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Application News

Inductively Coupled Plasma Atomic Emission Spectrometer ICPE™-9800 Series

Analysis of Elemental Impurities in Anode Materials for Lithium-Ion Secondary Batteries Using the ICPE-9820

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User Benefits

- Elemental impurities in the anode materials of lithium-ion secondary batteries can be measured.
- Even after measurement, elements and wavelengths can be added to check for unexpected elemental impurities in the anode materials.
- The system uses a mini torch that consumes less argon gas, thus reducing running costs.

■ Introduction

Lithium-ion secondary batteries (LIBs) are widely used in mobile devices, electric vehicles, hybrid cars, and more. One of the components of LIBs, the anode, accumulates and releases Li ions during charging and discharging. Graphite-based materials are mainly used as the anode material in LIBs. In China, one of the major producers, the analysis of elemental impurities in graphite, which is used as LIB anode material, is required by GB/T 24533-2019[1)] using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

In this Application News, elemental impurities in LIB anode materials were analyzed using the ICPE-9820. Spike recovery tests were performed to confirm the validity of the analytical values. Additionally, the "Acquisition for All Wavelength" feature allows for checking the presence of elemental impurities that were not subjected to quantitative analysis.

■ Samples and Sample Preparation

Graphite, which is employed as a LIB anode material, was used as the sample. Based on GB/T 24533-2019, approximately 0.5 g of graphite, 3 mL of nitric acid, and 9 mL of hydrochloric acid were added to a microwave digestion vessel. The mixture was decomposed using a microwave digestion system. After cooling to room temperature, the solution was filtered through a 0.45 µm PTFE membrane filter and diluted to a final volume of 50 mL with pure water. This solution was further diluted 2-fold to prepare the measurement solution. For the spike recovery test, a sample with a certain amount of standard solution of the elements was prepared. A method blank was also prepared following the same steps. The digestion procedure is shown in Fig. 1.

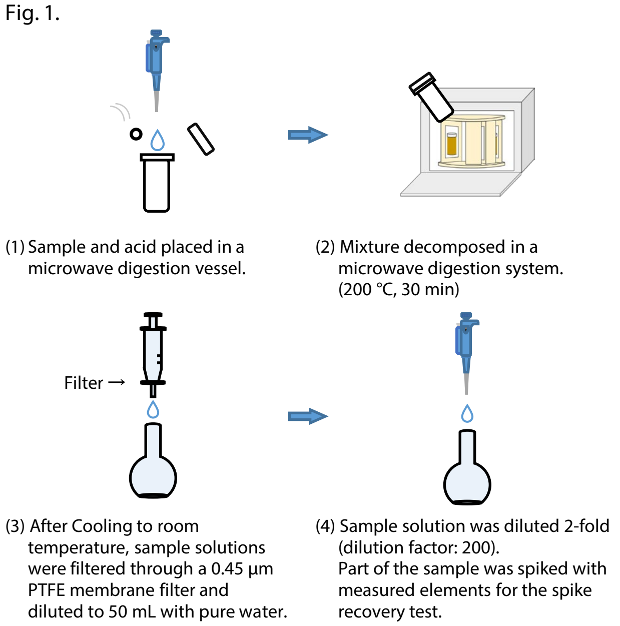

Fig. 1 Digestion Procedure

■ Calibration Standards

Calibration Standards were prepared by mixing commercially available standard solutions of Al, B, Co, Cr, Cu, Fe, Li, Mn, Mo, Na, Ni, P, S, Zn, and Zr with HNO_3 and HCl. The concentrations of the measured elements in each calibration standard are shown in Table 1.

Table 1 Concentrations of Measured Elements in Calibration Standards

Elements	Calibration Standards (mg/L)						
	STD0	STD1	STD2	STD3	STD4	STD5	STD6
Al, B, Co, Cr, Cu, Fe, Li, Mn, Mo, Na, Ni, Zn, Zr	0	0.025	0.1	0.25	0.5	1	2.5
P, S	0		0.1	0.25	0.5	1	2.5
HNO_3	3v/v%						
HCl	9v/v%						

■ Instrument Configuration and Analytical Conditions

The system configuration for ICP-AES is shown in Table 2. In order to reduce running costs, the analysis was performed using a mini torch, which consumes less argon gas than a conventional torch.

