MICAP-OES 1000

Trace elements analysis in Li-based battery cathodes with a microwave N_2 ICP-OES system

Jorge Pérez-Vázquez, Raquel Serrano, Luis Gras & Guillermo Grindlay
Analytical Atomic Spectrometry Group, University of Alicante, Spain

Introduction

The recent surge in electric vehicle adoption has driven a corresponding increase in the development and production of lithium-ion batteries (LiB). Among the various LiB variants, those with cathodes composed of lithium transition metal oxides, particularly the ternary cathode ($LiNi_xMn_yCo_{(1-x-y)}O2$, or NMC) have become the most common. The energy capacity, cycle stability, and cost of these batteries are directly influenced by the stoichiometry of the main cathode elements and the presence of impurities. Consequently, the accurate determination and precise quantification of primary elements (Li, Ni, Co, Mn) and impurities (e.g., Ca, Cd, Cr, Cu, Fe, Na, Pb) in final cathodes are essential for quality control in the LiBs-based industry.

This note describes the use of the simultaneous MICAP™ OES-1000 N_2 ICP-OES system for the analysis of major and impurity elements in binary and ternary Li-based cathodes. The analysis is performed in accordance with the established Chinese standard protocols. Analytical performance of the MICAP is presented to demonstrate accurate and stable performance during the analysis of several Li-based battery cathodes.

Instrumentation

The Chinese standard protocols represent the existing regulations that establish the maximum impurity content (i.e., Al, Ca, Cd, Cr, Cu, Fe, Mg, Na, Pb, and Zn) and the concentration of major elements (Co, Fe, Li, Mn, Ni) to ensure the quality of Li-based battery cathodes. These regulations establish the composition of major elements and maximum allowed trace metal impurities in LiB cathodes.

The MICAP-OES 1000 was configured with a standard sample introduction system. A cyclonic spray chamber and a pneumatic nebulizer were connected to a one-piece torch for introduction of samples into the N_2 plasma.

Microwave energy in the MICAP is coupled into the Cerawave™ ring utilizing a highly efficient process that creates the magnetic fields required to inductively couple energy into the robust N_2 plasma source. The 4 MP sCMOS camera simultaneously collects the emission lines from the high-resolution spectrometer.

Figure 1. MICAP-OES 1000 N_2 ICP-OES

Experimental Conditions

The analyses were performed on the simultaneous MICAP (Figure 1) utilizing the conditions listed in Table 1. The sample uptake path was rinsed between solutions using a customized rinse solution (ICP TRUE Rinse, Inorganic Ventures, Christiansburg, VA, USA) to speed rinse out of high concentration elements. Samples were introduced with an autosampler, with each sample analysis taking 3 minutes.

For the determination of both major elements (Li, Co. Mn and Ni) and impurities (Al, Ca, Cd, Cr, Cu, Fe, Mg, Na, Pb, & Zn), it is necessary control the level of signal impacting the camera. Without this, the major element peaks could easily overload the detector. The samples could either be analyzed at two different dilutions or measured at distinct data capture conditions. To ensure optimal simultaneous analysis performance without analyzing extra dilutions, two distinct exposure time conditions were automatically collected for each acquisition - 1000 ms for the impurities and 40 ms for major elements.

Table 2 provides specifics on the analyte wavelengths used for this analysis, along with the selected exposure times and resulting detection limits obtained from 3x standard deviation of 10 blank measurements. According to the Chinese standard protocols it is viable to analyze all the major and impurity elements as required; as the detection limits of MICAP are well below the legal thresholds.

Table 1. Operational conditions

Parameter	Value
Torch	Quartz 1-piece, 2.5mm injector
Spray Chamber	Cyclonic
Nebulizer	Pneumatic nebulizer
Sample Tubing	Blk/Blk (0.76 mm ID)
Drain Tubing	Blu/Yel (1.52 mm ID)
Rinse	ICP TRUE RINSE
Stabilization Time	20 sec
Power	1000 W
Coolant Gas Flow	14 L/min N_2
Auxiliary Gas Flow	0.3 L/min N_2
Nebulizer Gas Flow	0.9 L/min N_2
Peristaltic Pump	25 rev/min
Plasma Viewing	Axial
Camera Exposure A Camera Exposure B	30 sec (1000 ms @ 10 exps) 600 ms (40 ms @ 5 exps)
# of Repeats	3

Table 2. Analyte wavelengths and detection limits

Analyte Wavelength (nm)	Camera Exposure	Limit of Detection (mg/kg, ppm)*
Al I 396.152	A	1.2
Ca II 396.847	A	0.3
Cd I 228.802	A	0.8
Co I 345.350	B	5
Cr I 428.973	A	1.3
Cu I 327.396	A	0.6
Fe II 259.940	A	2
Li I 610.364	B	10
Mg II 279.553	A	0.07
Mn II 257.610	B	0.8
Na I 589.592	A	0.19
Ni I 345.847	B	4
Pb I 368.346	A	4
Zn I 213.857	A	2

** Expressed with respect to the solid LiB samples*

Samples

To assess the applicability of MICAP for the quality control of these LiB cathodes, 9 different cathode samples of lithium transition metal oxides were selected. This included a cathode Certified Reference Material (CRM) NMC11 BAM SO14 (Federal Institute for Materials Research & Testing (BAM), Berlin, Germany). These samples represent a wide range of compositions and manufacturing sources. The cathodes selected were four binary Li-based cathodes with different chemistries and four ternary cathodes with variable components of Li, Ni, Mn and Co. These cathodes compounds were acquired from various distributors and are listed in Table 3 below with their common name and specific stoichiometries.

