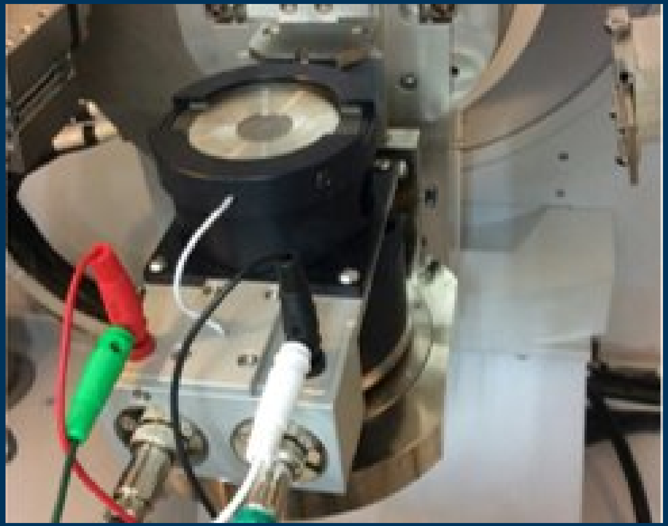
HBM Prenscia Technology Day

Virtual Seminar Series



Understanding Electrode Materials Stability with Charge Discharge Cycling

Presented by Mr. Umesh Tiwari
SMM, Advanced Materials
Malvern Panalytical

Session #1: Electric Vehicle Battery Testing

Understanding Electrode Materials Stability with Charge Discharge Cycling

Abstract

The electrodes in a lithium-ion battery undergo reversible electrochemical reactions as lithium enters and leaves the atomic structure of the intercalated lithium compounds. Particle size, shape and crystal structure of electrode materials play an important role in Li ion diffusion and their transportation during charge-discharge cycling. Reversibility of these electrochemical reactions with cycling largely governs the lifetime of the batteries. With certain battery chemistries, these electrochemical reactions render the electrode materials unstable state, pushing them into irreversible physical or structural changes, ultimately leading to battery degradation with cycling. Understanding the intricacies of these electrochemical reactions is, therefore, an important step to improve battery performance. X-ray diffraction (XRD) and scattering is well-suited to study these atomic phase changes, as well as a tool to understand and optimize the pathways that lithium uses to move through the electrodes. However, XRD investigation of battery materials requires special considerations that are different form the routine powder diffraction measurements.

This presentation will review the techniques related to dimensional measurements in battery electrode materials and how these relate to the battery capacity. Special focus would be on X-ray diffraction and scattering methods including considerations for experimental design. Some examples will be shared on how these considerations are applied to cathode material analysis, including Rietveld refinement, to quantify phase mixtures and atomic structure. A case study on the analysis of NCM based batteries with in-operando XRD, to track phase changes and potentially the degradation mechanisms during charge-discharge cycling, will be shared.

About the presenter, Umesh Tiwari

Umesh Tiwari has been working with Malvern Panalytical for more than 17 years in various roles starting as an application specialist for X-ray diffraction and scattering methods. Currently he is responsible for Energy, Electronics and Environment segments with special focus on Li ion batteries that are revolutionizing all these segments. After receiving his Ph.D. from Jawaharlal Nehru University, New Delhi, he worked for 6 years as research scientists in Solid State Physics Laboratory, Delhi, before joining PANalytical in 2003. In addition to his current segment focus, he is also responsible for the deployment of new innovations in X-ray analytical technology and feeding the future analytical developments with the voice of customers.

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a spectris company

Understanding Electrode Materials Stability with Battery Cycling

Umesh Tiwari, Ph.D.

Malvern Panalytical

Structural, Elemental and Morphology solutions

Almelo, The Netherlands

X-ray diffraction (XRD)
X-ray fluorescence (XRF)

Malvern, UK

Particle (morphology) analysis

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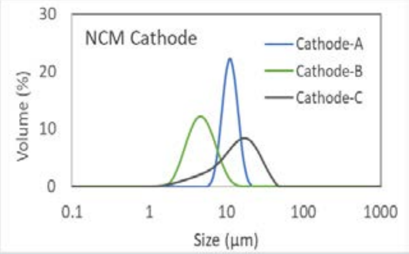
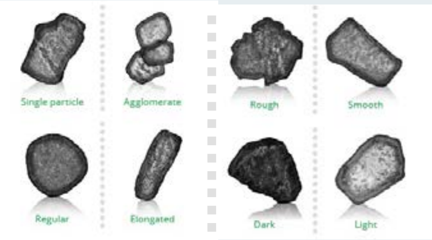
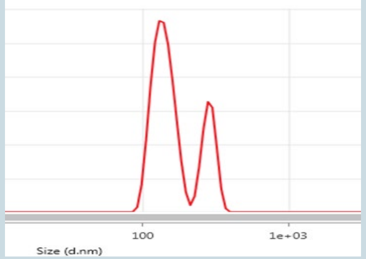
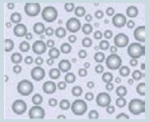
Battery Materials

	Product	Parameters analyzed	Sample types
	**Mastersizer3000** (Laser Diffraction)	Particle size distribution 	Dry powders and liquid dispersions / slurry
	**Morphology 4** (Optical Imaging)	Particle shape Analysis 	Dry powders and liquid dispersions / slurry
	**Zetasizer** (Dynamic light scattering and zeta potential)	Nano-particle size and Zeta potential 	liquid dispersions / slurry  

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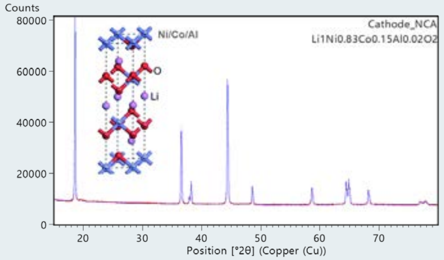
Battery Materials

	Product	Parameters analyzed	Sample types
	**Epsilon 4 / Zetium** (XRF)	Elemental composition Ni 80.4% Co 9.7% Mn 9.9%	Dry powders and liquid dispersions / slurry
	**Aeris / Empyrean** (XRD)	Crystal Phase analysis 	Dry powders and liquid dispersions / cells
	**OMNISEC** (GPC/SEC)	Polymer: Molecular size, weight and branching	Polymers

