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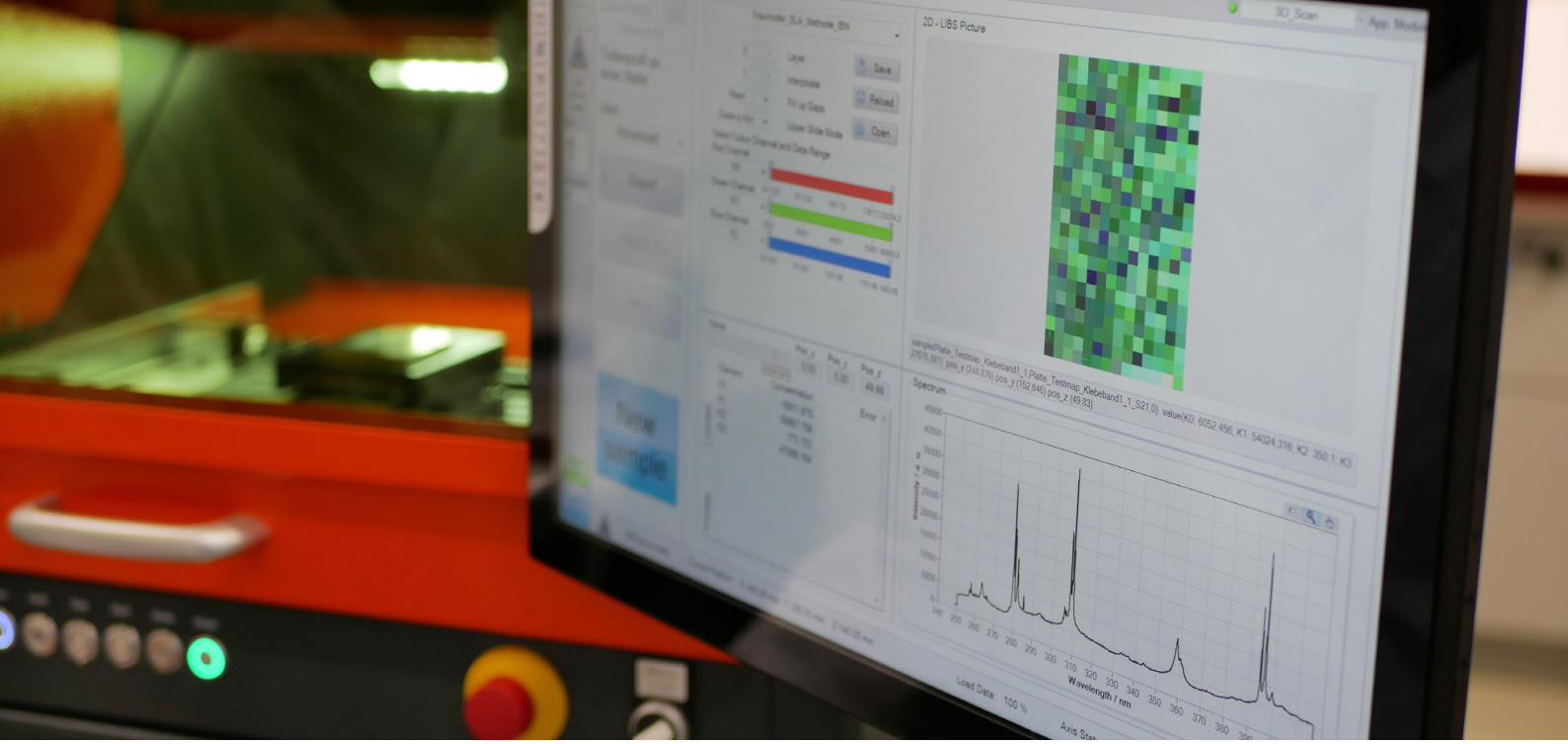
White Paper

Quantitative Analysis of Cathode Material of Lithium-Ion Batteries by Laser Induced Plasma Spectroscopy (LIBS)



Introduction

In lithium-ion batteries, mixed oxides of different compositions are used as cathode material. Nowadays, a mixed oxide of cobalt, manganese and nickel is primarily used. During the production of the batteries, but also during the recovery of the so-called »black mass«, a mixture of anode material (graphite) and cathode material (mixed oxide) resulting from mechanical recycling, it is necessary to monitor the composition.

