

# Application News

AIRsight™ Infrared/Raman Microscope

## Deterioration Evaluation of Lithium-Ion Battery Components Using Infrared/Raman Microscope and Airtight Cells

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### User Benefits

- ◆ Use of airtight cell allows infrared and Raman measurements of samples that are susceptible to degradation from atmospheric components when exposed to non-atmospheric conditions.
- ◆ Since AIRsight enables both infrared measurement and Raman measurement, the progress of deterioration of various battery components due to charging/discharging can be evaluated with a single instrument.

### Introduction

Lithium-ion batteries (LiBs) are used in many products, including smartphones and electric vehicles, owing to their outstanding features such as high energy density, long life, and large capacity, but because LiB components are subject to progressive deterioration with repeated charging/discharging, decreased battery capacity has become a problem. In response, research and development to clarify the causes of deterioration and delay its progress are underway. Since LiBs consist mainly of a positive electrode material, negative electrode material, separator, electrolyte, and a case, the causes of deterioration can be investigated by examining the changes in each of these components before and after charging/discharging. However, because many of these materials react with moisture and oxygen in the atmosphere, analyses must be conducted under conditions where the components are not exposed to the air. Moreover, as the substances used in these components include diverse organic and inorganic substances, evaluation using a combination of at least two instruments is inherently necessary.

Until now, analyses of organic substances and inorganic substances had been carried out using two different instruments. However, the AIRsight infrared/Raman microscope (Fig. 1) introduced in this article is a new type of microscope that makes it possible to analyze both types of substances with one instrument by incorporating a Raman unit in an infrared microscope. Since infrared and Raman spectra can be acquired at the same position, without moving the sample, the accuracy of qualitative analysis of micro areas is dramatically improved. By combining this instrument with an airtight cell (Fig. 2), it is possible to measure three types of LiB materials, the positive electrode material, negative electrode material, and separator, under non-atmospheric exposure conditions. This article introduces an example of an evaluation of the changes in these components before and after charging/discharging using the AIRsight microscope and airtight cells to isolate the samples from the atmosphere.

A model LiB was fabricated by assembling the materials in Table 1 and an electrolyte. The electrolyte was prepared by dissolving 1 mol/L of lithium hexafluorophosphate (LiPF<sub>6</sub>) in a solvent consisting of a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC) with a volume ratio of 1 : 1 : 1. A cycle sample was then prepared by applying 100 charge/discharge cycles with conditions of an end-of-charge voltage of 4.8 V and 40 °C to the fabricated LiB. This sample was disassembled and cleaned in a glovebox, and each of the components was enclosed in an airtight cell. The component parts of a new LiB, which had not been charged/discharged, were also enclosed in airtight cells in a similar manner, and a comparative evaluation of the new and cycle samples was conducted.

### Airtight Cells

Samples can be measured by infrared measurement and Raman measurement by the transmission method or reflection method without exposure to the atmosphere by placing the sample in an airtight cell under an inert atmosphere in a glovebox. Since the sealed environment can be maintained for 2 weeks, it is also possible to store or transport the samples in the sealed condition within this period. Although either calcium fluoride (CaF<sub>2</sub>) or quartz can be selected for the cell window plate, in this experiment, a calcium fluoride window plate was used in all the measurements. The analysis was conducted in a wavenumber range of 4000 to 880 cm<sup>-1</sup>.

### Measurement of Positive Electrode LiFePO<sub>4</sub>

The LiFePO<sub>4</sub> of the positive electrode was measured by infrared measurement. In the background measurement, an aluminum plate enclosed in the airtight cell together with the sample was used. Table 2 shows the measurement conditions, and Fig. 3 and Fig. 4 show the measurement results before and after a Kramers-Kronig (KK) analysis was carried out, respectively.



Fig. 1 Appearance of IRXross™ (Left) + AIRsight™ (Right)

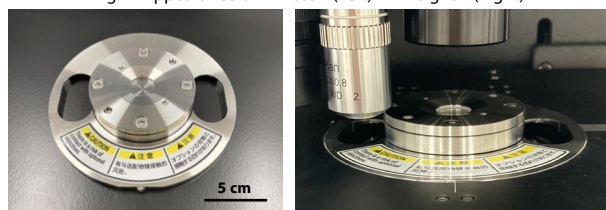


Fig. 2 Appearance of Airtight Cell (Right: Condition when Loaded in Instrument)

### Analysis Samples

Table 1 shows the samples used in these measurements.

