



## Application Notes AN R536

# Battery Research by Raman Microscopy

### Our world is electric

With a quick glance at the news you can tell - the world of energy storage is in transition. Whether lithium ion and solid-state batteries, ionic liquids or supercapacitors. Almost weekly a new breakthrough in battery technology is announced that may change our lives. Your smartphone, laptop, toothbrush and even your car is directly affected by the amount of electric energy we are able to store.

One of the most common battery types is the lithium polymer battery. It has obvious advantages over other battery technologies and most likely played a crucial role in today's ubiquity of mobile electronic devices.

Besides a large energy density per weight, it deliver high voltages, has no memory effect and exhibits a very well manageable degradation process. Yet still there is much untapped potential. Thus, Li-Po-batteries are being optimized and engineered as you are reading this, to satisfy the growing need for electrical energy storage.

During battery engineering and research it is very important to follow and understand the mechanistics involved. These insights are needed to investigate new electrode materials, tune the electrolytes and optimize battery performance.

Keywords	Instrumentation and Software
Battery Research	SENTERRA II Raman Microscope
Material Science	OPUS Spectroscopy Software
Carbon Allotropes	Ramanscope III FT-Raman
Lithium	OPUS/3D

### Raman spectroscopy in battery research

This application note features three real-life examples of Raman microspectroscopy and its benefits to battery research. Especially for the analysis of lithium based batteries, Raman spectroscopy allows gathering a wealth of information about the processes that take place in the battery, both *ex-* and *in-situ*.<sup>[1]</sup>

By combining a Raman spectrometer with an optical microscope it is possible to perform a chemical analysis in the micrometer range with a lateral resolution below 1  $\mu\text{m}$ .

The measurement employs a laser that interacts with the sample and grants molecular information about its vibrational properties. Furthermore, Raman spectroscopy is nondestructive and noninvasive and even allows to measure through optically transparent materials like glass or quartz.



Figure 1: Raman microscope SENTERRA was installed into glove box, to analyze sensitive materials in an inert atmosphere.<sup>[2]</sup>

### The classical lithium ion battery

This battery type consists of a graphite anode and a metal oxide cathode. Both are able to „store“ lithium ions, which is called intercalation. The ion transfer is mediated via a Li-ion conductive electrolyte like  $\text{LiPF}_6$  dissolved in an aprotic, water-free organic solvent. During charging, lithium moves to the anode and is stored (intercalated) within the carbon.<sup>[4]</sup>

During discharge the intercalated lithium ions leave the carbon matrix and are transported to the cathode. Raman microspectroscopy can elucidate all of the involved materials and processes. Since most samples are sensitive to air a successful measurement requires an inert atmosphere. In Figure 1,<sup>[2]</sup> the SENTERRA Raman microscope is installed in a glove box. This way, the researchers can safely work with samples containing elemental lithium. As an alternative, hermetically sealed cells can be used.

### Anode materials

Besides Graphite, many other carbon based materials like carbon nanotubes are in the focus of modern battery research. Indeed, Raman-spectroscopy is one of the most powerful tools for the analysis of carbon allotropes.<sup>[3]</sup>

In addition to the identification of the carbon-modification, further structural information can be obtained like the number of sheets in layered graphene<sup>[3]</sup> or information about defect concentrations and intercalated ions. These parameters can also be determined in time resolved *in-situ* experiments, showing the state of the anode during charge and discharge of the cell.

### Electrolytes

Raman spectroscopy can also be applied for the analysis of electrolytes. An example is the measurement of the salt concentration gradients in the electrolyte of a lithium battery. Here, the presence of polluting species and subsequent changes in the cathode could be measured.<sup>[4]</sup>



Figure 2: Close-up of the confocal Raman microscope SENTERRA II equipped with laser class 1 housing and fully stacked lens revolver.

### Cathode materials

Raman microspectroscopy is also sensitive to structural and chemical changes in cathode materials used in Li-ion batteries like  $\text{LiCoO}_2$ , lithium titanates or phospho-olivines.

It easily differentiates between different crystalline structures like anatase and rutile or cubic and hexagonal  $\text{LiCoO}_2$ . It is also sensitive on structural variations induced by the lithium insertion / deinsertion process in the lattice host.<sup>[1]</sup>

### About the instrumentation

The Raman measurements in the following examples were performed with Bruker Raman microscopes (see Figure 1 and 2). Thanks to the high level of automation of the SENTERRA II, excitation lasers or apertures change automatically, without manual modifications or adjustments.

In addition to the typical excitation wavelengths of 532 nm and 785 nm, the system can also be extended by a third laser with 488 nm or 633 nm. With the FT-Raman extension „RamanScope III“, a fourth excitation line with 1064 nm is available in the near infrared.

The wide selection of laser wavelengths makes it possible to adapt the measuring conditions to the sample with a single mouse-click. The high sensitivity of the SENTERRA II allows performing an analysis with very low laser power so that even sensitive samples such as carbon nanotubes or other carbon modifications can be investigated.

