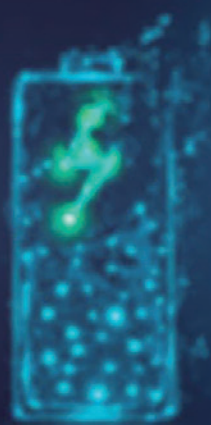![Malvern Panalytical, a spectris company]

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, 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.
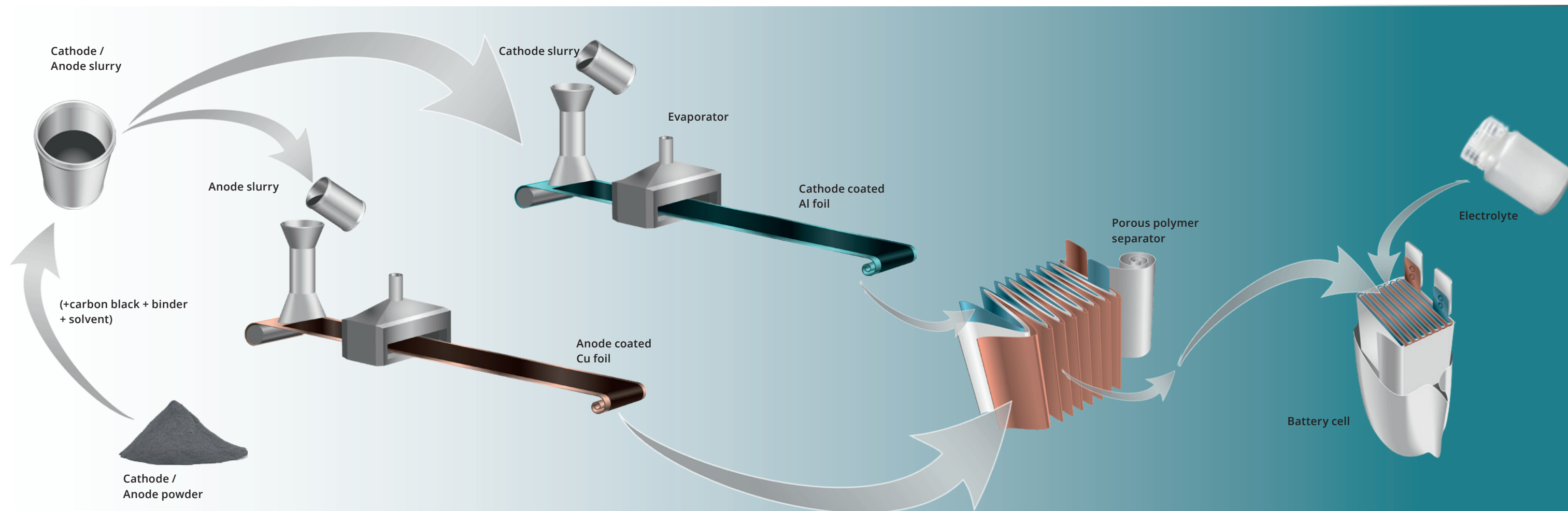
MONITOR AND OPTIMIZE AT EVERY STAGE

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, we've developed 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	Mastersizer 3000 Morphologi 4 Epsilon 4 / Zetium XRF Aeris compact XRD
Battery slurry	Particle size Particle shape	Laser diffraction Automated Imaging	Mastersizer 3000 Morphologi 4
Electrode coating	Coat weight Coating thickness	Photon sensor Micro caliper thickness sensor	Photon and Micro caliper sensors from NDC technologies
Battery cell	Degradation mechanism during cycling	*In operando* XRD	Empyrean XRD

Cathode / Anode slurry

Cathode slurry

Evaporator

Anode slurry

Cathode coated Al foil

(+carbon black + binder + solvent)