The analytical conditions are shown in Table 3. In this application, both axial and radial views of the plasma were used for the analysis. The axial view provides the advantage of higher sensitivity compared to the radial view. However, the axial view is more susceptible to ionization interferences than the radial view, as it only observes the high-temperature region of the plasma. In particular, the calibration curve of alkali metal elements such as Na and K in the axial view is known to bend in the high concentration range. Therefore, for the analysis of alkali metal elements, the axial view was used in the trace region and the radial view was used in the high concentration region. Using both the axial and radial views depending on the concentration range, the accuracy of the analysis can be expected to improve. Fig. 2 shows calibration curve for Na using axial and radial views.

Table 2 ICP-AES System Configuration

Instrument:	ICPE-9820
Nebulizer:	Nebulizer, 10UES
Chamber:	Cyclone Chamber, HE
Torch:	Mini-Torch
Auto Sampler:	AS-10

Table 3 Analytical Conditions

RF Power:	1.20 kW
Plasma Gas Flowrate:	10.0 L/min
Auxiliary Gas Flowrate:	0.60 L/min
Carrier Gas Flowrate:	0.70 L/min
View Direction:	Axial / Radial

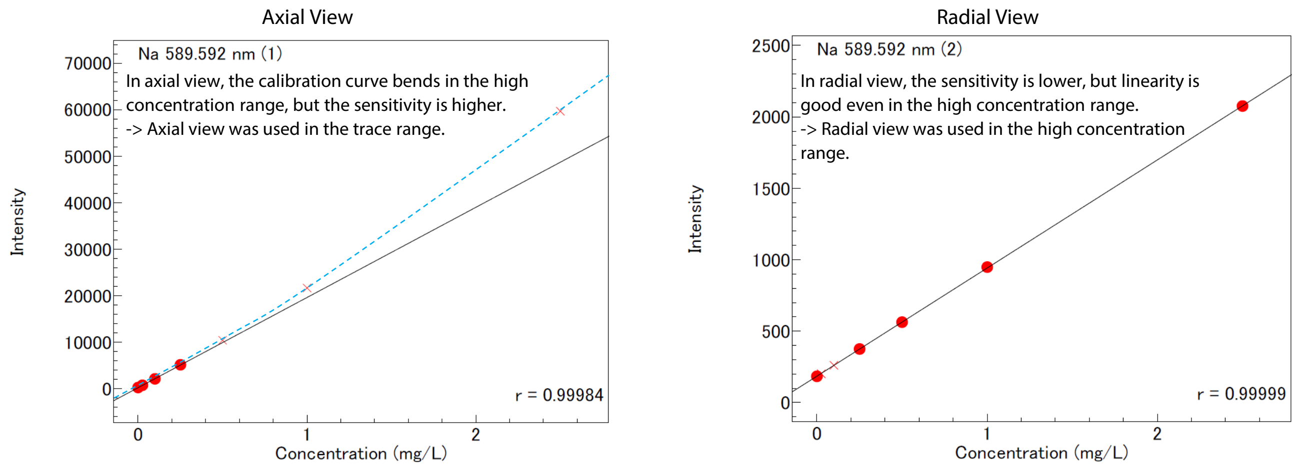

Fig.2 Calibration Curves for Na

■ Quantitative Analysis and Spike Recoveries

Calibration curves were made using the calibration standards shown in Table 1, and the elemental impurities in graphite used as a LIB anode material were quantitatively analyzed. The results of quantitative measurement and spike recovery test are shown in Table 4. Good 96 – 102 % spike recoveries were obtained, demonstrating that the ICPE-9820 can accurately analyze elemental impurities in LIB anode materials.