Battery cell Manufacturing

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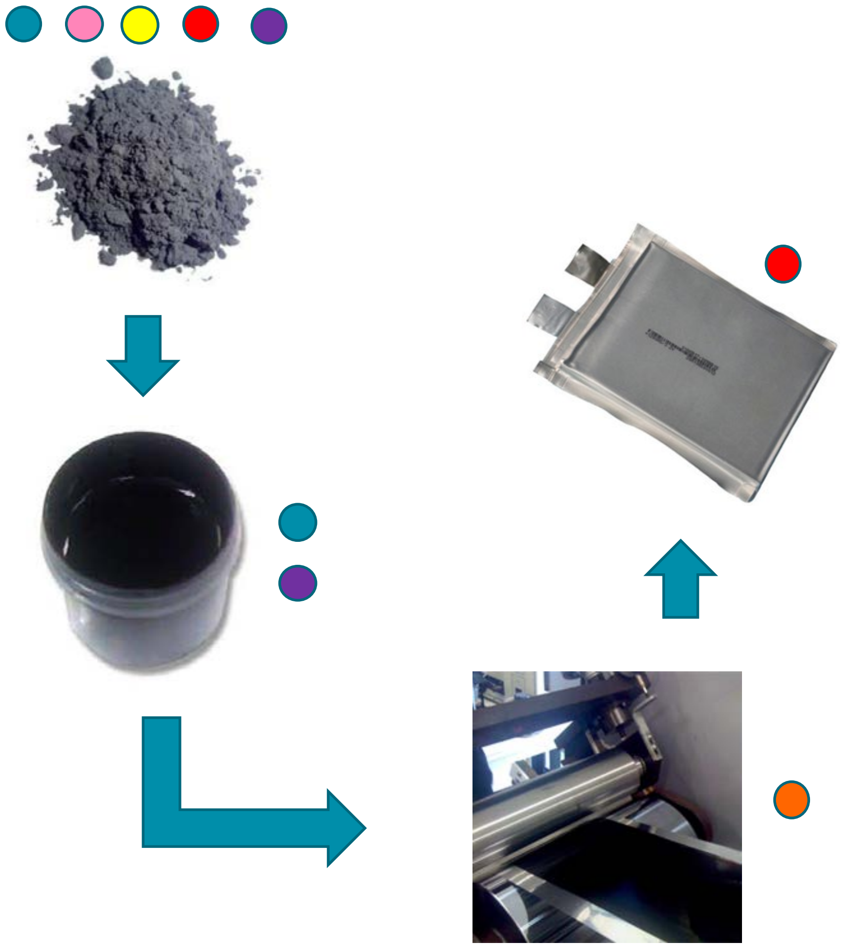


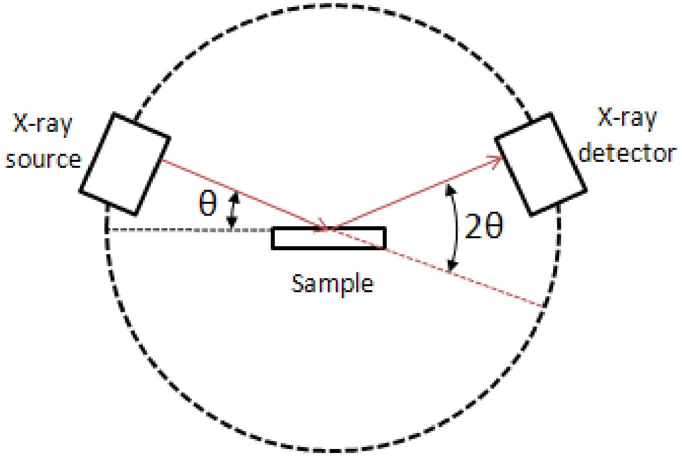
- Mastersizer
- Morphologi 4
- XRD (Aeris / Empyrean)
- XRF (Epsilon 4 / Zetium)
- Zetasizer
- MicroCaliper Thickness sensor (NDC)

X-Ray Diffraction

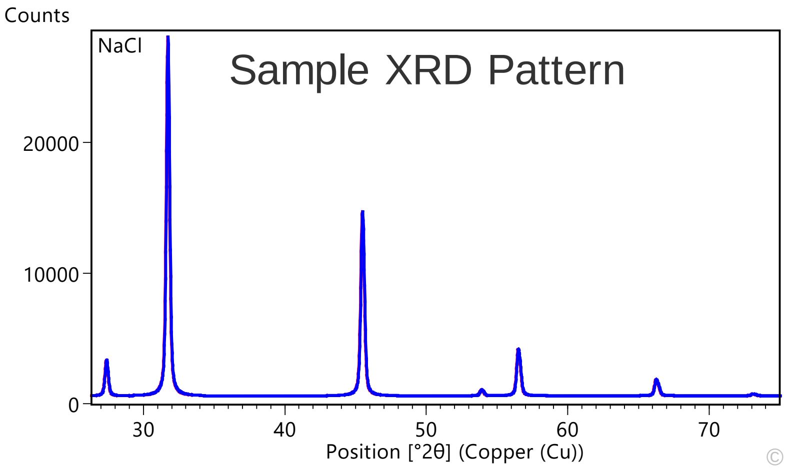
A technique to investigate crystal phase

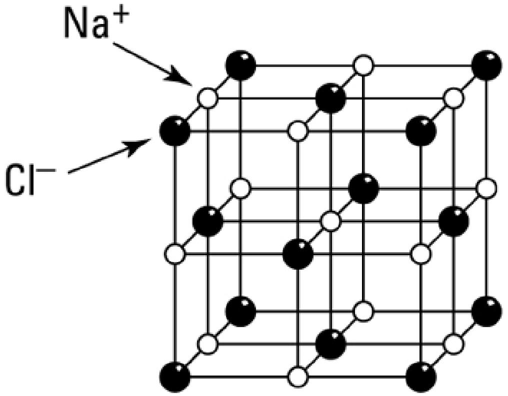
- X-ray Diffraction provides insight into the crystal phase at atomic scale. Crystal phase is usually the basis of materials physical properties