Anode coated Cu foil

Porous polymer separator

Electrolyte

Cathode / Anode powder
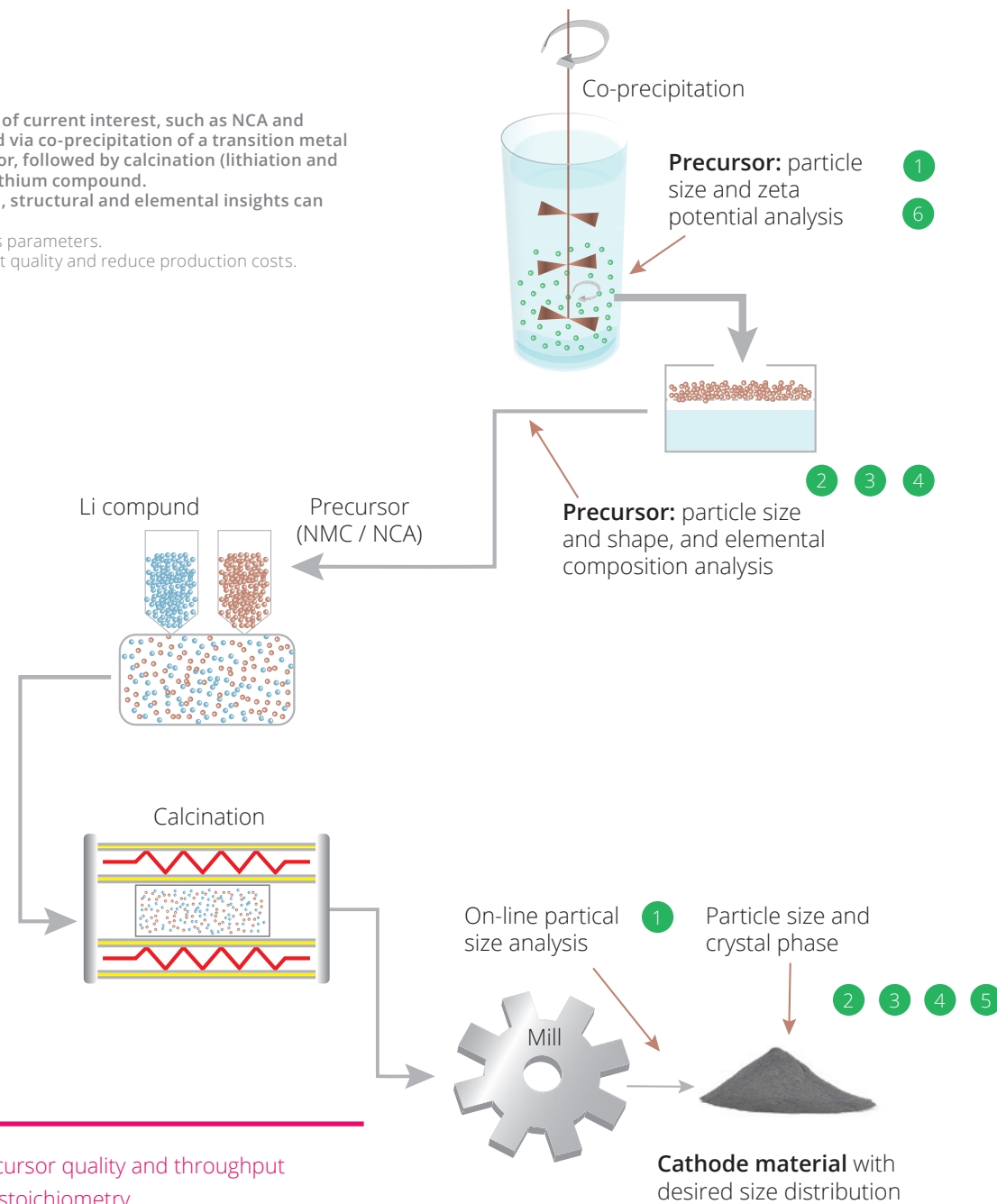
Battery cell

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.

Co-precipitation

Precursor: particle size and zeta potential analysis ①

⑥

Precursor: particle size and shape, and elemental composition analysis

② ③ ④

Li compound

Precursor (NMC / NCA)

Calcination

On-line partical size analysis ①

Particle size and crystal phase

② ③ ④ ⑤

Mill

Cathode material with desired size distribution

• 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.
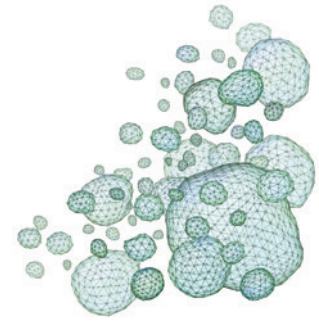
③ Particle shape

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.

