X-RAY FLUORESCENCE

Analysis of recycled NMC battery "black mass" powder

Lab Report 180

Introduction

Batteries in electric vehicles are responsible for a major part of the car manufacturing costs and contain a lot of critical resources, such as Lithium or Cobalt. Its recycling recovers materials from used batteries, reduces environmental impacts, and promotes sustainable resource management. It addresses the issue of battery waste due to the increasing demand for batteries in various industries.

The procedure involves sorting, dismantling, and separating different battery chemistries. Advanced technologies extract and recover metals like lithium, cobalt, nickel, and manganese. These materials can be reused in new batteries or other industries, reducing the need for mining.

Battery recycling conserves resources, reduces waste, and prevents the release of harmful substances.

There are several types of batteries often differentiated by their cathode active material (CAM). Lithium-ion NMC batteries, for example, are frequently used in electric vehicles and portable electronics. They have high energy density, excellent power capabilities, and relatively lower cost. Their CAM consists of Lithium, 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 N:M:C ratios affect the performance, cost, cycle life, and safety of the battery.

During the recycling process, cathode "black mass" powder is being produced and it's (sub-type) purity needs to be checked. This lab report shows the performance of the S2 PUMA Series 2 energy-dispersive X-ray fluorescence (EDXRF) spectrometer for the analysis of NMC "black mass" powder.

What is battery black mass?

Black mass is a graphite-containing black powder. It is a mixture of electrode materials, binders, additives, and electrolyte residuals. The grain size and homogeneity can differ substantially.

How is black mass produced?

There are several process routes for the recycling of lithium-ion batteries. Different steps can be combined, typically involving dismantling, mechanical crushing & separation, pyrometallurgy and hydrometallurgy. The black mass is produced during mechanical crushing and separation. In the hydrometallurgical step, the metals in the black mass (Li, Ni, Co, Cu, Fe) are being separated to produce high purity metal salts.

Why is elemental analysis needed?

There are mainly two reasons to analyze the black mass: for process control and to determine the value per ton. The analyses enable process monitoring of the mechanical crushing and separation step and ensure that black mass with appropriate quality is transferred to the hydrometallurgical step. The metal contents and NMC-type purity define the value of the black mass.

Optimal Spectrometer Configuration

The S2 PUMA Series 2, a versatile, high-performance benchtop EDXRF spectrometer, is an excellent analytical solution for black mass analysis. 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 1) enables high sample throughput while remaining completely flexible. You can load mixed batches (liquids, powders, solids …) and load, unload or prioritize samples at any time.

The large spot size of 34 mm in diameter combined with sample rotation allows to obtain highly representative results even for slightly heterogeneous samples like black mass.

Bruker's unique SampleCare™ technology protects important system components, such as X-ray tube and detector. Combined with the high-duty air filter, the S2 PUMA is ready for harsh and dusty environments. This guarantees high instrument uptime and ensures low cost of ownership.

Sample preparation

To enable fast process control, the reference materials and unknown samples were prepared as pressed pellets. The powders were pressed for 60 s at 25 tons.

A grinding step was not necessary since NMC black mass powders were already fine grained and homogenous (based on visual inspection).

However, if the powders are coarser or rather heterogenous, grinding the material for a few seconds can be beneficial (examples shown in Figure 2).

Figure 1
S2 PUMA Series 2 with XY-Autochanger for highest flexibility and sample throughput

Figure 2
Typical black mass powder samples. *Left:* Homogeneous sample, ready for immediate analysis as powder or pressed pellet. *Right:* Coarser, rather heterogeneous sample containing, e.g., Cu particles.

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 analyze. The measurements conditions (Table 1) were optimized to enable short time-to-result combined with high precision results even for trace element contaminants like Aluminum. Automatic current adjustment was selected to achieve the highest possible count rates for all samples. Vacuum mode was used for best light element performance and lowest operation costs, i.e., no expensive helium (He) purging gas needed! 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	kV	mA	Primary Filter	Mode	Time (s)	Sample Rotation
Co KA1, Mn KA1, Ni KA1, Zr KA1, W LB1	40	Automatic	Al (500 µm)	Vacuum	60	On
Al KA1	20	Automatic	none	Vacuum	60	On

Calibration

The compositions of the reference materials used for the calibration are provided in Table 2. The calibration curve and peaks for Ni are shown in Figure 3.

Table 2
Composition of the reference materials used for the calibration.

