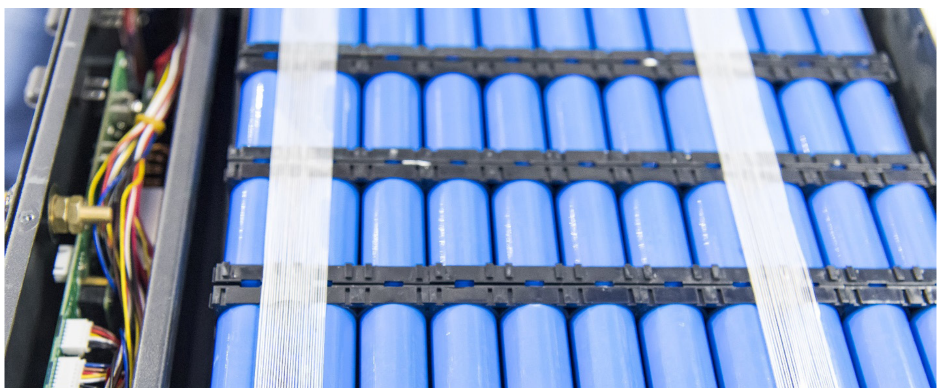
Application Note

Chemicals and Energy

Quick and Easy Material Identification of Salts Used in Lithium-Ion Batteries by FTIR

Using the Agilent Cary 630 FTIR Spectrometer to identify common LIB electrolyte salts



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Abstract

Rechargeable lithium-ion batteries (LIBs) are universally used in portable electronic devices and electric vehicles (EVs). Despite the rapid growth and use of LIBs, there is a need for batteries that can store more energy, are smaller and lighter, and can charge faster. A critical step in the advancement of LIB performance is the analysis of common electrolyte components used in the batteries. This application note demonstrates the use of the Agilent Cary 630 FTIR spectrometer with attenuated total reflectance (ATR) sampling technology for the fast and reliable material identification of LIB electrolyte salts.

Introduction

Lithium salts are one of the main components of LIBs. As such, the salts play a significant role in the ionic conductivity and thermal and electrochemical stability of the battery, as well as the corrosive properties of the system. Currently, lithium hexafluorophosphate ($LiPF_6$) dissolved in carbonate solvents is the main salt used in LIBs.[1] However, many research and development (R&D) teams working in both academia and industry are searching for new active and safer electrolyte salts.[2]

For battery safety and performance, it is mandatory for LIB manufacturers to ensure that the correct raw materials are used in manufacturing. Fourier transform infrared (FTIR) spectroscopy is a nondestructive technique that is widely applied in raw material identification studies. FTIR yields a characteristic chemical fingerprint of the sample by measuring the absorption of IR radiation. The easy-to-use technique, which does not require any sample preparation steps, provides rapid identification of materials.

There are many challenges associated with analysis and handling of lithium salts. Some salts are hygroscopic, toxic, combustible, readily decomposable, or they present safety hazards.[3,4] For example, $LiPF_6$ is susceptive to moisture as it reacts with water[5], leading to the release of highly toxic hydrogen fluoride (HF) gas.[4–6] It is therefore recommended that lithium salts are handled in an oxygen and moisture-controlled environment, such as a glove box.[7,8]

This study demonstrates the use and the benefits of the Agilent Cary 630 FTIR spectrometer (Figure 1) for the qualification of commonly used electrolyte salts for LIBs in a glove box. This application note describes the creation of a reference spectral library using the Agilent MicroLab software and uses a method-based approach to confirm the identity of various electrolyte salts.

Figure 1. The Agilent Cary 630 FTIR spectrometer with its ultracompact, lightweight design (20 × 20 cm and 3.6 kg) can easily be used in a glove box to produce high-quality results.

Experimental

Instrumentation and workflow

The Cary 630 FTIR spectrometer with a diamond ATR module was used in this study. The instrument was used to create a spectral reference library of the seven salts listed in Table 1. A routine material identification method was set up based on the user-generated library, which was then used to identify four "unknown" salt samples (Figure 2).

Table 1. LIB salts used as spectral reference materials for generation of the user-generated LIB-salts library.