Table 1 Samples Used in Measurements

Positive electrode material	: Lithium phosphate (LiFePO <sub>4</sub> )
Negative electrode material	: Graphite
Separator	: Polypropylene (PP)

Table 2 Infrared Measurement Conditions

Instruments	: IRXross, AIRsight
Measurement mode	: Reflection
Wavenumber range	: 4000 - 880 cm <sup>-1</sup>
Resolution	: 8 cm <sup>-1</sup>
Accumulation	: 100 times (positive electrode material) 40 times (separator)
Apodization function	: SqrTriangle
Aperture size	: 100 μm × 100 μm
Detector	: T2SL

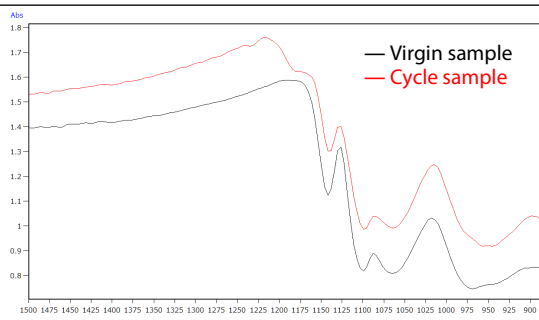


Fig. 3 Infrared Spectra of Positive Electrode Material LiFePO<sub>4</sub> (Before Kramers-Kronig analysis)

\* Wavenumber range in figure: 1500 - 880 cm<sup>-1</sup>

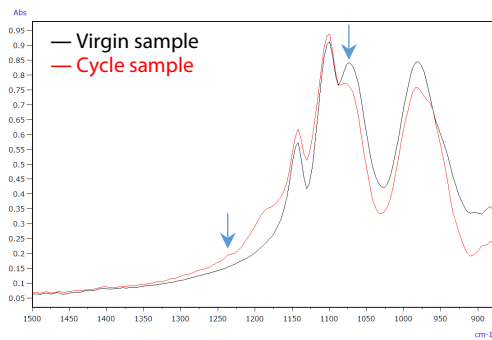


Fig. 4 Infrared Spectra of Positive Electrode Material LiFePO<sub>4</sub>  
(After Kramers-Kronig analysis)  
\* Wavenumber range in figure: 1500 - 880 cm<sup>-1</sup>

As can be seen in Fig. 4, the peak profiles of the virgin sample and the cycle sample are different. The peak at 1230 cm<sup>-1</sup> originated from stretching vibration of the PO<sub>3</sub> group. Together with the shift of the peak at 1075 cm<sup>-1</sup> to the higher wavenumber side, this is considered to be due to the deintercalation of Li and formation of FePO<sub>4</sub> that occur as a result of charging/discharging<sup>1)</sup>, and is evidence of progressive deterioration of the electrode due to repeated charging/discharging.

### ■ Measurement of Negative Electrode Graphite

The graphite of the negative electrode was measured by infrared measurement. Table 3 shows the measurement conditions, and Fig.5 and Fig.6 show representative examples of the measurement results obtained. The legend in Fig.6 also shows the intensity ratio I<sub>D</sub>/I<sub>G</sub> of the D-band to the G-band of the virgin sample and the cycle sample.

Table 3 Raman Measurement Conditions

Instruments	: IRXross, AIRsight
Wavenumber range	: 4000 - 150 cm <sup>-1</sup>
Accumulation	: 10 times
Exposure time	: 10 s
Objective lens	: 50x
ND filter	: 100 %
Excitation wavelength	: 532 nm
Detector	: CCD

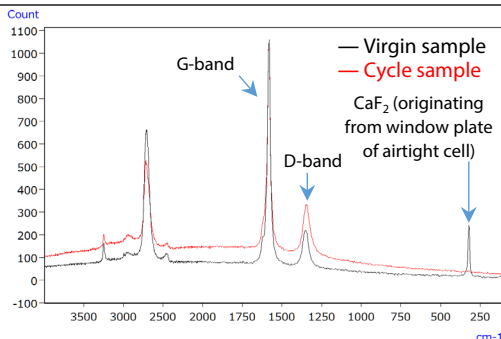


Fig. 5 Raman Spectra of Negative Electrode Graphite  
\*Without baseline correction.