NaCl Powder



X-ray Diffractometer





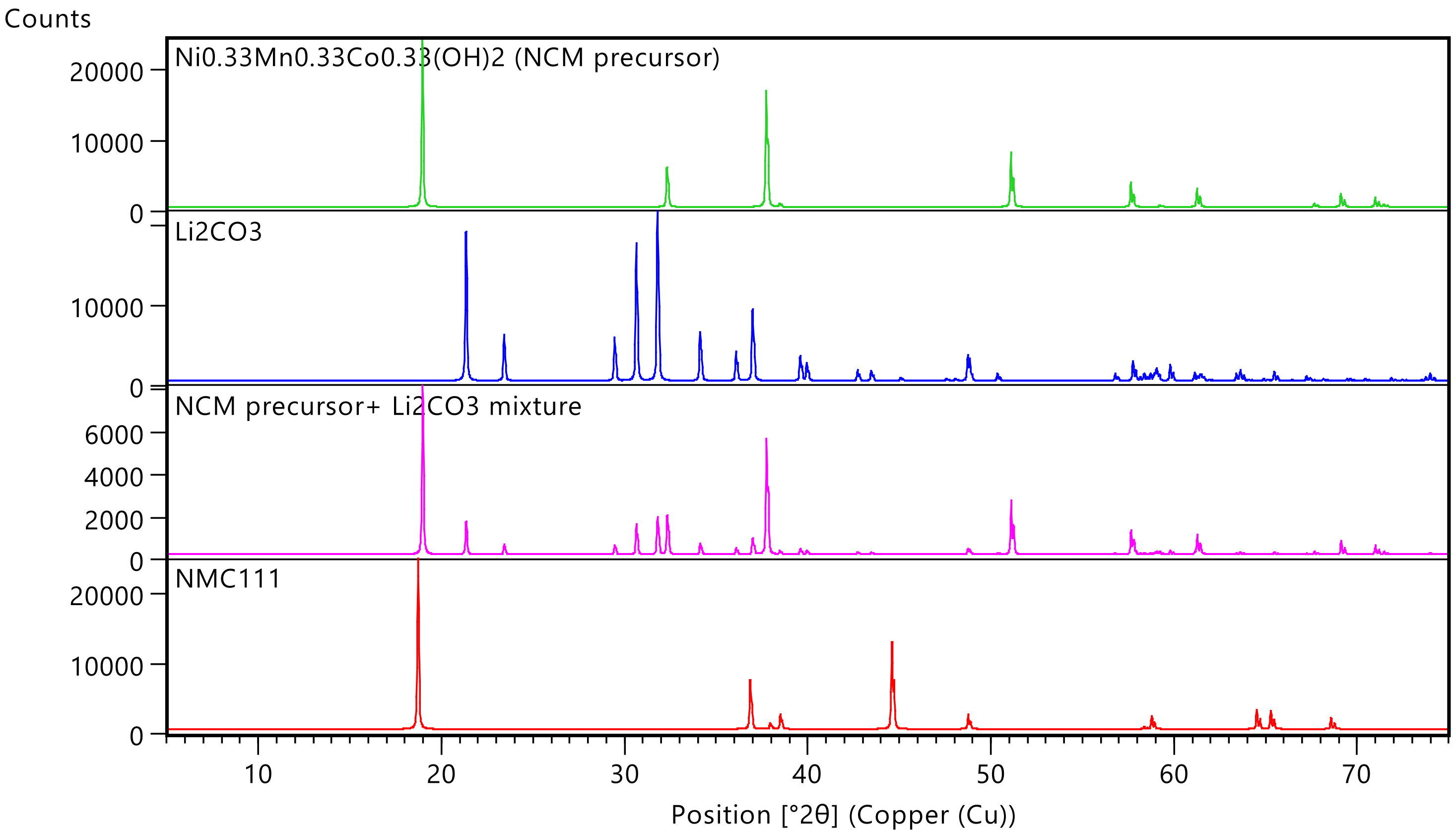
NaCl Crystal phase

XRD application: Crystal phase analysis

Precursor and cathode materials

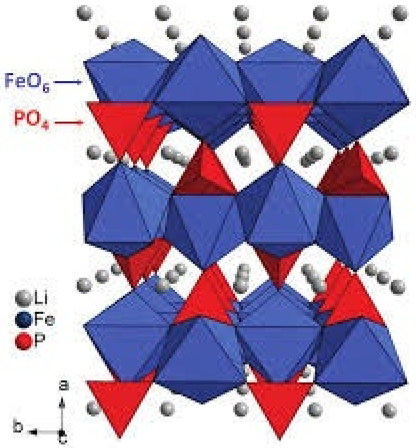
- XRD can analyze and verify crystal phases of precursors, reactants, and the synthesized cathode materials.

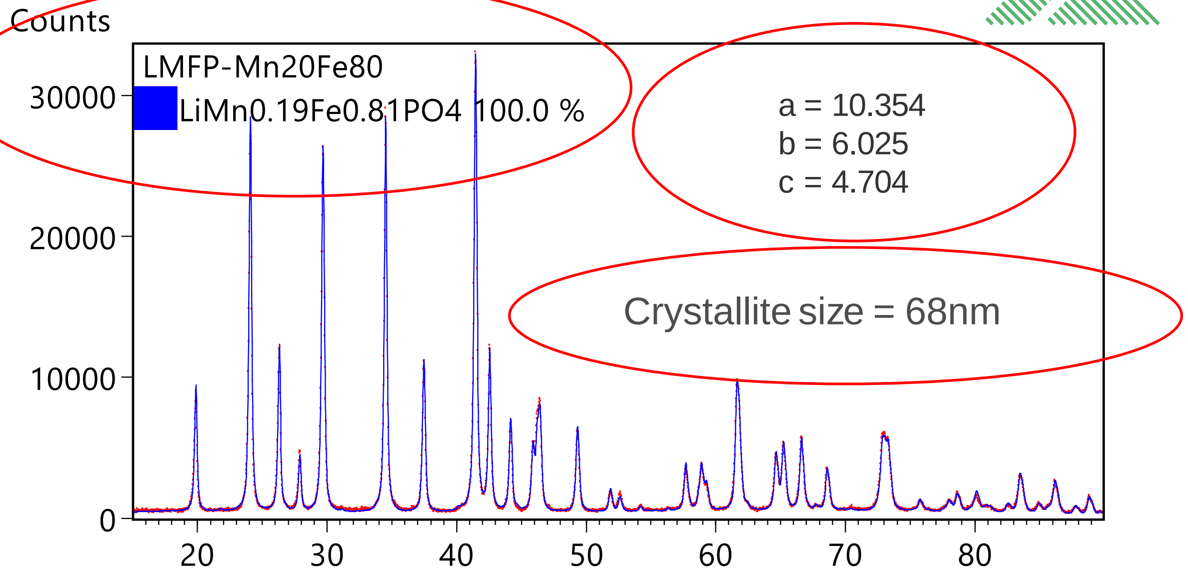
- Example XRD patterns of
  - NCM111 precursor,
  - Lithium carbonate,
  - mixture of precursor and Li2CO3,
  - synthesized NCM111 cathode material