Salt Name	Short Name	CAS	Supplier
Lithium Carbonate	Li_2CO_3	554-13-2	Sigma-Aldrich Co
Lithium Chloride Monohydrate	$LiCl{\cdot}H_2O$	16712-20-2	Merck
Lithium Chloride	LiCl	7447-41-8	Sigma-Aldrich Co
Lithium Iron Phosphate	$LiFePO_4$	15365-14-7	Sigma-Aldrich Co
Bis(Trifluoromethane) Sulfonimide Lithium Salt	LiTFSI	90076-65-6	Sigma-Aldrich Co
Lithium Hexafluorophosphate	$LiPF_6$	21324-40-3	Sigma-Aldrich Co
Lithium Tetrafluoroborate	$LiBF_4$	14283-07-9	Sigma-Aldrich Co

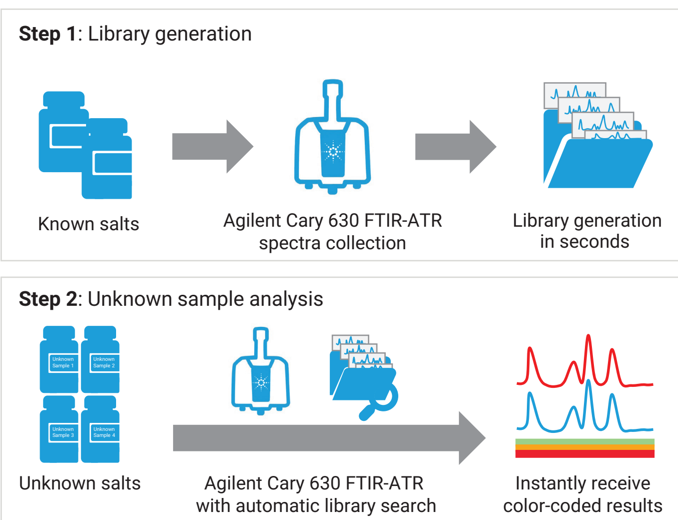


Figure 2. Workflow for LIB salts identification using the Agilent Cary 630 FTIR and Agilent MicroLab software.

Library generation and sample analysis

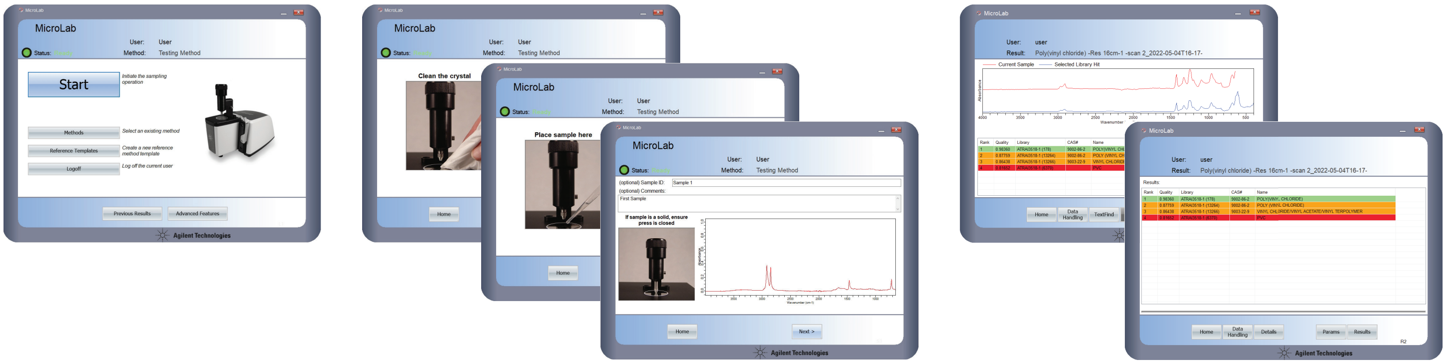
Spectral libraries can easily be created, maintained, and managed in the MicroLab software. A new library can be created in a few seconds. Spectra can be added to the library, either at the time of creation or at any other time, directly from the results screen. A user-generated LIB salts library was used to identify four independent "unknown" salt samples (the identity of those samples was stated on the container label). The library search method applied the Similarity search algorithm using the parameters shown in Table 2.

Table 2. Agilent Cary 630 FTIR–ATR operating parameters.

