

In situ Raman Analysis of Lithium Ion Batteries

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Abstract

The needs of the Li-ion battery customers can be segmented into *in situ* and *ex situ* modes of analysis. *In situ* analysis allows researchers to follow changes in a battery cell during its charge and discharge cycles. Recent improvements in Raman sensitivity enable these changes to be imaged on a dynamic time scale.

Introduction

The use of Raman spectroscopy for analysis of battery materials has been around for years. During the 1960s, researchers used Raman to elucidate many of the fundamental spectral features of the minerals and inorganic materials widely used in battery research today.^{1,2} Raman 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 that day and age, both Raman and far-infrared measurements were time consuming and difficult experiments.

Advances in instrumentation have greatly increased the ease-of-use of Raman making it a much more approachable technique. New areas of application ensued such as the exploding interest in rechargeable lithium ion batteries. Many researchers are involved and have published careful studies of materials specifically related to Li-ion batteries as well as next generation batteries. A review article by Baddour-Hadjean published in 2010 is an excellent resource for those wishing to get up-to-speed in this field.³ The focus of this application note is on the *in situ* application of Raman spectroscopy as it pertains to battery research.



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 a window on the case of a battery which lets you see the chemistry of what goes on when you charge and discharge a battery. There are very few commercially available cell designs compatible with spectroscopic measurements. Researchers have resorted to building their own cells to meet the needs of their experimental apparatus. Examples of such designs have been published along with experimental results.⁴⁻¹⁰

In situ cells analysis is generally targeted at 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 worked fine.

To answer these questions, researchers carefully disassemble a battery cell so the individual components can be examined. This type of analysis is termed *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. Please see the companion application note for details on *ex situ* analysis.

From Single Point Measurements to Raman Imaging

The majority of published research on Li-ion battery *in situ* Raman work is based on single point measurements acquired over time during charge/discharge cycles. An example is the excellent work done by Kostecki's group at Lawrence Berkeley National Lab.¹¹

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 which lets you 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. This technique provides confidence in understanding if changes are heterogeneous or hot spots.

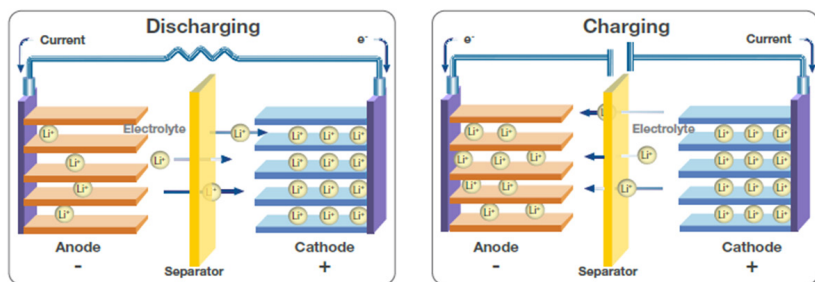


Figure 1: Movement of Li⁺ ions balance electrons during the charge and discharge cycles of a Li-ion battery

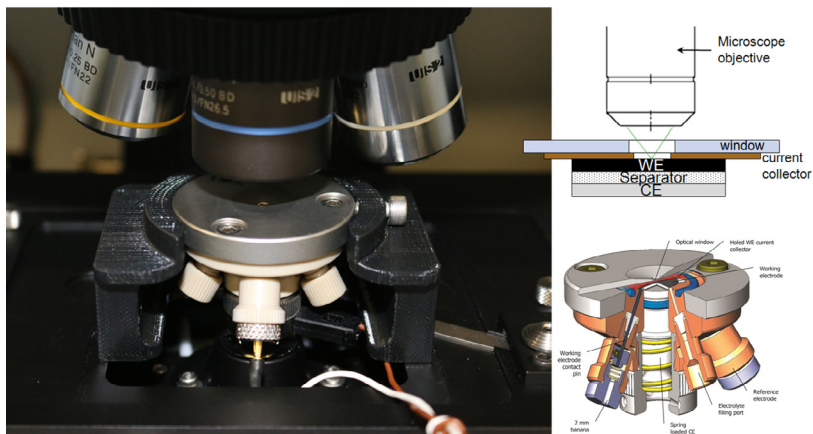


Figure 2: Experimental setup for the *in situ* example showing the electrochemical cell mounted on the stage of a Raman imaging microscope

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

Lithiation of Graphite

Graphite is widely used as an anode material for rechargeable Li-ion batteries.

