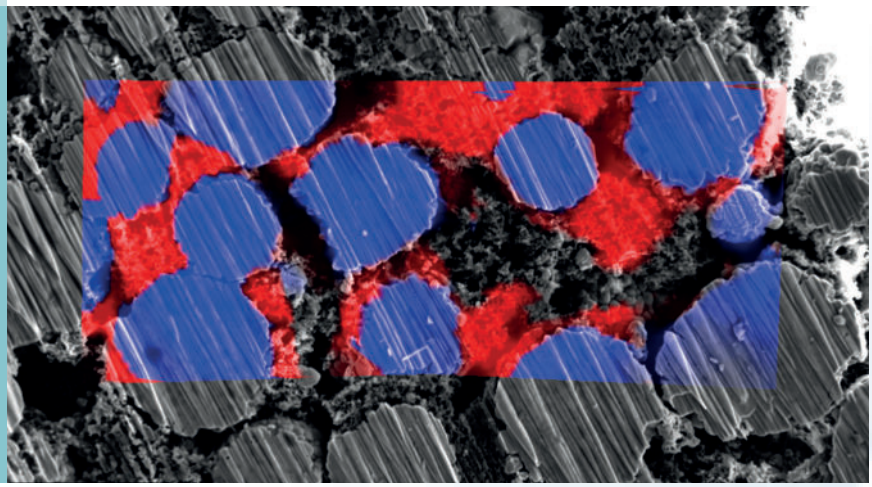
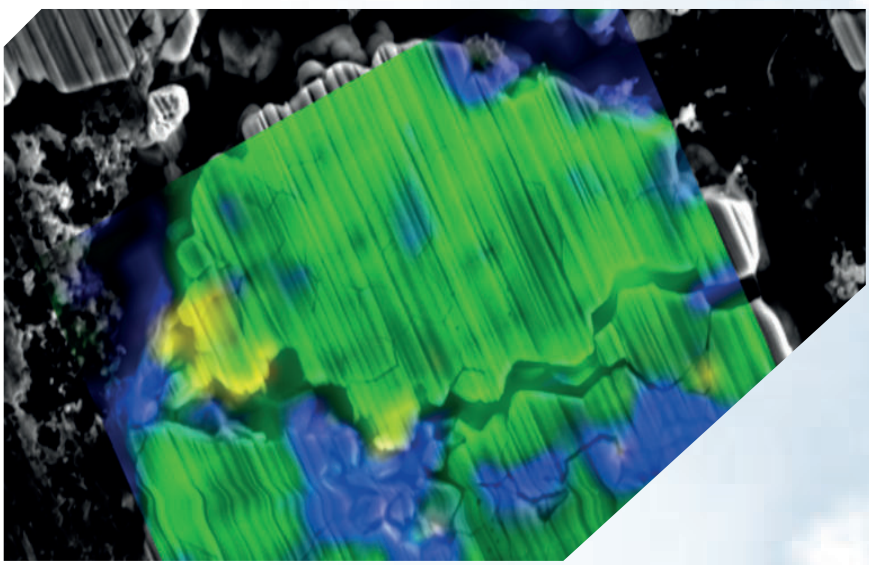
APPLICATION NOTE

Looking into Batteries with RISE Microscopy





Understanding structure-composition-property-performance relationships is fundamental in developing better batteries. RISE microscopy is an extremely useful technology for investigating these features.

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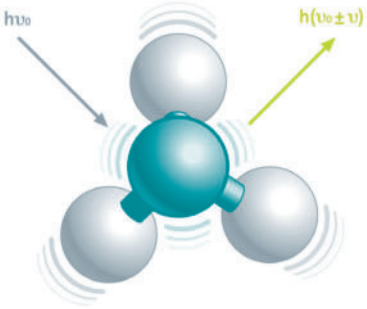
The Raman principle

The Raman effect is based on the inelastic scattering of light by the molecules of gaseous, liquid or solid materials. The interaction of a molecule with photons causes vibrations of its chemical bonds, leading to specific energy shifts in the scattered light. Thus, any given chemical compound produces a particular Raman spectrum when excited and can be easily identified by this individual "fingerprint."

Raman spectroscopy is a well-established, label-free and non-destructive method for analyzing the molecular composition of a sample.



Raman imaging

In Raman imaging, a confocal microscope is combined with a spectrometer and a Raman spectrum is recorded at every image pixel. The resulting Raman image visualizes the distribution of the sample's compounds. Due to the high confocality of WITec Raman systems, volume scans and 3D images can also be generated.