Up to now, measurement techniques such as X-ray diffraction (XRD), laser scattering or scanning electron microscopy (SEM) have been used for quality control in this area. These techniques can only provide a limited indication of the composition of the material. Therefore, complex offline analytical methods such as X-ray fluorescence analysis (XRF) or optical emission spectrometry using inductively coupled plasma (ICP-OES) are used. Concepts for in-situ measurement of material composition can make a significant contribution to process optimization and quality monitoring.

Laser induced breakdown spectroscopy (LIBS) is a method for sensitive elemental analysis that has recently been developed to industrial suitability. As a nearly non-destructive measurement method, LIBS combines adequate lateral resolution and sufficiently high sensitivity with very short analysis times. With suitable reference materials, quantification is possible. Thus, LIBS offers a unique possibility for inline monitoring of process stability and/or product quality.

This study was performed to demonstrate the usability of LIBS analysis for the quantitative determination of the composition of cathode material from lithium-ion batteries. For this purpose, various samples of Li, Mn, Co, Ni, and graphite were measured in the range of 0 to 40 wt.%. From the data obtained, calibration curves of the individual elements were generated. Potentially, this can be used to monitor material flows both in recycling and in the production of cathodes for lithium-ion batteries.

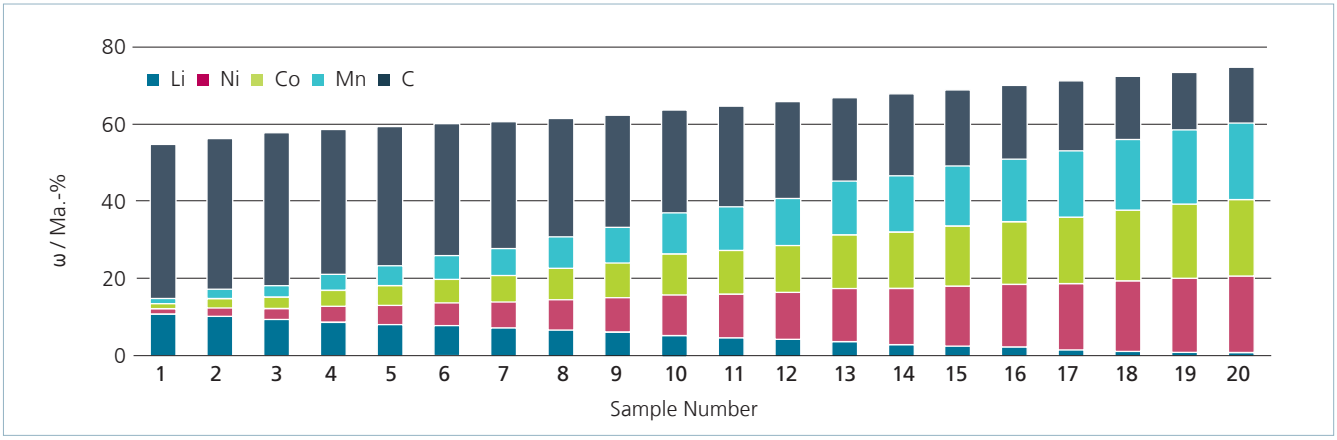


Figure 1: Composition of the measured calibration samples.

Experimental

Sample Preparation

For quantitative analysis of cathode material from lithium-ion batteries, samples of known composition of $LiCO_3$, Co_3O_4, MnO_2, Ni powder and C (in the form of graphite) were weighed. The obtained samples were mixed by a ball mill and measured in the form of a pressed tablet.

A total of 20 samples were prepared and measured, each with varying contents in the range of 0-10 wt.% (Li), 1-20 wt.% (Co), 1-20 wt.% (Mn), 1-20 wt.% (Ni) and a C content between 13-43 wt.%.

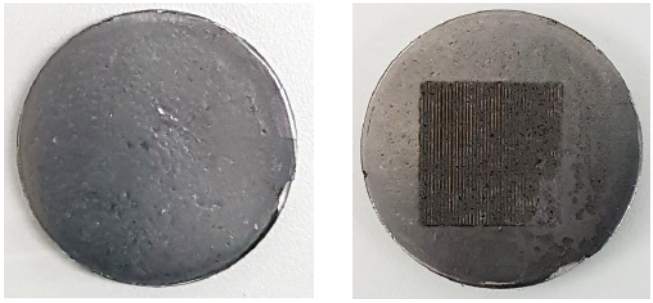


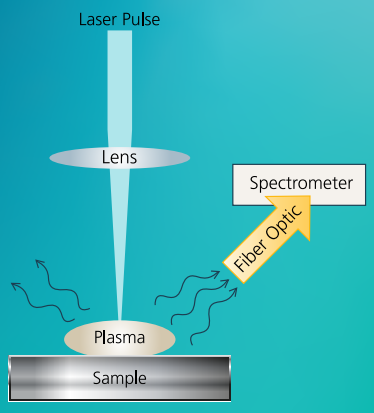
Figure 2: Pressed pellet of $LiCO_3$, Co_3O_4, MnO_2, Ni and C before (left) and after (right) a typical LIBS measurement.