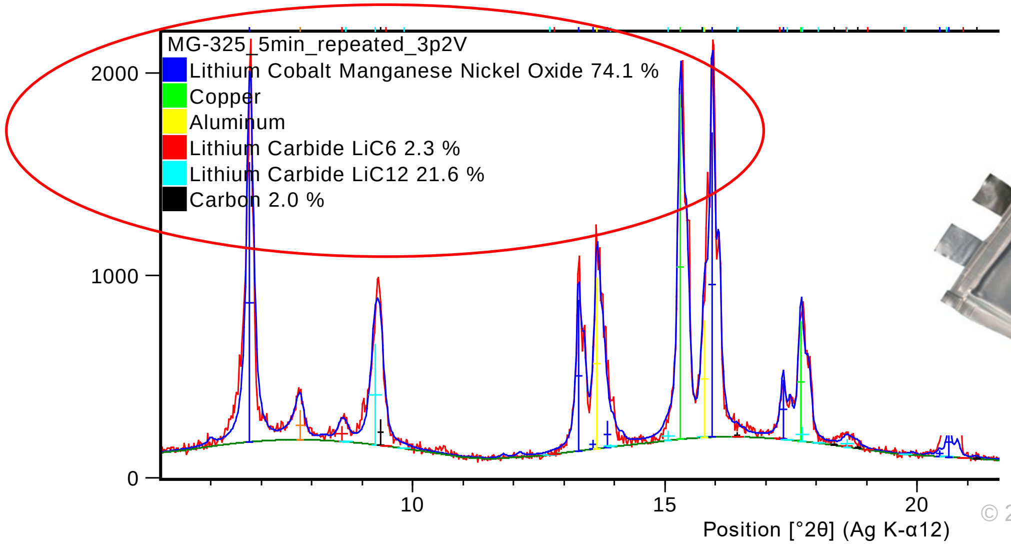


Crystal structure analysis

X-ray Diffraction





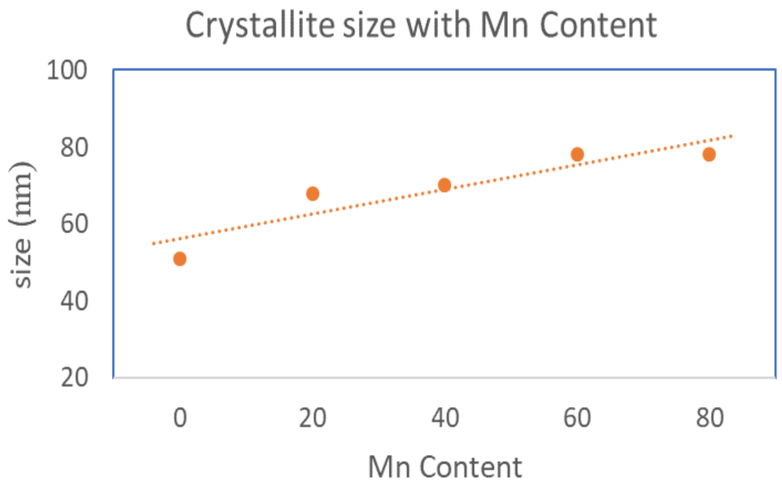


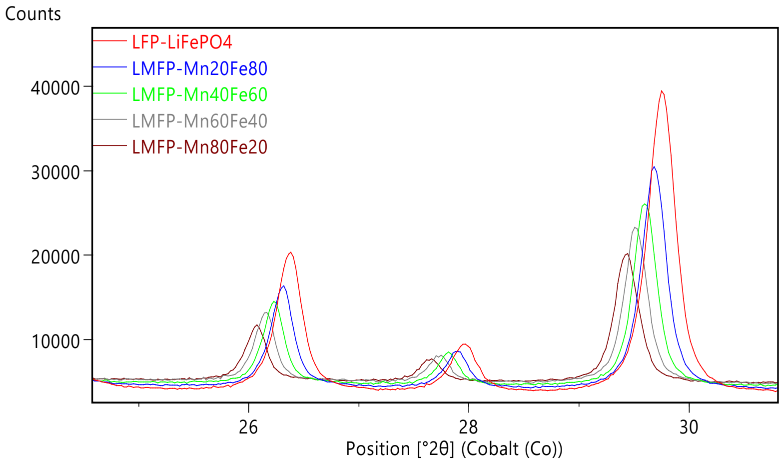
LMFP samples

Crystallite size

- Crystallite size and the primary particle size may influence the diffusion of Li ions, thus impacting the cell discharge capacity.

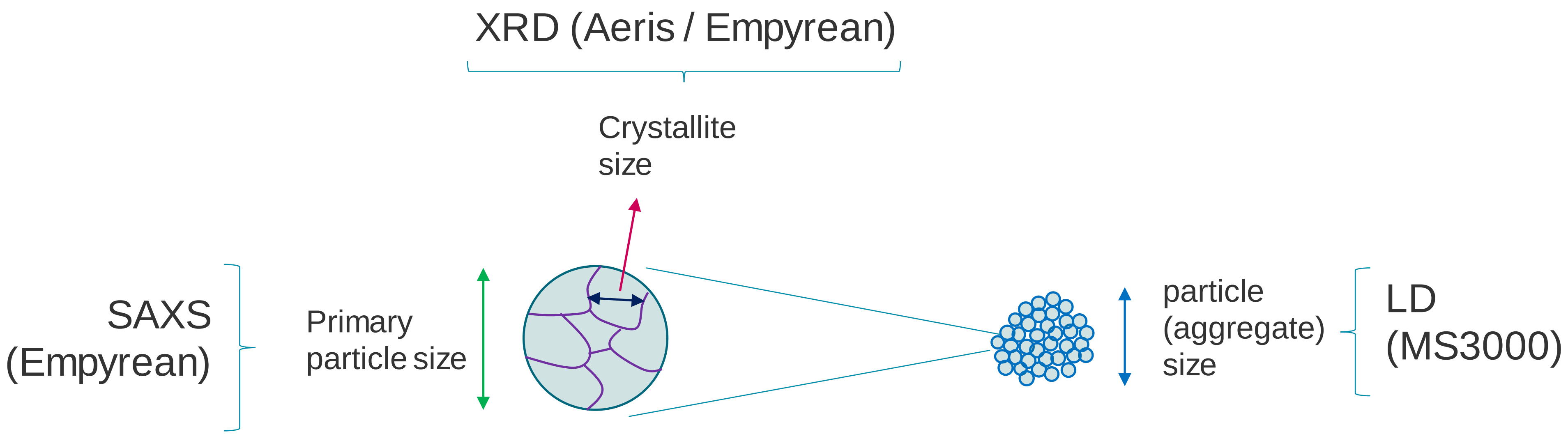
- A correlation was observed between decrease in discharge capacity with increasing crystallite size and





LMFP Samples

Comprehensive size analysis



	XRD size	SAXS size (D50)	LD size (D50)
Sample A	51 nm	55 nm	2.7 µm
Sample B	91 nm	128 nm	3.1 µm