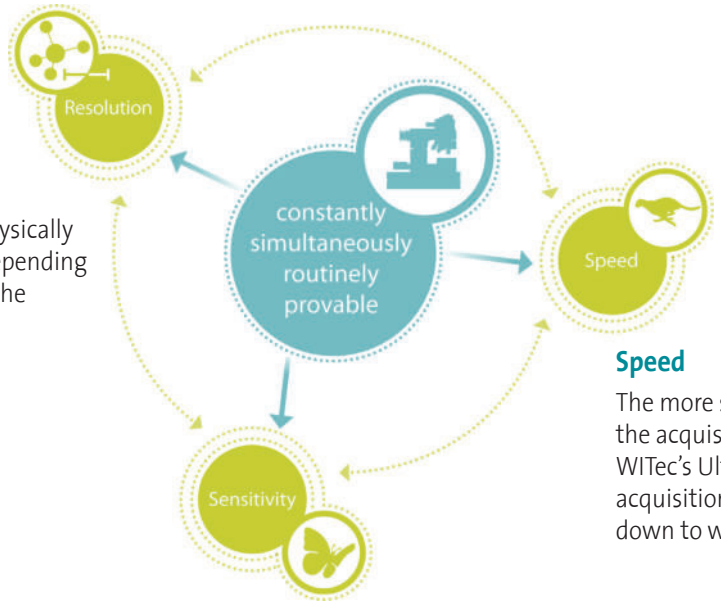
No need for compromises

The Raman effect is extremely weak, so every Raman photon is important for imaging. Therefore WITec Raman imaging systems combine an exceptionally sensitive confocal microscope with an ultra-high throughput spectrometer (UHTS). Precise adjustment of all optical and mechanical elements guarantees the highest resolution, outstanding speed and extraordinary sensitivity - simultaneously!

This optimization allows the detection of Raman signals of even weak Raman scatterers and extremely low material concentrations or volumes with the lowest excitation energy levels. This is an unrivaled advantage of WITec systems.

Resolution

Lateral resolution is physically limited to ~200 nm, depending on the wavelength of the incident light.



Speed

The more sensitive a system is, the shorter the acquisition time for a single spectrum. WITec's Ultrafast Raman Imaging reduces acquisition times for single Raman spectra down to well below 1 ms.

Sensitivity

A high confocality increases the signal-to-noise ratio by reducing the background. With the UHTS Series, WITec developed lens-based, wavelength-optimized spectrometers with a spectral resolution down to 0.1 cm^{-1} relative wavenumbers.

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Raman Imaging on Lithium Ion Batteries

Ever since Alessandro Volta invented the voltaic pile, the first electric battery, research on generating electricity from chemical reactions has continued and led to the development of many energy storage designs, culminating in lithium-ion batteries (LIBs) [1]. Significant improvements to LIBs resulted from the introduction of new cathode materials and the replacement of liquid electrolytes by solid materials.

Anodes usually consist of graphite and amorphous carbon. Cathode materials used in commercial LIBs include $LiCoO_2$ (LCO), $LiMn_2O_4$ (LMO), $LiNi_{0.84}Co_{0.12}Al_{0.04}O_2$ (NCA), $LiNi_xCo_{1-x-y}Mn_yO_2$ (NCM/NMC), and $LiFePO_4$ (LFP). Cobalt-free batteries such as spinel-structured $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) cells recently became a focus of research as they avoid requiring this expensive element.

Non-destructive Raman imaging microscopy can visualize structural and chemical information acquired from the battery's internal components such as their molecular composition, grain fractures, the formation of solid electrolyte interphase (SEI) layers and degradation processes at the electrodes.

In the following, we document changes of new and used electrodes with correlative Raman imaging and scanning electron (RISE) microscopy.

RISE™ Imaging: Correlative Raman Imaging and Scanning Electron Microscopy

The combination of SEM, energy dispersive X-ray spectroscopy (EDX) and Raman imaging is an ideal correlative approach for many applications. Scanning electron microscopy (SEM) uses the interaction of electrons with the investigated material to reveal the highest lateral resolution images of a specimen structure. The same focused electron beam can be used to generate energy dispersive X-ray spectra (EDX) for obtaining information on the chemical elements of the matter. This technique, though very powerful, cannot extract details of the bonding of atoms, which would disclose the nature of the molecules in a sample. This task can be achieved by fusing SEM with non-destructive Raman imaging.

