

X-RAY FLUORESCENCE

Battery Cathode Active Material: At-Line Process and Quality Control

Lab Report 181

Introduction

Batteries in electric vehicles (EV) are responsible for a major part of the car manufacturing costs. Within the batteries, the cathode active material (CAM) is the most significant cost driver, making process control and optimization important tasks for a cost-effective production.

There are several types of batteries often differentiated by their CAM. Lithium-ion NMC batteries, for example, are frequently used in EVs and portable electronics. 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, costs, cycle life, and safety of the battery.

Depending on the production process, different contaminations e.g., due to raw material impurities or incomplete solvent recovery, may affect the CAM purity and thus the cell quality and safety. Typical contaminants include, Sodium (Na), Aluminum (Al), Sulfur (S), Chromium (Cr) and Iron (Fe).

This lab report highlights the use cases of X-ray fluorescence (XRF) along the CAM production chain and shows the performance of the S2 PUMA Series 2 energy-dispersive XRF (EDXRF) spectrometer for liquid NMC precursor quality control.

Common types of Cathode Active Materials

Cathode Active Materials play a critical role for the battery performance, safety, and the production costs. Most common CAMs are:

- **Li-Ni-Mn-Co-Oxide (NMC)**, $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$
- **Li-Ni-Co-Al-Oxide (NCA)**, $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$
- **Li-Fe-Phosphate (LFP)**, LiFePO_4
- **Li-Mn-Oxide (LMO)**, LiMn_2O_4

The CAM production is different for each type but involves similar steps and analytical needs. In this report we focus on Li-NMC.

Li-NMC Production: Where to use XRF?

There are different ways to produce Li-NMC. One of the more common approaches is depicted 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).

Another important application of XRF is the identification and quality control of cathode and anode **raw materials**, e.g., sulfates, phosphates, hydroxides, carbonates, graphite, copper-foil, and aluminum-foil.

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.

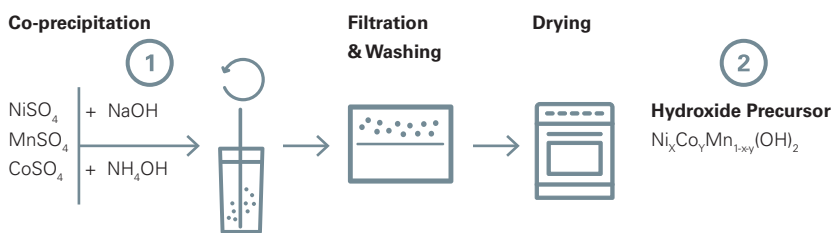
The ergonomic, easy-to-use TouchControl™ interface of the instrument allows for independent routine operation without external PC. And Bruker's unique SampleCare™ technology protects important system components, such as X-ray tube and detector, guaranteeing high instrument uptime and ensuring low cost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

Automated At-Line Production Monitoring

In high-throughput CAM production environments, fully automated analysis can be inevitable. The S2 PUMA is ready for the task!

- Samples can be fed directly, via robot or belt
- Full LIMS compatibility for data exchange
- Dedicated AXSCOM communication interface connects to the process control software
- Buffer sample positions compensate for delays in the lab automation
- The EasyLoad™ tray can be used for out-of-line samples

Preparation of the hydroxide precursor



Solid state synthesis to Li-NMC



Figure 1



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

Sample Preparation – Easy, Fast, Reproducible!

The optimal sample preparation depends on the sample type and analytical requirements. The latter includes the required time-to-result and analytical precision for the elements of interest. Fine grained powders like Cu-sulfate salt can be measured without any treatment in sample cups with a thin polymer foil at the bottom. For the analysis of coarser powders, a short-grinding step (1-2 min) will help to improving sample homogeneity and result quality. If light element like F or Na in powders are of interest, e.g., in hydroxide precursors, the samples need to be pressed into pellets. Pressed pellet sample preparation is easy, reproducible and takes only 1-2 minutes.

For this report, reference materials and **liquid precursors** have been measured in liquid cups equipped with a 4 µm Prolene® foil. A pipette was used to load 5 mL of sample into a cup.



Measurement Parameters

A S2 PUMA Series 2 equipped with a XY-Autochanger and a 50-Watt X-ray tube with Pd target was used for the analysis. The measurement conditions were optimized to enable short time-to-result combined with high precision (see Table 1). The sample rotation was switched on and a large 34 mm spot size was used to obtain most representative results.

