



# BATTERY RESEARCH AND QUALITY CONTROL SOLUTIONS

Benefit from physical, chemical and structural insight



# DISCOVER NEW HORIZONS IN BATTERY QUALITY

## Empower your research and production with advanced analytical solutions

The age of the battery is well underway. Lithium-ion batteries, for example, have already revolutionized our day-to-day lives – from smart mobile devices to pollution-free electric cars and intelligent power management solutions. And, looking ahead, batteries also have the potential to provide an economical solution for mass energy storage and complement renewable energy resources for power grid applications.

Despite these successes, gaps in battery technology remain, both in terms of safety and performance. What's more, for their mass-scale adoption in applications like electric vehicles, large cost reductions will be needed. Indeed, with regulators becoming more stringent and consumers more demanding, these core issues are driving not only research into new battery materials, but

also improvements in production efficiency to minimize production costs. When success is defined by such fine margins, today's manufacturers must be able to ensure total quality and performance – every time.

At Malvern Panalytical and NETZSCH Analyzing & Testing, we leverage over six decades of experience in the design, manufacture, and supply of analytical instruments to offer a complete range of laboratory and online analytical solutions. Whether you are a battery component manufacturer looking for greater process efficiency and better quality control, or a researcher trying to determine the performance parameters of newly emerging battery materials, our solutions will offer you the new levels of insight and control needed to power the production of superior-quality batteries.

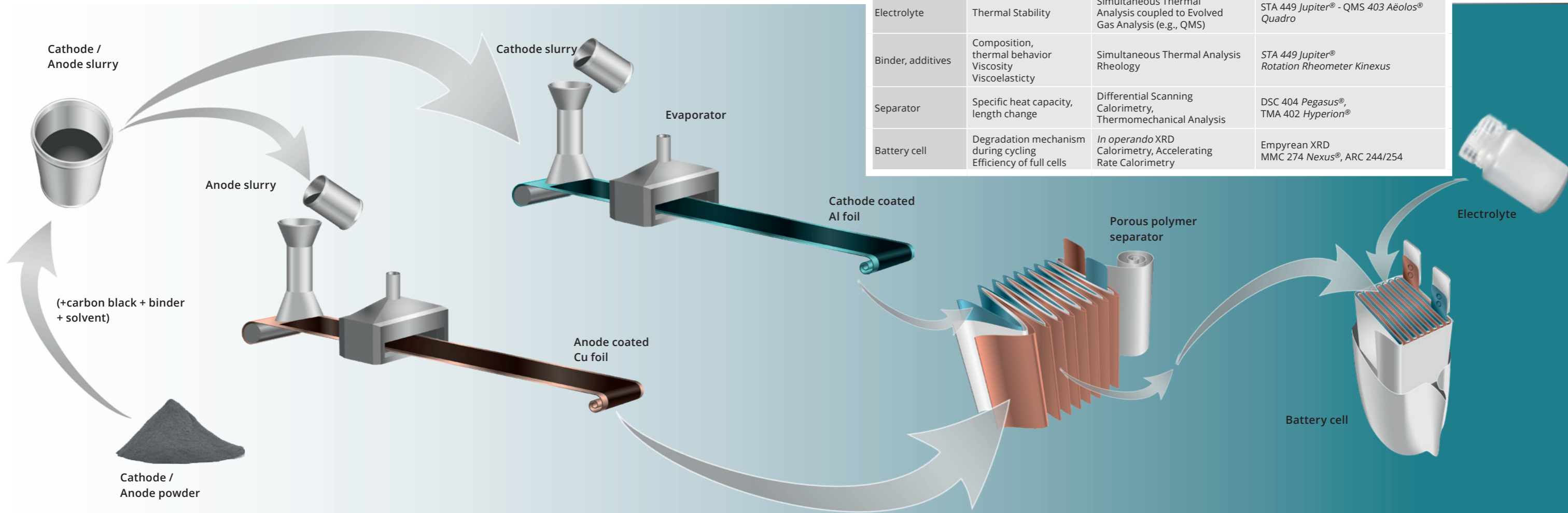
# MONITOR AND OPTIMIZE AT EVERY STAGE

Battery component manufacturers must not only deliver consistent overall quality – they must deliver it throughout the manufacturing process. The continuity of the manufacturing process means errors or impurities at an early stage will accumulate, resulting in much larger consequences further down the production line. Quality needs to be monitored at every stage – from raw materials through to cell assembly – to maintain production efficiency and minimize waste. Likewise, research into new battery materials must ascertain all the critical parameters that could affect battery performance throughout the entire manufacturing process.

At Malvern Panalytical and NETZSCH Analyzing & Testing, a range of research and quality control solutions to help manufacturers monitor and optimize every part of the battery manufacturing process. The unique set of physical, chemical and structural analysis possibilities that our technologies offer can be utilized across various stages of battery component production. From improving electrode material quality to accelerating the successful development of new high-performance battery materials, we've got you covered – enabling the development and production of the highest-performing batteries.

Table 1. Battery materials and analytical solutions along the battery value chain.

Battery materials	Critical Parameters	Analytical techniques	Product and solutions
Cathode precursor and electrode materials	Particle size Particle shape Chemical composition Crystal phase	Laser diffraction Automated Imaging X-ray fluorescence X-ray diffraction Simultaneous Thermal Analysis – Mass Spectrometer	Mastersizer 3000 Morphologi 4 Epsilon 4 / Zetium XRF Aeris compact XRD STA 449 Jupiter® - QMS Aëolos® Quadro
Battery slurry	Particle size Particle shape Viscosity Viscoelasticity Stability	Laser diffraction Automated Imaging Rotational Rheometry	Mastersizer 3000 Morphologi 4 Kinexus
Electrode and electrode coating	Coat weight Coating thickness Thermal management (thermal diffusivity/conductivity) Specific heat capacity	Photon sensor Micro caliper thickness sensor Laser/Light Flash Differential Scanning Calorimetry	Photon and Micro caliper sensors from NDC technologies LFA 467 HyperFlash® DSC 404 Pegasus®
Electrolyte	Thermal Stability	Simultaneous Thermal Analysis coupled to Evolved Gas Analysis (e.g., QMS)	STA 449 Jupiter® - QMS 403 Aëolos® Quadro
Binder, additives	Composition, thermal behavior Viscosity Viscoelasticity	Simultaneous Thermal Analysis Rheology	STA 449 Jupiter® Rotation Rheometer Kinexus
Separator	Specific heat capacity, length change	Differential Scanning Calorimetry, Thermomechanical Analysis	DSC 404 Pegasus®, TMA 402 Hyperion®
Battery cell	Degradation mechanism during cycling Efficiency of full cells	<i>In operando</i> XRD Calorimetry, Accelerating Rate Calorimetry	Empyrean XRD MMC 274 Nexus®, ARC 244/254