During the Li-ion battery charging cycle, positively charged Li⁺ ions move from cathode through the electrolyte, across a separator into the anode to balance the flow of electrons in the external circuit (Figure 1). This process of Li⁺ ions entering the graphitic structure of the anode is called intercalation. Intercalation causes changes in the anode structure – primarily a swelling of the graphite structure.

Experimental

The experimental setup for this example consists of a Thermo Scientific™ DXR™xi Raman imaging microscope and an EL-CELL® ECC-Opto-Std optical electrochemical cell. This cell enables the investigation of batteries in a so-called sandwich configuration where the working electrode (WE) material is placed under a sapphire (Al₂O₃) window. Electrode material (graphite powder in this example) is spread onto a copper grid serving as the current collector. This WE is sandwiched from below, with a glass fiber separator soaked with the electrolyte solution and lithium metal as the counter electrode (CE).

The Raman beam from the microscope objective impinges onto the backside of the WE material through the sapphire window (Figure 2). The advantage of investigating the backside of the electrode is that the pathway for the Raman beam is minimized, allowing the use of high magnification objectives, optimizing spectra quality. The drawback is the gradient of lithiation concentration along the depth of the electrode. Accordingly, the electrode must be charged very slowly in order to minimize this unwanted gradient.

The graphite electrode was cycled at a constant rate of approximately 0.06 C. The C-rate is measure of how rapidly a battery is charged/discharged. This rate of 0.06 C corresponds to 33 hours for a full charge/discharge cycle between 1.5 and 0.005 V against Li/Li⁺. Raman imaging was carried out during the initial 480 minutes of the charging (lithiation) process only.

Raman spectra were collected over a 30 μm × 30 μm area at 1 μm pixel spacing using 2 mW of 532 nm laser excitation, a 0.01 sec exposure time for each pixel, and 50 scans per image. Higher laser powers and/or longer exposure times resulted in burning of the graphite and boiling of the electrolyte.

Results

A Raman image is a hyperspectral data set with each pixel in the image being a complete Raman spectrum. Using a variety of spectral processing techniques, this hyperspectral Raman data generates image contrast pertaining to specific chemical features. It is this capability that visualizes minute differences within a sampled area. By collecting a sequence of Raman images, we now have the ability to monitor changes in both space and time. As mentioned earlier, a variety of chemical images can be created from each data set showing changes within the sampled area. Alternatively, the Raman spectral data within each data set can be averaged to produce a single spectrum for each time slice. 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.

In Figure 3, the 3D view (bottom left) shows changes in the Raman spectrum as a function of time over 8.3 hours (1–500 min). During this time, the battery cell is in the charging (lithiation) process only. This portion of the electrochemical cycle is shown in the lower right of Figure 3.

The spectrum of graphite exhibits a prominent peak at $1580\ \text{cm}^{-1}$ attributed to the E_{2g2} mode (G band). At potentials between 0.42 and 0.31 V (specific charge 33 and 45 mAh/g), the band gradually disappears along with the simultaneous emergence of a peak centered at $1590\ \text{cm}^{-1}$. This peak shift is attributed to the Li^+ ions intercalated into the graphite structure. This is more easily seen in the center, 2D Raman image. The inset shows Raman spectra before and after the change.

Towards the end of the charge cycle at 8.3 hours (496 min), where the voltage is less than 0.15 V (specific charge greater than 146 mAh/g), a strong Raman band centered at $154\ \text{cm}^{-1}$ begins to appear. This Raman band has not been previously reported so its assignment is not conclusive. Strong Raman bands in this region have been attributed to TiO_2 , Sb, and metal chlorides.

The type of views shown in Figure 3 are “spectrum-centric” because they show changes in the Raman spectra captured at different times during a time based analysis. Figure 4 shows another way of exploring the same Raman imaging data set from an alternative “image-centric” point-of-view. Here, we are not as interested in the Raman spectrum itself but rather its use as a tool to enhance differences within the image (image contrast).

