Application Note

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Determination of Elemental Impurities in Graphite-based Anodes using the Agilent 5110 ICP-OES

Accurate determination for lithium battery anodes

Authors

Ni Yingping, Feng Wenkun

Agilent Technologies (China) Co., Ltd.

Introduction

As one of the four main components of lithium ion batteries, the anode material allows the reversible transfer of lithium ions. At present, the mainstream anode material used in lithium battery production is a graphite-based material. As the energy density of the battery increases, the capacity utilization rate of the graphite-based anode material gradually approaches the theoretical value, and the compaction density is higher and higher, which requires the stability of the graphite-based anode material.

The impurity content present in the graphite-based anode material can have an effect on its stability, so the analysis and removal of trace impurity elements in the graphite-based anode material is particularly important.

For instance, the presence of iron (Fe) is an important indicator for the efficiency of graphite anode materials. The lower the Fe content, the more efficient the charge transfer from the anode. In addition, in order to optimize the cycle performance of the battery (increase the number of charge and discharge cycles), the graphite-based

anode is coated and doped with an active material, which is often carried out in the production process of the anode. During these processes, there is the possiblity of introducing other elements, which can affect product quality, therefore accurate determination of these elements is required. ICP-OES is suitable technique for the determination of these elements, as described in China's GB/T 24533-2009 Lithium-ion battery graphite anode material method. This application focuses on the fast and accurate determination of Fe, Al, As, Ba, Be, Cd, Co, Cr, Cu, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn in graphite-based anode materials using the Agilent 5110 Vertical Dual View (VDV) ICP-OES.

Experimental

Instrumentation

All measurements were performed using the Agilent 5110 Vertical Dual View (VDV) Inductively Coupled Plasma Emission Spectrometer (ICP-OES). The instrument is well suited to the analysis of impurities in graphite anode materials due to its high sensitivity providing accurate measurement at low concentrations. Equipped with Vista Chip II detector with processing speeds up to 1 MHz over the entire wavelength range, the 5110 delivers high throughput, high sensitivity and the largest dynamic range. The 5110 ICP-OES features a solid state RF system (SSRF) which has the capability of coping with variable plasma loads and a range of sample types, achieving long term analytical stability.

Table 1. Microwave digestion temperature program for graphite anode material samples.

Step	Temperature (°C)	Time (min)
1	150	10
2	150	5
3	180	5
4	180	20

Standard and sample preparation

Calibration standards were prepared using Agilent 10 mg/L multi-elemental standard 2A at 10, 20, 50, 100 and 200 µg/L in 2% (V/V) nitric acid solution (High-purity nitric acid purchased from Suzhou Jingrui Company).

Two commercially available graphite anode material samples (Sample 1 and Sample 2) were purchased for this study and prepared for analysis by microwave digestion using the Milestone ETHOS ONE Microwave Digester. 0.5 g of each sample was accurately weighed. 5 mL aqua regia (high-purity nitric acid and high-purity hydrochloric acid, Suzhou Jingrui Company) and 5 mL deionized water was added to the samples, and placed in the microwave digester according to the temperature program in Table 1. After the digestion was completed, digests were made up to 50 mL using high purity deionized water. Digests were prepared in duplicate, as well as duplicate digestion blanks. The sample introduction system consisted of SeaSpray concentric glass nebulizer, double-pass glass cyclonic spray chamber and a standard 1.8mm ID injector torch. Instrument operating parameters are shown in Table 2.

Table 2. Agilent 5110 ICP-OES instrument and method parameters.

Parameter	Setting
Read time (s)	10
Replicates	3
Sample uptake delay (s)	12
Stabilization time (s)	10
Pump speed (rpm)	12
Fast pump during uptake (rpm)	60
RF power (kW)	1.2
Plasma flow rate (L/min)	12
Aux flow (L/min)	1.0
Nebulizer flow (L/min)	0.65
Viewing mode	Axial
Sample pump tubing	White/white
Waste pump tubing	Blue/blue
Background correction	Fitted

Results and Discussion

Calibration linearity

Linear calibrations were obtained for all 18 elements examined, with correlation coefficients greater than 0.9995. The elemental wavelengths and correlation coefficients are listed in Table 3, and the calibration curve for Fe 238.204 nm is shown in Figure 1.

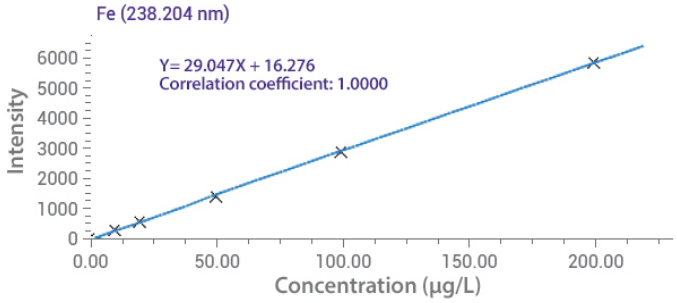

Figure 1. Calibration curve for Fe 238.204 nm.

Table 3. Elemental wavelengths and correlation coefficients for 18 elements concentration range 0 - 200 µg/L.