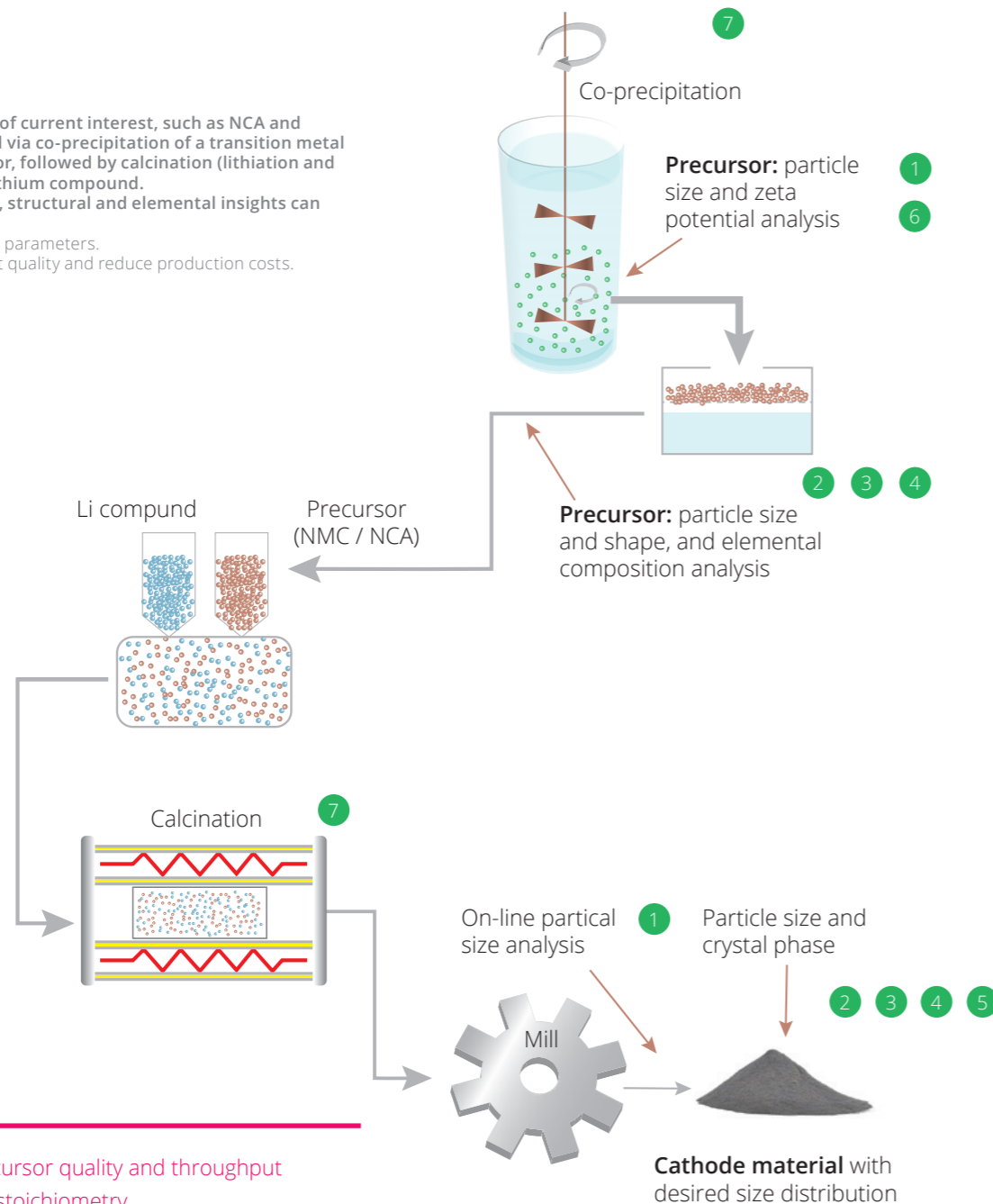
# OPTIMIZE CATHODE MATERIALS

Cathode material production is just one example of how our solutions enable quality at every stage of the manufacturing process. As one of the first stages in battery production, quality control is especially important to cathode manufacturing – and battery manufacturers must implement it all while minimizing costs.

Our solutions can be used as cathode characterization tools at several stages of the cathode production process, from co-precipitation and precursor quality control, down to optimizing calcination and the final material. By providing manufacturers with morphological, structural, and elemental insights, these solutions enable them to optimize process parameters accordingly to ensure the highest cathode quality.

Cathode materials of current interest, such as NCA and NMC, are produced via co-precipitation of a transition metal hydroxide precursor, followed by calcination (lithiation and oxidation) with a lithium compound. Our morphological, structural and elemental insights can help to:

- Optimize process parameters.
- Ensure consistent quality and reduce production costs.

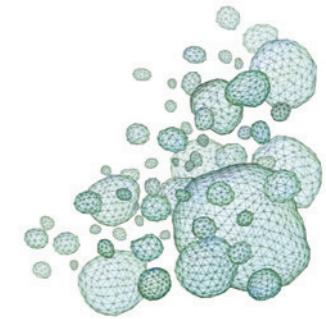


- Improve precursor quality and throughput
- Ensure right stoichiometry
- Optimize calcination process
- Control particle size and morphology

# CHARACTERIZATION TOOLS

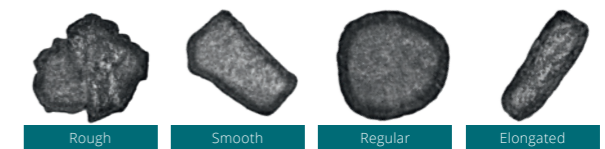
## Particle size

- 1 Consistent cathode-material particle size starts with the precursor – with our **Insitec** online tool, manufacturers can analyze particle size in real time at the precursor or milling stage.
- 2 Fine control over particle size distribution plays an important role in the quality of the electrode coating. With the **Mastersizer 3000**, you can analyze particle size with accuracy and ease.



## Particle shape

Particle shape influences critical parameters like electrode slurry rheology and packing density. Analyze particle size and shape at the precursor stage with **Morphologi 4** imaging - automatic analysis of thousands of particles with high statistical accuracy.



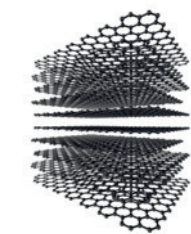
## Elemental composition

Combined with fusion sample preparation recipes, our **Epsilon 4** benchtop X-ray fluorescence (XRF) spectrometer or high-end **Zetium** spectrometer can simplify the chemical composition and elemental impurity analysis of electrode materials.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	L	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	A															
		L	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		A	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

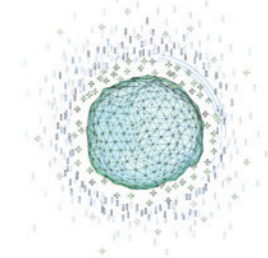
## Crystalline phase

Crystalline phase and crystallite size are the key attributes defining the quality of electrode materials. Our **Aeris** compact X-ray diffractometer sets the industry benchmark for crystalline phase composition analysis, which can be used to optimize the calcination process.



