Challenge
Highly detectable and accurate quantification of impurities in anode material

Solution
The high-resolution ICP-OES PlasmaQuant 9100 Elite with its industry-leading optical system delivers excellent measurement sensitivity and matrix tolerance for trace analysis in anode material

Intended audience
Research, development and quality assurance of anode materials for lithium-ion batteries

Elemental Analysis of Anode Material using HR Array ICP-OES

Introduction

Lithium-ion batteries mainly consist of anode material, cathode material, separator and electrolyte. The anode material is the carrier of lithium ions and electrons during the charging process of the battery and has the function of storing and releasing energy. Impurities in anode materials refer to other components beyond the main elements and the cladding and doped elements. The chemical analysis of graphite and silicon oxide plays a crucial role in the ongoing development of anode materials for lithium-ion batteries, which are used as key components in numerous electronic devices and electric vehicles. Researchers and engineers are working to exploit the potential of various anode materials beyond graphite. Silicon-based anodes, for example, promise significantly higher performance as silicon can absorb more lithium ions. The production of anode materials for lithium-ion batteries faces complex challenges, as the quality and purity of these materials have a direct influence on the performance and safety of the batteries. Graphite and silicon oxide are two key components used in the anode side of the battery cell. Impurities in these materials can not only impair the specific capacity of the battery, but also catalyze undesirable side reactions that can negatively affect the service life and safety of the battery. Precise knowledge of the chemical composition is therefore of crucial importance for quality control and optimization of the manufacturing process. This application note focuses on the analytical challenges of manufacturing such anode materials, in particular the use of graphite and silicon oxide. It also discusses the importance of the ICP-OES (Inductively Coupled Plasma-Optical Emission Spectroscopy) method for the accurate measurement of chemical elements in these materials. The ICP-OES method has established itself as an extremely effective tool for the precise measurement of the chemical composition of materials. Especially in the analysis of graphite and silicon oxide, this method offers high sensitivity and precision. In the Chinese standardization landscape, three major standards have emerged that define the quality control of anode materials for lithium-ion batteries.

GB/T24533-2009 focuses on graphite as the first commercially used cathode material, while YS/T825-2012 sets specific requirements for lithium titanate. The national standard GB/T30836-2014 goes further and covers titanate lithium-ion batteries and their carbon composite cathode material. These standards provide clear guidelines for manufacturers and emphasize the need for precise analytical methods such as ICP-OES to ensure compliance with these standards and ensure high-quality anode materials for lithium-ion batteries. In this application note, the use of ICP-OES methods in this context will be discussed and their importance for quality assurance and the further development of anode materials will be emphasized.

Materials and Methods

Samples and reagents

- Sample material: Mixture of graphite and silicon dioxide
- Nitric acid (HNO_3)
- Hydrofluoric acid (HF)
- Multi-element standard solution with 100 mg/L Mo, Zn, Pb, Ni, Cd, Co, Fe, Cr, Cu, Al, Na (National Nonferrous Metals)
- Single element standard solutions with 1000 mg/L each of Hg, S and Au (National Nonferrous Metals)

Calibration

Table 1 below lists the concentrations of the standard solutions used for external calibration.

Sample preparation

As an open digestion on a hotplate can lead to losses of volatile elements (e.g. Hg), a closed microwave digestion was carried out. For this purpose, 0.2 g of each sample was accurately weighed, and 2 mL of concentrated nitric acid (HNO_3) and 4 mL of hydrofluoric acid (HF) were added. After the immediate reaction had subsided, the temperature was gradually increased to 180 °C (120 °C, 160 °C, 180 °C) and the final temperature was maintained for 20 minutes. After cooling the digestion vessels to room temperature, the solutions were each transferred to a graduated 50 mL PP centrifuge tube and filled to 50 mL with deionised water. As the resulting solutions still contained black carbon particles, filtration was then carried out using a 0.45 µm membrane filter.

Table 1: Concentrations of the calibration standards

Standard	Concentration [mg/L]		
	Hg, Mo, Zn, Pb, Ni, Cd, Co, Cu, Al	**Na**	**S**
Cal0	0	0	0
Std. 1	0.01	0.5	0.1
Std. 2	0.05	1	0.3
Std. 3	0.15	2	0.5
Std. 4	0.2		1

Instrumentation

A PlasmaQuant 9100 Elite ICP-OES equipped with a hydrofluoric acid resistant sample introduction system (HF kit) was used for the analysis. The settings and device parameters used are listed in Table 2. The evaluation parameters for the analysis are listed in Table 3.

Table 2: Device configuration and settings

Parameters	Specification
Performance	1200 W
Plasma gas flow	15 L/min
Auxiliary gas flow	0.5 L/min
Nebulizer gas flow	0.5 L/min
Nebulizer	PFA; 1 mL/min
Spray chamber	0.5 L/min
Outer tube/inner tube	Syalon/aluminium oxide
Injector	Ceramic, ID 2 mm
Pump tubing	PVC
Pump rate	1.0 mL/min
Torch position	0 mm

Table 3: Method parameters

Element	Line [nm]	Plasma observation	Integration	Measurement time [s]	Evaluation			
					Selection pixel	Baseline adjustment	Polynom	Correction
S	182.565	axial	Peak	2	3	ABC	auto	-
Hg	194.159	axial	Peak	2	3	ABC	auto	-
Mo	202.030	axial	Peak	1	3	ABC	auto	-
Zn	206.200	axial	Peak	1	3	ABC	auto	-
Pb	220.353	axial	Peak	1	3	ABC	auto	-
Ni	221.648	axial	Peak	1	3	ABC	auto	-
Cd	228.802	axial	Peak	1	3	ABC	auto	-
Co	228.615	axial	Peak	1	3	ABC	auto	-
Fe	259.940	axial	Peak	1	3	ABC	auto	-
Cr	267.716	axial	Peak	1	3	ABC	auto	-
Cu	324.754	axial	Peak	1	3	ABC	auto	-
Al	396.152	axial	Peak	1	3	ABC	auto	-
Na	589.592	axial	Peak	1	3	ABC	auto	-

ABC: Automatic Baseline Correction

Results and Discussion

The measurement results for the two analysed samples are listed in Table 4 below. In addition, a sample solution was spiked with an analyte concentration of 0.1 mg/L in order to check the influence of the sample matrix on the signal intensities and the accuracy of the measurement results. Recovery rates of 90-110% indicate an undisturbed analysis. The analyte lines show no spectral overlaps due to other matrix components, so that a spectrally undisturbed analysis can also be assumed. Examples of analyte spectra are shown in Figure 1.

