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Total Organic Carbon Analyzer, AIRsight™ Infrared/Raman Microscope

Application News

Evaluation of Surface Carbon on Lithium-Ion Battery Cathode Active Materials Using a TOC Analyzer and Infrared/Raman Microscope

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User Benefits

- The TOC solid sample measurement system enables quantitative evaluation of carbon coatings on cathode active material surfaces.
- The AIRsight infrared/Raman microscope enables evaluation of the carbon layer structure.
- Carbon content and structure can be evaluated using a small amount of sample.

■ Introduction

The cathode active materials used in lithium-ion batteries (LiBs) for electric vehicles (EVs) are broadly classified into two categories depending on their application: nickel-based materials (NCM/NCA/NCMA) and phosphate-based materials (LFP: $LiFePO_4$, LMFP: $LiFe_xMn_{1-x}PO_4$). Nickel-based materials are characterized by high energy density as well as excellent low-temperature and high-power performance, making them indispensable for long-range driving and high-performance vehicle segments. In contrast, phosphate-based materials offer superior safety, long cycle life, and cost advantages, and their use is expanding primarily in standard-range and mass-market segments.

Because LFP and LMFP compounds are intrinsically low in electronic conductivity, a carbon coating on the surface of the active material is essential to compensate for that limitation and improve performance. Accordingly, quantitative control of carbon content is of great importance. For that type of carbon analysis, the TOC solid sample measurement system (Fig. 1), which combines a TOC-L total organic carbon analyzer with an SSM-5000A solid sample combustion unit, is effective.

Furthermore, the conductivity of the surface carbon layer is closely related to the degree of graphitization and defect structure of the carbon, making structural evaluation of the carbon layer equally important. The AIRsight infrared/Raman microscope (Fig. 2) enables such structural evaluation.

This Application News presents examples of evaluating carbon on the surface of LMFP cathode active materials, with carbon quantitation using a TOC-L + SSM-5000A system and carbon layer structure evaluation using the AIRsight infrared/Raman microscope.

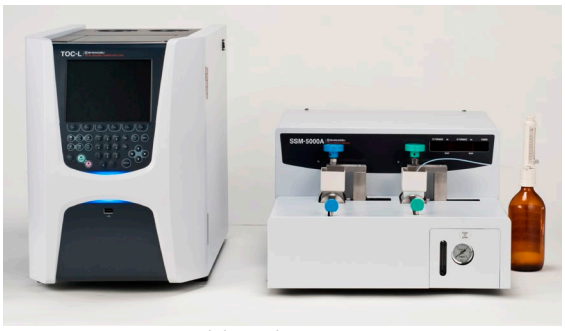

Fig. 1 TOC Solid Sample Measurement System
TOC-L (Left) and SSM-5000A Solid Sample Combustion Unit (Right)

Fig. 2 IRTracer™ (Left) + AIRsight™ (Right)

■ Analysis Sample

LMFP cathode active material (LMFP: $LiFe_{0.4}Mn_{0.6}PO_4$)

Fig. 3 LMFP Cathode Active Material

■ Quantitative Evaluation of Carbon

Analysis Method

The TOC solid sample measurement system quantifies total carbon (TC) or inorganic carbon (IC) by detecting carbon dioxide (CO_2), generated either by combustion oxidation of solid samples or by acidification of the sample.

In this analysis, TC analysis was performed for carbon quantitative evaluation. This system enables rapid, straightforward, and accurate analysis simply by weighing the sample into a sample boat (Fig. 3) and loading it into the instrument.

In practical research, cathode active materials are often available only in limited quantities, so analysis with minimal sample consumption may be required. Therefore, 15 mg or 30 mg of sample was weighed for a single measurement (n = 1) in this analysis, taking into account the absolute carbon content of the sample and the limit of quantitation (LOQ) of the instrument. Assuming triplicate analysis (n = 3), the sample consumption per sample would be 45 to 90 mg.

The measurement conditions are shown in Table 1.

Table 1 Measurement Conditions

Instrument	TOC solid sample measurement system (TOC-L_{CPH} total organic carbon analyzer + SSM-5000A solid sample combustion unit)
Cell Length	Short cell
Carrier Gas	500 mL/min oxygen gas
TC Measurement Method	Combustion catalytic oxidation (TC furnace: 980 °C)
Measurement Items	TC
Calibration Curve	TC: One-point calibration curve using calcium carbonate powder reagent
Sample Amount (n = 1)	15 mg, 30 mg
Limit of Quantitation	0.1 mgC (absolute carbon amount)*1

*1 Further sensitivity improvement is possible by using the optional cell switching valve set.

Measurement Results

The TC results of the carbon coating on the LMFP surface are presented in Table 2. Comparable TC values were obtained for sample quantities of 15 mg and 30 mg, and the coefficients of variation (CV) were less than 2.0 %, indicating good reproducibility.

In addition, if the absolute carbon content falls below the LOQ (0.1 mgC), the sample amount should be increased.

