APPLICATION NOTE

Measurement of Battery Materials with Laser Diffraction - an overview

Introduction

The optimization and safety of lithium-ion batteries in the reduction of cell aging is very important. In this case one of the most critical factors is the particle size of the active materials like cathode, anode and separator material.[1] In figure 1 the general set up of a lithium-ion battery is shown.

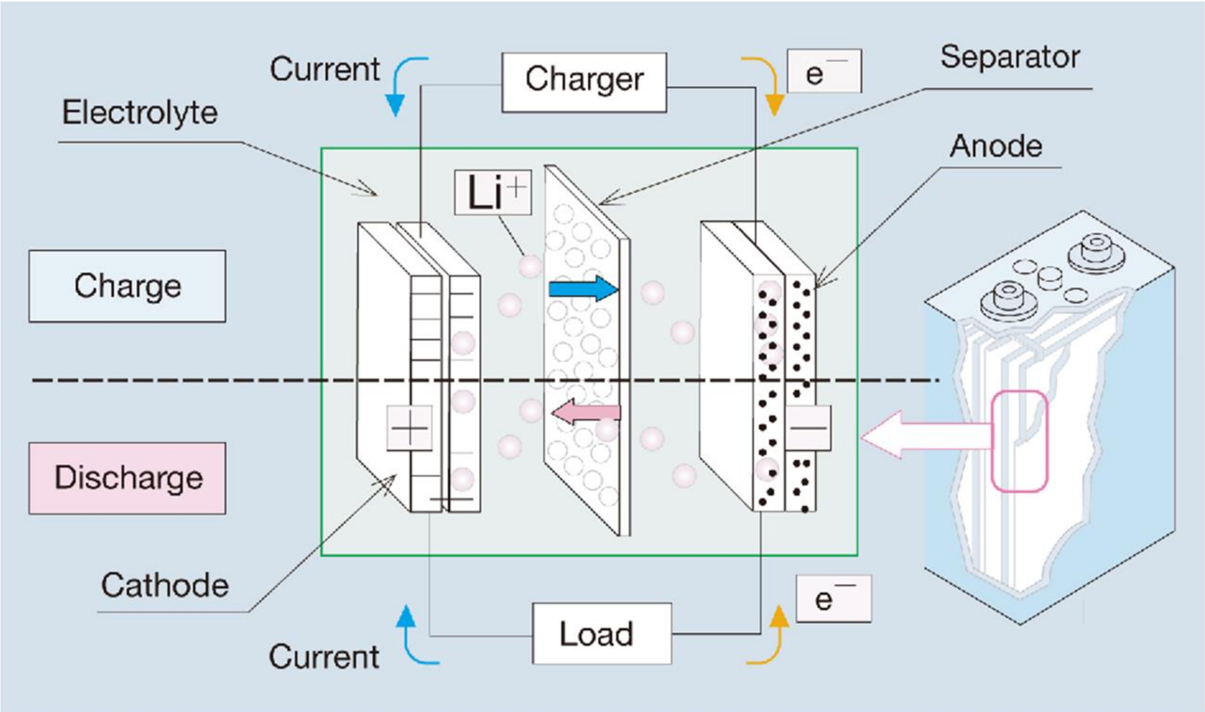
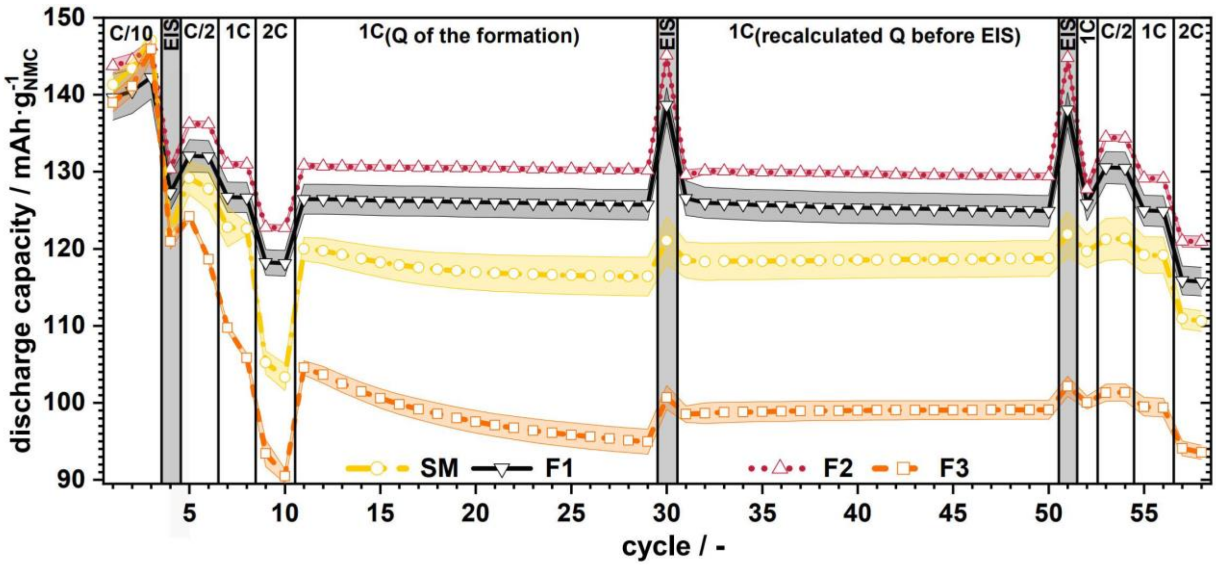