Table 3. Cathode materials analyzed

Li-based Cathodes	Li Ni Mn Co (NMC) Cathodes
LFP $LiFePO_4$	**NMC111** $LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$
LCO $LiCoO_2$	**NMC442** $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$
LMO $LiMn_2O_4$	**NMC532** $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$
NCA $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	**NMC622** $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$

Sample preparation

All samples were digested in triplicate using a Ultrawave microwave oven (Milestone s.r.l., Sorisole, Italy) according to the manufacturer's recommendations, by adapting the conditions defined in the Chinese standard protocols. A 0.15 g aliquot of each sample was digested with 4 mL of aqua regia. After the digestion process samples were brought to a final weight of 15 g with ultrapure water (UPW). The digestates were then diluted 1:2 with UPW prior to analysis.

Multi-element solutions containing 10 mg/kg of each analyte were formulated in synthetic matrices designed to replicate the elemental composition of cathodes sample digests in accordance with Chinese standard protocols. These solutions were used to investigate spectral interferences arising from major constituents (i.e., Co, Fe, Li, Mn and Ni). Working standards for major elements were prepared by diluting 1000 mg/kg multi-element stock standards (Sigma-Aldrich, Steinheim, Germany) in UPW while for impurities analysis calibration standards were prepared simulating the elemental composition of each cathodes sample digest.

Results

The MICAP was calibrated as described above and all wavelengths were viewed in the Radom Intuitive Software (RIS) Profiles View to verify no spectral interferences existed and to set peak integration points. The emission lines utilized for quantitation were selected from numerous line options available. The simultaneous, full wavelength range data collection also provided the ability during method development to confirm accurate measurements across multiple emission lines (see Figure 2) for major (i.e., Co, Fe, Mn, Ni) and trace impurity elements (i.e., Al, Ca, Cd, Cr, Cu, Fe, Mg, Na, Pb, and Zn).

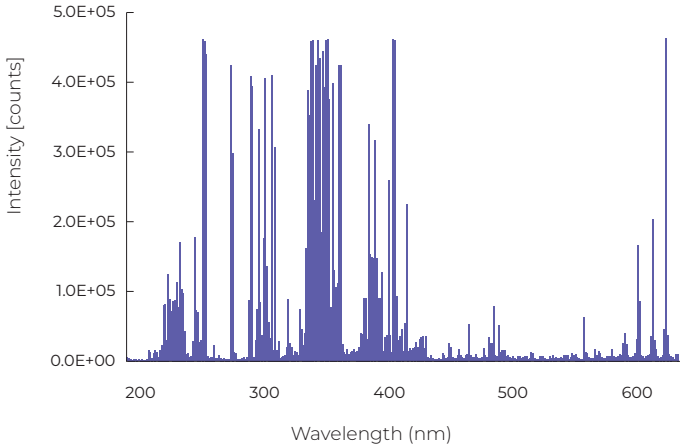

Figure 2. Emission spectra for NMC 111 ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$) cathode digest.

Figure 3 provides an example emission signal for the analyte of Mg. Note the clear baseline resolution between the Mn 279.482 nm and Mg 279.553 nm emission lines, demonstrating the high resolving power of the spectrometer between a major element of the LiB matrix and the Mg impurity element. The high-resolution performance of the MICAP ensures the analyte peaks of interest are not impacted by nearby spectral interferences from other potential elemental components present.

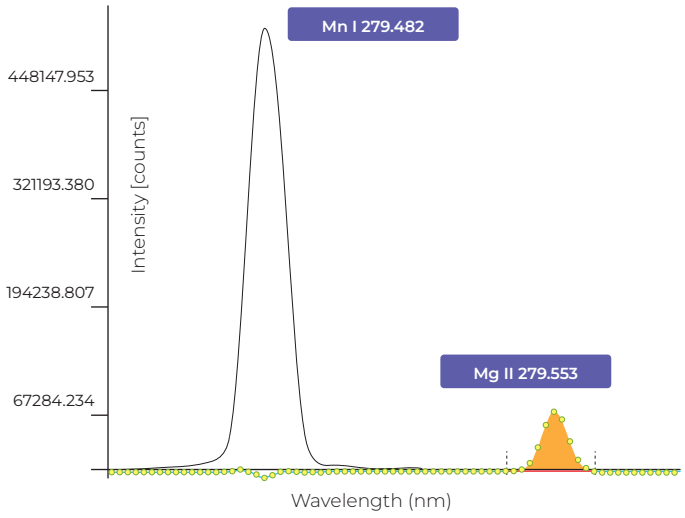

Figure 3. Profiles view of Mn and Mg emission lines in 2 mg/Kg spiked NMC cathode sample.