Table 2 TC Analysis Results

Sample Weight (mg)	Absolute Carbon (mgC)	TC Conc. (%)	Average TC Conc. (%)	CV (%)
15.7	0.2653	1.690	1.694	1.30
15.2	0.2544	1.674		
15.7	0.2694	1.717		
30.2	0.5136	1.701	1.705	0.94
30.4	0.5140	1.691		
30.3	0.5218	1.722		

■ Structural Evaluation of Carbon

Analysis Method

The LMFP surface was measured using the Raman measurement function of the AIRsight microscope. Preliminary investigations showed that higher laser intensities altered both the appearance and the Raman spectra before and after measurement. To minimize laser irradiation, the ND filter was set to 7.5 %, enabling acquisition of high-quality Raman spectra without sample damage.

The detailed measurement conditions are shown in Table 3.

Table 3 Raman Measurement Conditions

Instruments	IRTracer-100, AIRsight
Accumulation	5 times
Exposure Time	25.0 sec
Objective Lens	100x
ND Filter	7.5 %
Excitation Wavelength	532 nm
Detector	CCD

Measurement Results

A representative Raman spectrum of the LMFP surface is shown in Fig. 4. Carbon materials exhibit a peak near 1580 cm^{-1}, known as the G band, and a peak near 1340 cm^{-1}, known as the D band. A strong D band indicates a high degree of structural defects. The intensity ratio of the D band to the G band (I_D/I_G) is used as an indicator of electrical conductivity and crystallinity. For reference, the I_D/I_G ratio is indicated in Fig. 4. The carbon coating was found to be not highly crystalline graphite, but rather to contain structural defects, as indicated by the D band.

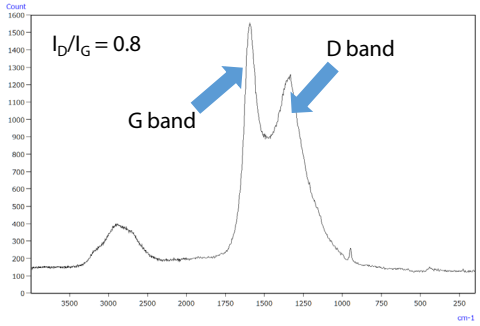

Fig. 4 Raman Spectrum of the LMFP Surface

■ Validation of the Carbon Results by Raman

To confirm that the carbon coating on the LMFP surface was completely reacted and quantified by the TOC solid sample measurement system, Raman measurements were also performed on the LMFP residue obtained after TC analysis (Fig. 5). Representative Raman spectra of the LMFP material and the LMFP residue after TC analysis are shown in Fig. 6.

As shown in Fig. 6, the peaks near 1580 cm^{-1} and 1340 cm^{-1} disappeared for the LMFP residue after TC analysis. Since no Raman peaks derived from carbon were observed, it is inferred that only a negligible amount of carbon remained on the surface of the LMFP residue. Accordingly, the carbon present on the LMFP surface is considered to have reacted sufficiently and been appropriately quantified by the TOC solid sample measurement system.

In addition, a new peak near 1300 cm^{-1} was observed after TC analysis. This peak is presumed to originate from oxides formed during the high-temperature oxidation reaction.

Fig. 5 LMFP Residue after TC Analysis

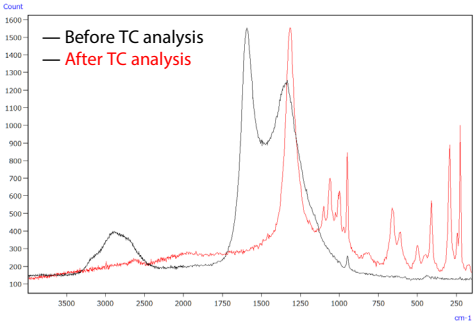

Fig. 6 Raman Spectra of the LMFP Material and the LMFP Residue

■ Conclusion

Quantitative analysis of the carbon coating on the LMFP surface was performed using the TOC solid sample measurement system (TOC-L + SSM-5000A), and structural evaluation of the carbon layer was conducted using the AIRsight microscope. In addition, Raman analysis of the LMFP residue after TC analysis was carried out to verify the validity of the carbon quantitation results.

The TOC solid sample measurement system (TOC-L + SSM-5000A) is capable of not only TC analysis in solid samples, but also of IC and TOC analysis. Furthermore, by simply changing the software settings, carbon analysis of liquid samples (TOC, TC, and IC) can also be performed using the TOC-L main unit. This system can also be applied to carbon analysis of water-extractable TOC in black mass, lithium extraction solutions, and lithium carbonate, all of which are relevant materials in lithium-ion battery recycling.

The AIRsight is capable of both Raman and infrared measurements. Therefore, in addition to the Raman measurements introduced here, it can be used, with a single microscope system, to evaluate degradation caused by charge and discharge cycles in various battery components, such as negative electrode materials and separators.

Related Applications

1. Evaluation of Organic Impurities in Lithium Carbonate by TOC Analysis Application News No. 01-01098A-en
2. Deterioration Evaluation of Lithium-Ion Battery Components Using Infrared/Raman Microscope and Airtight Cells Application News No. 01-00997A-en

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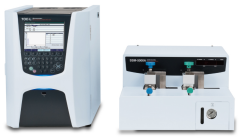

› SSM- 5000A
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› AIRsight™
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