In a Raman spectrum, carbon materials have a peak at 1580 cm<sup>-1</sup> called the G-band and a peak at 1350 cm<sup>-1</sup> called the D-band. The G-band is assigned to sp<sup>2</sup> bonds of graphite, and the D-band is assigned to sp<sup>3</sup> bonds associated with disorder of the crystallographic structure. Graphite has a planar plate-shaped 3-dimensional structure. However, as a characteristic feature, the G-band appears relatively strongly in the basal plane of the graphite structure, while the D-band is relatively strong near the edges (edge surface)<sup>2)</sup>.

As can be seen in Fig. 6, compared to the G-band, the D-band appears more strongly in the cycle sample than in the virgin sample. Based on this result, it is suggested that changes have occurred in the crystallographic structure or the 3-dimensional arrangement of the graphite due to repeated charging/discharging.

It may be noted that the peak around 310 cm<sup>-1</sup> in Fig.5 originated from the CaF<sub>2</sub> window plate. Since a Raman-grade CaF<sub>2</sub> window plate with few impurities is used in the airtight cells, only one peak with a narrow halfwidth appears, indicating that impurities in the window material do not influence the analysis of the Raman spectrum of graphite.

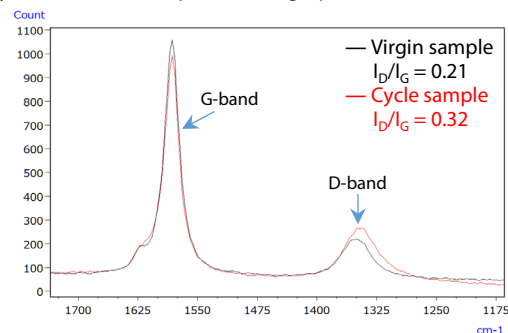


Fig. 6 Raman Spectra of Negative Electrode Graphite  
\*With baseline correction.

### ■ Measurement of PP Separator

The PP of the separator was measured by infrared measurement. As in the measurement of the positive electrode, an aluminum plate enclosed in the airtight cell together with the sample was used in the background measurement. The measurement conditions were the same as in the above Table 2, and the measurement results are shown in Fig. 7.

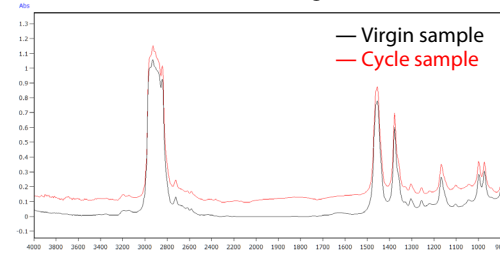


Fig. 7 Infrared Spectra of PP Separator  
(Without Kramers-Kronig analysis)

In Fig. 7, no differences could be seen in the PP of the separators of the new and cycle samples, and no changes in the spectrum indicative of PP deterioration could be observed under the charge/discharge conditions of this experiment.

### ■ Conclusion

A deterioration evaluation of the positive electrode material LiFePO<sub>4</sub>, the negative electrode material graphite, and the polypropylene (PP) of the separator obtained from a model LiB after charging/discharging was carried out by comparing virgin samples and cycle samples based on infrared measurement and Raman measurements with an AIRsight infrared/Raman microscope. It was possible to measure all components under inert atmosphere by using airtight cells. It was found that changes in the structures of the positive electrode material LiFePO<sub>4</sub> and the negative electrode material graphite occurred as a result of repeated charging/discharging. The AIRsight enables both infrared measurements and Raman measurements with only one instrument, and can be used to evaluate various LiB components under inert conditions when used in combination with airtight cells.

### <References>

- 1) A. Ait Salah, P. Jozwiak, K. Zaghib, J. Garbarczyk, F. Gendron, A. Mauger, C. M. Julien, "FTIR features of lithium-iron phosphates as electrode materials for rechargeable lithium batteries". *Spectrochimica Acta Part A* 65, 1007-1013, 18 January 2006.
- 2) Gen Katagiri, "Raman Spectroscopy of Graphite and Carbon Materials and Its Recent Application," *TANSO (Journal of The Carbon Society of Japan)*, No. 175, 304-313, 1996.

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