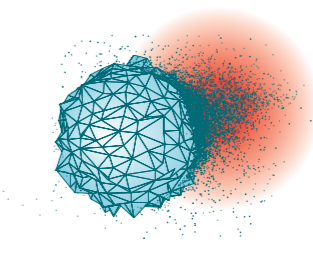
## Zeta potential

Zeta potential can be used to optimize process parameters like pH and concentration to control slurry stability, agglomeration, and sedimentation behavior. Our **Zetasizer** can analyze zeta potential of a dispersion and also the size and agglomerate state of nanosized materials.



## Heat treatment

Characterization of raw materials and calcination: Simultaneous monitoring of the thermal behavior and gases released during heat treatment enables coupling of the **NETZSCH QMS Aëolos® Quadro** mass spectrometer to the **NETZSCH STA 449 Jupiter®** Simultaneous Thermal Analyzer (Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)). This combination provides a deep insight into both the raw materials and the calcination process.



# OUR RESEARCH AND QUALITY CONTROL SOLUTIONS

## Superior particle size distribution measurement

Delivering an optimal and consistent particle size distribution doesn't just add value to electrode materials, it's key to ensuring final product quality – enabling manufacturers to optimize; slurry viscosity and flow behavior; coating packing density and porosity; battery cell charge rate capacity and cycling durability.

To meet this need, Malvern Panalytical offers an industry-standard particle size measuring tool; the Mastersizer 3000. Based on laser diffraction, it offers industrial-level performance, delivering more reliable

and faster measurements than sieving, faster measurements than sedimentation, and statistically superior information compared to microscopy. The Mastersizer 3000 laser diffraction particle size analyzer delivers rapid, accurate particle size distributions for both wet and dry dispersions with the minimum of effort. Measuring over the nanometer to millimeter particle size ranges, it packs exceptional performance into the smallest of footprints, bringing operator-independent measurements that every user can rely on.

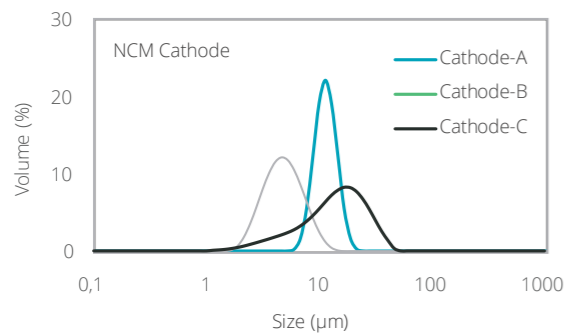


Figure 1. Particle size distribution of three batches of NCM811 cathode materials synthesized with different processing parameters.

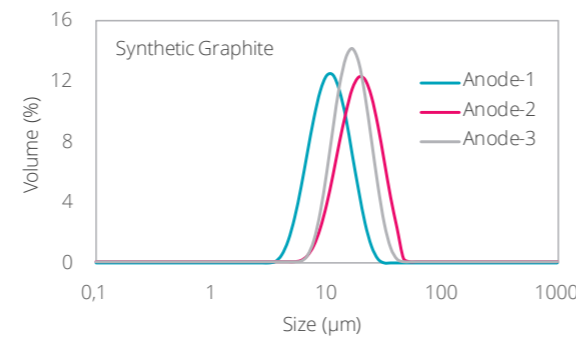


Figure 2. Particle size distribution of three batches of synthetic graphite synthesized with different heating conditions.

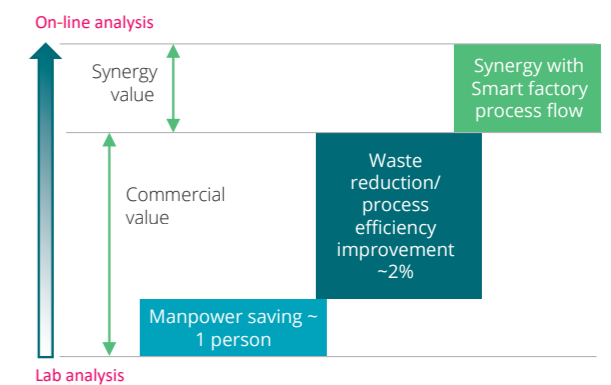


## REAL-TIME PROCESS AUTOMATION

### Optimizing process parameters

Manufacturers also need to monitor particle size as the production process continues. And, if you're manufacturing at industrial scale with limited human resources, finding an efficient way to analyze particle size in real time can be difficult. Usually, lab analysis will deliver feedback in about an hour, whereas for optimum quality control, a feedback loop of a few minutes is required.

Our on-line, automated Insitec particle size analyzer is ideal to meet this need in a production environment, delivering real-time analysis every few seconds using a feedback loop. It can be used to control precursor particle size evolution over time, or just after milling to control electrode particle size – enabling manufacturers to reduce waste and align their processes with smart factory manufacturing flows.



Typical value gain for a cathode manufacturing plant with Insitec online particle size analysis of precursor slurry, in comparison to lab analysis.

# THERMAL MANAGEMENT

## Controlling battery thermal characteristics – Separator, Electrode and Electrode Coating

Like the human body, the operating temperature of a battery should always be monitored, protected and kept at an optimal level. If the ambient temperature is too low, it will not deliver its full power. If the ambient temperature rises too high, the battery can even swell, catch fire, explode and release toxic gases. Proper battery thermal management ensures longer lifespan by keeping the cells within a limited temperature range during storage, operation and charging. Understanding how much heat can be dissipated by the cells requires understanding of the basic heat transfer properties of the cell design. Measuring the thermal diffusivity and thermal conductivity along with the specific heat capacity form the basis for comprehensive understanding. To investigate these thermophysical properties, NETZSCH offers Laser/Light Flash Analysis systems (LFA) as well as Differential Scanning Calorimeters (DSC). Thermal management system failures can be avoided.

### Laser Flash Analysis



Thermal conductivity and diffusivity are the most important thermophysical parameters for the description of the heat transport properties of a material or a component (Figure 3). The Laser/Light Flash technique has proven itself a fast, versatile and absolute method for measurement of the thermal diffusivity. NETZSCH offers three models, covering the widest temperature range for the broadest spectrum of materials. For the investigation

of electrodes, electrode coating, separators, the LFA 467 *HyperFlash*® is the right instrument. Between -100°C and 500°C, this LFA system contactless measures the temperature increase of samples between 6 mm and 25.4 mm with an IR detector. The patented *ZoomOptics* allows the detector's field of view to be adjusted until the only temperature increase registered is that of the sample and no influences by the surroundings may have any effect.

### Differential Scanning Calorimetry



Specific heat capacity ( $c_p$ ) is determined by means of the LFA method or Differential Scanning Calorimetry (DSC). DSC is the most employed Thermal Analysis method. It allows for the precise detection of thermal characteristics such as melting/crystallization temperatures and enthalpies, glass transition temperatures, reaction temperatures and enthalpies, cross-linking reactions (curing), and more.