Rough   Smooth   Regular   Elongated
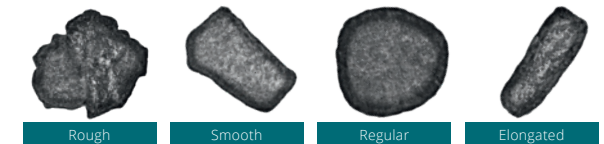
④ Elemental composition

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.

⑤ 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.
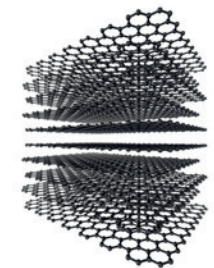
⑥ Zeta potential

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.
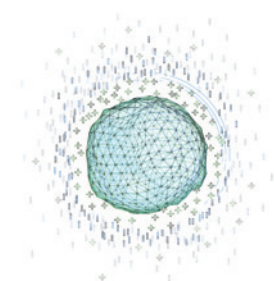
OUR RESEARCH AND **QUALITY CONTROL SOLUTIONS**

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.
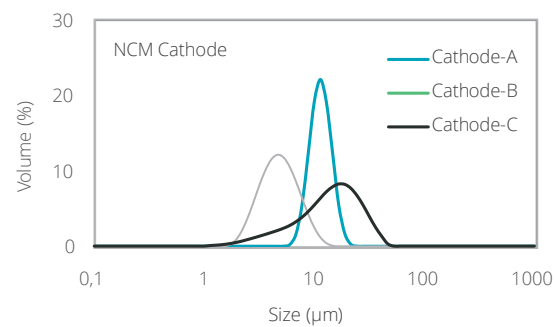

Figure 1 Particle size distribution of three batches of NCM811 cathode materials synthesized with different processing parameters
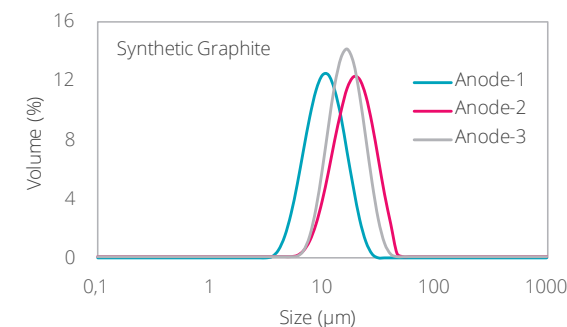

Figure 2 Particle size distribution of three batches of synthetic graphite synthesized with different heating conditions


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.
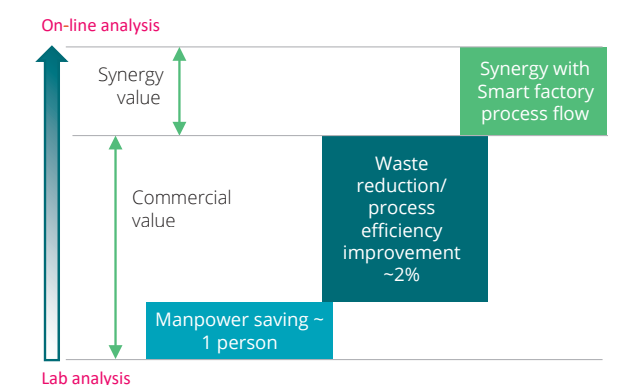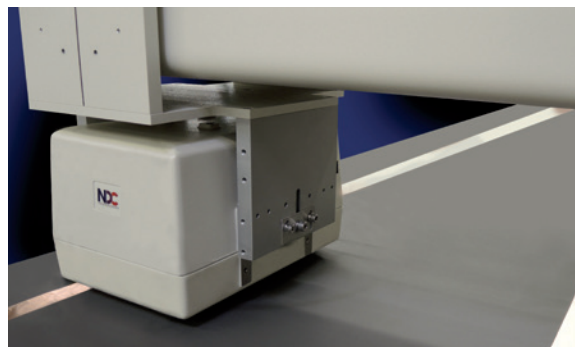

Typical value gain for a cathode manufacturing plant with Insitec online particle size analysis of precursor slurry, in comparison to lab analysis.

