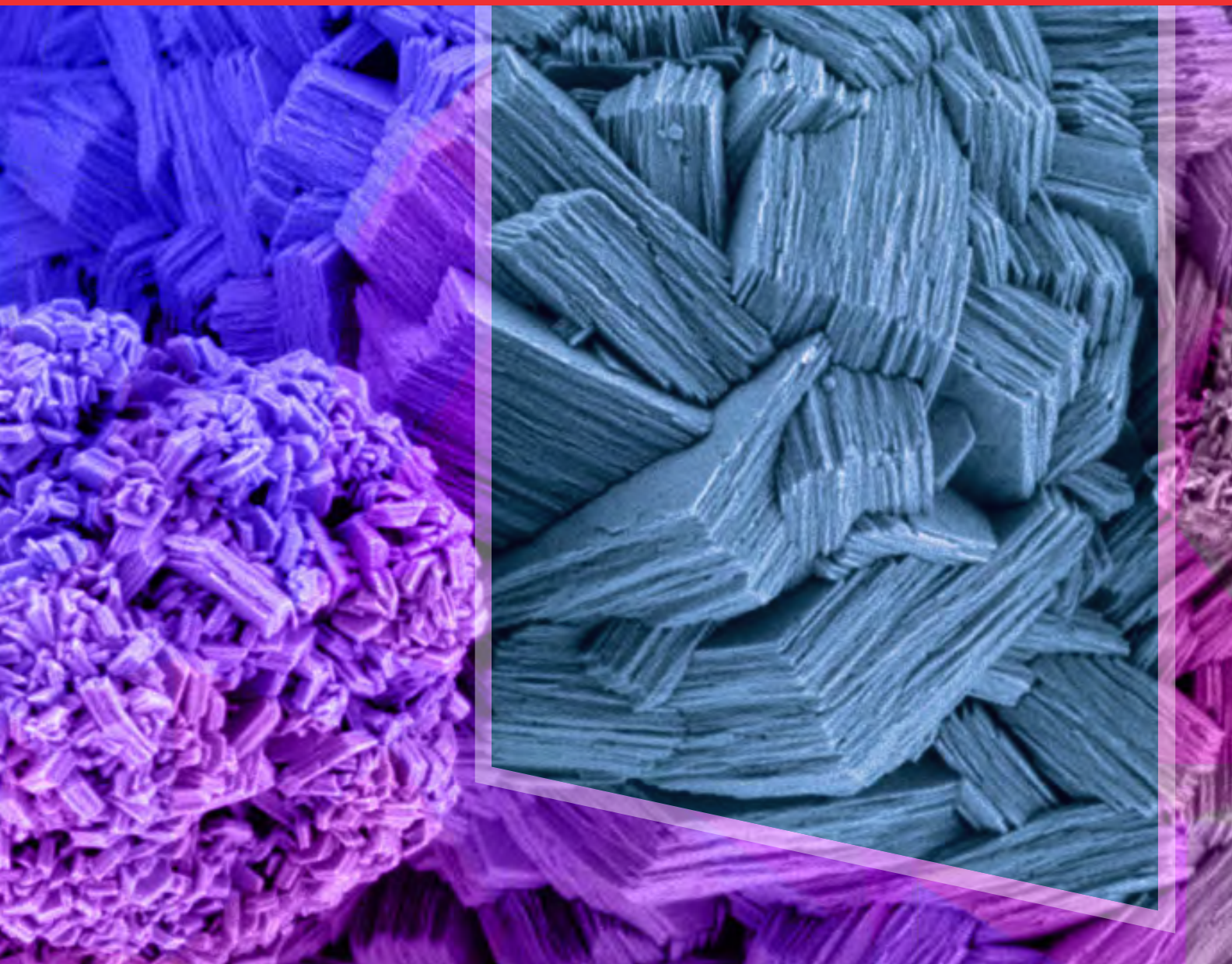


thermo scientific



Analytical solutions for improved
battery and energy storage products

ThermoFisher
SCIENTIFIC



The global lithium-ion battery market is expected to reach USD 93.1 billion by 2025. This is largely driven by increased usage in electric vehicles, grid storage, and portable consumer electronics where its higher energy density over that of lead-acid batteries is of primary importance.

However, in order to increase performance and to obtain a better understanding of the different degradation mechanisms further research is required. Battery performance is dependent on the active materials used and in the morphology of the battery. While fundamental degradation mechanisms occur inside active cathode materials and are affected by chemical interactions during charging-discharging cycles.