Table 4 Quantitative Result and Spike Recovery

Element	Wavelength (nm)	View	Detection Limit (mg/L)	Method Blank (mg/L)	Unspiked Sample (mg/L)	Quantitative Result in Graphite (mg/kg)	Low Conc. Spike			High Conc. Spike		
							Spike Conc. (mg/L)	Spiked Sample (mg/L)	Recovery (%)	Spike Conc. (mg/L)	Spiked Sample (mg/L)	Recovery (%)
Al	396.153	Axial	0.001	0.005	0.017	2.4	0.025	0.041	96	1	1.01	99
B	249.773	Axial	0.0005	0.0008	0.0013	0.1	0.025	0.0259	98	1	0.995	99
Co	228.616	Axial	0.0007	N.D.	N.D.	N.D.	0.025	0.0255	102	1	0.996	100
Cr	267.716	Axial	0.0006	0.0018	0.0031	0.26	0.025	0.0275	98	1	0.999	100
Cu	327.396	Axial	0.0007	N.D.	0.0014	0.28	0.025	0.0260	98	1	0.989	99
Fe	259.940	Axial	0.0006	0.0016	0.0857	17.1	0.025	0.111	101	1	1.07	98
Li	670.784	Axial	0.00004	0.00025	0.00022	N.D. (Axial)	0.025	0.0242 (Axial)	96 (Axial)	1	1.00 (Radial)	100 (Radial)
		Radial	0.005	N.D.	N.D.							
Mn	257.610	Axial	0.00007	N.D.	0.00100	0.2	0.025	0.0260	100	1	0.992	99
Mo	202.030	Axial	0.001	0.001	0.001	N.D.	0.025	0.0259	100	1	0.986	99
Na	589.592	Axial	0.0004	0.0034	0.0400	7.44 (Axial)	0.025	0.0645 (Axial)	98 (Axial)	1	1.04 (Radial)	100 (Radial)
		Radial	0.01	N.D.	0.04							
Ni	231.604	Axial	0.001	N.D.	0.004	0.8	0.025	0.028	96	1	0.992	99
P	213.618	Axial	0.005	N.D.	N.D.	N.D.	0.1	0.100	100	1	0.985	99
S	180.731	Axial	0.01	N.D.	0.12	24	0.1	0.22	100	1	1.11	99
Zn	213.856	Axial	0.0002	0.0021	0.0052	0.63	0.025	0.0296	98	1	1.00	99
Zr	343.823	Axial	0.0002	0.0006	0.0019	0.26	0.025	0.0266	99	1	0.991	99

Detection Limit = 3 × σ (Standard Deviation of STD0) × Slope of Calibration Curve
N.D.: Below the Detection Limit
Quantitative Result in Graphite = (Unspiked Sample – Method Blank) × Dilution Factor
Recovery (%) = (Spiked Sample – Unspiked Sample) / Spike Conc. × 100

■ Acquisition for All Wavelength

To check for the presence of elemental impurities other than the quantified elements, the qualitative data of all elements was retrieved from the quantitative analysis data without remeasuring. As a result, It is found that elements such as Ca, Mg, Si, and Sr were also present in the anode materials, in addition to the elements that were quantitatively analyzed. As an example, Fig. 3 shows the spectra of Si and Sr, which were added as qualitative elements after the measurement.

In this way, the ICPE-9820 has the "Acquisition for All Wavelength" feature that allows for checking the data of unregistered elements and wavelength after the measurement. Therefore, even after the measurement, adding elements and wavelengths and checking the spectra and qualitative and quantitative analysis results is possible. If there is an interference or overflowing intensity at the analytical wavelength, it is possible to change to a different wavelength and check the quantitative results without remeasuring.

■ Conclusion

In this Application News, an analysis of elemental impurities in LIB anode materials was performed using the ICPE-9820. Good spike recoveries were obtained, confirming the accuracy of the analysis. Additionally, elements and wavelengths were added after the measurement to identify elemental impurities other than the analyzed elements present in the anode materials.