SUPERIOR **END-TO-END GAUGING SOLUTIONS**

Opening new process control possibilities

When it comes to electrode coatings, coat weight and thickness consistency is vital: Slight discrepancies in coat weight or thickness uniformity may drastically affect process efficiency and final battery performance. And, when the measurements are so critical, component manufacturers need fast, efficient ways to measure these variations. To address these challenges and deliver unparalleled process visibility and control,

Malvern Panalytical and sister company NDC have teamed up to deliver an end-to-end gauging system. From the basis weight measurement of electrode battery coatings to final product thickness measurement following the roll press line, these tools open new levels of control and precision that deliver outstanding process reliability and ultimately industry-leading, quality batteries.

Photon Sensor
Delivering unparalleled coat weight accuracy
Even the smallest of discrepancies in anode or cathode weight measurement can make a big difference. Coats too thin or too thick, or any type of irregularity on aluminum and copper foil substrates, can seriously compromise final battery performance.

Thanks to NDC's dedicated Photon Sensor, these issues are a thing of the past. Specifically, this highly innovative solution offers the industry's highest coat weight accuracy, and delivers ultra-fast measurements on patch, zone, and continuous coating lines.

For more information, visit:
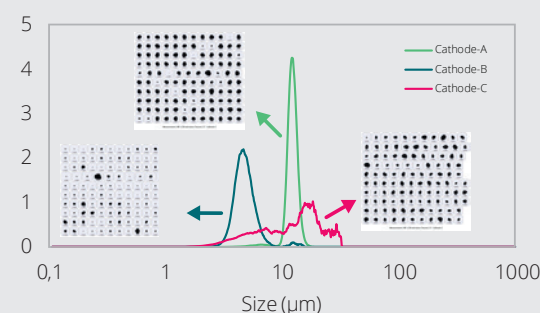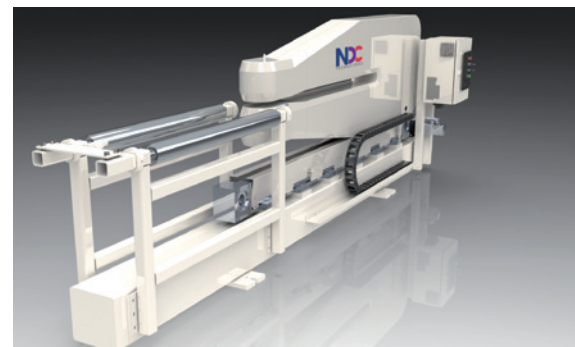www.ndc.com/film-extrusion-and-converting/industry-solutions/battery

MicroCaliper Thickness System
Driving roll press process quality
All too often, the roll press process can affect the quality of battery component coatings. This, in turn, can compromise the process efficiency, throughput volume, and final product quality.

NDC's specialized MicroCaliper Thickness Sensor tackles this issue by delivering repeatable, sub-micron accuracy for better insight into thickness variations – enabling battery manufacturers to produce the most consistent, highest-quality products on the market.
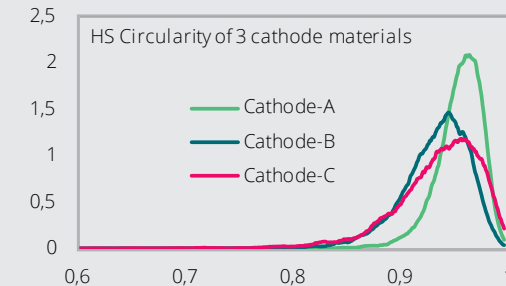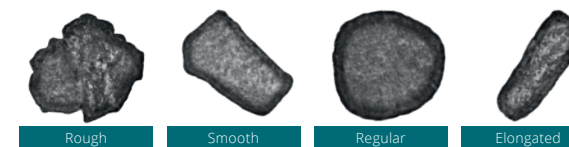
PARTICLE MORPHOLOGY