The accuracy and precision of the method was evaluated through the direct analysis of a certified reference material (NMC111 BAM S014) analysed in triplicate (n=3) and recovery tests by spiking cathode samples with 0.5 mg/kg of Al, Ca, Cd, Cr, Cu, Fe, Mg, Na, Pb, and Zn.

As it can be observed in Table 4, the CRM experimental values obtained for the major elements and impurities agreed well with the certified values and there was no significant difference for a probability p-value of <0.05.

The method accuracy for the LiB samples was further evaluated by spiking each of the samples with 0.5 mg/kg levels for each analyte. The recovery tests (Table 5) demonstrate that all the recoveries obtained for the LiB cathode materials were quantitative, ranging within 90-110%.

The precision of the method (i.e., relative standard deviation) was within the 0.1–4% range for all the elements evaluated regardless the sample considered. The method reproducibility was evaluated by measuring each sample three times across five different days, and it was lower than 7% for all the samples tested.

Table 4. NMC111 BAM S014 CRM values for major elements (in%) & impurities (mg/kg) along with measured precision.

Major Element	Certified Value (%)	Found Value (%)
Li	7.62 ± 0.17	7.63 ± 0.14
Ni	19.76 ± 0.16	19.59 ± 0.07
Mn	18.22 ± 0.17	17.47 ± 0.08
Co	19.80 ± 0.16	19.49 ± 0.10
Impurities	**Certified Value (mg/kg)**	**Found Value (mg/kg)**
Al	14.1 ± 1.9	13.6 ± 1.6
Fe	26 ± 4	26 ± 3
Na	512 ± 13	495 ± 3

Table 5. Analyte percent recoveries (mean ± SD, n = 3) obtained for impurities in the cathode types analyzed. Each cathode material was spiked with 0.5 mg/kg (ppm) for all elements analyzed.

Element	LCO	LFP	LMO	NCA	NMC 111	NMC 442	NMC 532	NMC 622
Al	108 ± 7	97 ± 4	95 ± 4	-	94.9 ± 0.3	95 ± 6	101.4 ± 0.8	111 ± 5
Ca	101 ± 2	109 ± 3	104 ± 2	102 ± 7	103 ± 5	103 ± 5	94.2 ± 1.0	107 ± 4
Cd	97 ± 4	100.5 ± 0.9	99 ± 6	100.5 ± 0.6	92 ± 4	97 ± 3	98.1 ± 1.9	105 ± 6
Cr	105 ± 3	101 ± 5	104 ± 2	98.2 ± 0.9	106 ± 2	102.6 ± 1.1	105.1 ± 0.3	95.2 ± 1.2
Cu	100 ± 2	105 ± 2	103 ± 3	95 ± 3	101.4 ± 0.7	99.6 ± 0.5	97.8 ± 0.2	102 ± 4
Fe	107 ± 2	-	104.2 ± 0.8	98 ± 3	106.6 ± 1.5	99 ± 4	93.6 ± 1.0	96.4 ± 0.2
Mg	98 ± 6	106.2 ± 0.6	102.5 ± 1.5	108.3 ± 1.4	105.3 ± 1.2	102.6 ± 1.5	94.9 ± 1.8	101 ± 3
Na	105 ± 3	104.7 ± 0.9	93 ± 5	93.4 ± 1.5	97.9 ± 0.8	104.2 ± 1.7	100 ± 5	98 ± 4
Pb	90 ± 5	108 ± 4	97 ± 4	103 ± 4	90.2 ± 1.4	90 ± 4	96.2 ± 1.9	105.8 ± 1.7
Zn	100 ± 4	92 ± 3	95 ± 3	105 ± 6	98 ± 6	95 ± 5	103 ± 3	104 ± 2

Note: Al and Fe are major elements for NCA and LCO cathodes, respectively, and recovery values are not included.

Conclusions

The MICAP-OES 1000 N_2 ICP-OES clearly demonstrated its capability for the quality control of LiB battery cathodes in accordance with the Chinese standard protocols. No significant spectral interferences were detected and no salt deposition from the samples was observed on the MICAP torch throughout this application work. Both impurities and major elements can be simultaneously determined in a single run by the appropriate selection of operating conditions and the calibration strategies (i.e., matrix-matched calibration standards and multi-exposure data collection). It is also important to highlight that this methodology can easily be extended to the quality assessment of materials recovered from LiB-based black mass samples, supporting its relevance for both manufacturing and recycling operations.

References

1. GB/T 20252-2014, Chinese standard method for Lithium Cobalt Oxide ($LiCoO_2$)
2. YS/T 1027-2024, Chinese standard method for Lithium Iron Phosphate ($LiFePO_4$)
3. YS/T 677-2016, Chinese standard method for Lithium Magnesium Oxide ($LiMn_2O_4$)
4. YS/T 1125-2023 Chinese standard method for Lithium Nickel Cobalt Aluminium Oxide ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$)
5. YS/T 798-2012, Chinese standard method for Lithium Nickel Cobalt Manganese Oxide ($LiNi_xMn_yCo_{(1-x-y)}O_2$)

Scan the code to access our website for additional information and our resources