Element and wavelength (nm)	Correlation Coefficient
Al 396.152	1.0000
As 188.980	0.9998
Ba 455.403	0.9999
Be 313.107	1.0000
Cd 214.439	1.0000
Co 230.786	0.9999
Cr 267.716	1.0000
Cu 327.395	1.0000
Fe 238.204	1.0000
K 766.491	0.9997
Mg 279.553	1.0000
Mn 257.610	1.0000
Na 589.592	0.9999
Ni 216.555	0.9999
Pb 220.353	0.9996
Sr 407.771	1.0000
V 311.837	1.0000
Zn 213.857	0.9999

Method detection limits

The method detection limits (MDL) were based on three sigma of eleven replicate measurements of the digestion blank solution during the analytical run. The method detection limits for the 18 elements examined are shown in Table 4.

Table 4. Method detection limits for 18 impurity elements. The MDLs were calculated based on sample preparation (0.50 g sample in 50 mL final volume).

Element and wavelength (nm)	MDL (mg/kg)	Element and wavelength (nm)	MDL (mg/kg)
Al 396.152	0.076	K 766.491	0.056
As 188.980	0.188	Mg 279.553	0.021
Ba 455.403	0.010	Mn 257.610	0.026
Be 313.107	0.012	Na 589.592	0.095
Cd 214.439	0.017	Ni 216.555	0.027
Co 230.786	0.020	Pb 220.353	0.108
Cr 267.716	0.028	Sr 407.771	0.015
Cu 327.395	0.052	V 311.837	0.062
Fe 238.204	0.049	Zn 213.857	0.056

The two graphite anode material samples, sample A and sample B were analyzed using the Agilent 5110 ICP-OES. The graphite anode material, sample B was selected for the spike recovery experiment. Since the limit of most impurity elements is less than 5 mg/L (*1*), according to GB/T 24533-2009 method, the spiked concentrations of sample B was 0.025 mg/L for all 18 elements. The sample analysis results and spike recoveries are displayed in Table 5. The spike recovery results for sample B are within ± 10% of the spike concentration value, across all elements.

Table 5. Sample analysis concentration and spike recoveries results of impurity elements in the graphite anode material samples.

Element and Wavelength (nm)	Sample A Measured concentration (mg/kg)	Sample B		
		Measured concentration (mg/kg)	Spiked measured concentration (mg/kg)	Spike recovery (%)
Al 396.152	0.85	0.91	3.32	96
As 188.980	0.43	0.40	2.89	100
Ba 455.403	0.16	0.16	2.62	98
Be 313.107	ND	ND	2.46	98
Cd 214.439	ND	ND	2.51	100
Co 230.786	ND	ND	2.57	103
Cr 267.716	ND	ND	2.56	102
Cu 327.395	ND	ND	2.57	103
Fe 238.204	3.50	4.11	6.77	106
K 766.491	ND	ND	2.33	93
Mg 279.553	0.43	0.40	2.87	98
Mn 257.610	ND	ND	2.53	101
Na 589.592	11.11	11.23	13.97	110
Ni 216.555	3.23	3.13	5.60	99
Pb 220.353	ND	ND	2.58	103
Sr 407.771	0.22	0.20	2.71	100
V 311.837	11.67	12.10	14.57	99
Zn 213.857	ND	ND	2.53	101

* ND: below detection limit

Long-term stability

Long-term stability experiments were carried out using a spiked solution of graphite-based anode sample B (with a spiked concentration of 0.025 mg/L). The sample spiked solution was analysed continuously over a 2.5 hour period. The relative standard deviation (RSD) of the measured impurity element results is shown in Table 6. The RSD of all 18 elements examined was less than 1.6%, demonstrating the robustness of the solid state RF system of the Agilent 5110 ICP-OES for long-term stability analysis of impurities in graphite-based anode materials.

Table 6. Long-term stability results, %RSD of 18 elements in a spiked solution of graphite-based anode sample B.

Element and Wavelength (nm)	RSD (%)	Element and Wavelength (nm)	RSD (%)
Al 396.152	0.9	K 766.491	0.9
As 188.980	1.5	Mg 279.553	0.9
Ba 455.403	0.6	Mn 257.610	0.7
Be 313.107	0.7	Na 589.592	1.1
Cd 214.439	0.6	Ni 216.555	0.4
Co 230.786	0.4	Pb 220.353	1.3
Cr 267.716	1.0	Sr 407.771	1.1
Cu 327.395	0.8	V 311.837	0.9
Fe 238.204	0.4	Zn 213.857	0.6

Conclusions

At present, the Chinese domestic lithium battery industry mainly judges the purity level of graphite anode materials by the Fe content, but the presence of other metal elements also affects the quality of the anode materials (*1*).

In this application, a method for the accurate detection of 18 impurity elements (including Fe) in graphite-based anode materials was established using the Agilent 5110 Vertical Dual View (VDV) ICP-OES.

The spike recovery of this method was between 90% and 110%, and the relative standard deviation (RSD) of the 2.5 h stability test results was less than 1.6% The Agilent 5110 ICP-OES provided a method with good accuracy and stability making it suitable for the analysis of impurity elements in graphite-based anode materials.

The reliability of the instrument proved to be a powerful tool for the grading of higher purity anode materials in the future.

References

1. GB/T 24533-2009 Lithium-ion battery graphite anode material

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