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.

| Rough | Smooth | Regular | Elongated |

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.
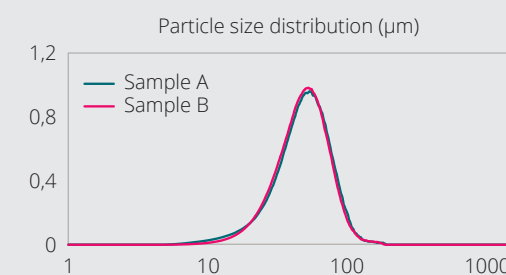

Figure 3

Figure 4

Example Cathode Materials Circular Equivalent (CE) size distribution of three NCM cathode materials, as obtained from Morphologi 4 (Figure 3). These are the same samples as those measured with the Mastersizer 3000 in Figure 1. Circularity for these samples is compared in Figure 4. 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 5

Figure 6

Example Graphite electrode material: size distribution of two samples as measured with Mastersizer 3000 (Figure 5) and circularity of the same samples (Figure 6) as measured with Morphologi 4. Though the samples have similar circular equivalent size distribution, sample A is more irregular in shape.
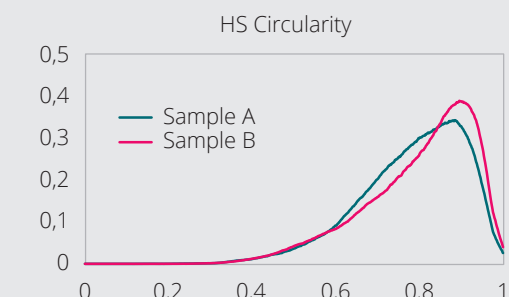
ELEMENTAL COMPOSITION

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.
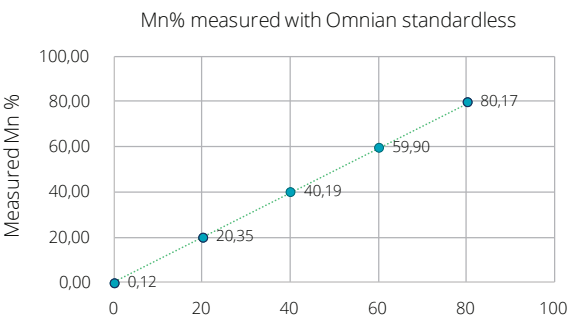
Mn% measured with Omnian standardless

Figure 7

Composition and impurities analysis on five samples of $LiFe_xMn_{1-x}PO_4$ 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 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	$LiFe_{02}Mn_{08}PO_4$	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	$LiFe_{04}Mn_{06}PO_4$	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	$LiFe_{06}Mn_{04}PO_4$	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	$LiFe_{08}Mn_{02}PO_4$	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	$LiFePO_4$	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
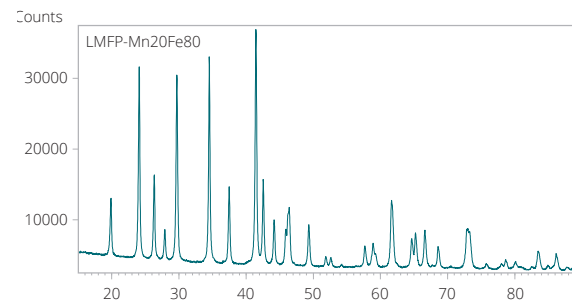
Typical XRD pattern of a Lithium Manganese Iron Phosphate (LFMP) cathode material

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.
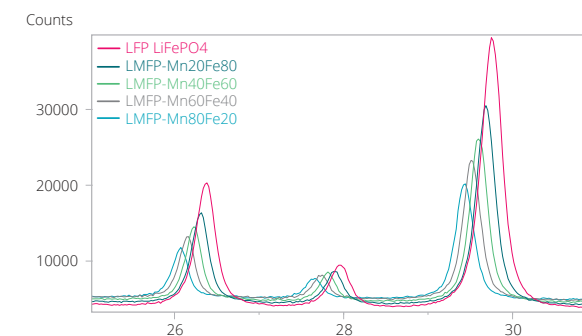