In-operando XRD

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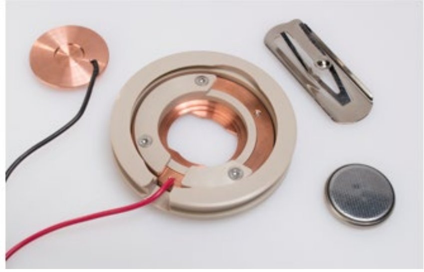
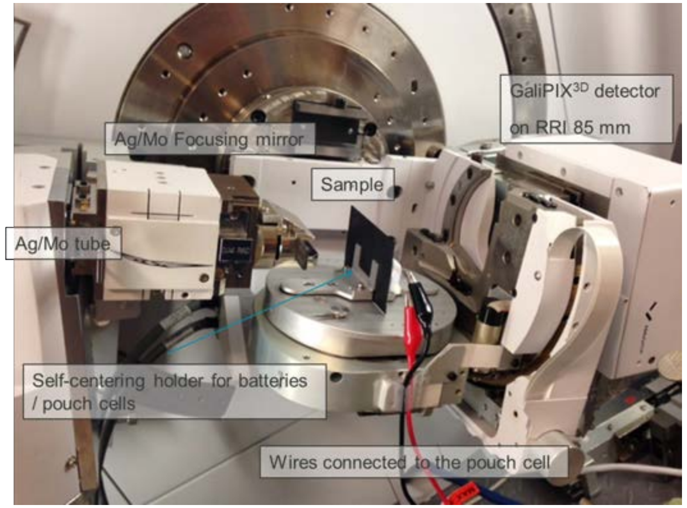
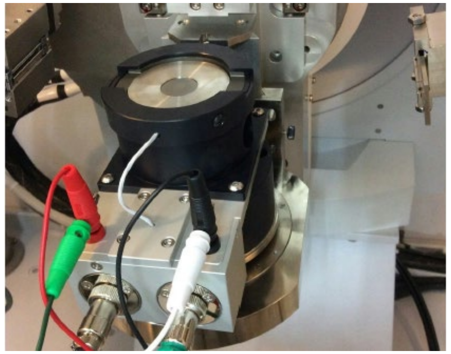


- Understand the cause of battery failure with in-operando X-Ray Diffraction (XRD)
  - Particle cracking
  - Li ion retention in anode
  - Li coating with fast charge
  - Undesired phase formations



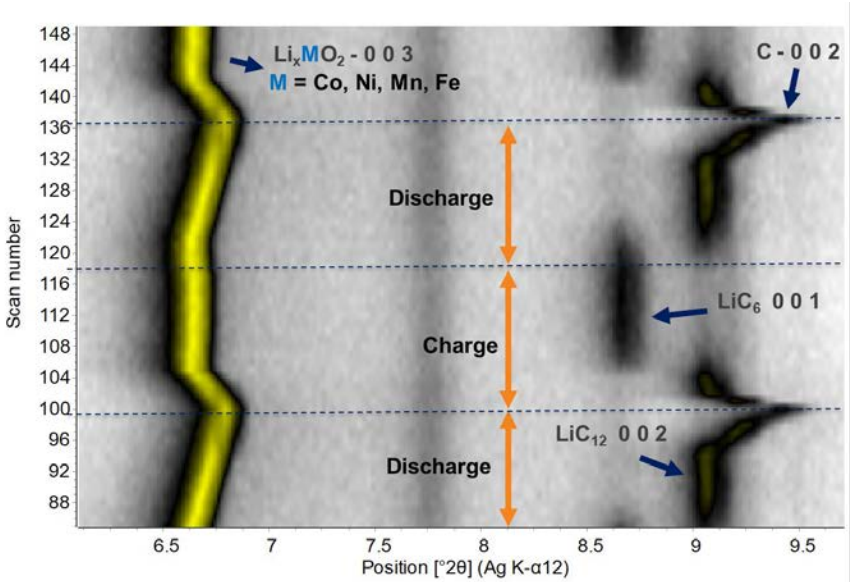
- Investigated cell types
  - Pouch Cell
  - Coin cell
  - Electrochemical cells
  - Heating and cooling option

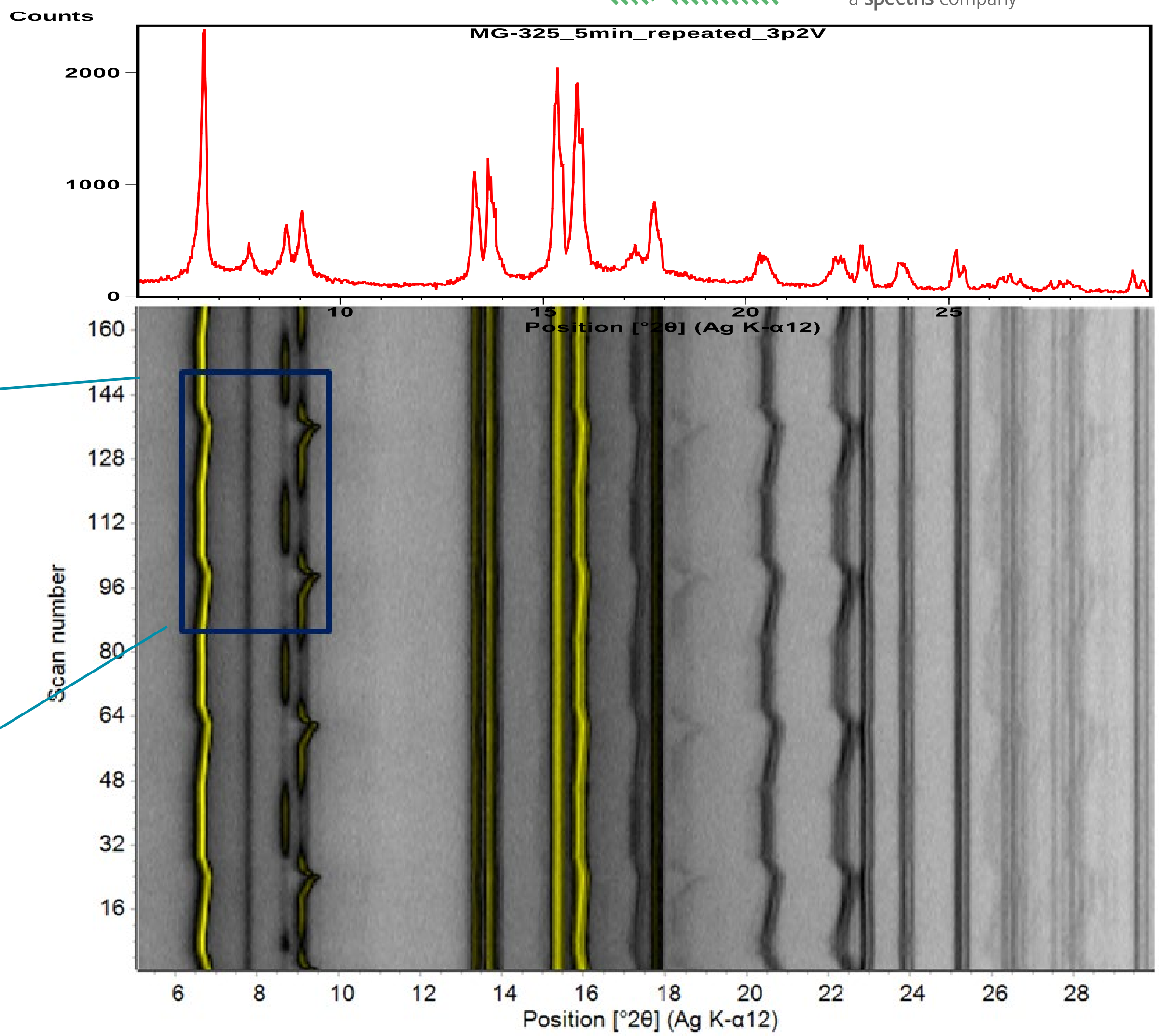


Experimental

charge-discharge measurements

- Four charge/discharge cycles
  - 5 minutes per scan.
  - 166 scans: 4 hours,
- 20 peaks in the angular range 5° to 30° 2ϴ of Silver radiation (~100° of Cu).