Table 4: Measurement results for the two analysed samples and recovery rate of the spiking

Element	Sample 1	Sample 2	
	Measured concentration [mg/kg]	Measured concentration [mg/kg]	Recovery of the spiking (0.1 mg/L)[%]
S	26.3	23.8	91.2
Hg	< LOD	< LOD	110
Mo	< LOD	< LOD	99.0
Zn	2.85	1.63	105
Pb	< LOD	< LOD	106
Ni	3.89	3.82	101
Cd	< LOQ	< LOD	104
Co	< LOD	< LOQ	96.2
Fe	16.1	12.4	90.4
Cr	2.53	2.18	95.8
Cu	0.49	0.52	99.6
Al	19.97	17.8	93.6
Na	8.48	8.43	90.3

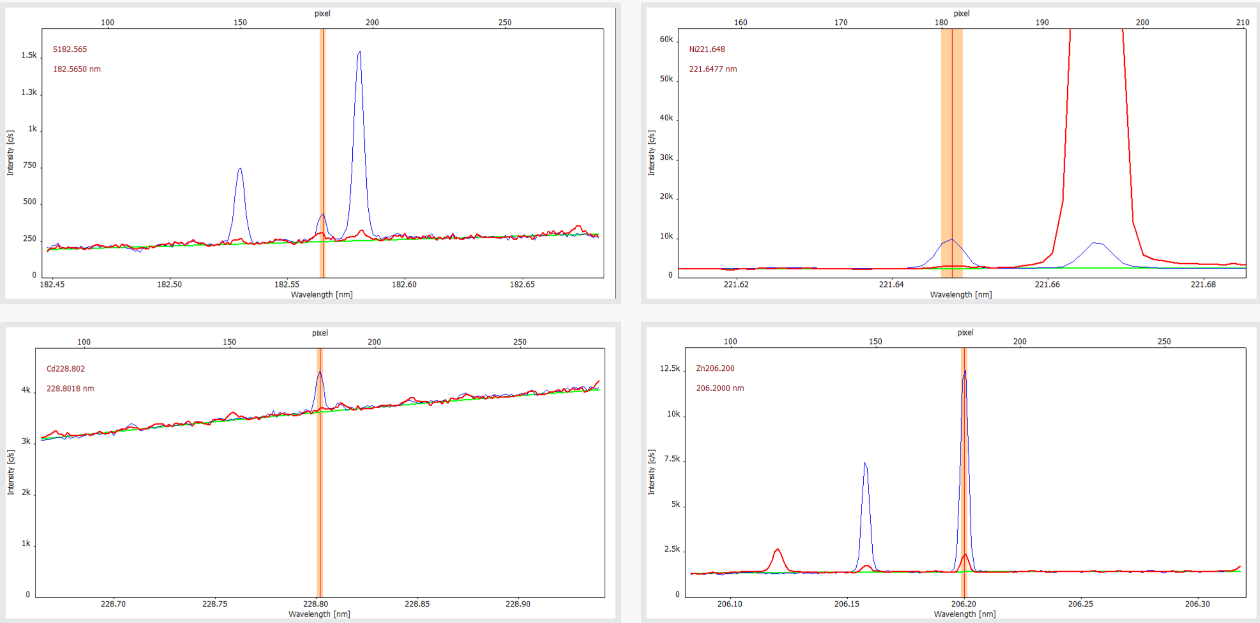

Figure 1: Examples of analytical spectra of the analysed sample matrix

--- Baselines (ABC) --- Sample --- Calibration standard (1 mg/L S; 0,2 mg/L Ni/Zn; 0,01 mg/L Cd)

Summary

The analysis of anode materials for lithium-ion batteries is an essential process in the battery manufacturing process. In this context, the PlasmaQuant 9100 Elite proves to be a robust and easy-to-use instrument with a unique spectrometer that is ideally suited for the analysis of anode materials.
The spectrometer is characterized by a high spectral resolution of 2 pm at 200 nm, which enables precise examination of the analyte peaks. In conjunction with the ABC software tool (Automatic Baseline Correction), exact and reliable measured values can be achieved without time-consuming manual spectrum evaluation.
Particularly noteworthy is the use of the most sensitive emission lines for trace analysis, even in complex matrices. This guarantees maximum sensitivity when determining the elemental composition. The use of the PlasmaQuant 9100 Elite and the ABC software tool is therefore a decisive step in the production of anode materials for lithium-ion batteries, as it enables precise characterization of the elements.

Figure 2: PlasmaQuant 9100 Elite

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
PlasmaQuant 9100 Elite	818-09101-2	High-resolution ICP-OES
Teledyne Cetac ASX 560	810-88015-0	The ASX-560 from Teledyne CETAC Technologies with integrated flushing function
HF-Kit	810-88007-0	Sample introduction system for samples containing hydrofluoric acid
Consumables set HF Kit ICP-OES	810-88042-0	Consumables set for HF kit

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