Figure 8

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.
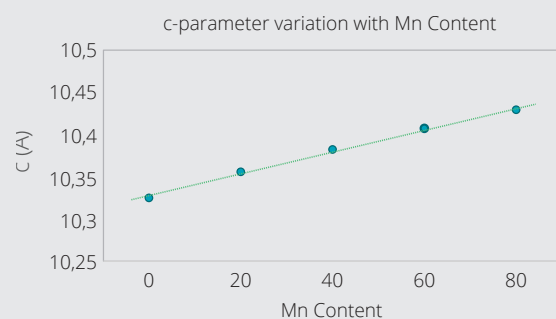
ZETA POTENTIAL ANALYSIS

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 9

Figure 10

Example LMFP Cathode Materials with varying Mn content:
Lattice expansion along c-axis (Figure 9) with increasing Mn content. For unknown batch samples, c-parameter can be measured, and composition deduced using calibration graph (Figure 9). XRD also reveals that crystallite size increases with Mn content (Figure 10) – higher Mn facilitates larger crystallite size. Crystallite size usually has a close relationship to the primary particle size.
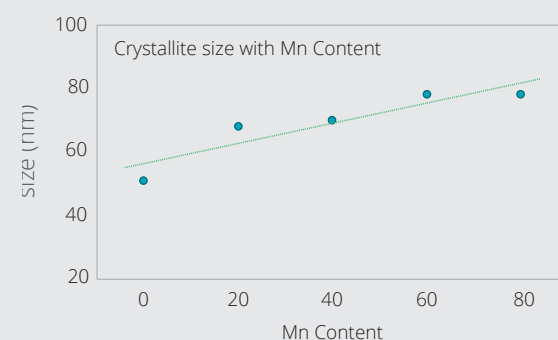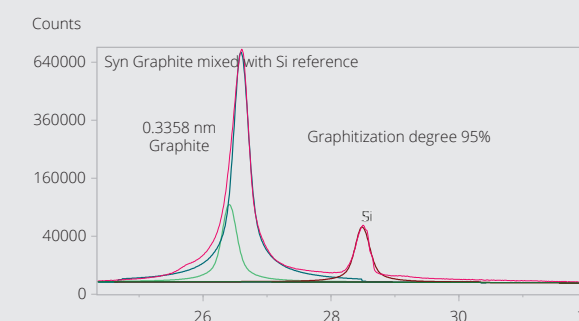

Figure 11

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 11 shows the measurement of the degree of graphitization in one such material.

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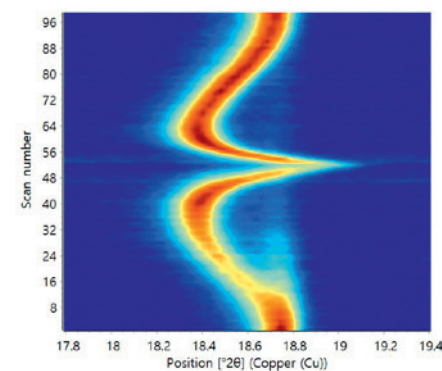
Another solution is the electrochemical cell, with an X-ray transparent window made from beryllium or glassy carbon. We supply the electrochemical cells with the option of heating and cooling that are mounted on the Empyrean XRD.
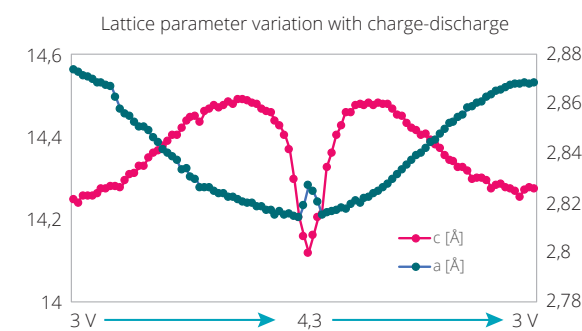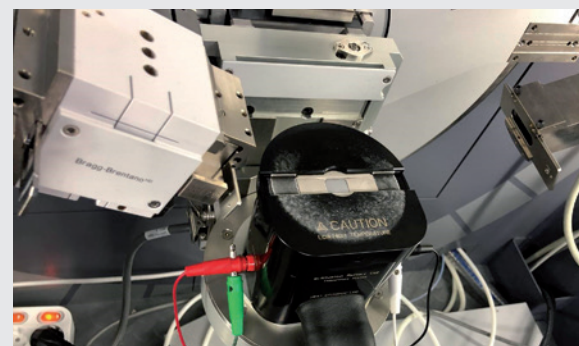