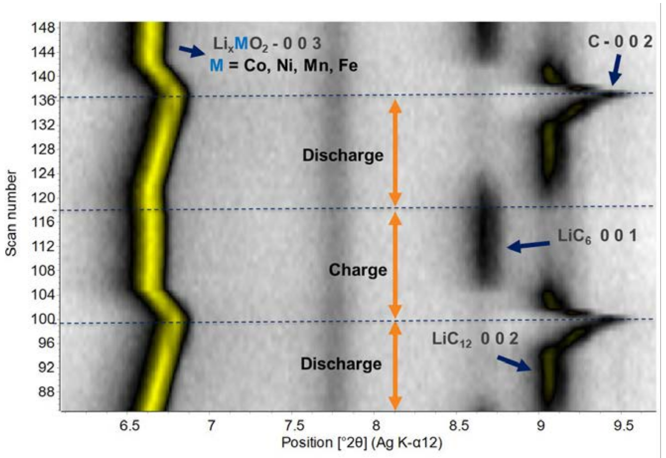


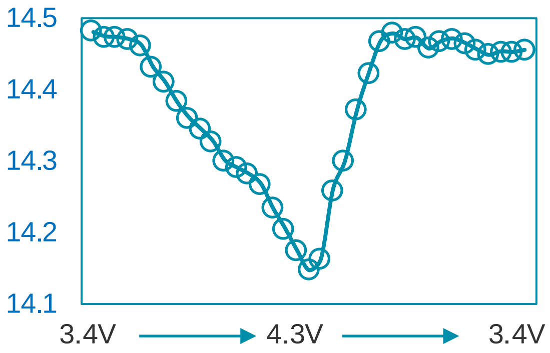


In-operando XRD

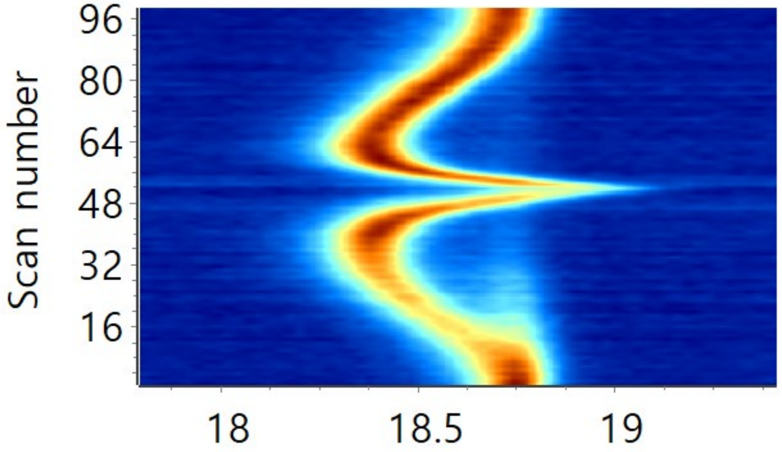
Lattice parameter variation

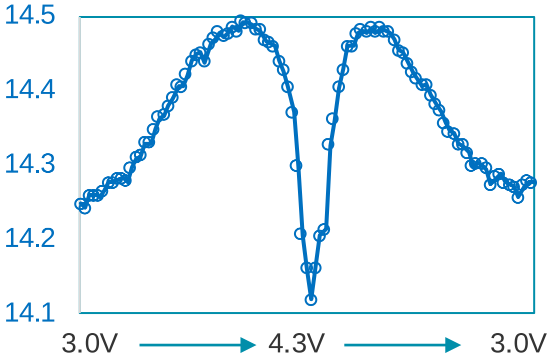
NCM333





NCM811

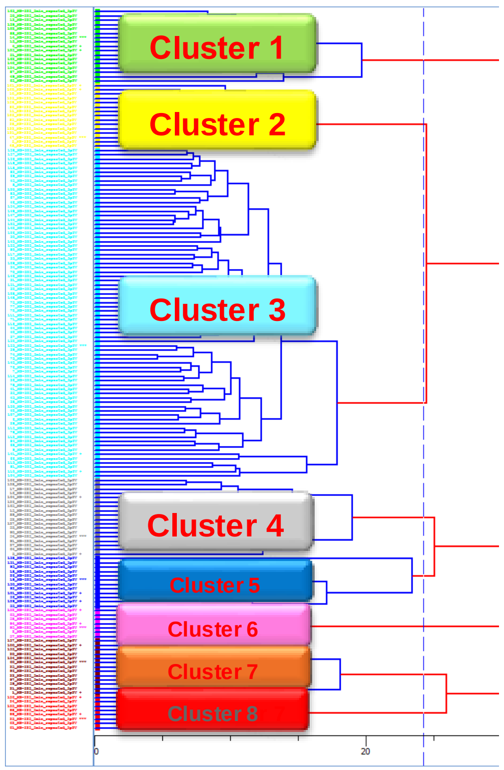




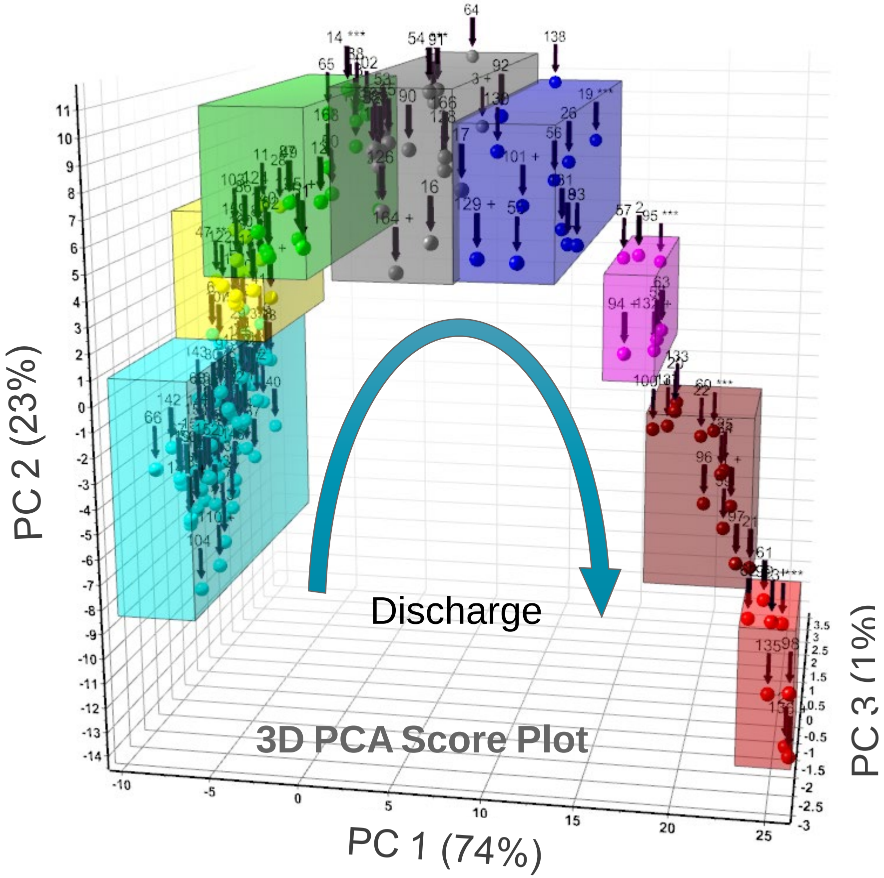
Statistical correlation – Cluster analysis