Evaluation of batteries and battery components requires a variety of analytical methods that study bulk materials and component surfaces at various scales. As the world leader in advancing science, Thermo Fisher Scientific provides the widest range of analytical instrumentation for battery analysis and product formulation, including X-ray photoelectron spectroscopy (XPS/ESCA), electron microscopy (SEM, TEM and FIB-SEM), optical spectroscopy (FTIR, Raman, & NIR), mass spectrometry (GC-MS, HPLC, LC-MS, HREMS-MS, TEA), microCT, nuclear magnetic resonance (NMR), X-ray diffraction, X-ray fluorescence, torque rheometry and extrusion, and viscometry.

Imaging techniques such as Raman, microCT, and electron microscopy are mainly used to study the 2D and 3D morphology of battery components at different stages in the lifecycle. These techniques cover the full length scale from the cell level with Raman and microCT down to the atomic scale with TEM. 3D imaging provides complete geometric evolution of the cathode microstructure upon cycling. Geometric parameters such as volume fraction, surface area, particle size distribution and tortuosity are typically assessed using a combination of microCT and FIB-SEM techniques.

Spectroscopy, NMR, X-ray diffraction and mass spectrometry are key to study the evolution of structural changes and the defect formation in battery electrodes. These techniques permit the analysis of electrode materials as they change during the redox reactions; and give information on both crystalline and amorphous phases. Local differences in Raman spectral changes can create a state-of-charge (SOC) distribution map showing the composite electrode. The composition of the Solid Electrolyte Interface (SEI) is commonly studied with *ex situ* XPS and *in situ* FTIR and Raman spectroscopy to monitor the SEI formation.

The rheometry and viscometry systems measure the dispersiveness and coating capability of battery materials in the electrode slurry. Torque rheometers deliver information about melting behavior, influence of additives on processability and temperature or shear stability; all critical parameters for the production of polymer separators.



Electron microscopy

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TEM

Thermo Scientific Themis Z Transmission Electron Microscope



FIB



Thermo Scientific Helios G4 PFIB CXe DualBeam Microscope



On the cover: Cross section of a lithium carbonate (Li_2CO_3) particle and nickel manganese cobalt (NMC) particles which provide the lithium to a battery system.

Electron microscopy at a glance

High resolution 2D Imaging in the SEM

- Structural characterization of electrodes and separator
- Cathode active particle morphology

Quick and easy imaging in the desktop SEM

- For fast analysis, even inside the glovebox.
- Quality control on graphite particles in the anode

3D imaging at the cell level with microCT

- Micrometer resolution, optimized for cylindrical samples
- Quality control of cathode sheets

3D imaging at the electrode level with PlasmaFIB

- Representative volumes for transport property calculations
- A 100 micrometer wide section of a battery cathode as part of a 3D reconstruction

3D Imaging at the active material level with FIBSEM

- Nanometer resolution with high contrast in 3D
- Section through an NMC cathode particle

Atomic scale characterization with TEM

- Structural characterization of the SEI and different active material chemistries
- Direct imaging of Li-atoms in the lithium oxide crystal structure

2D and 3D Image Analysis with the Avizo Software Suite

- Visualization, segmentation and modeling based on 2D and 3D datasets
- Three phase segmentation of a battery cathode

FTIR

Fourier-transform Infrared Spectroscopy (FTIR) is a commonly used vibrational spectroscopy that reveals molecular information about the sample. FTIR spectrometers accommodate an array of sampling accessories. Several third-party companies also offer a number of specialized FTIR sampling accessories useful in battery research.

The Thermo Scientific™ Nicolet™ iS50 FTIR spectrometer accommodates technique modules for FT-Raman, IR-TGA, IR-GC and a dedicated NIR unit. All of our spectrometers use our award-winning Thermo Scientific™ OMNIC™ software that provides fast and easy materials identification, and features designed for time-resolved experiments, kinetics and advanced spectroscopic studies such as phase modulation infrared reflection-absorption (PM-IRRAS) spectroscopy.

Enabling maximum sample ease-of-use on all Thermo Scientific FTIR spectrometers are attenuated total reflectance (ATR) sampling. Simply place the sample over the reflectance crystal (diamond, germanium), clamp down the material and acquire data. The use of Raman and IR spectroscopy as complementary techniques means that Raman can be used to examine structural changes in the electrode material and IR to probe the interface between the lithium and the organic electrolyte.

In developing research for battery materials FTIR has been shown to be useful in providing specific information about chemical bonds and functional groups used to identify transient lithium species. FTIR is non-destructive and supported by a comprehensive library of IR spectra for common lithium species. FTIR supports researchers actively exploring batteries alternatives like Li-S, Li-O₂, Na-ion, Mg batteries and different metal-organic batteries.

