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IRSpirit™ Fourier Transform Infrared Spectrophotometer

Application News

Measurement of Electrolyte Solutions for Lithium-Ion Secondary Batteries with IRSpirit Glove Box System

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User Benefits

- IRSpirit can be controlled via wireless communication.
- Installing the IRSpirit in a glove box enables sample measurements in an environment purged with inert gas.
- Anaerobic samples such as cell components of lithium-ion secondary batteries can be analyzed with FTIR.

■ Introduction

When cell components of lithium-ion secondary batteries are affected by water vapor and oxygen in the atmosphere, the battery characteristics are significantly affected. It is therefore desirable to handle and characterize the cell components under an atmosphere not affected by water vapor or oxygen.

The IRSpirit, a compact FTIR, can be installed in a glove box, thus enabling the evaluation of cell components in a high purity argon atmosphere with low dew point and low oxygen concentration.

This article introduces an example of the measurement of organic electrolyte solutions, commonly used in lithium-ion secondary batteries.

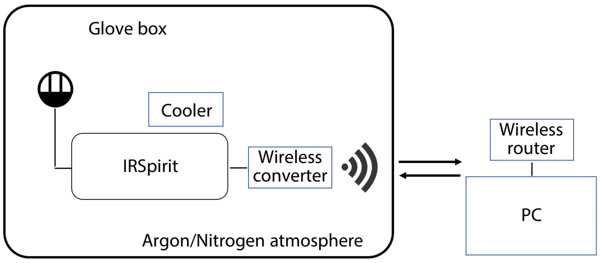

Fig. 1 Schematic Diagram of IRSpirit Glove Box System
(Cooler installed as necessary)

■ IRSpirit Glove Box System

Since IRSpirit can be controlled wirelessly, sample can be measured while the FTIR unit is installed in a glove box (custom order required). Communication is established via a wireless converter and a wireless router. Fig. 1 shows the schematic diagram of IRSpirit glove box system.

Fig. 2 shows an example of a system where IRSpirit is installed in a flow-type glove box (Glovebox Japan, GBJA100). With this system, FTIR analysis can be conducted under an atmosphere of argon, nitrogen, etc.

Fig. 3 shows the inside of the glove box. In the glove box, the IRSpirit unit, a wireless converter, and if necessary, a cooler (fan) and a mouse for controlling the PC are installed. The PC is placed outside the glove box, and analysis is performed via wireless communication between the IRSpirit and PC.

Note that since thermal conductivity is different between argon and air, the heat exhaust mechanism of the instrument may not function properly, thereby preventing acquisition of correct infrared spectra. To avoid this, we used a cooler to enhance heat exhaustion in this analysis, and controlled the dew point in the glove box to -70 ˚C (moisture content of 2.58 ppm) or lower, and the oxygen concentration to 0.3 ppm or lower. Analysis in a glove box thus enables highly accurate measurements without being affected by water vapor or oxygen.

Fig. 2 Example of IRSpirit Glove Box System

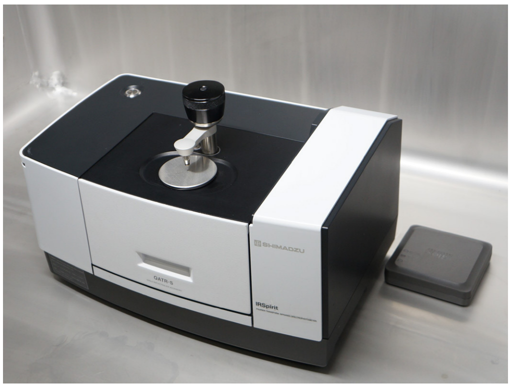

Fig. 3 IRSpirit (Left) and Wireless Converter (Right) in Glove Box

■ Effect of Atmospheric Gases on Measurement of Electrolyte Solutions for Lithium-Ion Secondary Batteries

An electrolyte of EC (ethylene carbonate) + DEC (diethyl carbonate) (3 : 7) solution containing 1M $LiPF_6$ (lithium hexafluorophosphate), an organic electrolyte solution commonly used in lithium-ion secondary batteries, was measured under air and argon atmospheres. Fig. 4 shows the measured infrared spectra and Fig. 5 shows the enlarged region between 2800 and 4000 cm^{-1} in Fig. 4.

Although the optical properties of argon and air are very different, Fig. 4 shows that the infrared spectra acquired under both atmospheres were almost identical, appearing to be unaffected by the difference of atmosphere.

Note that in Fig. 5, the broad absorption of symmetric and antisymmetric OH-stretching vibrations from water molecules were observed between 3400 and 3700 cm^{-1} under the air atmosphere. Meanwhile, the influence was negligible in the infrared spectrum under the argon atmosphere.