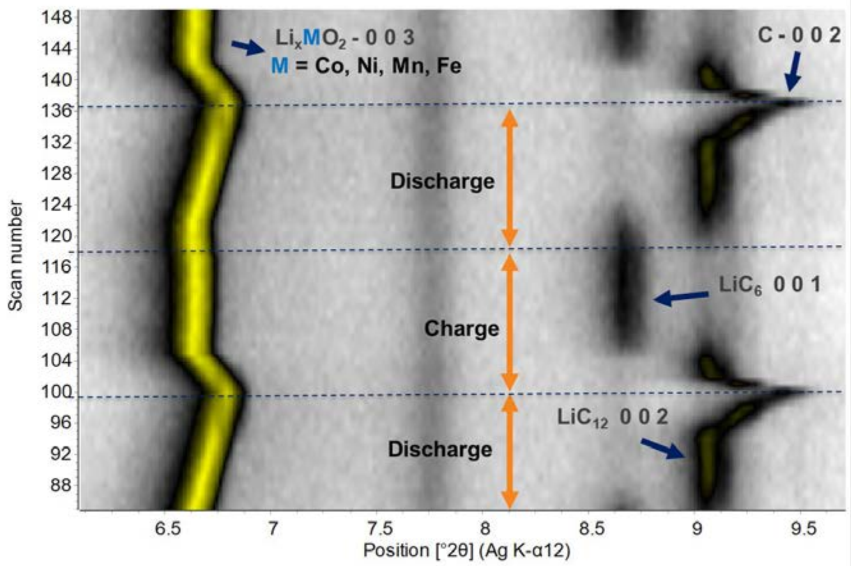
- The correlation matrix forms the input for all subsequent cluster analysis steps.
- **Agglomerative Cluster Analysis** and **Principle Component Analysis** clearly reveal a "charge/discharge axis" and do expose several groups of similar scans along this axis:

Dendrogram



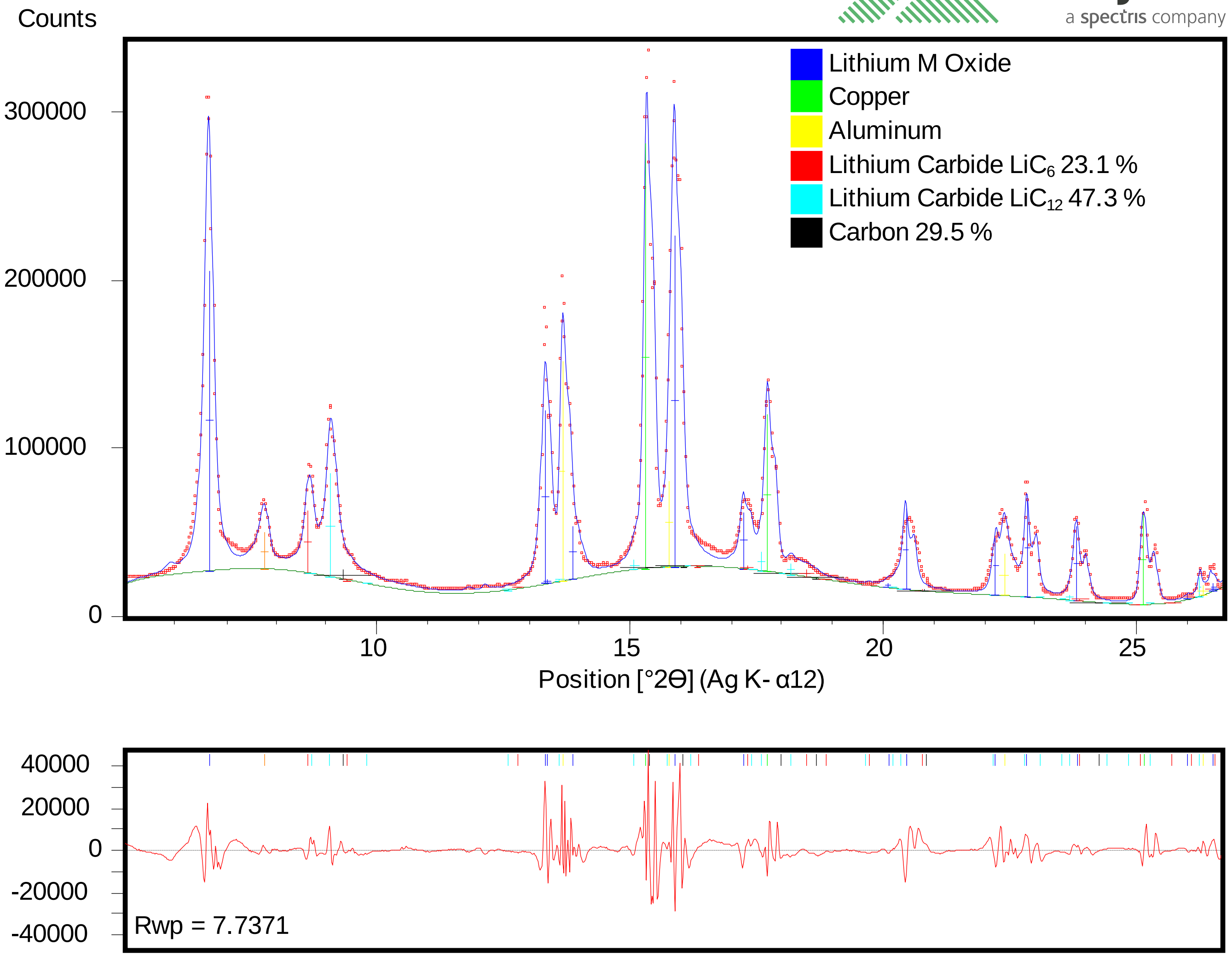
Dissimilarity Scale





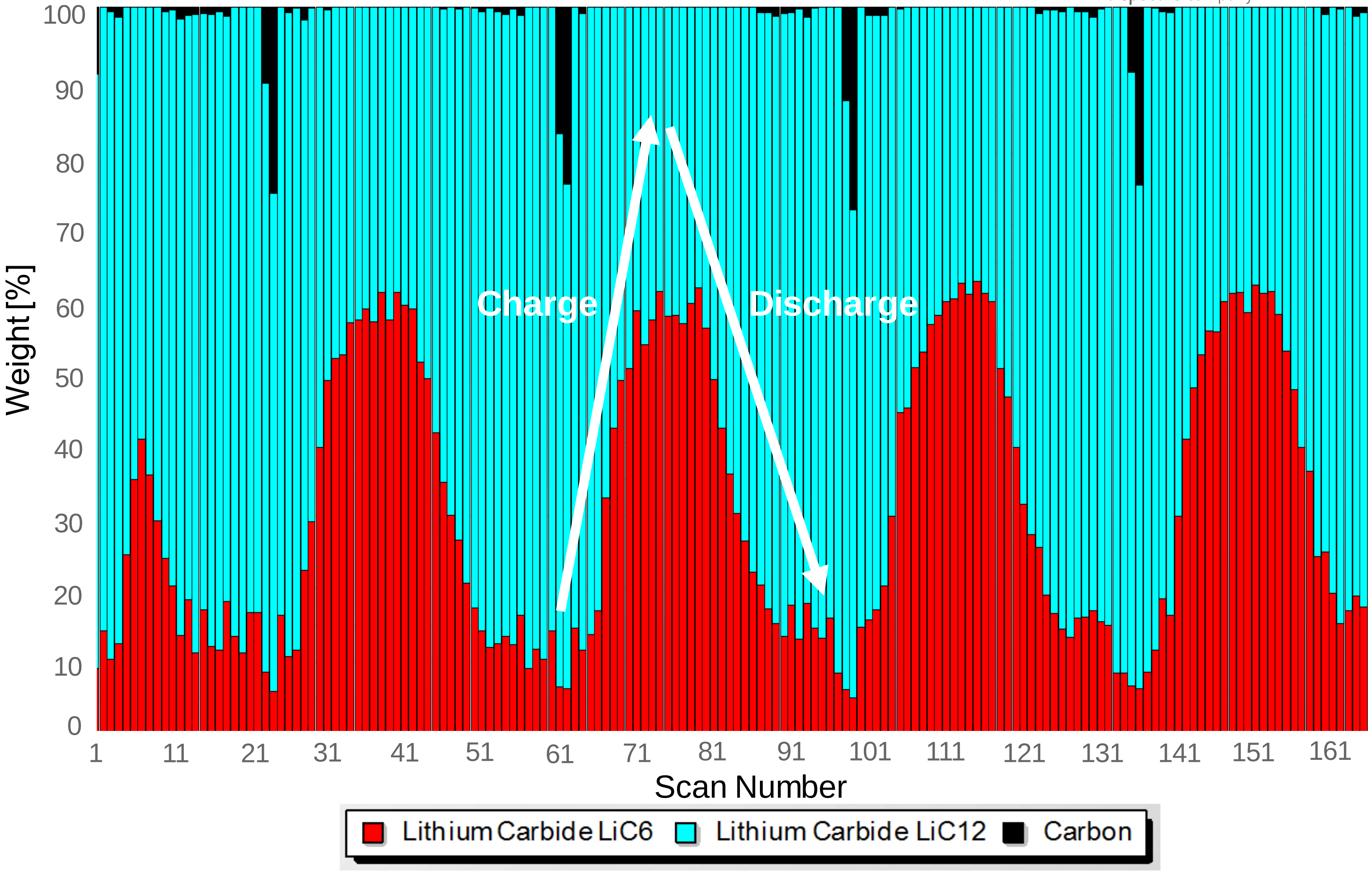
Analysis – Physical model – Fitting

- Initially we fitted the complex 6 phase model to the sum of all scans.
- The refined “average” model (with some box constraints on lattice parameters) was then used as starting point for consecutive automated fits of all individual scans.
- This allowed automated extraction of phase quantities as well as lattice parameters.



Analysis – Physical model – Fitting – QPA

- The Rietveld method allows quantification of all model phases based on the refined scale factors.
- The bar graphics shows the quantification of the 3 relevant phases appearing and vanishing during charge/discharge cycles, LiC_6, LiC_{12} and Carbon, for all 166 scans.



More details

- Website (battery page)
  - https://www.malvernpanalytical.com/en/industries/battery-and-energy-storage
- White Paper
  - https://www.malvernpanalytical.com/en/learn/knowledge-center/whitepapers/WP171005AnalyticalToolkitBatteryElectrodes
- Recorded Webinar
  - https://www.malvernpanalytical.com/en/learn/events-and-training/webinars/W200422BatteryXRD
  - Focus on Battery Research: Studying Battery Cathode Materials using in-operando X-Ray Diffraction

www.malvernpanalytical.com

Q&A

- Filmon Tsegai (AeroVironment, USA)
  - What's the best material/chemistry that renders most reliable battery?
    - *Currently NCM811 is regarded as the best chemistry in terms of energy density, while LFP is the safest. However, the future is with solid state batteries (with solid electrolyte) which will push the energy density by as much as 3 times in addition to offering the highest safety.*

- Anonymous
  - What is the maximum thickness of pouch cell can be analysed?
    - *If there is no metal casing, then there is no limit on the thickness. The middle of the pouch cell can be analysed for up to 5mm thick pouch cells, while the edge can be analysed for any thickness.*
  - Can you detect Li plating or dendrites?
    - *Yes, Li plating or dendrites will show a distinct Li peak in the X-ray diffractogram.*
  - Is there an advantage using X-ray fluorescence over ICP mass spectrometry?
    - *XRF is non-destructive, ICP is destructive. XRF does not require sample dissolution in acids and frequent calibrations. XRF analysis is accurate for major elements (at low % level) as it does not require any sample dilution. ICP has advantages when impurities at sub ppm level are to be detected.*

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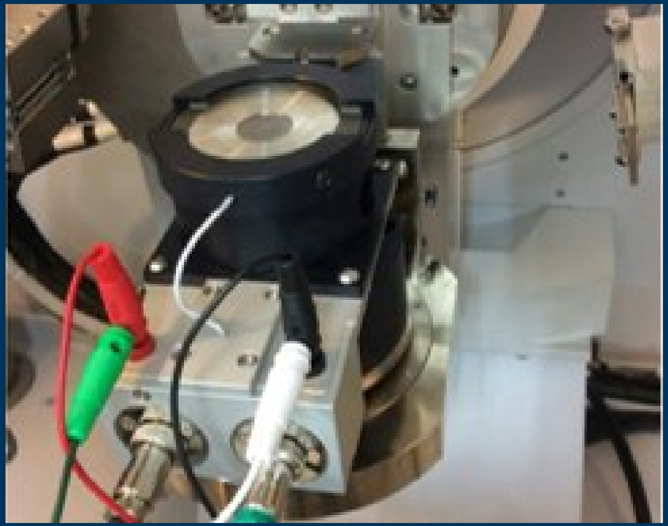

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