X-RAY FLUORESCENCE

Battery Li-NMC Powder: Rapid & Easy Production and Quality Control

Lab Report 188

Introduction

The type and quality of the cathode active material (CAM) used in a rechargeable Lithium-ion battery (LIB) is critical for its performance, safety, and cycle lifetime. The CAM is the most significant cost driver of LIBs, making process control and optimization vital tasks for a cost-effective production.

Li-NMC batteries are frequently used in electric vehicles (EVs) due to their high energy density. Their CAM consists of Lithium (Li), Nickel (Ni), Manganese (Mn) and Cobalt (Co). The sub-types, such as NMC 333, 632, and 811, indicate the Ni:Mn:Co molar ratio. The different NMC ratios affect the performance, cost, cycle life, and safety of the battery.

X-ray Fluorescence (XRF) spectrometry is a powerful analytical technology which enables rapid and accurate elemental analysis of CAM, like Li-NMC powder, without sample digestion and dilution.

This lab report demonstrates the performance of the S2 PUMA Series 2 energy-dispersive XRF (EDXRF) spectrometer for Li-NMC powder quality control. Accurate results are achieved within less than 10 minutes including sample preparation.

Production of Li-NMC Cathode Active Material

There are different ways to produce Li-NMC. One of the more common approaches is depict in Figure 1. Here, XRF is used to determine the stoichiometry and purity of liquid precursors (1), dried hydroxide precursors (2) and calcined CAM (3).

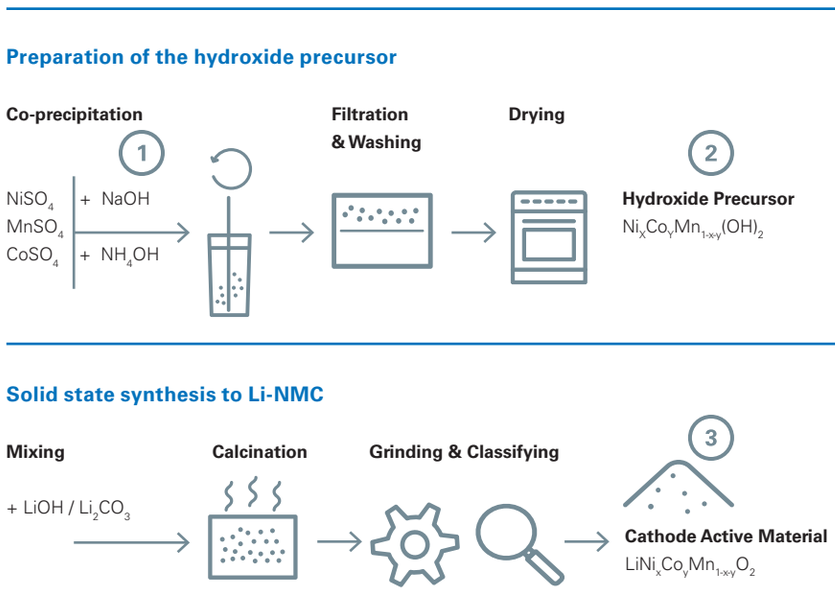


Figure 1 Li-NMC production process.

NMC Quality Criteria

Key quality criteria for NMC cathode active materials are the Ni, Mn, and Co contents and their ratios. These can be accurately monitored using XRF along the production process to ensure that the final CAM is within specifications.

Other elements that can be monitored by XRF for quality and production monitoring purposes include Aluminum (Al), Sulfur (S) and Zirconium (Zr). Sulfur, one the one hand, is usually seen as a contaminant stemming from the production process which often start with the preparation of Ni-, Mn-, Co-sulfate solutions. On the other hand, Zirconium oxide (ZrO_2) and Aluminum oxide (Al_2O_3) are typical additives. Doping or coating with ZrO_2 and/or Al_2O_3 is used to improve the structural stability and electrochemical performance of Ni-rich cathode materials at high voltages and elevated temperatures.

Optimal Spectrometer Configuration

The S2 PUMA Series 2, a versatile, high-performance benchtop EDXRF spectrometer, is an excellent solution for many analytical tasks along the CAM production chain. The optimized beam path, the 50-Watt power X-ray tube, and the HighSense™ Silicon Drift Detector (SDD) ensure short time-to-results in combination with outstanding precision and accuracy.

The XY-Autochanger (Figure 2) enables high sample throughput while remaining completely flexible: You can load mixed batches (liquids, powders, solids …) and load, unload or prioritize new samples at any time.

The ergonomic, easy-to-use TouchControl™ interface of the instrument allows for independent routine operation without external PC. And Bruker's unique SampleCare™ technology protects important system components, such as X-ray tube and detector, guaranteeing high instrument uptime and ensuring low cost of ownership.

Figure 2
S2 PUMA Series 2 with XY-Autochanger and optional automation interface.

Reference Materials, Sample Preparation, Calibration

A set of nine secondary reference materials covering different NMC types (e.g., 111, 424, 532, 662) and including one NCA sample (Ni-Co-Al) was used for calibration. The concentration ranges for the three major (Ni, Mn, Co) and three minor (Al, S, Zr) elements covered by the calibration are listed in Table 1.

The samples were already fine grained. Nine (9) grams of sample powder was mixed thoroughly with 1 gram of wax and pressed into a pellet.