Due to its versatile sample handling capabilities and large accessory chamber, FTIR is now found in several *in operando* experiments to investigate the decomposition process of the electrolyte solutions. *In situ* FTIR can provide real-time information about the chemical nature of adsorbates and solution species as well as intermediate/product species involved in the electrochemical reactions.

FTIR at a glance

- Acquires infrared spectra of solids, liquids and gases
- Provides information about chemical bonds and functional groups
- Spectral fingerprinting enables rapid identification of unknowns
- ATR sampling provides quick and easy data collection
- Multiple sampling capabilities for specialized studies
- Monitors time-based and dynamic events
- *In operando* and *in situ* sampling capabilities



Thermo Scientific Nicolet iS50 FTIR spectrometer

Raman microscopy

Raman spectroscopy provides a structural fingerprint by which molecules in a sample can be identified. The Raman technique measures the energy shift in light scattered photons that yields molecular and structural information. Combining small spot microscopy with precision stage movement enables chemical mapping across a sample area. Raman spectroscopy is an important technique in analyzing various forms of carbon such as graphene and graphite, and diamond-like materials.

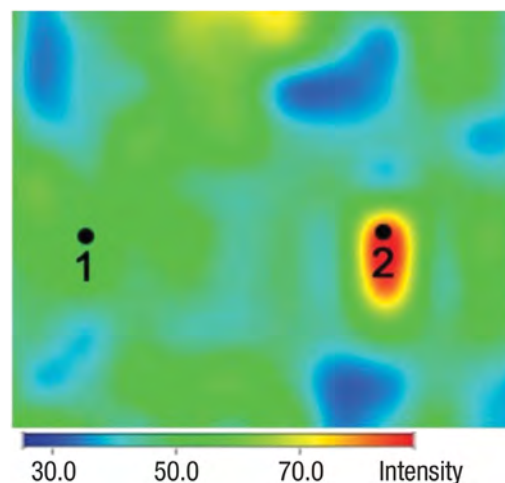
Raman is a useful technique in developing alternatives to lithium cobalt oxide cathodes, such as manganese spinel material. Raman is useful in looking at lithium cobalt doping with transition metals to synthesize materials with different morphologies.

In developing anode materials, Raman has been useful in studying carbon allotropes besides graphite. Raman spectral data can be used to determine the number of sheets of graphene in a stack, provide information on defects and disorder in the structure of graphene, and determine diameters of single wall carbon nanotubes.

Raman spectroscopy can be used to study the degree of association of electrolyte ions in solutions and in polymer materials. The association of ions has a direct effect on the ion mobility and ion conductivity and thus affects battery performance. Raman can measure the effects of additives used to suppress the crystallinity of the polymer matrix and to improve the mechanical and electrochemical properties of the resulting composite polymer electrolytes.

Raman at a glance

- Visualize chemical compositional distribution on component surfaces
- Profile chemical changes during battery cycling
- Evaluate the spatial distribution of phases in a sample
- Ideal for studying allotropes of carbon and transition metals



A Raman map showing the distribution of the two different spinel phases in a sample. The red-yellow locations (such as location 2) indicate areas of the P4332 phase whereas the blue-green areas (such as location 1) represent areas of the Fd3m phase. Mapping data collected using a DXR2 Raman microscope with a motorized stage and AtIus software.*

Raman



Thermo Scientific DXR2xi Raman Imaging microscope

*Adapted with Permission from Xialong Zhang, Fangyi Cheng, Kai Zhang, Yanliang Liang, Siqi Yang, Jiang Liang, Jun Chen, RSC Advances, 2, 2012, 5669–5675. Copyright 2012 RSC Publishing

XPS

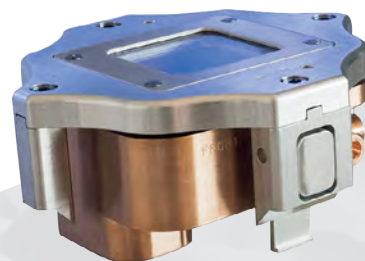
X-ray Photoelectron Spectroscopy (XPS) is a surface analysis technique that provides elemental and chemical state information about the top layer(s) of a material. XPS detects photoelectrons emitted from a surface exposed to an X-ray beam. Under typical laboratory conditions, these photoelectrons have relatively low kinetic energies meaning that only the top few nanometers of the sample are observed.

XPS instrumentation provides a quantified composition of not only the elements present, but also their chemical state. Instruments are usually equipped with an ion beam for removing material from the sample so that analysis can be extended deeper into surface. All elements from lithium and above in the periodic table can be detected.