LIBS Analysis

For this work, a LIBS laboratory instrument based on a Nd:YAG laser with a wavelength of 1064 nm (FiberLIBS, SECOPTA analytics GmbH) was used. The samples are mounted in a sample holder system. The focal height of the samples was determined using the 4-point measurement mode, where only the

Measuring Principle of LIBS

A high-energy laser pulse is irradiated onto the surface to be examined. The high intensity of the exciting radiation leads to heating, vaporization and partial ionization of a part of the sample surface. Since only a short period of interaction and ablation of the material takes place, there is hardly any heat transport into the sample. The recombination of electrons and ions produces a characteristic radiation which allows a precise elemental determination.



focal height of the four corner points was determined, while all other points were interpolated.

All samples were analyzed with a x/y grid of 200 x 200 points with an increment of 0.1 mm in each direction. Thus, the measured area was 20 mm x 20 mm. The analysis was performed »while motion« with one laser pulse per integration time (shot per burst) at a laser shot repetition rate of 1000 Hz. In each case 200 spectra in a vertical line were averaged directly during the measurement. A further averaging of the values was obtained in each case from all even-numbered and non-even-numbered spectra, so that exactly two averaged spectra per sample were available for the calibration curve. The partial least square (PLS) method of the instrument-specific software SEC Analyzer was used for evaluation.

The spectra were processed by means of various filters, in which both the wavelength ranges were limited and a normalization was carried out. For the elements cobalt, nickel and carbon an additional smoothing of the spectra was performed. By means of the PLS method, not only complete calibration curves were generated, but also the corresponding detection limits and coefficients of determination of the calibration curves were calculated.

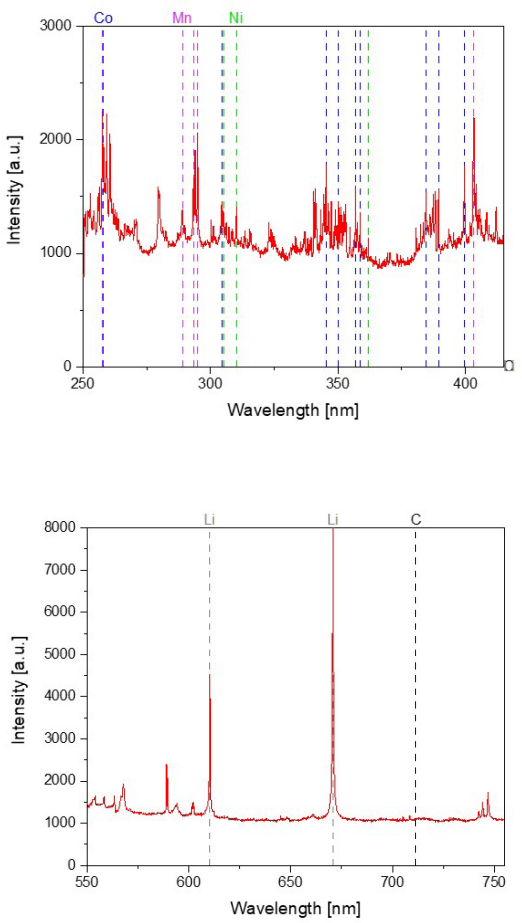


Figure 3: LIBS spectrum in the UV region (top) and VIS region (bottom) with markings of the Mn, Co, Ni and Li lines.