Table 1 Concentration range covered by the secondary reference materials. (*NCA is nominally Mn-free)

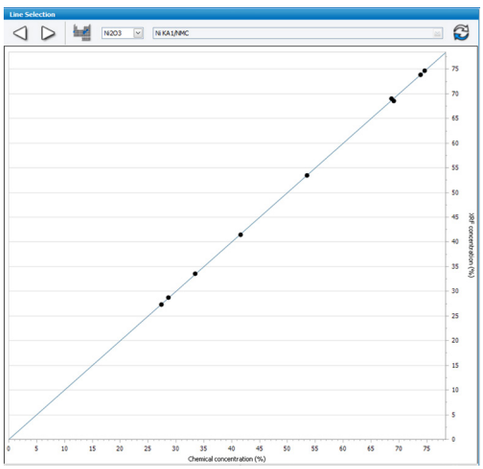
Compound	Concentration Range	R^2
Ni (%)	27.42 – 74.64	0.99984
Mn (%)	0* – 22.21	0.99983
Co (%)	2.94 – 20.42	0.99954
Al_2O_3 (ppm)	280 – 17610	0.99968
SO_3 (ppm)	106 – 4980	0.99856
ZrO_2 (ppm)	523 – 5543	0.99621

Table 2 Measurement conditions

Elemental Lines	Voltage	Current	Filter	Counting time	Sample Rotation	Spot Size	Mode
Al KA, S KA	20 kV	Automatic	None	120 s	On	34 mm	Vacuum
Mn KA, Co KA, Ni KA, Zr KB	40 kV	Automatic	Al (500 µm)	120 s	On	34 mm	Vacuum

The measurement conditions are summarized in Table 2. Vacuum mode was chosen to enhance the sensitivity for Sulfur (S) and Aluminum (Al). If Al and S are not of interest, measurements can be conducted in air mode, without compromising analytical performance for heavier elements (e.g. Ni, Mn, Co, Zr).

Figure 3 displays the calibration curve and peaks for Ni KA. To ensure representative analysis, sample rotation and a large 34 mm spot size were used, addressing the inherent inhomogeneity of powder and pellet samples.



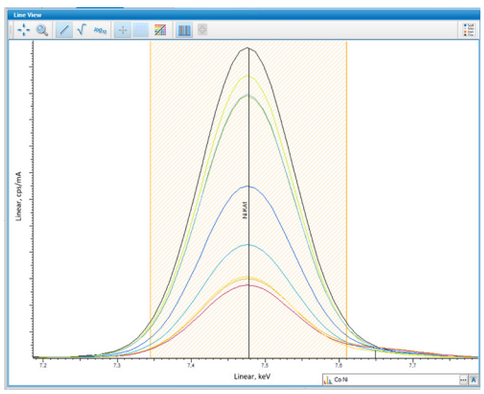


Figure 3
Ni KA calibration curve (left) and peaks (right).

Analytical Performance

The analytical performance was tested by analyzing the Li-NMC certified reference material BAM-S014 ten times. The results are summarized in Table 3 revealing an outstanding precision and accuracy for Ni, Mn, Co and S. Another repeatability test was performed on a Li-NMC powder with unknown composition. The results demonstrate again excellent precision for Ni, Mn, and Co as well as for lower contents of S and the important additives Al and Zr (Table 4).

Table 3 Repeatability and accuracy test. CRM BAM-S014 (NMC 111) was prepared as pressed powder pellet and measured 10 times.

Rep#	Ni (%)	Mn (%)	Co (%)	S (ppm)
BAM S-014_1	19.48	18.18	19.64	1384
…	…	…	…	…
BAM S-014_10	19.47	18.18	19.64	1374
Average	**19.48**	**18.18**	**19.64**	**1377**
Std.Dev.	**<0.01**	**<0.01**	**0.01**	**7**
Rel.Std.Dev.	**0.03%**	**0.04%**	**0.05%**	**0.50%**
Certifed value	**19.76**	**18.22**	**19.80**	**1421**

Table 4 Repeatability test. A Li-NMC powder with unknown composition was prepared as pressed powder pellet and measured 10 times.

Rep#	Ni (%)	Mn (%)	Co (%)	Al (ppm)	S (ppm)	Zr (ppm)
NMC_1	48.62	2.72	6.95	2162	210	2312
…	…	…	…	…	…	…
NMC_10	48.63	2.72	6.95	2203	214	2252
Average	**48.63**	**2.72**	**6.95**	**2181**	**217**	**2283**
Std.Dev.	**<0.01**	**<0.01**	**<0.01**	**79**	**8**	**27**
Rel.Std.Dev.	**0.02%**	**0.18%**	**0.08%**	**3.63%**	**3.87%**	**1.18%**

Conclusion

This lab report showcases the excellent performance of the S2 PUMA Series 2 in production and quality control of Li-NMC cathode active materials. Utilizing HighSense detector technology, vacuum mode, large spot size (34 mm) and sample rotation, it delivers accurate results in under 10 minutes, including pressed pellet sample preparation. Opting for pressed pellet preparation and vacuum mode minimizes operational costs (e.g., no Helium gas, no plastic cups for powders).

Several options are available to tailor the analytical approach to your needs. For example, sample preparation time can be reduced by measuring the CAM powder directly in disposable plastic cups. And, if lighter elements are not of interest, measurements can be conducted in air mode and using a single kV range. This reduces the measurement time substantially without compromising analytical performance for Ni, Mn, and Co.

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