### SureCal™ enhanced performance

A high wavenumber precision is ensured by Bruker's unique SureCal™ technology. This guarantees, that observed band shifts are truly caused by the sample and not by instrument misalignment.

Guided measurements, efficient data acquisition and a high-precision sample stage allow rapid Raman imaging at sub-micron spatial resolution.

### Example #1: carbon analysis in flexible electrodes

Flexible batteries are of interest for wearable electronics, smart cards, flexible displays and medical devices. The approach on Lui et al. employs a flexible, binder-free, three-dimensional ordered macroporous TiO<sub>2</sub> electrode (3DOM).<sup>[5]</sup>

This binder-free 3DOM TiO<sub>2</sub> electrode is fabricated by depositing a polystyrene (PS) template on pure carbon cloth (CC), using a simple dipcoating technique. The TiO<sub>2</sub> then infiltrates the templated carbon cloth via a sol-gel solution. Afterwards, the raw electrode is heat-treated under air (3T-CC) or argon (3T-C-CC) to crystallize TiO<sub>2</sub> and remove the template. Figure 4 shows the Raman spectra of the electrode variants.

The spectrum of 3T-CC (red) is in accordance to the literature spectrum (blue) of plain carbon cloth and shows the characteristic D band (1344 cm<sup>-1</sup>) and G band (1590 cm<sup>-1</sup>) as well as a small 2D peak at approx. 2679 cm<sup>-1</sup>.

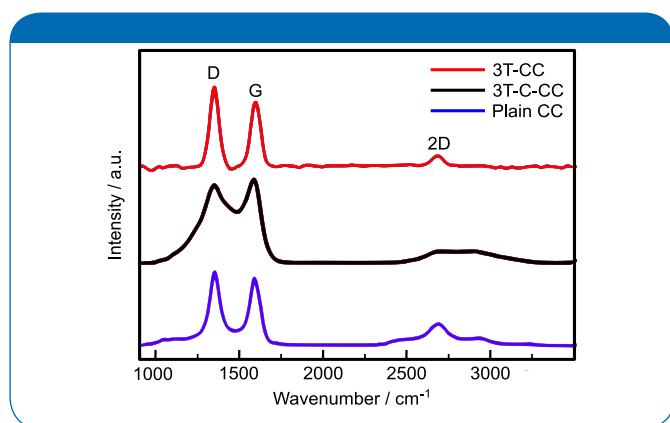


Figure 4: Raman spectra of different electrode types.<sup>[5]</sup>

If the template was heat-treated in argon, a thin layer of carbonized polystyrene remained on the carbon cloth.

Therefore, the 3T-C-CC spectrum (black) shows an obvious change in the relative intensities of the D and G bands ( $I_D/I_G$ ), in addition to a broadened 2D band. The change in the D and G band shows that the carbon stemming from the carbonized polystyrene has a different structure than the one from the carbon cloth.

Furthermore, it is evident via the decreased  $I_D/I_G$  - ratio, that the degree of disorder in the graphitic structure is decreased with the addition of carbonized polystyrene which suggests that it is amorphous.<sup>[5]</sup>

### Example #2: mapping of the SEI on lithium

The work of Schmitz et al. used Raman mapping to visualize the Solid Electrolyte Interphase (SEI) of a lithium metal battery model that uses a copper electrode partially electroplated with lithium.<sup>[6]</sup> Lithium as a substrate enhances the Raman signal by many orders of magnitude via the SERS effect (Surface Enhanced Raman Scattering), also copper shows a good enhancement factor.

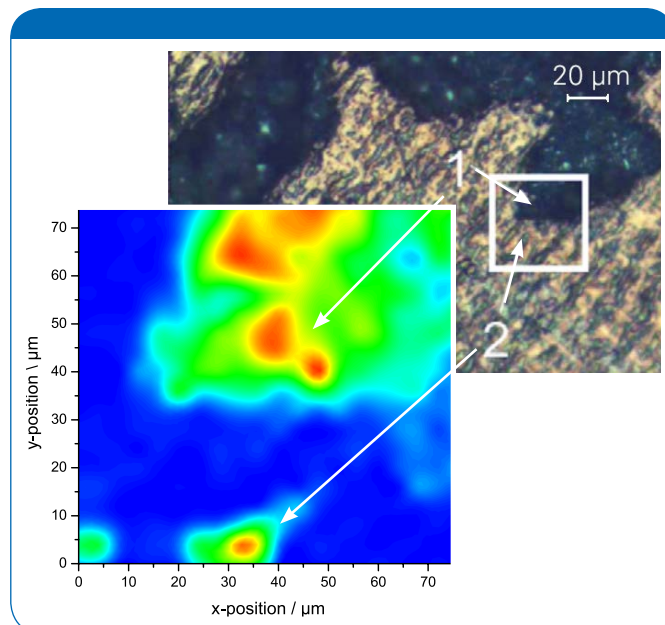


Figure 5: The upper right shows the visual image (10x magnification) of the copper foil (2, metallic) electroplated with lithium (1, dark). Measured area is indicated by white square. On the left, the chemical Raman image collected from within the white square is depicted. The image is color coded based on the integral of the Li<sub>2</sub>C<sub>2</sub>-band at 1856 cm<sup>-1</sup>. Red indicates high concentrations, blue the absence of Li<sub>2</sub>C<sub>2</sub>.<sup>[6]</sup>