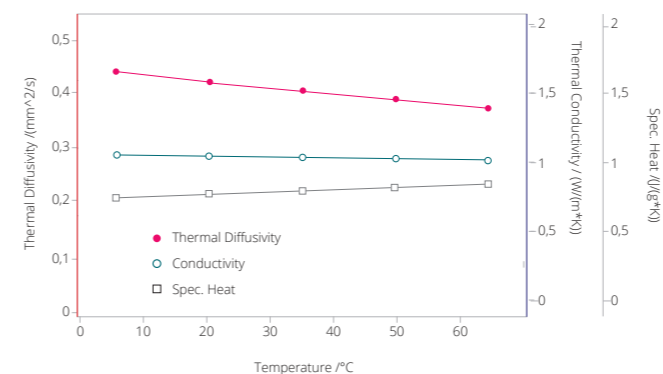


Figure 3. Aluminum electrode coated on both sides: The thermal conductivity (petrol curve) is determined by measuring the thermal diffusivity with the NETZSCH LFA 467 *HyperFlash*® (rubine red curve) and specific heat capacity,  $c_p$  (gray curve). In this example,  $c_p$  was determined using the DSC 404 F1 *Pegasus*®.

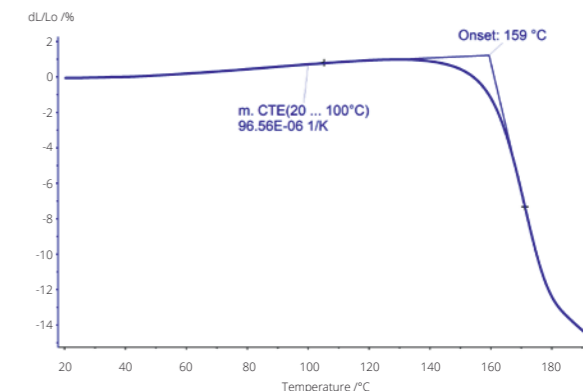


Figure 4. TMA measurement on a polymer film between RT and 190°C at a tensile force of 5 mN. Shrinkage starts at 159°C (extrapolated onset).

### Thermomechanical Analysis

Each time a material is exposed to temperature changes – it shows a variation in its dimension. Whether it is in the course of its regular thermal expansion or by passing a phase transition, the substance will either be shrunk or elongated. For example, polymer separators can shrink significantly at elevated temperatures which affects the battery performance. To predict the deformation and stresses in the separator in battery cells, it is necessary to measure the expansion/shrinkage behavior.

This is achieved by Thermomechanical Analysis (TMA), expressed by the coefficient of thermal expansion (CTE). The length change phenomena can be studied by means of thus revealing information regarding their thermal behavior and about process parameters or curing kinetics.

Under a defined mechanical force, the TMA 402 *Hyperion*® series allows for monitoring the volumetric and linear thermal expansion, shrinkage steps, glass transition temperature, density change, and anisotropic behavior.



TMA 402 *Hyperion*®

# THERMAL STABILITY

## Safety is ensured when deterioration of stability is avoided

Electrolytes are characterized by high conductivity, good electrochemical stability and the ability to perform at low temperatures. However, the thermal stability of many electrolyte solutions is restricted even at moderate temperatures. Due to overcharging, batteries can overheat to the point that they catch fire.

Besides various metals (e.g., cobalt, aluminum or manganese, etc.), the cathode material of Li-ion batteries contains nickel. There is a positive correlation between the nickel content and the battery capacity. Since nickel is relatively cheaper than cobalt, adding more nickel lowers the unit cost of, e.g., electric vehicle (EV) batteries.

However, nickel reduces the stability of the battery as it reacts easily to the external environment. The nickel content in batteries can increase to 80% or higher, and the consequent deterioration in stability must be improved to ensure safety.

The thermal stability can be investigated by means of Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG or called Thermogravimetric Analysis TGA). A combination of both methods represents the Simultaneous Thermal Analyzer (STA). The STA 449 *Jupiter*® series combines configuration flexibility and unmatched performance in just one instrument. Pluggable interchangeable DSC and TGA sensors and various furnaces allow for precise thermoanalytical measurements. By supplementary MS coupling, even more comprehensive analyses are possible.

The NETZSCH QMS 403 *Aëolos*® *Quadro* is a compact mass spectrometer with a heated capillary inlet system for routine analysis of gases and, in particular, volatile decomposition products. The software is unique: fully integrated MS software for measurement and analysis allows for direct correlation between the mass-loss steps and gases released. This coupling is especially suitable for studying the thermal degradation of electrolytes.

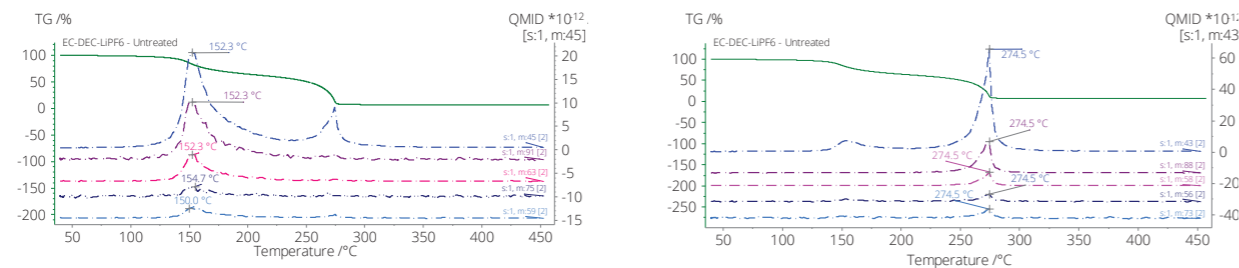
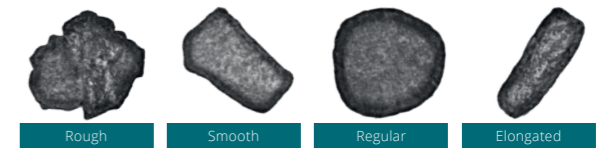


Figure 5. STA-MS measurement on 8 to 10 mg 1.0 M LiPF6 in EC/DEC=50/50 (v/v). The left plot indicates that the 1<sup>st</sup> mass-loss step is most likely due to the evaporation of DEC; the right plot shows mass numbers attributed to ethylene carbonate (43, 56, 58, 73 and 88) indicating the evaporation of EC during the 2<sup>nd</sup> mass-loss step.

# PARTICLE MORPHOLOGY

## Enabling better insight into electrode material morphology

The role of particle shape in battery electrode materials is usually ignored or underestimated. However, this may be the key to unlock full potential of a given battery material to be translated into the best performing battery. Particle shape affects slurry rheology as well as the electrode coating in terms of packing density, porosity and uniformity. To achieve the highest level of battery performance, manufacturers must also understand and optimize the particle morphology.



Do your particles have the right morphology?

To help manufacturers resolve these critical questions, we offer our powerful optical imaging tool, Morphologi 4. Equipped with fully automated image analysis, it enables manufacturers to measure parameters such as circularity, elongation/aspect ratio, Circular Equivalent (CE) diameter, and transparency.



With analysis based on 10,000 – 500,000 particles from 0.5 µm onwards, manufacturers can gain reliable insight into the shape of the smallest particles with high statistical accuracy. What's more, the Morphologi 4-ID combines automated static imaging features of the Morphologi 4 with chemical identification of individual particles using Raman spectroscopy - enabling automated measurement of particle size, particle shape and chemical identity, on a single platform.

