Application Brief

Energy and Chemicals

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ICP-MS Analysis of Trace Elements in LIB Cathode Materials

Low-level analysis of contaminants that affect lithium-ion battery performance and safety

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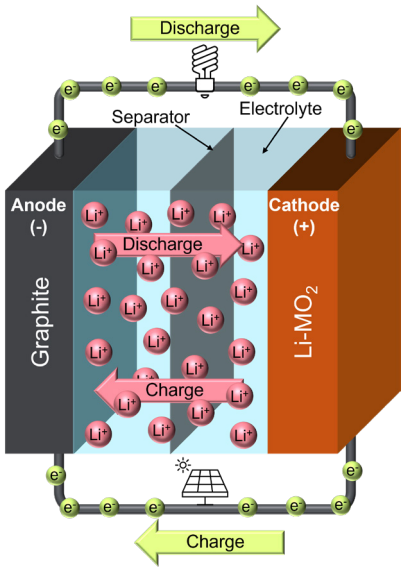

Figure 1. Lithium-ion battery schematic.

Lithium-ion battery performance and cathode composition

Rechargeable batteries—mainly lithium (Li)-ion batteries (LIBs)—are used in products from consumer electronics to grid storage. LIBs are also increasingly used in electric vehicles (EVs), as manufacturers seek to reduce reliance on fossil fuels.

The performance of a LIB is highly dependent on the cathode material, which determines characteristics such as the battery's energy density, charge capacity, and capacity retention after repeated charge/discharge cycles. The cathode active material (CAM) of a LIB usually consists of Li combined with a metal oxide compound such as cobalt (Co) oxide (LCO), nickel (Ni) Co aluminum (Al) oxide (NCA), Ni Co manganese (Mn) oxide (NCM or NMC), or Ni Mn Co Al oxide (NMCA).

The cathode is responsible for around 25% of the weight and cost of a typical LIB, with the Co content being responsible for much of the cost (*1*). The high cost of Co has led to the development of cathode materials with lower Co content, for example, NMC 622 (molar % of 60 Ni, 20 Mn, 20 Co) has replaced NMC 111 (equal Ni, Mn, and Co). Co-free materials have also been developed, including Li iron (Fe) phosphate (LFP) and Li Mn oxide (LMO) (*2*). Depending on manufacturer, most EV batteries currently use cathodes made from LFP, NMC, NCA (*3*), or newer, high-Ni, quaternary materials such as NMCA. The cathode raw material is doped and coated with other elements and compounds to give the required electrochemical properties (*4*).

The cathode's capacity, stability, and lifetime are strongly affected by the CAM's morphology and purity, so control of contaminants in raw materials and during production is critical to the industry. LIBs for EVs are mainly produced in China, and standards and methods have been published to define maximum impurity and contaminant levels to ensure LIB quality and safety.

For cathode materials, the relevant (non-mandatory) State product quality standard is GB/T 6300-2020, and the industry standard is YS/T 928.4-2013. The standards define maximum contaminant levels for specified elements and include the recommended analytical method. For most elemental contaminants, the standards recommend Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for the analysis. The most critical contaminants in cathode materials are elements such as Cr, Fe, Cu, Zn, and Pb, which manufacturers aim to control at levels of <1 mg/kg (ppm). With the development of more advanced battery technologies, contaminant levels are becoming too low to measure reliably by ICP-OES, so manufacturers are investigating ICP-MS as an alternative. The Agilent 7900 ICP-MS has very low detection limits for almost all elements and includes UHMI aerosol dilution technology to enable high matrix levels to be run routinely. Agilent ICP-MS systems also provide good control of spectral overlaps, as they include an optimized helium (He) mode ORS[4] collision/reaction cell to attenuate matrix-based polyatomic ion interferences.

Routine analysis of NMC cathode material

A 7900 ICP-MS was used to run a four-hour sequence consisting of multiple NMC samples, spiked samples, and QCs. Continuing calibration verification (CCV) standards at the midpoint of the calibrations were run every 12 samples. The plot shown in Figure 2 confirms that all CCV recoveries were within the method requirements of 90 to 110%.

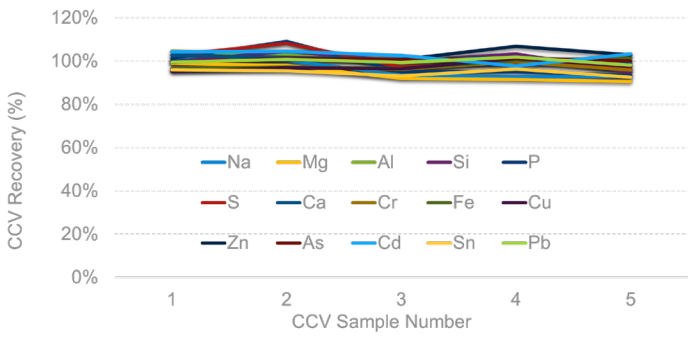

Figure 2. CCV recoveries were within ±10% for all analytes throughout the four-hour NMC sample analysis sequence.

Quantitative analysis of NMC by ICP-MS

The 7900 ICP-MS sequence focused on the quantitative analysis of priority impurity elements in four NMC cathode material samples with Ni content varying from 50 to 60 mol% (5 Series) to >90 mol% (9 Series). There are no certified reference materials for NMC cathode materials, so the accuracy of the 7900 ICP-MS method was confirmed by running multiple spike recoveries for each matrix.

The mean spike recoveries for the four different NMC compositions are shown in Table 1. Almost all the recoveries were within ±10%, demonstrating the accuracy of the 7900 ICP-MS method for low-level contaminant analysis in varied, high matrix NMC cathode materials.

Table 1. Spike recoveries for contaminant elements in NMC cathode materials. All elements measured in He mode except Si and Ca, H_2 mode. *All spike concentrations in µg/L except S, mg/L.

Mass, Element	Spike Level (µg/L)	Mean Spike Recovery (%) in NMC			
		5 Series	6 Series	8 Series	9 Series
23 Na	125	100	99	99	111
24 Mg	125	92	96	93	91
27 Al	10	90	105	109	126
28 Si	10	110	97	99	103
31 P	10	99	94	100	95
34 S	**2***	**115**	**106**	**102**	**97**
40 Ca	125	95	101	101	100
52 Cr	10	96	94	94	96
56 Fe	10	91	94	92	105
63 Cu	10	92	94	91	95
66 Zn	10	91	92	93	94
114 Cd	0.5	97	114	99	97
118 Sn	10	107	98	99	98
208 Pb	10	100	99	97	97

References

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