Figure 12

Lattice parameter variation with charge-discharge

Figure 13

Example of *in operando* cycling of an NCM cathode and graphite anode in an electrochemical cell. Fig. 12 shows how the 003 peak shifts during cycling. Fig. 13 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.

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 **GaliPIX³ᴰ** 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 Kα radiation** and the **GaliPIX³ᴰ** detector. Every XRD scan over 5-30 2θ 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° 2θ is the 003 peak of the NCM cathode and its changing position reflects changes in c-parameter with cycling. The discontinuous peak around 9° 2θ is from the graphite anode, which changes from C to LiC_6 or LiC_{12} during the charge cycle and then reverses back to LiC_{12} and then C during the discharge cycle.

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.
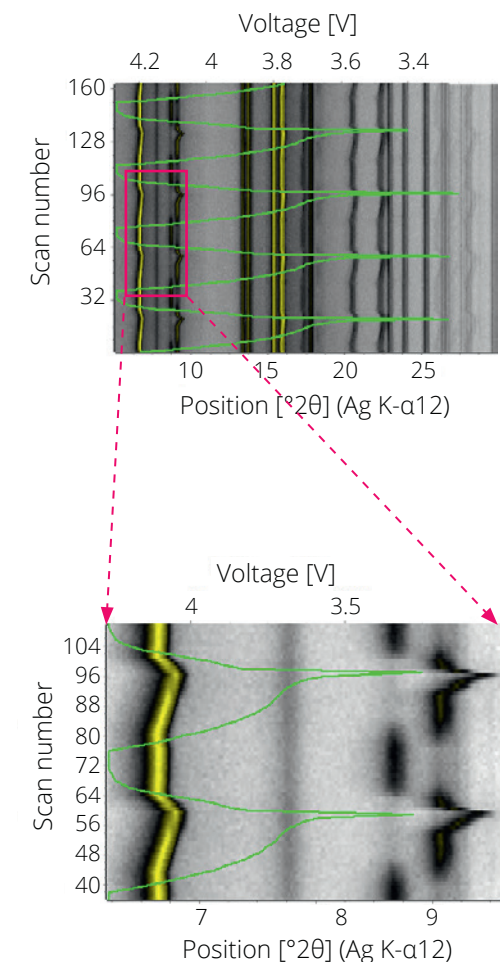

Pouch and prismatic cell mounting on the Empyrean XRD. A mechanism to apply pressure on the pouch cell is also supported.

Our **GaliPIX³ᴰ** detector with 100% efficiency from Cu to Ag radiation makes fast measurements possible on cells up to 5 mm thick.

WHY CHOOSE **MALVERN PANALYTICAL**?

We are global leaders in materials characterization, creating superior, customer-focused solutions and services which supply tangible economic impact through chemical, physical and structural analysis.

Our aim is to help you develop better quality products and get them to market faster. Our solutions support excellence in research, and help maximize productivity and process efficiency.

Malvern Panalytical is part of Spectris, the productivity-enhancing instrumentation and controls company.

www.spectris.com

SERVICE & **SUPPORT**

Malvern Panalytical provides the global training, service and support you need to continuously drive your analytical processes at the highest level. We help you increase the return on your investment with us, and ensure that as your laboratory and analytical needs grow, we are there to support you.

Our worldwide team of specialists adds value to your business processes by ensuring applications expertise, rapid response and maximum instrument uptime.

- Local and remote support
- Full and flexible range of support agreements
- Compliance and validation support
- Onsite or classroom-based training courses
- e-Learning training courses and web seminars
- Sample and application consultancy

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