This powerful combination is realized in one instrument for Raman Imaging and Scanning Electron (RISE) microscopy. Due to an intelligent positioning system the instrument enables diffraction limited confocal Raman imaging from exactly the same sample area as the SEM image.

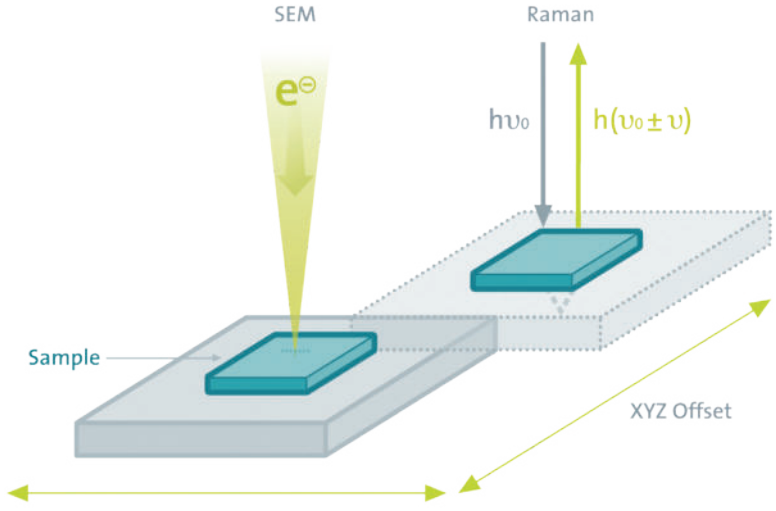

Fig. 1: Principle of RISE microscopy

Samples are automatically transferred from one measuring position to the other within the vacuum chamber of the combined Raman-SEM instrument, streamlining the workflow and drastically improving ease of use.

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Raman-EDS analysis of type 18650 Li-ion batteries before and after charging

High-resolution scanning electron microscopy (SEM) enables the detailed analysis of the electrodes' ultrastructure and energy-dispersive X-ray spectroscopy (EDS) detects most of their incorporated elements. Lithium itself evades EDS detection because it is too light. However, Li-containing molecules are identifiable by their Raman spectra, which can reveal changes in their localization and concentration. Raman spectroscopic imaging can also differentiate polymorphic variations of molecules such as amorphous carbon and graphite, which EDS is not able to do.

All high-resolution Raman measurements were performed using a WITec alpha300 confocal Raman microscope integrated with an SEM system to enable the quick and easy correlation of ultrastructural and chemical properties of the sample. An alpha300 microscope can also operate as a stand-alone, remotely controlled instrument that provides the opportunity to carry out the entire process of delicate sample preparation and Raman imaging within the controlled gaseous environment of a glove box.

We examined two type 18650 Li-ion batteries, one in its initial condition, while the other cell had been cycled over 480 times, resulting in state of health of approximately 64%. Cross sections were prepared under an argon atmosphere in a glove box. The SEM-EDS measurement of the new battery reveals that the cathode consists of Co/Ni (pink) and Mn-rich parts (cyan) (Fig. 2a). The separator and the anode are not visible, as the two polymers as well as the two carbon molecules cannot be distinguished from each other. Also, lithium cannot be detected.

However, Raman imaging can visualize graphite (cyan) and amorphous carbon (blue) in the anode and amorphous carbon and lithium with manganese oxides (red) in the cathode (Fig. 2b). The separator is built up from a layer of polyethylene (PE)