As a surface technique, XPS is essential for understanding the interfaces between electrolytes and electrodes. Cathode and anode materials of Li-ion cells can be investigated to confirm changes in composition following cycling, to understand the oxidation states of the cathode components, and to determine the variation with depth of the solid electrolyte interphase layer as it develops. XPS has been proven useful in studying surface pre-treatment of graphitic electrode materials to significantly reduce the irreversible consumption of material during battery charging.

XPS at a glance

- Detect top ~10 nm of sample
- Quantified chemical state analysis
- Depth profiling of hard and soft materials
- Vacuum Transfer Module for air-sensitive materials



The vacuum transfer module allows samples that have been prepared in an inert environment to be transferred *ex situ* into the spectrometer chamber without exposure to air.

XPS



Thermo Scientific Nexsa Surface Analysis System

XRF

X-ray Fluorescence (XRF) spectroscopy is an elemental analysis technique that identifies and quantifies the composition of a broad range of materials. XRF measures characteristic X-rays emitted from atoms in the sample that have been energized.

Energy-dispersive XRF (EDXRF) is a rapid screening technique that captures X-ray energies across the spectral range from fluorine to uranium, identifying specific elements or unknowns.

Wavelength-dispersive XRF (WDXRF) uses crystals to disperse the fluorescence spectrum into individual wavelengths of each element (beryllium to americium), providing high resolution and low background spectra for accurate determination of elemental concentrations.

Quickly identifies elements and their concentrations within battery/energy storage product materials. XRF can also perform elemental mapping and small spot analysis for identifying defects, inclusions or inhomogeneities down to 0.5 mm. XRF determines the thickness of layers; both conducting and insulating films, non-destructively and consistently.

XRD

X-ray Diffraction (XRD) is a structural analysis technique that is typically used to identify and quantify mineral composition, phases or compounds in powder materials or thin films and layers.

X-ray diffraction systems can be used to do *in situ* and *in operandi* measurements to optimize formulations with suitable structural forms of the lithium and related materials such as polymers and/or graphite based materials.



Thermo Scientific ARL PERFORM'X



Thermo Scientific ARL QUANT'X



Thermo Scientific EQUINOX 100

EDXRF at a glance

- Analyzes bulk solids, granules, powders, thin films and liquids
- Qualitative or quantitative elemental analysis
- Identifies major, minor and trace elements
- Simultaneous identification of elements from Li to U.

WDXRF at a glance

- Bulk elemental analysis with mapping and small spot analysis
- Analyze materials in varied sizes, coatings, layers, heterogeneities and inclusions
- Covers wide concentration ranges and varied samples matrices

XRD at a glance

- Real-time rapid determination of polymorphic structures
- Measure percentage of crystallinity and study phase transitions
- Observe the stability of the materials at high temperatures, reactivity, texture and stress

Rheology

Rheology is the study of flow and deformation of materials.

The techniques investigate properties that correlate strongly with the microstructure of a material and are an indicator for any structural changes.

Rheometers are high performance instruments used for extended quality control applications as well as for research purposes.

The electrodes of lithium batteries are made by coating concentrated solid suspensions (slurries) onto metal foils, forming a thin porous layer. The electrochemical performance of a lithium ion battery is determined by how homogeneously the active components are distributed within the slurry and how uniform the slurry is coated onto the substrate. To optimize this performance, the rheometer provides critical information about the complex viscoelastic properties of battery slurries.

Twin-screw extrusion

Extrusion is a formulation and manufacturing process that melts and compounds viscous materials with additives and fillers. The extruder transports materials through specialized screws and heating zones to mix ingredients or create new compounds. The Thermo Scientific Process 11 Twin-screw Extruder is a bench-top instrument capable of supporting the end-to-end process of battery/fuel cell manufacturing.

An important topic in lithium-ion battery (LIB) technology is the use of solid-state polymer electrolytes (SPE). Twin-screw extrusion methods can play an essential role in developing a molecular dispersion of the polymer matrix with lithium salts and other additives, and thus help the search for improved formulations.

Rheology at a glance

- Investigate viscosity, yield stress and the viscoelastic moduli in formulations
- Study the complex viscoelastic properties of battery slurries
- Determine flow properties in a coating process that produce a continuous and even coating

Twin-screw extrusion at a glance

- Develop separator films using either a dry or wet compounding process
- Produce graphene and lithium cobalt oxide (LiCoO_2) slurries
- Flexible setup and low sample volumes
- Screw geometries comparable with larger equipment for efficient scale-up to manufacturing



Rheology

Thermo Scientific HAAKE MARS Rheometer



Extrusion

Thermo Scientific Process 11 Twin-screw Extruder

If you'd like to speak to an application specialist please visit thermofisher.com/specinquiry

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