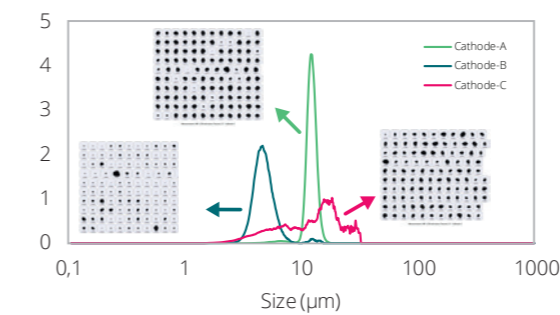


Figure 6.

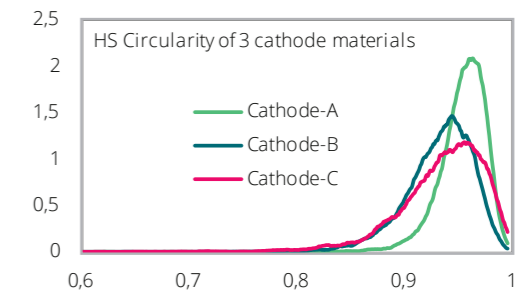


Figure 7.

Example Cathode Materials Circular Equivalent (CE) size distribution of three NCM cathode materials, as obtained from Morphologi 4 (Figure 6). These are the same samples as those measured with the Mastersizer 3000 in Figure 1. Circularity for these samples is compared in Figure 7. Circularity index 1 corresponds to perfect spheres and smaller values to larger deviation from circularity. A narrow distribution in circularity means uniform shape particles, whereas broad distribution represents large variance in particle shapes. Cathode A has circular particles, whereas B and C are irregularly shaped with large shape variations.

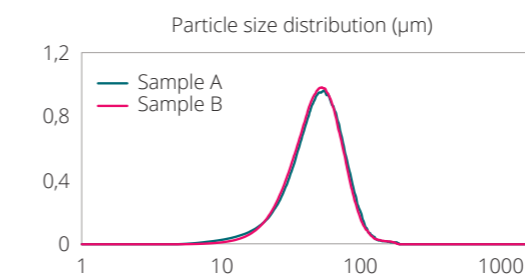


Figure 8.

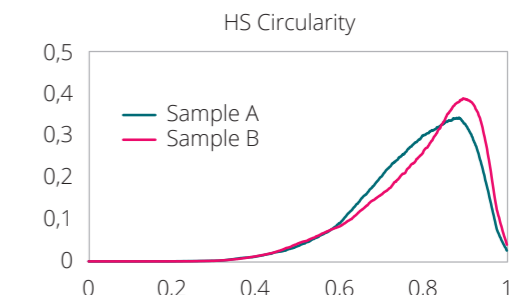


Figure 9

Example Graphite electrode material: size distribution of two samples as measured with Mastersizer 3000 (Figure 8) and circularity of the same samples (Figure 9) as measured with Morphologi 4. Though the samples have similar circular equivalent size distribution, sample A is more irregular in shape.

# ELEMENTAL COMPOSITION

## Simplifying chemical composition and impurity analysis

Deviations in chemical composition or impurities in electrode materials can significantly affect final battery performance. For this reason, chemical composition and elemental impurity analysis are an integral part of the battery manufacturing process. However, the often-used inductively coupled plasma (ICP) analysis is not always the best tool for this. Requiring sample digestion and frequent calibration, ICP is inefficient and expensive for most elemental analysis needs.

To provide a simpler way to analyze elemental composition and detect impurities down to ppm level, we offer X-ray fluorescence (XRF) solutions that require no sample digestion or frequent calibration and are up to three times cheaper in terms of per sample analysis. In particular, chemical composition analysis of cathode materials at low-percentage elemental levels is more reliably measured with X-ray fluorescence.

Specifically, our **Epsilon 4** benchtop energy dispersive XRF spectrometer can accurately measure elemental composition in just a few minutes. When better light element sensitivity is desired, our **Zetium** wavelength dispersive XRF spectrometer is recommended. These solutions can help manufacturers optimize cost and use of human resources, while saving ICP for very low-level impurity detection.

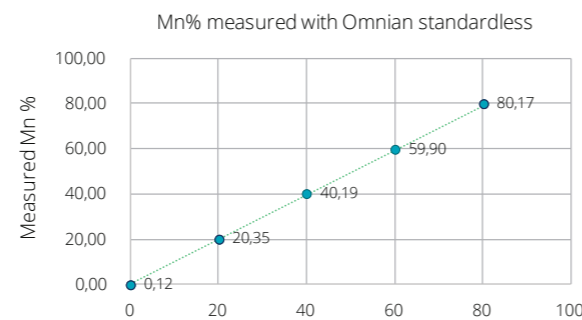


Figure 10. Composition and impurities analysis on five samples of  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$  measured on the Epsilon 4 is shown in the table below. Measured Mn composition (Figure 7) shows a straight-line calibration with Target Mn composition in these samples.

Table 2. Typical elemental composition analysis on a LFMP cathode material using XRF

Sample	Target Material	Measured composition and impurities													
		Mn %	Zr	Al	Ca	Cl	Co	Cr	Cu	Ni	S	Si	Ti	Y	Zn
SMP1	$\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$	80.2	0.11	0.011	0.014	0	0	0.017	0	0.026	0.008	0.022	0.009	0.006	0
SMP2	$\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$	59.9	0.19	0.012	0	0	0.001	0.024	0.018	0.013	0.004	0.02	0.01	0.009	0.006
SMP3	$\text{LiFe}_{0.6}\text{Mn}_{0.4}\text{PO}_4$	40.2	0.117	0.041	0	0	0.003	0.034	0.011	0.023	0.006	0.024	0	0.007	0.005
SMP4	$\text{LiFe}_{0.8}\text{Mn}_{0.2}\text{PO}_4$	20.4	0.161	0.008	0.014	0.037	0	0.042	0.009	0.015	0	0.02	0	0.006	0.006
SMP5	$\text{LiFePO}_4$	0.1	0.155	0.015	0	0	0	0.055	0.009	0.024	0.007	0.024	0	0.009	0.004



# SAMPLE PREPARATION FOR XRF

## Ensuring more accurate analysis

Sample preparation is a major source of error in elemental composition analysis. All too often, preparation methods such as pressed pellets (in XRF) or acid digestion (in ICP) are affected by mineralogical or particle size effects in metal samples, compromising the accuracy of the results.

To meet the need for reliable sample preparation for XRF or ICP, Malvern Panalytical offers a high-performance fusion solution. Fusion involves dissolving a fully oxidized sample at high temperature in a suitable solvent (a flux) in a platinum, zirconium or graphite crucible. The melted mixture is agitated and poured into a mold to create a glass disk for XRF analysis. It can also be poured into a beaker to create a solution for Atomic Absorption Spectroscopy (AAS) or ICP analysis.