References

1) GB/T24533-2019 Graphite negative electrode materials for lithium ion battery

<Related Applications>

1. Analysis of Elemental Impurities in Lithium-Ion Secondary Battery Electrolytes Using the ICPE-9800 Series, [Application News 01-00702-EN]

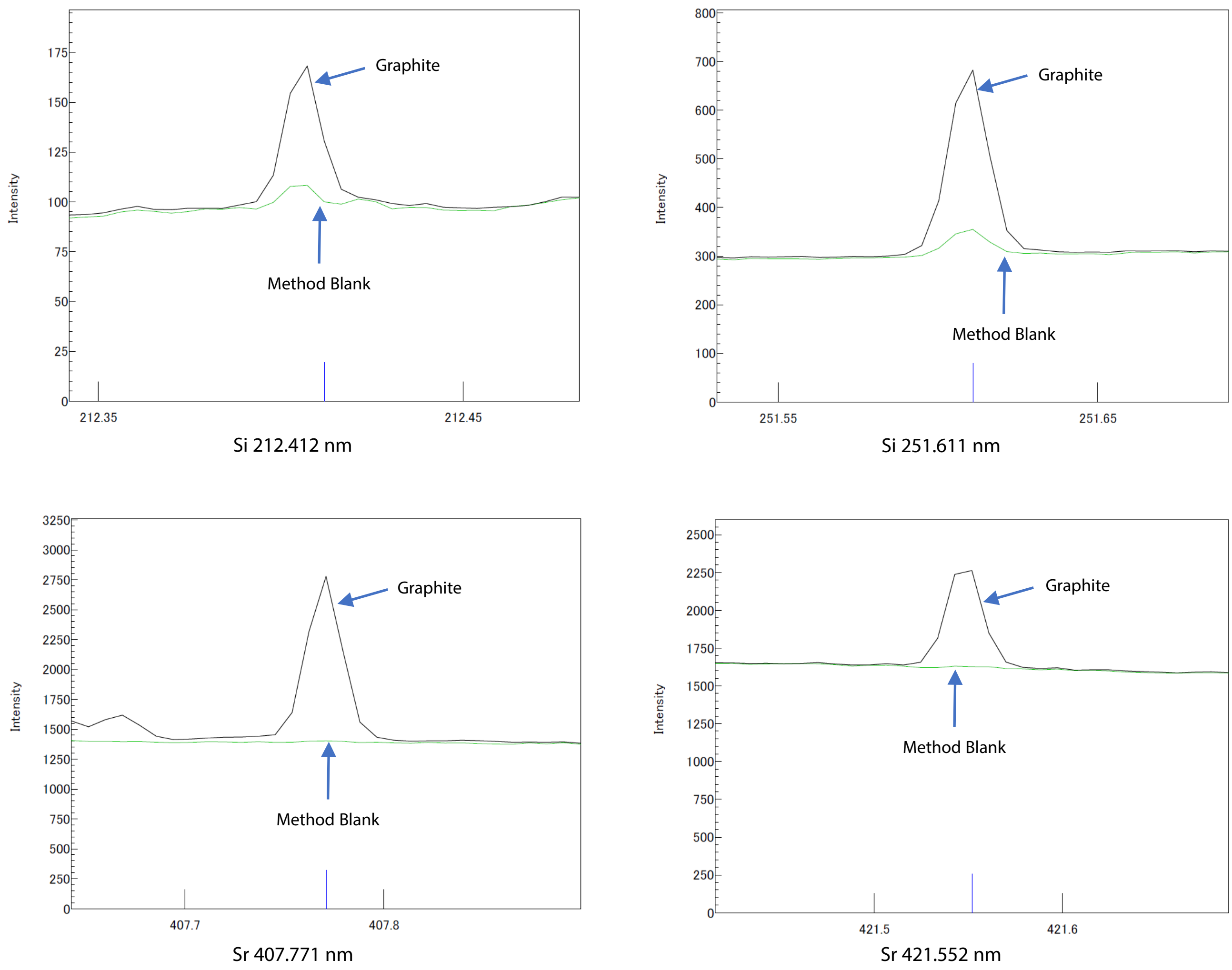

Fig.3 Spectra of Si and Sr

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