Parameter	Setting
Method	Library search
Library Used	User-generated LIB salts library
Search Algorithm	Similarity
Spectral Range	4,000 to 650 cm^{-1}
Background Scans	32
Sample Scans	32
Spectral Resolution	4 cm^{-1}
Background Collection	Argon
Zero Fill Factor	None
Apodization	HappGenzel
Phase Correct	Mertz
Color-Coded Confidence Level Thresholds	Green (high confidence): >0.95 Yellow (medium confidence): 0.90 to 0.95 Red (low confidence): <0.90

Software

The Cary 630 FTIR spectrometer was controlled using MicroLab software, which uses a pictorial interface to guide users through the steps of the analysis, from sample introduction to reporting (Figure 3).



1 Start the analysis

2 Follow picture-driven software guidance

3 Instantly receive color-coded, actionable results

Figure 3. The intuitive Agilent MicroLab software makes finding answers with the Agilent Cary 630 FTIR spectrometer as easy as 1, 2, 3. The picture-driven software also reduces training needs and minimizes the risk of user-based errors.

Results and discussion

The Cary 630 FTIR and the $LiPF_6$ salt sample were kept in a glove box under dry, inert gas (argon) until use. When ready for analysis, a small quantity of the solid sample was placed onto the ATR crystal, and contact was ensured using the ATR swivel press. The IR measurement was taken, and after completion, the crystal was wiped clean using a light solvent and a low-lint wipe.

Using the Similarity algorithm to search the user-generated spectral library, all unknown samples 1 to 4 were identified correctly (according to each sample label). The hit quality index (HQI) for each sample was above 0.98, as shown in Table 3.

Table 3. LIB salts identification results obtained using the Agilent Cary 630 FTIR–ATR and Similarity search algorithm.

Sample Name	Material Identification	Hit Quality Index
Unknown Sample 1	Lithium carbonate	0.99815
Unknown Sample 2	Lithium iron phosphate	0.99791
Unknown Sample 3	Bis(trifluoromethane)sulfonimide lithium salt	0.98530
Unknown Sample 4	Lithium hexafluorophosphate	0.99382

The HQI, which is automatically calculated for each library item by the software, indicates how well the measured spectrum and the library spectrum match. The HQI is often used as pass/fail criteria in material identification and confirmation workflows. Analysts can set their own HQI-based thresholds in the MicroLab software.

Color-coded results

For easy review of the data generated by the Cary 630 FTIR, the material identification results obtained for each sample are color-coded based on user-defined confidence level thresholds (Figure 4).

In this study, results with an HQI above 0.95 were color-coded in green, indicating a good spectral match and providing confidence in the identification of the material for all samples. Color-coding the results turns the Cary 630 FTIR system into an easy-to-use, turnkey solution that enables quick decision making. Once the sample has been measured, the MicroLab software shows the final answer directly on screen, without any input needed by the user. The software automatically performs the library search and provides the operator with the final color-coded results, reducing the complexity of the analysis and the risk of user-based errors.

The Cary 630 FTIR spectrometer is a compact and flexible instrument that can perform various applications due to its unique modular design. It is ideal for glove box-based applications because of its simplicity, ease-of-use, and robustness under different environmental conditions.