At Malvern Panalytical, you can count on our 40-plus years of expertise in designing and delivering fusion recipes for various kinds of complex samples. What's more, we offer two fusion instruments. Our robust LeNeo instrument is ideal for battery sample fusion. This automatic electric instrument can prepare glass disks for XRF analysis, as well as borate and peroxide solutions for AA and ICP analysis. With one fusion position, it delivers excellent ease of use, operator safety, and superior analytical performance in the laboratory – eliminating doubt and driving high-precision quality control. To meet high sample throughput, our TheOx advanced instrument, which has six fusion positions, can be used.



# CRYSTALLINE PHASE COMPOSITION

## Unlocking atomic-level exploration

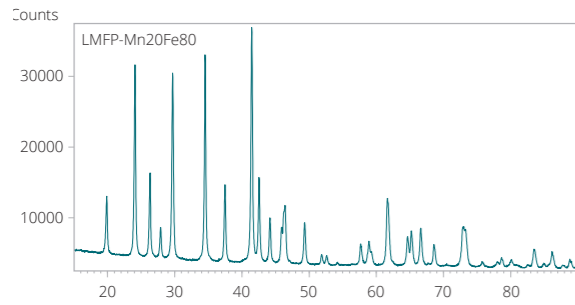


Figure 11. Typical XRD pattern of a Lithium Manganese Iron Phosphate (LMFP) cathode material.



Crystalline phase is an important factor in battery electrode materials, governing lithium-ion transport at atomic level. To analyze crystalline phase composition and quality in synthesized powder materials, X-ray diffraction (XRD) is routinely used.

In battery cathode materials, XRD can be used to ensure that reactants have completely fused to the desired and stable crystalline phases during the calcination process. It can also be used to measure chemical composition or to estimate the size of primary particles (from the measurement of crystallite size), which plays an important role in ion migration. In anode materials, XRD can measure the degree of graphitization in synthetic graphite, which significantly affects anode energy density.

These applications can be carried out easily with our Aeris compact X-ray diffractometer. Thanks to its automated analysis, sample measurement on Aeris requires no prior XRD expertise. Moreover, the Aeris is built for industrial automation. It meets requirements for industrial high

throughput sampling, since typical sample measurement takes just a few minutes. Samples can be fed either manually or via a belt automation.

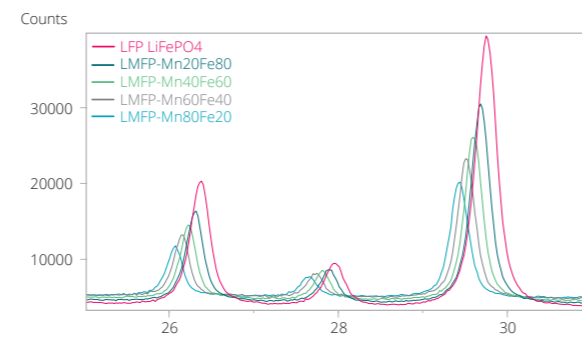


Figure 12.

Example LMFP Cathode Material: Section of XRD pattern (Figure 8) showing peak shift to lower angles as the Mn content increases, meaning lattice expansion along c-axis.

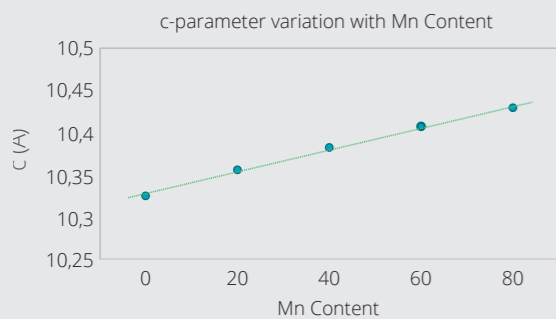


Figure 13.

Example LMFP Cathode Materials with varying Mn content: Lattice expansion along c-axis (Figure 13) with increasing Mn content. For unknown batch samples, c-parameter can be measured, and composition deduced using calibration graph (Figure 13). XRD also reveals that crystallite size increases with Mn content (Figure 14) – higher Mn facilitates larger crystallite size. Crystallite size usually has a close relationship to the primary particle size.

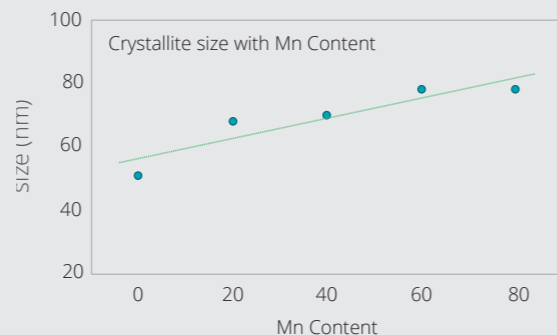
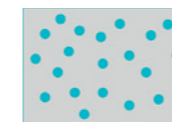


Figure 14.

# ZETA POTENTIAL ANALYSIS

## Enabling slurry stability insight

In electrode slurry production, zeta potential (related to charge charge on particle) plays an important role in slurry stability. Low zeta potential can result in agglomeration and aggregation of particles – causing unstable particle dispersion in slurries and, in turn, compromising battery quality. So, being able to accurately monitor and optimize zeta potential isn't just useful to battery manufacturers – it's essential.



High zeta potential = stable dispersion



Low zeta potential = unstable dispersion / agglomeration



To meet this need, we offer the **Zetasizer**. Whether it's to understand agglomeration and sedimentation in precursor slurry, or to ensure electrode slurry stability, or to understand slurry wetting behavior on flat surfaces, this tool measures zeta potential with excellent accuracy, repeatability, and consistency. And, for high-concentration and highly conducting samples, its specialized cell and constant current mode have you covered – enabling manufacturers to optimize Ph and concentration for stable slurries to manufacture high quality electrodes.

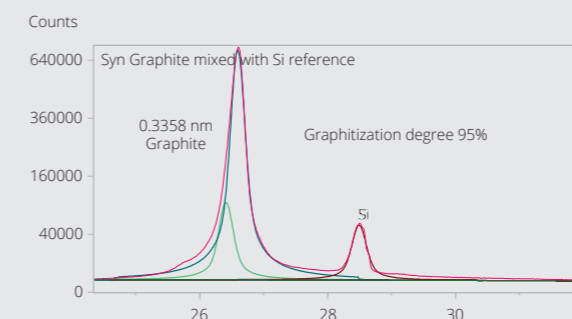


Figure 15.

Example Synthetic graphite: Degree of graphitization and orientation index are important attributes of synthetic graphite, which is a commonly used anode material due to its superior consistency and purity compared to natural graphite. Aeris can measure both the graphitization degree and orientation index. Figure 15 shows the measurement of the degree of graphitization in one such material.



# PROCESSING PROPERTIES AND LEVELING CHARACTERISTICS

## How to apply battery slurry onto the electrode

A battery slurry is typically processed by blade coating or slot die coating. During these processes, the slurry is undergoing mid-level shear rates for a short period of time, followed by gravitational stresses acting on the slurry after the coating process. This has impact on the leveling behavior at low shear rates and film uniformity.