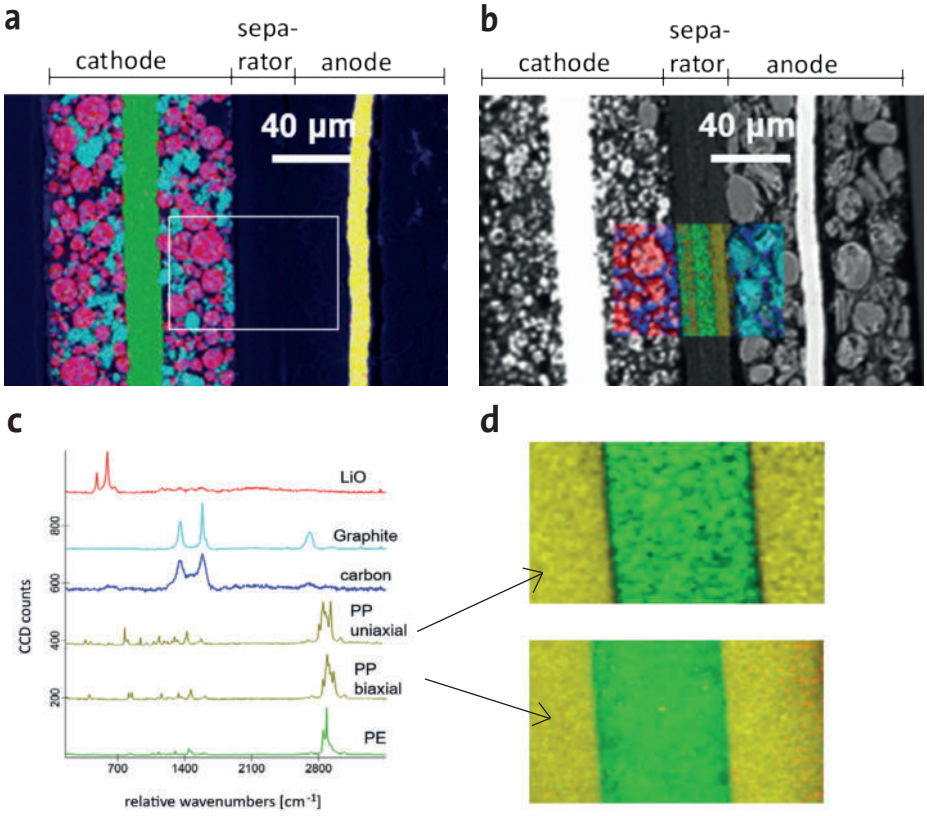

Fig. 2: Raman microscopy and SEM-EDX mapping investigation of 18650 cell LMO batteries.

(a) SEM-EDX image of a cross section of a new battery. The cathode consists of Co/Ni-rich regions (pink) and Mn-rich parts (cyan). The separator and the anode cannot be differentiated (black). Lithium is not detectable by EDX.

(b) The area indicated by an inset in (a) was analyzed by Raman microscopy. The resulting Raman image was overlaid on a white-light image. The anode consists of graphitic (cyan) and amorphous carbon (blue), the separator is made up of polypropylene (yellow) and polyethylene sheets (green), and the cathode is comprised of LMO (red) and amorphous carbon (blue).

(c) Raman spectra of the battery's components. Colors as in (b).

(d) Raman images of the separator before (above) and after (below) cycling. The process induced changes in structure of the polypropylene sheets.

Sample courtesy of Timo Sörgel and Gerhard Schneider, Aalen University of Applied Sciences, Germany.

(green) between two layers of poly propylene (PP) (yellow). All of the molecules mentioned were identified by their Raman spectra (Fig. 2c). During cycling the separators' polymers undergo molecular deterioration (Fig. 2d). While the outer layers of the separator of the new battery include only uniaxial PP, the polymer chains change their directions during cycling, appearing as bi-axial PP in the used battery. It has been described that changes in the composition of separators influence significantly the performance of a Li-ion battery.

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Impact of fast charging cycles on Li-NMC batteries

We performed analyses of NMC batteries that underwent fast recharging. Rapid charging of empty batteries is in great demand in the automotive sector, yet it impairs the batteries' performance. The investigated NMC cell was subjected to 400 cycles, leading to a 40% loss of capacity. Changes in performance are often a result of inhomogeneous degradation in battery electrodes.

Local deterioration of microstructure in NMC battery electrodes subjected to fast charging and long-term cycling was studied using a Raman system integrated with a Tescan SEM that includes a focused ion beam (FIB). Cross sections were created with the FIB for imaging.

In the RISE image of the new, charged cathode (Fig. 3a) its particles appear to consist of uniform lithium nickel cobalt manganese oxide. The components were identified by their typical spectral peaks around 580 (Li-NMC, blue), 1300 cm^{-1} and 1550 cm^{-1} (amorphous carbon, red) wavenumbers (Fig 3c).

Rapid cycling induced significant changes in lithiation of the particles as indicated by changes in the Raman spectra (green) (Fig. 3b). Raman peaks have broadened and shifted (Fig. 3d). The Raman data reveals local variations even at the single particle level.

In Fig. 3b one particle is characterized by two spectra, one of which corresponds to the Li-NMC spectrum of the native electrode, indicating that this particle might not have participated in the cycling process. Lorentzian fitting of the spectral peak positions of another particle also shows a high level of inhomogeneity and degradation in the form of cracks (Fig. 3e). More significant cracking was detected near the separation membrane (not shown).