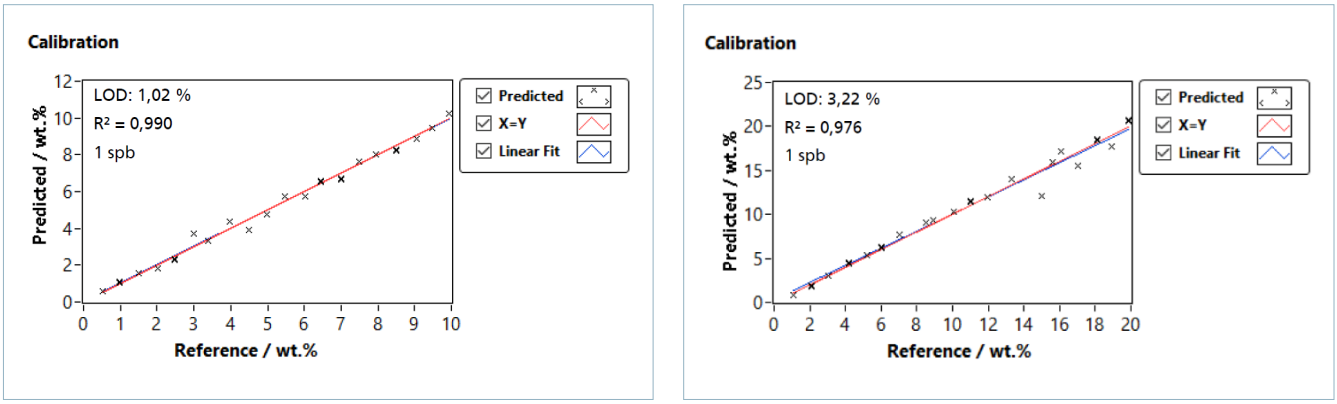


Figure 4: Calibration curves for lithium (left) and nickel (right).

Results and Discussion

Calibration curves could be generated for all elements investigated. Figure 4 shows the calibration curves for lithium and nickel as examples. The calibration curves have a high coefficient of determination and sufficiently low limits of detection (LOD).

Table 1: Limits of Detection (LOD) and Coefficients of Determination of the Calibration Curves

Element	ω / Ma.-%	LOD / %	R²
Li	0-10	1,02	0,99
Mn	0-20	6,33	0,92
Co	0-20	5,99	0,91
Ni	0-20	3,22	0,98
C	10-40	6,17	0,97

For the nowadays used mixed oxides, such as NMC622 (lithium-nickel-manganese-cobalt oxide), NMC532, NMC111, NCA (lithium-nickel-cobalt-aluminum oxide) and LCO (lithium-cobalt(III) oxide), these detection limits are sufficient (see Figure 5). The low cobalt and manganese contents in NMC811 are very close to the detection limit. An extension of the calibration to Fe and P to also analyze the cathode material of lithium iron phosphate (LFP) batteries will be considered in the future.

During the production of cathode material for lithium-ion batteries, the composition can be determined and possible production errors detected. In the recycling process the obtained stream of cathode material can be analyzed and stoichiometrically supplemented with fresh oxides to form a reusable cathode material. Combined with the low measurement time in the range of a few seconds and the low sample consumption, LIBS offers a powerful method for quality or incoming goods control of mixed oxides and »black mass« in the production and recycling of lithium-ion batteries, which is potentially inline-capable.

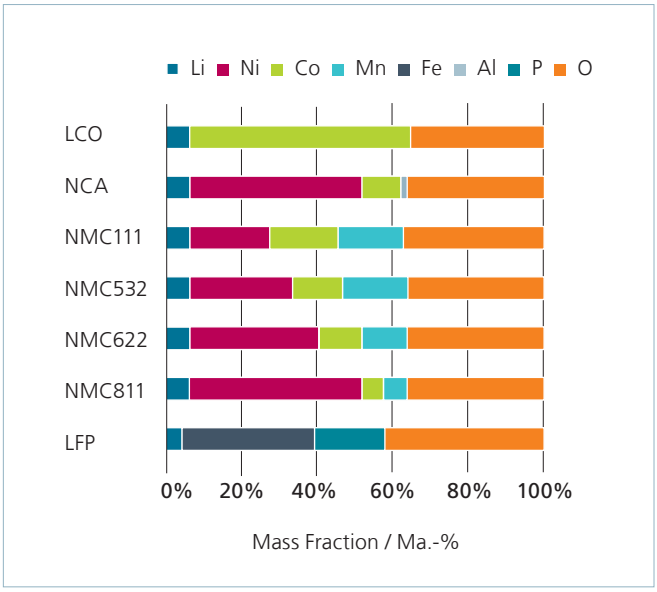


Fig. 5: Element Content in Weight Percent According to Cathode Technology.

Imprint

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