Rheology provides access to these flow properties of battery slurries. Different low-shear behavior can influence the leveling. With high solid content, shear thickening might occur in processing shear rate range and causes difficulties during the coating process. In addition to the shear viscosity function, the elasticity of the slurry under shear flow is important. It can lead to flow instabilities, such as film rupture or uneven edges of the coating layer. Elasticity of the slurry, however, helps prevent sedimentation of the particles at rest and needs to be balanced against the negative impact of elastic normal stresses on the processing.

### Critical factors influencing rheology of the slurry:

- Volume fraction
- Particle size and distribution
- Shape
- Electrostatic interactions
- Molecular weight
- Intrinsic viscosity

### Critical factors when processing battery slurries:

- Slurry stability
- Flow properties (viscosity and elasticity) during coating
- Flow instability
- Film structure / leveling behavior

### Viscosity and visco-elasticity control of the coating process

The rheometer measurement with the NETZSCH Kinexus shows that the addition of PVDF to NMP drastically increases viscosity relative to NMP alone and the viscosity remains largely independent of the shear rate (Newtonian behavior). Adding carbon black increases viscosity and the resulting slurries both showed shear rate dependence (non-Newtonian behavior). The slurry made with Carbon A yielded a much higher viscosity than Carbon B at low and high shear rates, which would likely increase the resistance to sedimentation on standing (low shear process) and result in a thicker electrode film on coating (high shear process).

To avoid sedimentation at all, the slurry structure at rest needs to be dominated by elasticity. This can be investigated by oscillatory shear experiments, which allows for characterization of the viscoelastic properties and thus enables a stability forecast for the slurry before it is coated.

The higher viscosity may also make the coating process more difficult to control, potentially leading to uneven coating and variable layer density which, in turn, results in a variable ion transfer rate and hence battery lifetime (and recharge cycle time).

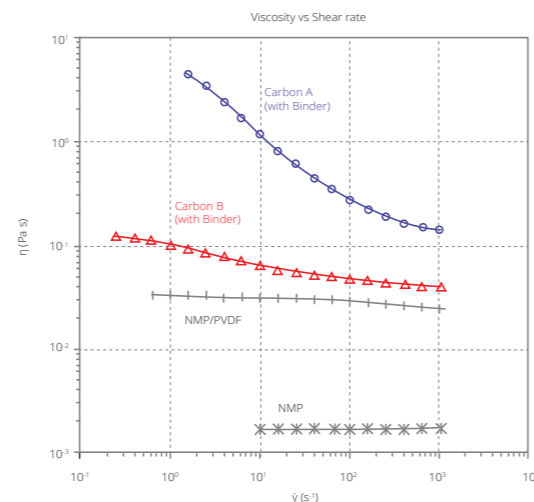
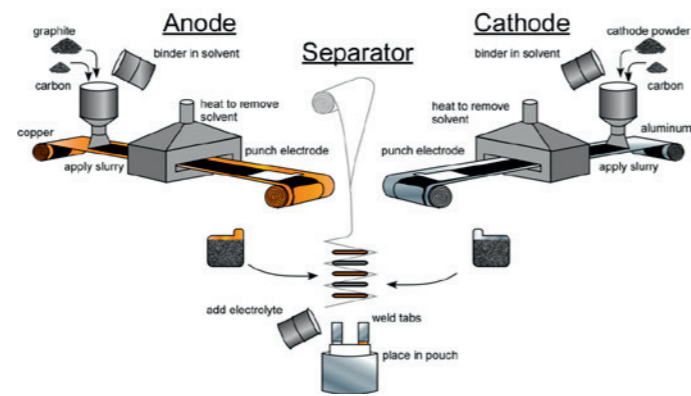


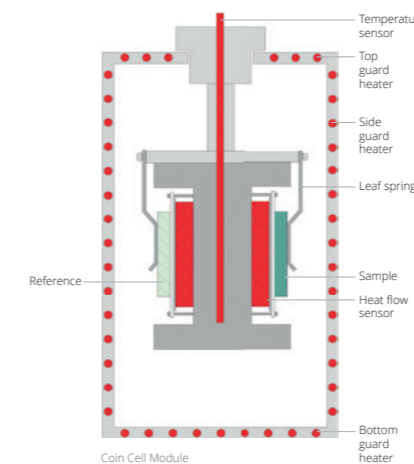
Figure 16. Rheological measurements on 4 different slurries measurement carried out at shear rates ranging between 0.1 to 1000s<sup>-1</sup>.

# CHARACTERIZATION OF COIN CELLS AS A WHOLE

## Heat signature as key information for battery development and testing

Specifically, understanding of the heat generation during charging/ discharging cycles is crucial for improving the cell efficiency, performance and lifetime of batteries. Measuring the heat signature of coin cells during cycling provides insight into the underlying processes and provides a quantitative way of comparing changes in chemistry above and beyond current and voltage measurements. Some of these processes are reversible, some occur during the initial few cycles, and others take place over a period of weeks, months, or even years. The amount of heat released or absorbed during all these physicochemical changes and the rate of energy change within the coin cell provide additional pieces of the puzzle and can accelerate the development process.

Using the unique coin cell module of the NETZSCH MMC 274 Nexus® Multiple Module Calorimeter allows for analysis of the behavior of a complete coin cell instead of individual components to mimic cell performance in the real world. This special differential measuring principle for improved stability and sensitivity captures even weak heat signals from coin cells. Characterization of coin cells can be achieved by isothermal charging/discharging and scanning tests.



The MMC 274 Nexus® offers three interchangeable calorimeter modules: ARC for process safety investigations, Scanning for high reaction enthalpies and Coin Cell for battery testing.

### Efficiency Tests for Coin Cells

The key component of the coin cell module is the sensor. It features an innovative differential measurement design based on thermopiles for improved sensitivity and stability in heat-flow measurements. The calorimetric block is equipped with a Resistance Temperature Device (RTD) in order to precisely monitor and control its temperature using the surrounding furnace. When the coin cell releases or absorbs any heat due to charging/ discharging or internal physical changes, the sensor detects this heat. To nullify the effect of external disturbances, the signal coming from the reference heat flow meter is subtracted from the signal detected by the sample heat flow meter, thus yielding a true differential measurement. This technique is much more accurate and sensitive than that of a single-sensor system.

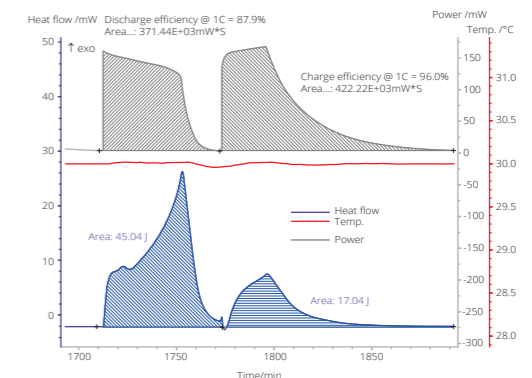


Figure 17. From the heat signature of the LiR2032 during three cycles of discharging and charging, the efficiency is calculated by dividing the electrical energy by the total energy (electrical energy + heat flow) during discharging and charging.

