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Inductively Coupled Plasma Atomic Emission Spectrometer ICPE™-9800 Series

Application News

Analysis of Elemental Impurities in Lithium-Ion Secondary Battery Electrolytes Using the ICPE-9800 Series

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User Benefits

- The ICPE-9800 Series allows for simultaneous multi-element analysis.
- It is possible to accurately and precisely analyze elemental impurities in lithium-ion secondary battery electrolytes.
- Lithium-ion secondary battery electrolytes can be injected using a hydrofluoric acid-resistant injection system and an organic solvent torch.

■ Introduction

Lithium-ion secondary batteries (LIBs) are widely used in mobile devices, electric vehicles, hybrid cars, and more. Impurities in LIB electrolytes can cause a decrease in battery performance and safety. Therefore, in China, the management of elemental impurities in electrolytes using inductively coupled plasma atomic emission spectroscopy (ICP-AES) is required by the HG/T4067-2015[1)] standard.

LIB electrolytes are typically composed of lithium hexafluorophosphate ($LiPF_6$) dissolved in an organic solvent, requiring an injection system for organic solvents. However, $LiPF_6$ can hydrolyze to generate hydrofluoric acid (HF), which poses a risk of corrosion to the glass-based injection systems commonly used in ICP-AES.

In this Application News, the ICPE-9820, a hydrofluoric acid resistant injection system and an organic solvent torch were used to analyze elemental impurities in LIB electrolytes. Spike recovery tests and replicate analysis were performed to confirm the validity and precision of the analysis.

■ Samples

Two types of LIB electrolytes were prepared as samples. One is an electrolyte containing 1.0 mol/L $LiPF_6$ dissolved in ethyl methyl carbonate (EMC) (hereinafter referred to as $LiPF_6$ in EMC), and the other is an electrolyte containing 1.0 mol/L $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) in a ratio of 50:50 (v/v%) (hereinafter referred to as $LiPF_6$ in EC/DMC).

■ Sample Preparation

- Dilution solvent

The dilution solvent was prepared by mixing EMC, ethanol, and pure water in a volume ratio of 1:4:5.

- Unspiked samples of LIB electrolyte

The $LiPF_6$ in EMC and $LiPF_6$ in EC/DMC electrolytes were each diluted 10 times with the dilution solvent to prepare unspiked samples.

- Spiked samples of LIB electrolyte

Spiked samples were prepared by adding a mixture of commercially available standard solutions of Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Na, Ni, Pb, and Zn to electrolytes diluted 10 times with the dilution solvent. Spiked concentrations of each element in the solution were 0.1 mg/L (equivalent to 1 mg/kg in the electrolyte).

■ Calibration Standards

Commercially available standard solutions of Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Na, Ni, Pb, and Zn were mixed and added to the dilution solvent to prepare the calibration standards. Lithium carbonate was also added to calibration standards for matrix matching. Li concentration in each calibration standard is 0.1 mol/L. 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)			
	STD1	STD2	STD3	STD4
Al, As, Ca, Cd, Cr, Cu, Fe, Hg, K, Mg, Na, Ni, Pb, Zn	0	0.1	0.5	1
Li	0.1 mol/L			

■ Instrument Configuration and Analytical Conditions

The nebulizer (Fig. 1-A), chamber (Fig. 1-B), and drain (Fig. 1-C) used in this analysis are made of HF-resistant materials to avoid corrosion by HF, as they have much contact with the samples. For the torch, which has minimal contact with the sample and is less affected by HF corrosion, an organic solvent torch made of quartz (Fig. 1-D) was used. In addition, the standard glass extension pipe was replaced with a quartz one. The system configuration for ICP-AES is shown in Table 2.

The analytical conditions are shown in Table 3.

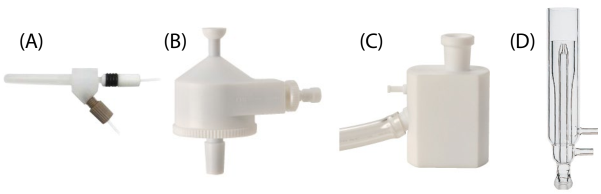

Fig. 1 Hydrofluoric Acid Resistant Injection System and Organic Solvent Torch

Table 2 ICP-AES System Configuration

Instrument:	ICPE-9820
Nebulizer:	Nebulizer, PFA1S
Chamber:	Cyclonic Chamber for Hydrofluoric Acid
Extension Pipe:	Made of Quartz
Torch:	Organic Solvent Torch
Drain:	Hydrofluoric Acid Resistant Drain
Auto Sampler:	AS-10

Table 3 Analytical Conditions

RF Power:	1.40 kW
Plasma Gas Flowrate:	20.0 L/min
Auxiliary Gas Flowrate:	0.70 L/min
Carrier Gas Flowrate:	0.75 L/min
View Direction:	Axial

■ Quantitative Analysis

Calibration curves were made using the calibration standards shown in Table 1, and the elemental impurities in the two types of LIB electrolytes were quantitatively analyzed. The quantified results, converted to the concentrations in LIB electrolytes, are shown in Table 4. The detection limits are lower than the regulation values in HG/T4067-2015, demonstrating that the ICPE-9820 has sufficient sensitivity for analyzing impurities in LIB electrolytes.