In Figure 4, Raman images are presented in which the image contrast is generated by multivariate curve resolution (MCR) analysis. In this case, MCR finds the differences not only within each image but also across the entire time sequence. A different color is assigned to each resolved component. This is analogous to the use of dyes in

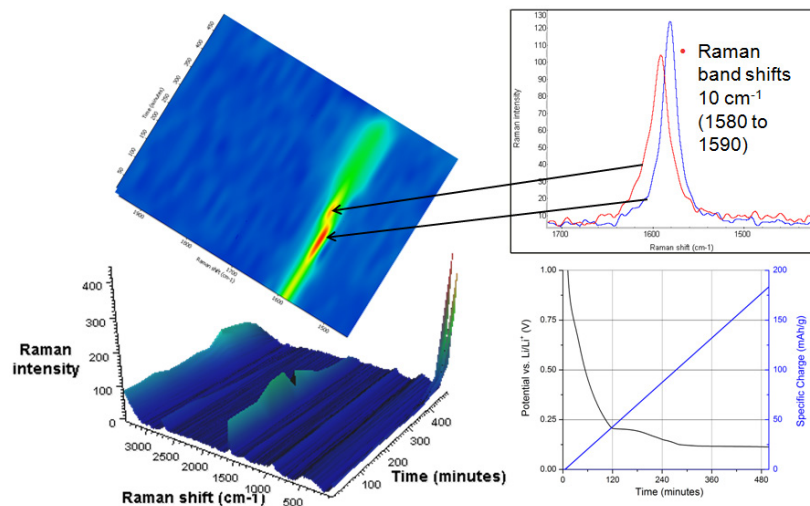


Figure 3: Different views rendered from the time lapse hyperspectral Raman data provide a wealth of experimental information

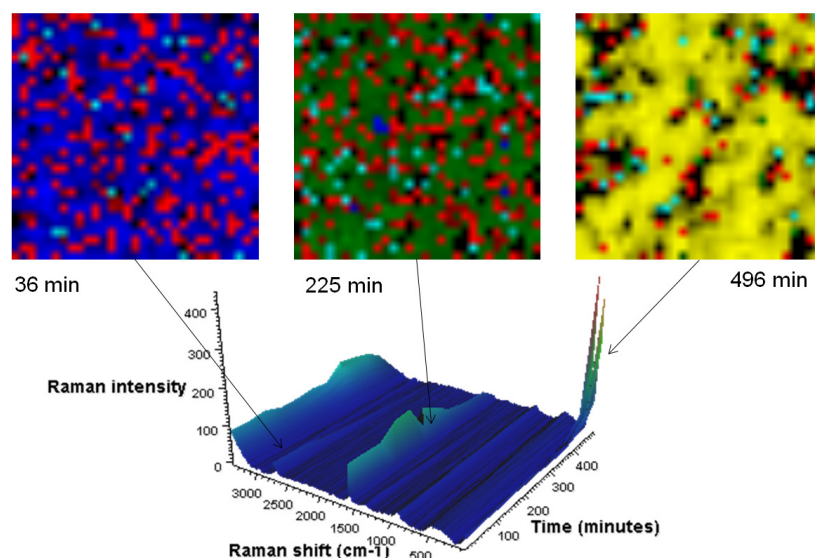


Figure 4: Raman images from different time slices in the graphite lithiation experiment

biological fluorescence imaging which tag different parts of a cell. Each image is from the same $30\ \mu\text{m}$ square portion of the anode. The blue MCR component is indicative of the $1580\ \text{cm}^{-1}$ band; green the $1590\ \text{cm}^{-1}$ band; yellow the $154\ \text{cm}^{-1}$ band; red represents carbon black, a conductivity enhancer.

It can be challenging to visualize the information content with such a massive wealth of data. Figure 4 shows just three frames to demonstrate this type of analysis. The changes are easier to grasp using a time lapse viewer of the complete time sequence:

- 3D time lapse: <http://youtu.be/Ic0MFABSU4M>
- Time lapse: <http://youtu.be/geq6mbYVARE>

Conclusion

The high sensitivity of Raman imaging is a benefit for Li-ion battery analysis. *In situ* Raman imaging techniques show the spatial distribution of phase changes in electrodes over time. This is a capability that was not possible with single point measurements using traditional Raman microscopy.

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