# BATTERY CELL CHARACTERIZATION

## Delivering *in operando* X-ray diffraction

The biggest issue faced when developing new battery materials with high energy density is capacity degradation with cycling. Causes of capacity degradation can include particle cracking, lithium retention in electrodes, electrolyte degradation, and dendrite formation. Understanding these degradation mechanisms is therefore an important step towards the successful development of new battery materials.

*In operando* X-ray diffraction (XRD) can investigate these failure mechanisms by analyzing underlying crystal structure changes during battery cycling. Our Empyrean XRD platform offers options for the *in operando* cycling of various types of battery cells – from coin cells and electrochemical cells to pouch cells and prismatic cells.

# COIN AND ELECTROCHEMICAL CELLS

## Opening possibilities for non-ambient exploration

All types of coin cells with at least one side with an X-ray transparent window can be studied on the Empyrean XRD. We provide a specialized coin cell holder, which can be used for charge-discharge cycling.

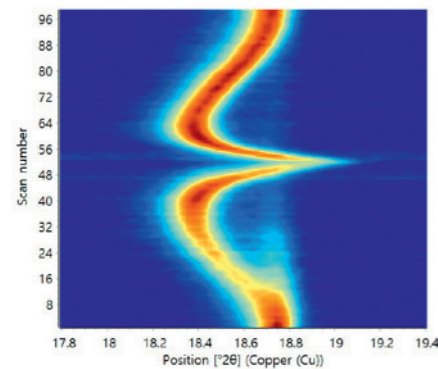


Figure 18.

Example of *in operando* cycling of an NCM cathode and graphite anode in an electrochemical cell. Fig. 17 shows how the 003 peak shifts during cycling. Fig. 18 shows how c and a lattice parameters change during charge and discharge. Any abrupt change in lattice parameter is usually associated with crystal phase changes and may cause particle cracking.

Another solution is the electrochemical cell, with an X-ray transparent window made from beryllium or glassy carbon. We supply the electrochemical cells with the option of heating and cooling that are mounted on the Empyrean XRD.

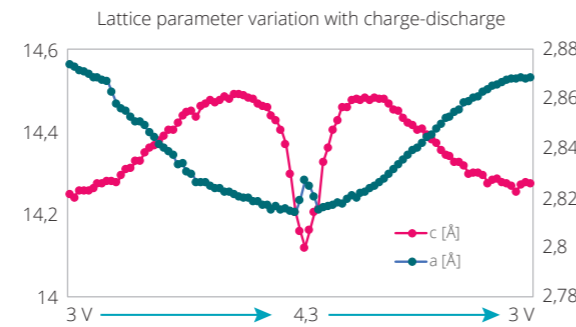
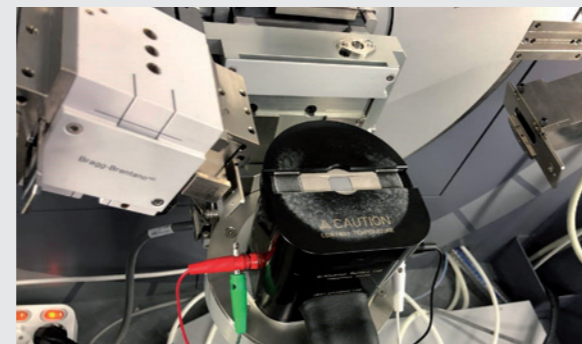


Figure 19.

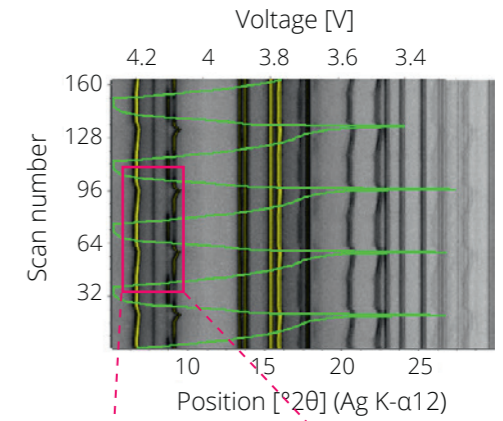


An electrochemical cell supported on the Empyrean XRD platform: it is also possible to heat or cool the cell and investigate cycling durability at non-ambient temperatures.

# POUCH AND PRISMATIC CELLS

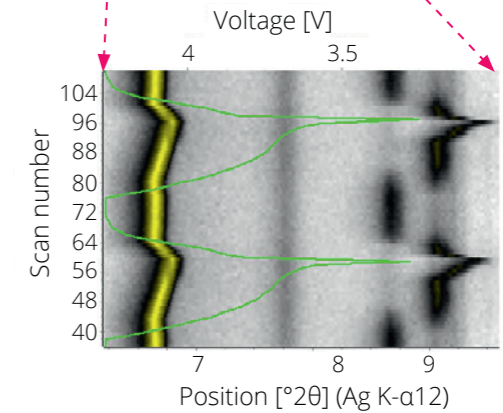
## Unlocking the full story with hard radiation transmission

What's more, multilayer **pouch cells** up to 5 mm thick can also be analyzed on the Empyrean XRD platform, when equipped with high energy **Ag radiation** and a **GaliPIX<sup>3D</sup>** detector. The Empyrean supports 60 kV excitation, enabling the high-intensity 22.16 keV Ag radiation suitable for pouch cell research. Special multilayer focusing mirrors deliver high resolution and a high brilliance X-ray beam, further shortening the measurement times.



Example of *in operando* cycling of a pouch cell. Measurements were performed on the **Empyrean XRD** platform configured with **Ag K $\alpha$  radiation** and the **GaliPIX<sup>3D</sup>** detector. Every XRD scan over 5-30  $2\theta$  range was measured in just five minutes. A total of 166 scans were measured over five complete charge-discharge cycles.

The voltage variation (3.2V in discharged state to 4.3V in fully charged state) is plotted in green line colour. The isoline plot shows cathode and anode peak positions as the cell is charged or discharged. The peak around 6.8°  $2\theta$  is the 003 peak of the NCM cathode and its changing position reflects changes in c-parameter with cycling. The discontinuous peak around 9°  $2\theta$  is from the graphite anode, which changes from C to LiC<sub>6</sub> or LiC<sub>12</sub> during the charge cycle and then reverses back to LiC<sub>12</sub> and then C during the discharge cycle.



Pouch and prismatic cell mounting on the Empyrean XRD. A mechanism to apply pressure on the pouch cell is also supported.



Our **GaliPIX<sup>3D</sup>** detector with 100% efficiency from Cu to Ag radiation makes fast measurements possible on cells up to 5 mm thick.



## WHY CHOOSE US?

**When you make the invisible visible,  
the impossible is possible.**

Our analytical systems and services help our customers to create a better world. Through chemical, physical and structural analysis of materials, they improve everything from the energies that power us and the materials we build with, to the medicines that cure us and the foods we enjoy.

We partner with many of the world's biggest companies, universities and research organizations. They value us not only for the power of our solutions, but also for the depth of our expertise, collaboration and integrity.

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