

Ex situ Raman Analysis of Lithium-Ion Batteries

Abstract

The needs of lithium-ion (Li-ion) battery customers can be segmented into *in situ* and *ex situ* modes of analysis. *Ex situ* lets researchers study battery components removed from the operating battery cell.

Introduction

The use of Raman spectroscopy to analyze battery materials has been around for years. During the 1960s, researchers used Raman spectroscopy to elucidate many of the fundamental spectral features of the minerals and inorganic materials widely used in battery research today.^{1,2} Raman spectroscopy is a good fit for these materials because many of the characteristic vibrational and rotational modes occur in the low-wavenumber region of the spectrum, typically accessible only by far-infrared measurements. In the past, both Raman and far-infrared (FIR) measurements were time-consuming and difficult experiments.

Instrumentation advances have made Raman spectroscopy a much more approachable technique, mainly by increasing the ease of use. New application areas ensued, such as the exploding interest in rechargeable Li-ion batteries. Many have published careful studies of materials specifically related to Li-ion batteries as well as next-generation batteries. The review articles published by Julien in 2018 and Baddour-Hadjean in 2010 are excellent resources for learning more about the developments in this field.^{3, 5} The focus of this application note is on the *ex situ* application of Raman spectroscopy as it pertains to battery research.



Thermo Scientific DXR3xi Raman Imaging Microscope

Analysis techniques: *in situ* versus *ex situ*

The term *in situ* is used to describe experiments where the battery components are studied in an assembled cell under operating conditions. Think of *in situ* as the window to the chemical reactions that happen inside a battery, such as charging and discharging a battery.

While *in situ* cells provide valuable information, their use is generally targeted at the research and development of new materials for Li-ion batteries. Once a formulation is designed, a candidate battery is scaled up through pilot production to actual product samples. At this stage of development, researchers are most interested in characterizing failure modes and a better understanding of performance differences. For example, what makes one production run work better than another, and why did one battery fail yet its siblings from the same batch work fine?

To answer these questions, researchers carefully disassemble a battery cell to examine the individual components. This type of analysis is called *ex situ* because the battery components are removed from the operating battery cell. The goal is to prepare the samples for analysis in as close to a native state as possible.

Battery disassembly for *ex situ* analysis is carried out in an inert environment such as an argon-filled glove box to protect the battery components from moisture and oxidation. For example, the anode-separator-cathode sandwich must be carefully separated and rinsed to remove excess electrolytes.

Once the samples are prepared, they must be kept in an inert environment to protect against changes during analysis. When space is available, instruments are installed inside the glove box so the samples can be analyzed. In most cases, the sample must be removed from the glove box and transferred to an external instrument for analysis. This is where an *ex situ* transfer cell becomes a key component of the workflow. It preserves the inert environment around the sample so it can be studied.

From single point measurements to Raman imaging

The majority of published research on Li-ion battery Raman work is based on single point measurements acquired over time during charge/discharge cycles. Single point measurements can be misleading because there is no way of knowing if the sampled point is representative of the entire electrode. It is important to make multiple measurements to be sure. Because the Raman signals are weak, it takes many minutes to generate enough signal-to-noise ratio at each measurement point. A complete, multi-point experiment can be quite time-consuming to complete.

Today, Raman imaging is a viable alternative that enables you to quickly make thousands of measurements over an area of the electrode rather than just single point measurements. Each pixel in a Raman image is a complete Raman spectrum, so you can tell if changes are heterogeneous or hot spots.

The following experimental results demonstrate the flexibility of using Raman imaging for the *ex situ* analysis of Li-ion batteries and their components.

Characterization of Li-ion anodes

After safety concerns, a leading area of interest in Li-ion battery research is understanding the cause of performance degradation over time. Research indicates that the solid electrolyte interphase (SEI) layer formed on the surface of the electrode is key to performance. The SEI layer is formed by the deposition of organic and inorganic compounds during the first several charge/discharge cycles.⁴ It stabilizes the electrode from further decomposition and promotes reversible capacity. Because of the complexity of the SEI layer, results from any and all analytical techniques contribute to an incremental understanding of this behavior.

As you might expect, it is a messy business to extract electrodes from a used battery so the SEI can be studied. It takes great care to prepare the sample so as to preserve its integrity for *ex situ* analysis. This is usually achieved by working in an argon-filled glove box to prevent sample degradation due to atmospheric exposure. A transfer cell with a window is used to seal the sample in the inert argon environment so it can be removed from the glove box for analysis using a Raman microscope.

Experiment

Anode samples from a disassembled Li-ion battery were cut and mounted in a Thermo Scientific transfer cell so that a cross-section of the anode could be imaged.

The transfer cell (**Figure 1**) maintains an inert environment surrounding the sample so it can be analyzed using instruments outside a glove box. The cell body accepts various industry-standard sample holders (stubs) developed for scanning electron microscope (SEM) analysis. A 90° stub was used to hold the cut edge of the anode facing the window. A cap containing a calcium fluoride (CaF₂) window seals the sample under an argon blanket. The cap is screwed on until the window height is just above the sample. This provides a minimum working distance between a microscope objective and the sample. A short working distance is an advantage because it allows the use of high magnification objectives having a large numerical aperture (N.A.).



Figure 1. Transfer cell maintains sample in an inert environment for *ex situ* analysis of Li-ion battery materials.