Table 4 Quantitative Results in LIB Electrolytes

Elements	Wavelength (nm)	Detection Limit (mg/kg)	HG/T 4067-2015 Regulation Value (mg/kg)	Quantitative Result (mg/kg)	
				$LiPF_6$ in EMC	$LiPF_6$ in EC/DMC
Al	396.153	0.02	1	0.21	N.D.
As	193.759	0.3	1	N.D.	N.D.
Ca	396.847	0.003	1	N.D.	N.D.
Cd	226.502	0.008	1	N.D.	N.D.
Cr	205.552	0.03	1	0.04	N.D.
Cu	327.396	0.01	1	0.02	0.01
Fe	259.940	0.01	1	0.12	N.D.
Hg	184.950	0.05	1	N.D.	N.D.
K	766.490	0.02	1	N.D.	N.D.
Mg	280.270	0.0005	1	0.017	N.D.
Na	589.592	0.02	2	0.02	0.04
Ni	231.604	0.03	1	0.09	0.07
Pb	220.353	0.07	1	N.D.	N.D.
Zn	213.856	0.009	1	N.D.	N.D.

Detection Limit: 3 × σ (standard deviation of STD1) × slope of calibration curve × dilution factor (10 times)
N.D.: below the detection limit

■ Spike Recovery Tests and Repeatability

Spike recovery tests for the two types of LIB electrolytes were performed. Additionally, for the spiked samples of $LiPF_6$ in EMC, 10 repeated measurements were conducted to verify repeatability. The results are shown in Table 5.

Good spike recoveries ranging from 89 % to 107 % for the two types of LIB electrolytes were obtained, confirming the accuracy of the analysis of elemental impurities in LIB electrolytes using the ICPE-9820.

In the 10 repeated measurements of the spiked samples of $LiPF_6$ in EMC, 6.9 % or less repeatability was obtained, indicating that elemental impurities at concentrations equivalent to the regulation values can be precisely analyzed.

■ Conclusion

In this Application News, analysis of elemental impurities in LIB electrolytes was performed using the ICPE-9820, a hydrofluoric acid resistant injection system and a torch for organic solvents. Good spike recoveries were obtained, confirming the accuracy of the analysis. Additionally, the repeated measurements demonstrated good analytical precision.

References

1) HG/T4067-2015 Cell liquor of lithium hexafluorophosphate https://www.chinesestandard.net/PDF/English.aspx/HGT4067-2015 (February 20th, 2024)

Table 5 Spike Recoveries and Repeatability

Elements	Wavelength (nm)	Detection Limit (mg/L)	Spike Conc. (mg/L)	$LiPF_6$ in EMC				$LiPF_6$ in EC/DMC		
				Unspiked Sample (mg/L)	Spiked Sample (mg/L)	Spike Recovery (%)	Repeatability (%)	Unspiked Sample (mg/L)	Spiked Sample (mg/L)	Spike Recovery (%)
Al	396.153	0.002	0.1	0.021	0.128	107	3.0	N.D.	0.098	98
As	193.759	0.03	0.1	N.D.	0.099	99	6.9	N.D.	0.096	96
Ca	396.847	0.0003	0.1	N.D.	0.0934	93	1.2	N.D.	0.0937	94
Cd	226.502	0.0008	0.1	N.D.	0.100	100	0.9	N.D.	0.103	103
Cr	205.552	0.003	0.1	0.004	0.105	101	1.3	N.D.	0.102	102
Cu	327.396	0.001	0.1	0.002	0.103	101	2.0	0.001	0.101	100
Fe	259.940	0.001	0.1	0.012	0.111	99	1.1	N.D.	0.101	101
Hg	184.950	0.005	0.1	N.D.	0.091	91	3.5	N.D.	0.100	100
K	766.490	0.002	0.1	N.D.	0.095	95	0.8	N.D.	0.095	95
Mg	280.270	0.00005	0.1	0.00172	0.106	104	1.3	N.D.	0.103	103
Na	589.592	0.002	0.1	0.002	0.099	97	1.1	0.004	0.105	101
Ni	231.604	0.003	0.1	0.009	0.109	100	1.2	0.007	0.108	101
Pb	220.353	0.007	0.1	N.D.	0.093	93	3.6	N.D.	0.089	89
Zn	213.856	0.0009	0.1	N.D.	0.094	94	0.9	N.D.	0.095	95

Detection Limit: 3 × σ (standard deviation of STD1) × slope of calibration curve
N.D.: below the detection limit

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