Figure 5 shows the visual image of the Li plated copper foil, darker areas are plated with lithium and its reaction products while brighter areas are copper. The 40x40 μm area indicated by the white rectangle was mapped by a series of automated Raman measurements with a distance of 2 μm between each measurement point.

The chemical image on the left was generated by the integration of the Li<sub>2</sub>C<sub>2</sub>-band at 1856 cm<sup>-1</sup>. In accordance with the visual image, the highest concentrations were found in the upper right corner.

Remarkably, Raman microscopy also reveals lowly concentrated amounts of Li<sub>2</sub>C<sub>2</sub> at Spot #2, that would have otherwise remained undetected.

### Example #3: carbon coated LiFePO<sub>4</sub> particles.

Lithium Ion batteries that use LiFePO<sub>4</sub> (LFP) based cathodes are known to be very safe and show no risk of thermal runaway. A drawback of LFP is its low electrical conductivity which limits the performance at high charge/discharge rates.

A very thin carbon coating on the LFP particles can be used to improve its conductivity, however. Metzger et al. used Raman spectroscopy in order to analyze <sup>13</sup>C coated LFP particles. They were synthesized as a model compound to study the stability of carbon coated cathode materials.<sup>[7]</sup>

Figure 7 shows the Raman-spectra of uncoated LFP in green. The symmetric stretching vibration of the PO<sub>4</sub> unit at 950 cm<sup>-1</sup> dominates the spectrum. This intense peak is only barely visible in the coated LFP particles, clearly demonstrating the homogeneity of the carbon coating.

Additionally, an isotopic shift of the carbon bands is visible when comparing the <sup>13</sup>C coated LFP particles to the <sup>12</sup>C coated particles, its value is within the theoretically expected range.

### Application summary

Raman microspectroscopy offers a wide range of possibilities in the field of battery research for both *ex-* and *in-situ* measurements.

All components of a battery like anode/cathode materials and electrolytes can be analyzed with a very high lateral resolution. Especially the Raman spectra of carbon, which is very widely used in batteries, can be used to distinguish all of its allotropes and provide further information like defect concentration.

The technique is nondestructive and noninvasive and measures through optically transparent materials like glass or quartz which is especially of interest for *in-situ* setups.

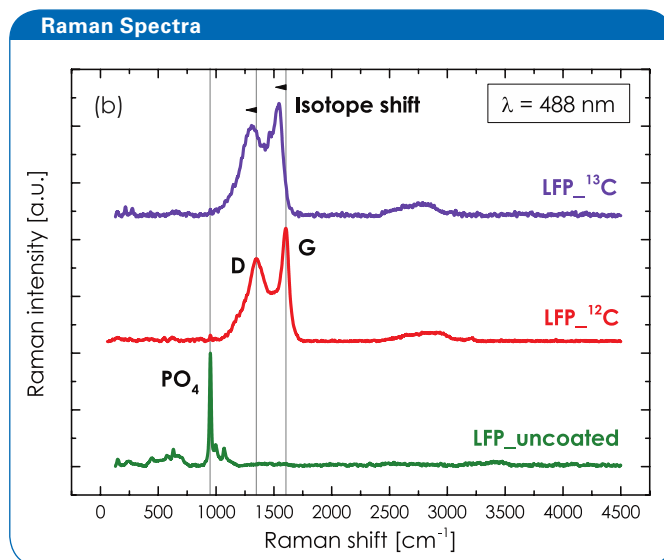


Figure 7: Raman spectrum of uncoated LFP (green) and <sup>13</sup>C coated LFP (violet) in comparison to commercial <sup>12</sup>C coated LFP (red).<sup>[7]</sup>

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### ● Bruker Optik GmbH

Ettlingen · Deutschland  
Phone +49 (7243) 504-2000  
Fax +49 (7243) 504-2050  
info.bopt.de@bruker.com

### Bruker Optics Inc.

Billerica, MA · USA  
Phone +1 (978) 439-9899  
Fax +1 (978) 663-9177  
info.bopt.us@bruker.com

### Bruker Shanghai Ltd.

Shanghai · China  
Phone +86 21 51720-890  
Fax +86 21 51720-899  
info.bopt.cn@bruker.com

[www.bruker.com/optics](http://www.bruker.com/optics)

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