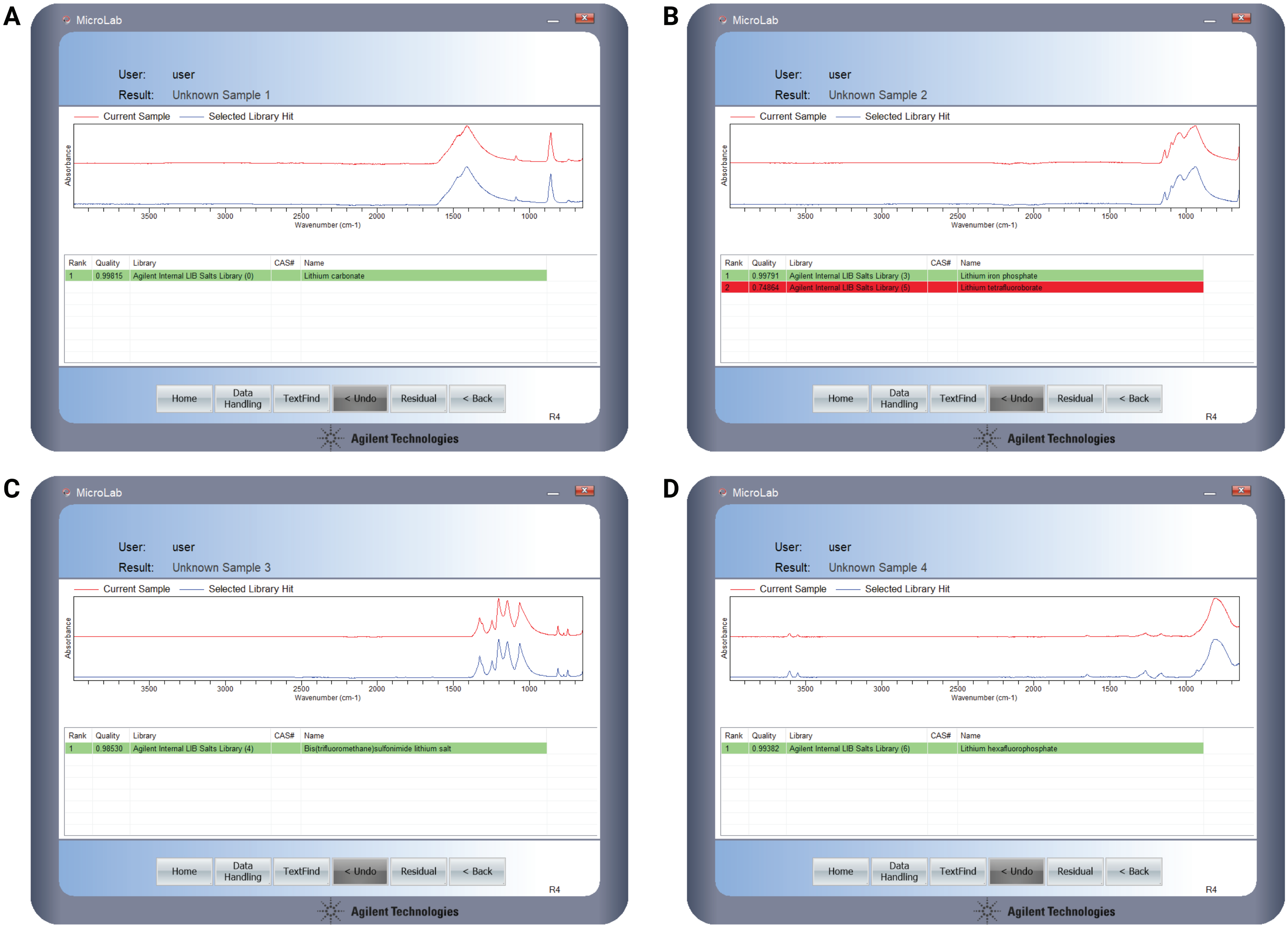


Figure 4. The Agilent Cary 630 FTIR spectrometer identification analysis of the four LIB salts samples (red traces) and library hit (blue traces). The table shows the hit quality, the library used, and the hit name for unknown samples 1 to 4 (labeled A to D, respectively).

Conclusion

The Agilent Cary 630 FTIR spectrometer provided a simple-to-use solution for material identification of salts used in lithium-ion batteries. As the world's smallest and lightest benchtop FTIR spectrometer, the Cary 630 FTIR can perform the potentially hazardous analysis of lithium salts in a moisture-controlled environment within a glove box.

The Cary 630 FTIR and MicroLab software facilitated the quick and easy generation of a LIB salts spectral library, which enabled the fast and accurate identification of four unknown salt samples (HQI >0.98). The MicroLab software applied color-coding to the identification results based on the HQI, making it quick and easy to review the quality of the data.

This study has shown the robustness of the Cary 630 FTIR fitted with the ATR sampling module for material qualification as required by manufacturers. The methodology also supports R&D groups working within the chemical, materials, and energy sectors to develop next-generation batteries.

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Further information

Agilent Cary 630 FTIR Spectrometer

MicroLab FTIR Software

MicroLab Expert

FTIR Analysis & Applications Guide

FTIR Spectroscopy Basics – FAQs

ATR-FTIR Spectroscopy Overview

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DE20351012

Printed in the USA, July 5, 2023
5994-6243EN

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