Raman spectra were collected over a single $76\ \mu\text{m} \times 160\ \mu\text{m}$ area at a spatial resolution of $1.0\ \mu\text{m}$ per pixel using a Thermo Scientific™ DXR™xi Raman Imaging Microscope. Laser power at the sample was $2.0\ \text{mW}$ at $532\ \text{nm}$ with a $0.2\ \text{sec}$ exposure time and four image scans. An Olympus $50\times$ long working distance $0.5\ \text{N.A.}$ microscope objective was used to focus through the transfer cell window. Higher laser powers and/or longer exposure times were avoided because they can heat the sample, causing changes that mask the native state of the electrode.

Results

A Raman image is a hyperspectral data set with each pixel in the image being a complete Raman spectrum. Using various spectral processing techniques, this hyperspectral Raman data generates image contrast pertaining to the specific chemical features. This capability is used to visualize minute differences within a sampled area.

A variety of chemical images can be created from each data set, showing changes within the sampled area. For this experiment, image contrast is generated by multivariate curve resolution (MCR) analysis. MCR finds the major components within each image and a different color is assigned to each. This is analogous to the use of dyes in biological fluorescence imaging that tag different parts of a cell.

Alternatively, multiple regions of the sample can be imaged, and the Raman spectral data within each region can be averaged to produce a single spectrum. In this mode, the Raman imaging data set is used as a means of homogenizing any differences in the electrode area. This average spectrum represents a single point measurement, yet each point represents a $30\ \mu\text{m}$ square compared with the typical $1\ \mu\text{m}$ sample area from a standard Raman microscope.

Figure 2 is a micrograph of the anode cross-section. The copper current collector is in the center, with anode material coated on both surfaces. Superimposed is the Raman image created from the spectral differences shown by the inset Raman spectra. The Raman image clearly shows that the coating on one side of the copper current collector is dominated by carbon black (red) whereas the other side has a much greater density of the active graphite phase (blue).

This example demonstrates the advantage of Raman imaging over traditional single point measurements. The major differences in the two coatings could easily have been missed by single point measurements depending on where the points were measured.

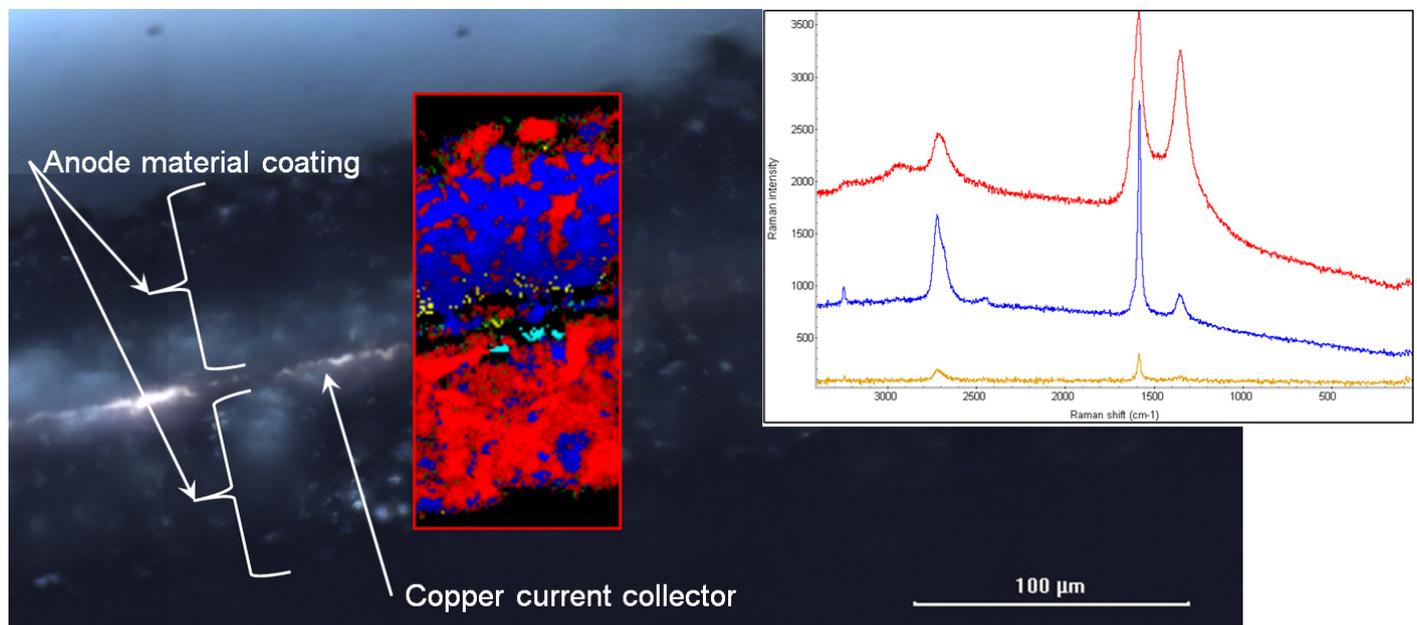


Figure 2. Cross section view of a Li-ion battery anode. Raman image indicates a difference in the anode coating on each side. Inset Raman spectra are color-coded to the areas in the Raman image.

Conclusion

The high sensitivity of Raman imaging is a benefit for Li-ion battery analysis. *Ex situ* Raman imaging measurements give results with a higher degree of confidence compared to single points.

The data were collected using an older model instrument, the Thermo Scientific DXRxi Raman Microscope. Currently, Thermo Fisher Scientific offers an improved model, the Thermo Scientific DXR3xi Raman Microscope, which offers superior speed and performance over its predecessor models

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