Standard	Co (wt%)	Mn (wt%)	Ni (wt%)	Al (ppm)	W (ppm)	Zr (ppm)
1	20.14	18.81	20.07	965.8	7922	1624
2	19.65	18.38	19.58	1063	8574	1546
3	1.57	19.29	38.4	970	1.57	1.57
4	6.41	15.86	36.47	–	–	–
5	11.76	10.9	35.74	1871	2720	1657
6	3.04	1.66	53.53	813	–	1414
7	3	0.61	56.35	334	–	1637
8	4.23	15.93	39.49	1084	2262	1612
9	4.31	16.03	39.44	1072	2044	1585

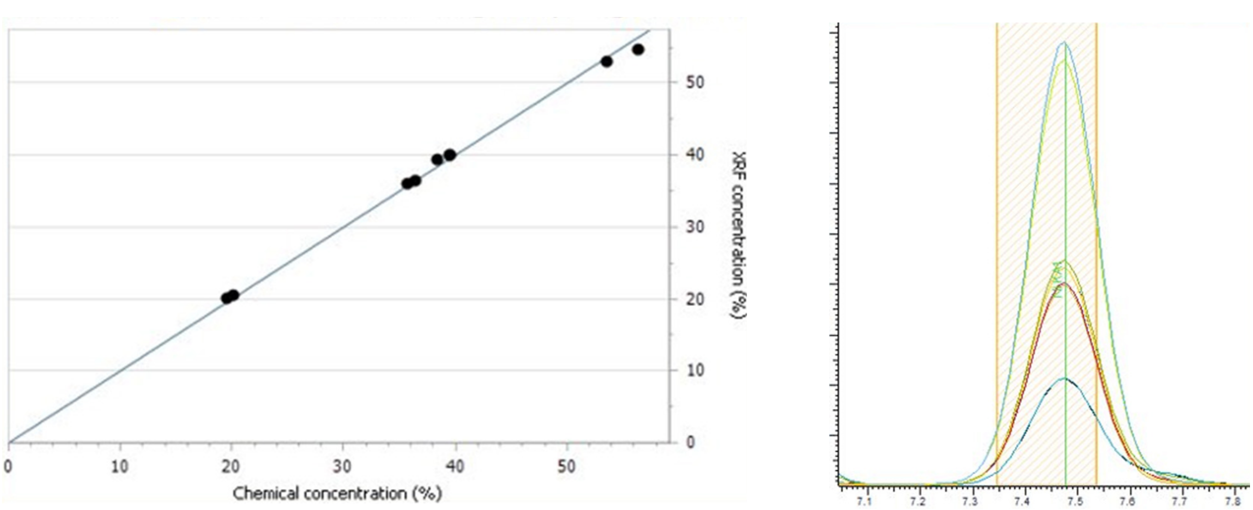

Figure 3
Ni KA1 calibration curve and integrated peaks; standard deviation 0.81%, R^2 = 0.99775.

Results

The analytical repeatability was tested by analyzing two unknown samples. The results reveal an excellent precision even for the trace elements Al, W, and Zr (see Tables 3 and 4). The NMC molar ratios for both samples are close to the common NMC type 631. The measured ratios can be used as a process control parameter to monitor the varietal purity after mechanical shredding and, thus, to verify the presorting and material input processes.

Table 3
Results of repeatability test 1.

Sample 1	Co (wt%)	Mn (wt%)	Ni (wt%)	Al (ppm)	W (ppm)	Zr (ppm)	N (Ni,mol%)	M (Mn,mol%)	C (Co, mol%)
Average	41.28	16.38	4.45	569	–	420	6.53	2.77	0.70
Std. Dey	0.02	0.02	<0.01	6	–	18	<0.01	<0.01	<0.01
Rel. Std. Dev	0.05%	0.12%	<0.01%	1.04%	–	4.26%	0.02%	0.07%	0.06%

Table 4
Results of repeatability test 2.

Sample 2	Co (wt%)	Mn (wt%)	Ni (wt%)	Al (ppm)	W (ppm)	Zr (ppm)	N (Ni,mol%)	M (Mn,mol%)	C (Co, mol%)
Average	39.69	15.68	4.32	1274	1772	1521	6.53	2.76	0.71
Std. Dey	0.06	0.03	0.01	14	27	11	<0.01	<0.01	<0.01
Rel. Std. Dev	0.16%	0.16%	0.13%	1.14%	1.53%	0.70%	0.04%	0.06%	0.11%

Conclusion

The high analytical precision demonstrates the excellent suitability of the S2 PUMA Series 2 to determine the elemental composition of recycled NMC black mass powder. The advanced detector technology of the Series 2 allowed us to achieve outstanding counting statistics in just 120 seconds. In combination with the optimized workflow, the time-to-result, including sample preparation and automatic sample handling by the XY-Autochanger, was about 5 minutes.

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