Table 1 Measurement parameters.

Element line	Voltage	Primary filter	Mode	Measurement time	Sample Rotation
Mn KA1	40 kV	Al (500 µm)	Air	60 s	On
Co KA1					
Ni KA1					

Reference Materials and Calibration

A set of aqueous Ni-, Mn-, and Co- sulfate reference solutions was prepared for the calibration of the instrument. The weighed-in properties were used to determine the reference metal concentrations. The calibration curves for the three element lines are shown in Figure 3 and the peaks are displayed in Figure 4.

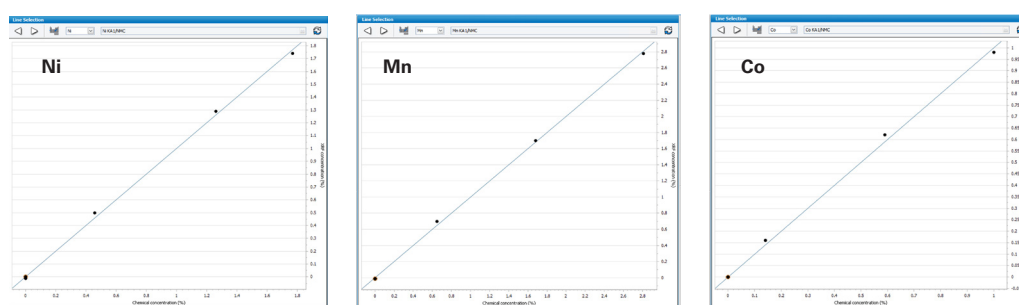


Figure 3
Calibration curves for Ni KA1, Mn KA1, and Co KA1 (left to right).
 R^2 (Ni) = 0.99901,
 R^2 (Mn) = 0.99952,
 R^2 (Co) = 0.99849.

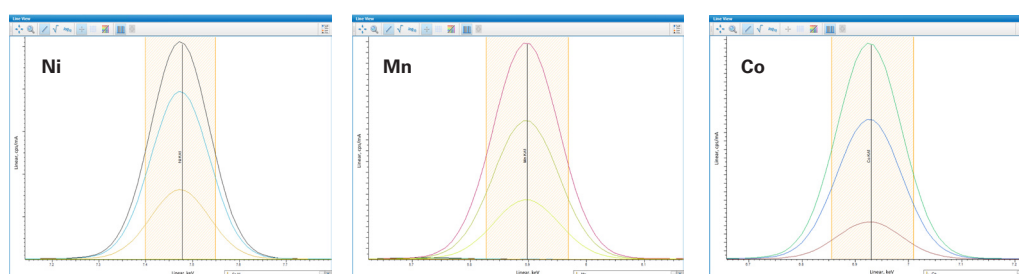


Figure 4
Peaks and integration range (orange shaded area) of the reference solutions: Left to right: Ni KA1, Mn KA1, Co KA1.

Results: Analytical Performance

A liquid precursor solution with a nominal 6:2:2 (Ni:Mn:Co) molar ratio was prepared to test the analytical repeatability. A fresh sample was prepared for each measurement. This way we are not just testing the analytical precision but also the influence of the sample preparation. The results highlight that the Ni/Mn/Co stoichiometry of liquid precursors can be verified within very tight thresholds (see standard deviation in Table 2).

Table 2 Results of NMC 622 repeatability test.

Sample ID	Ni ratio	Mn ratio	Co ratio
622_1	5.901	1.968	2.004
622_2	5.894	1.965	1.999
622_3	5.908	1.968	2.005
...
622_12	5.900	1.972	2.005
Average	5.907	1.969	2.007
Std.Dev.	0.008	0.002	0.004
Rel.Std.Dev.	0.1%	0.1%	0.18%

Conclusion

The S2 PUMA Series 2 is an excellent solution for production and quality control along the CAM production chain. It can handle different tasks, from raw material identification to precursor monitoring and final CAM quality control. It enables rapid and accurate determination of the metal stoichiometry (Ni:Mn:Co, Ni:Co:Al, Fe:P) in CAM intermediate and final products as shown in this report for liquid NMC precursors. The advanced detector technology of the Series 2 allows us to achieve outstanding results in no time: Prepare a liquid cup, pipette 5 mL sample into the cup, load it onto the XY-Autochanger, start the measurement on the TouchControl™, check the results on the screen!

All done in a few minutes!

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