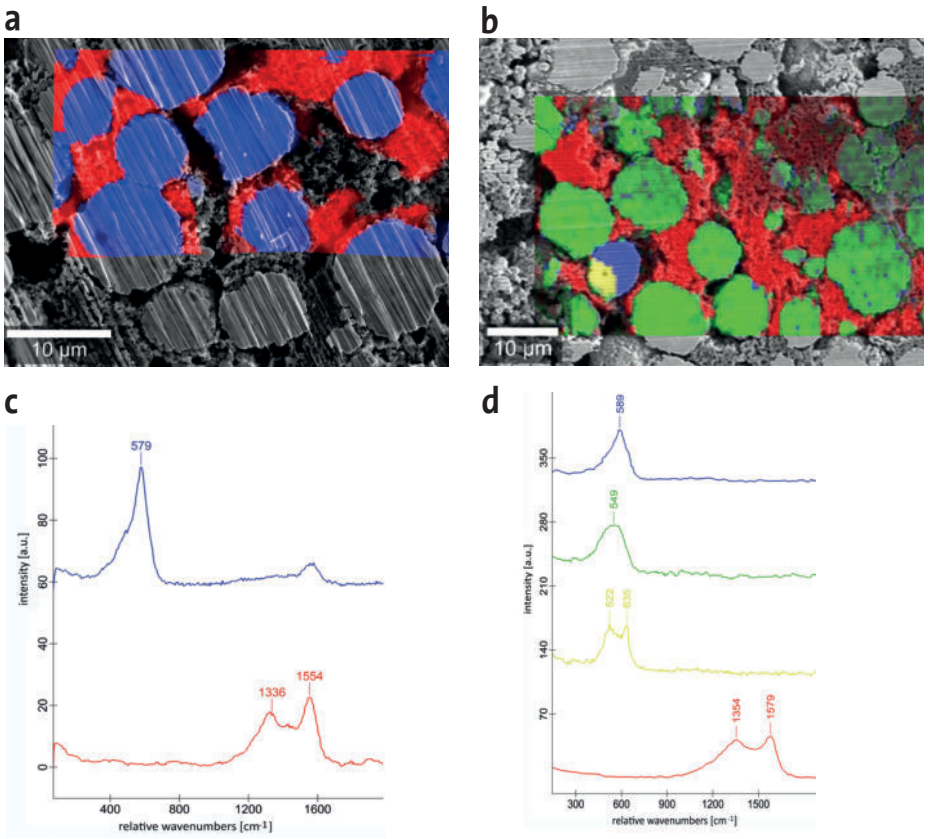


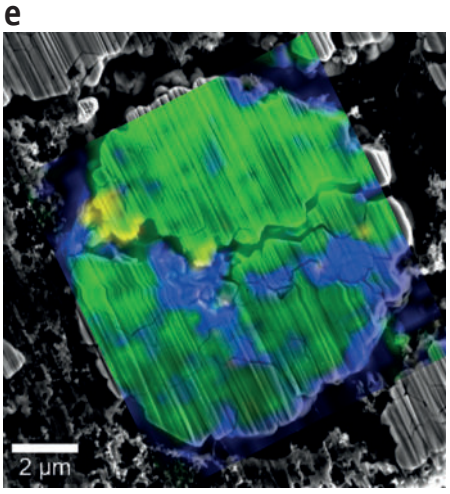
Fig. 3 RISE analysis of the cathode of a fast-cycled Li-NMC battery.

(a) Cross section of an uncycled cathode. Particles embedded in amorphous carbon (red) contain uniformly-distributed lithium nickel cobalt manganese oxide (blue).

(b) Cross section of a cycled and rapidly charged cathode. Compared to the uncycled cathode the particles appear inhomogeneous. One particle (bottom left) shows a completely different composition, including a spectrum (blue) identical to the Li-NMC spectrum of the uncycled electrode.

(c) Typical Raman spectra of Li-NMC (blue) and amorphous carbon (red) of the uncycled cathode.

(d) Raman spectra of molecules detected in the cycled cathode. Changes in peak positions and peak width indicate variance of Li-NMC composition.



(e) RISE image of a particle of a cycled cathode that reveals changes in Li-NMC composition and substantial structural degradation.

Sample courtesy of Dean Miller (Tescan USA)

WITec Microscope Series

alpha300 S: Scanning Near-field Optical Microscope

alpha300 A: Atomic Force Microscope

alpha300 R: Confocal Raman Microscope

alpha300 Ri: Inverted Confocal Raman Microscope

RISE: Raman Imaging – Scanning Electron Microscope

alpha300 *apyron*: Automated Confocal Raman Microscope

alpha300 *access*: Confocal Micro-Raman System

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