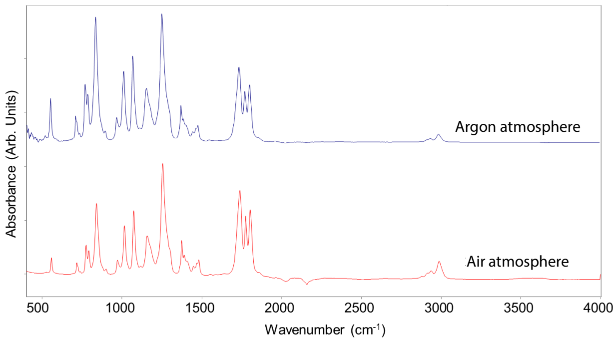

Fig. 4 Infrared Spectra of EC+DEC (3 : 7) Electrolyte Solution Containing 1M $LiPF_6$

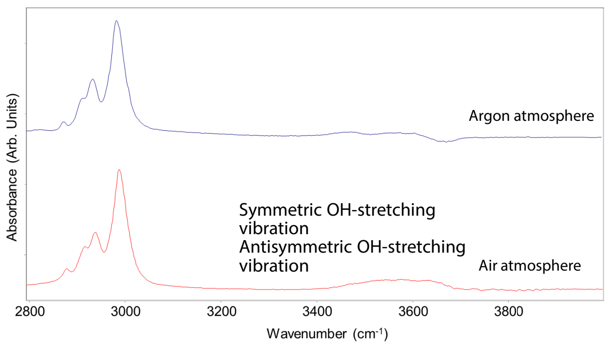

Fig. 5 Infrared Spectra of EC+DEC (3 : 7) Electrolyte Solution Containing 1M $LiPF_6$ (Enlarged)

■ Measurement of Electrolyte Solution for Lithium-Ion Secondary Battery in Inert Atmosphere

Organic electrolyte solutions are used as the electrolyte solution for lithium-ion secondary batteries, and their moisture content is strictly controlled. Such an electrolyte solution was measured by FTIR in an argon atmosphere.

Fig. 6 shows the infrared spectra of EC+DEC (3 : 7) electrolyte solution with 1M $LiPF_6$ and EC+DEC (3 : 7) solution without 1M $LiPF_6$. The only difference between the two samples is the presence or absence of $LiPF_6$.

* In this application, measurements were performed under specific conditions and environments since glove boxes and argon atmospheres reduce the heat exhaust function and may prevent proper instrument operation. Please contact for details.

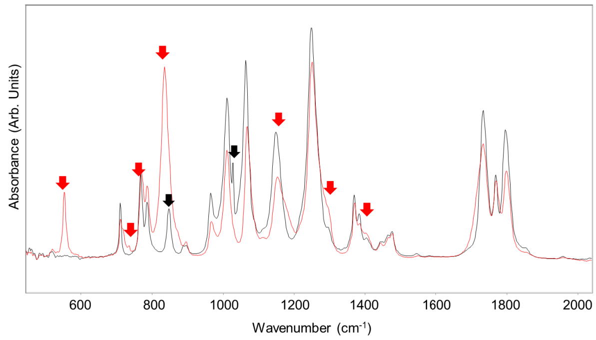

Fig. 6 Infrared Spectra of EC+DEC (3 : 7) Electrolyte Solution Containing 1M $LiPF_6$ (red) and EC+DEC (3 : 7) Solution (black)

The absorptions indicated with red and black arrows in Fig. 6 are characteristic to each component. To clarify the difference between the two spectra, Fig. 7 shows the difference spectrum where the black line in Fig. 6 was subtracted from the red line.

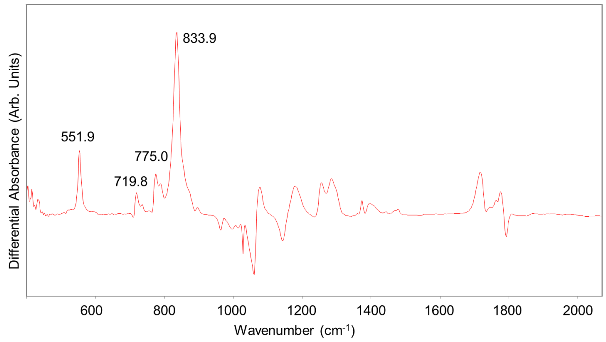

Fig. 7 Difference Spectrum between EC+DEC (3 : 7) Electrolyte Solution Containing 1M $LiPF_6$ and EC+DEC (3 : 7) Solution

We can see in Fig. 7 that the differences in absorption intensity appeared at 551.9 cm^{-1}, 719.8 cm^{-1}, 775.0 cm^{-1}, and 833.9 cm^{-1}. These absorptions cannot be explained simply by the vibrational mode of $LiPF_6$. Given that characteristic vibration modes of solvation between either EC or DEC and lithium ions appear in the 700 cm^{-1} to 1000 cm^{-1} frequency range[1)], the four absorption lines shown in Fig.7 are probably characteristic absorption lines of lithium ions solvated by EC or DEC.

■ Conclusion

We introduced an application example of the IRSpirit glove box system. Although FTIR measurements are usually performed in air, the IRSpirit can also handle anaerobic samples such as cell components of lithium-ion secondary batteries by installing the instrument in a glove box for measurements under inert atmosphere. In addition, even though the measurement wavenumber region of FTIR includes the infrared absorption of water vapor and carbon dioxide, such influences effected by air can be reduced by measurement under inert atmosphere using a glove box.

<Acknowledgment>
The data shown above was provided by Associate Professor Takashi Ito at Frontier Research Institute for Interdisciplinary Sciences, Tohoku University. We would like to take this opportunity to express our sincere gratitude. Please also see the article in FTIR TALK LETTER Vol. 35.

<Reference>
(1) Masayuki Morita, Research of Solvation Structures by Raman Spectroscopy, Electrochemistry, 81(12), 2013, pp.991-994.

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