AND *OPERANDO* X-RAY DIFFRACTION (XRD)

In situ X-ray diffraction analysis allows the structural analysis of electrode materials within the electrochemical cell at specific states of charge, as opposed to the more conventional *ex situ* analysis which requires the disassembling of the cell and the extraction of the electrodes for the XRD analysis.
The *operando* (Latin word for "operating") technique allows the characterization of the structural evolution of the crystalline phases contained in batteries and pouch cells, simultaneous with the operation of the reaction, under non-equilibrium and real-time conditions [4,5].
The combination of *in situ* with *operando* X-ray powder diffraction is then an even more powerful tool, and is widely used today by the research community [6].
Below, an example of *in situ* and *operando* XRD experiment on a Li battery is shown (4 complete cycles of charge/discharge, 5 minute/scans, Ag radiation, GaliPIX^{3D} detector):







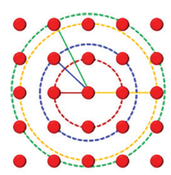


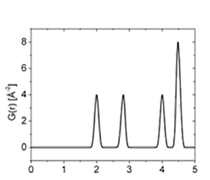
C. PAIR DISTRIBUTION FUNCTION (PDF)

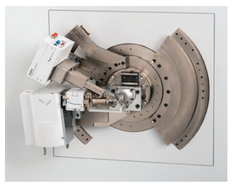
A Pair Distribution Function (PDF) provides the probability of finding atoms separated by a certain distance, from which local structure and distortions can be studied. In order to reach sufficient atomic resolution, high energy X-rays must be used (Ag or Mo radiation).

The PDF is applicable to nanocrystalline and amorphous materials, and even liquids, and can be used for the analysis of:

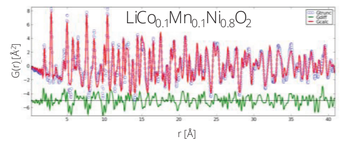
- Short-range order (local structure).
- Long range order.
- Size of coherently scattering domains (average crystallite size).







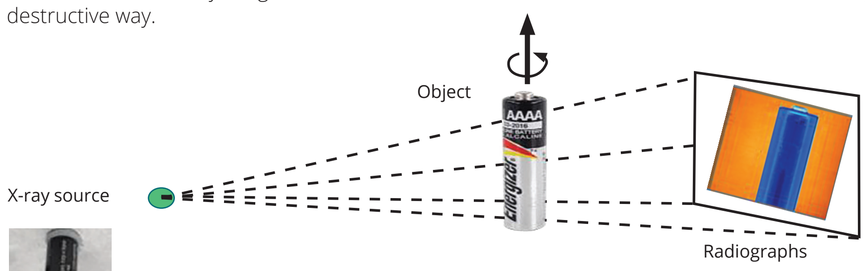
Example of PDF analysis of $LiCo_{0.1}Mn_{0.1}Ni_{0.8}O_2$ powder.
Setup: focusing mirror for Ag radiation, GaliPIX^{3D} detector [7].
Measurement time: 7 hours.

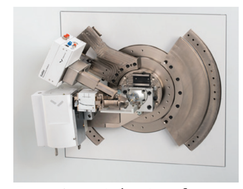


PDF generated by Malvern Panalytical HighScore Plus software v. 4.5 [8];
PDF fit performed with PDFgui software [9], with experimental data (blue points), calculated profile (red line) and difference curve (green line).

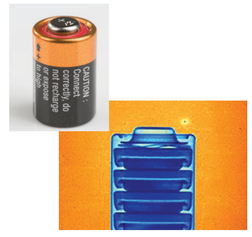
D. X-RAY RADIOGRAPHY (2D IMAGES)

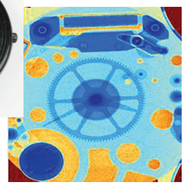
The same type of diffractometer (Malvern Panalytical Empyrean) which can be used for *in situ/operando* XRD and for the PDF analysis, can also be employed for X-ray Radiography and Computed Tomography (see next section). A sample (for instance a complete battery) is placed in the X-ray beam, the radiation transmitted through the object is recorded by the detector and stored as 2D X-ray image. Several information on the internal structure can be derived by the radiographs, in a non-destructive way.





Experimental setup for X-ray Radiography and Computed Tomography.

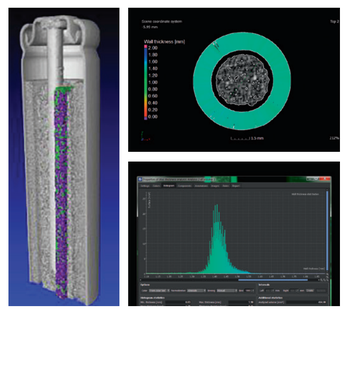




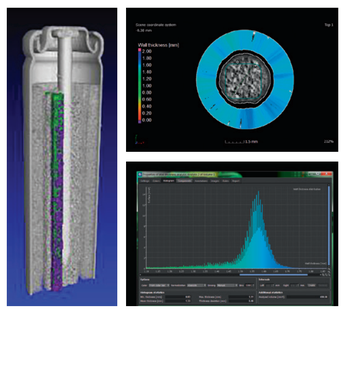
E. X-RAY COMPUTED TOMOGRAPHY (CT)

Computed Tomography (CT) is an imaging method which can provide detailed and non-destructive information about the object of interest, e.g. its structure, the materials it is made of, defects, inclusions and pore sizes, as well as their distribution. Digital processing of a large series of 2D X-ray images (radiographs) generates a 3D object (reconstructed volume). This provides information not only of the surface of the sample, but also of the internal parts of the object. The experimental setup for CT is the same as the one used for the X-ray radiographs, the only difference being that the sample is being rotated during a CT experiment [10].

Volume reconstruction
charged AAAA battery
(1.5 V) Porosity: 18.9 %



Volume reconstruction
discharged AAAA battery
(0.9 V) Porosity: 14.5 %



The volume reconstruction shows lower porosity and higher wall thickness in the discharged battery

References

[1] E. Talaie et al., Energy & Environmental Science 8, 2512-2523 (2015).
[2] Z. Liu et al., Chemistry of Materials 26(8), 2513-2521 (2014).
[3] H.M. Rietveld, J. Appl. Cryst. 2, 65 (1969).
[4] I. Buchberger et al., Journal of The Electrochemical Society 162(14), A2737-A2746 (2015).
[5] N. Sharma et al., ChemSusChem , 8, 2826-2853 (2015).
[6] E. Talaie et al., Chemistry of Materials, DOI: 10.1021/acs.chemmater.6b02726 (2016).
[7] G. Confalonieri et al., Powder Diffraction Journal, 30(2), Supp. 1, S65 (2015).
[8] T. Degen et al., Powder Diffraction 29 (S2) (2014).
[9] C.L. Farrow et al., J. Phys.: Cond. Matter, 19, 335219 (2007).
[10] H. Pöllmann et al., Proceedings 34th Int. Conf. on Cement Microscopy 2012, 266 – 288, Halle, Germany (2012).

Conclusions

X-ray techniques can give invaluable insights to develop new battery materials. In this contribution we showed various examples of what can be learned from the different materials of a battery using X-ray analysis, as well as *in situ* and *operando* measurements of batteries during charge/discharge.
For more information about the Malvern Panalytical X-ray solutions for battery materials, please visit our website: www.malvernpanalytical.com