***Figure 1**: setup of a lithium-ion battey.[2]*

The particle size of anode, cathode, and separator material affects the electrochemical performance of batteries. A smaller particle size will lead to shorter pathways in solid materials and decreased over potential leading to improvements in the charge/discharge rate (C rate).[1]

Smaller particle size results in larger surface area which leads to a larger proportion of passivation at the solid electrolyte interphase which can reduce battery capacity. This loss of capacity will be irreversible.[1]

The following example shows how important the particle size distribution is for the charging and discharging process and the aging of the battery. In Figure 2 the specific discharge capacity vs. cycles for full cells of materials with different particle sizes are shown.[1]



Sample	X_{10} / µm	X_{50} / µm	X_{90} / µm	X_{98} / µm
SM	1.44	12.90	28.63	39.62
F1	0.84	1.53	2.82	4.01
F2	3.96	5.86	8.65	10.43
F3	10.34	17.45	30.89	69.68

***Figure 2**: Specific discharge capacity vs. cycles for full cells with source material (SM) and F1 to F3 with C-rate variations; the coloured range indicates the corresponding standard deviation.[1]*

In Figure 3 is shown which materials used in the manufacture of batteries.

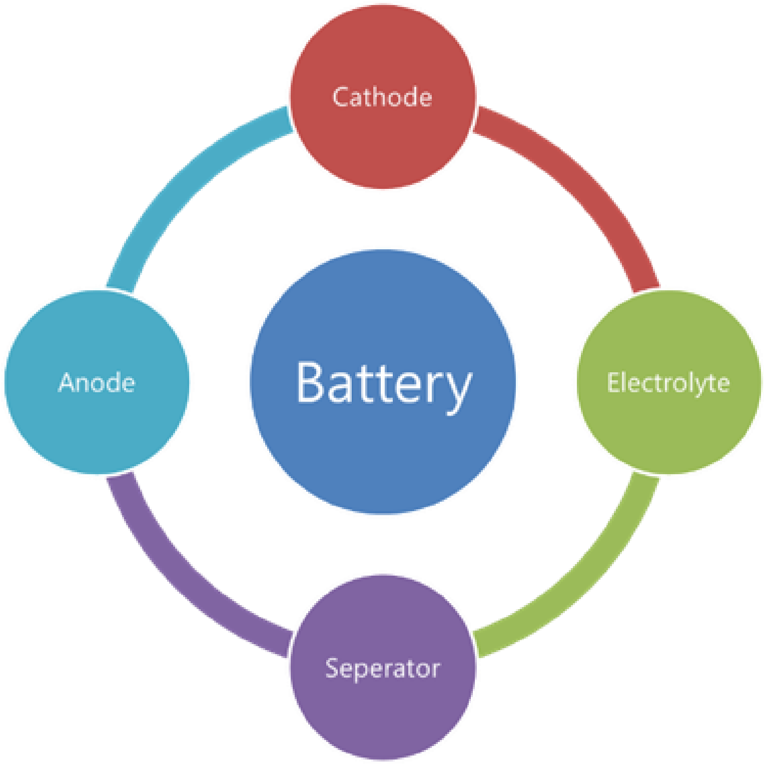


***Figure 3**: Battery Components*

In the present example, the particle size distributions of all battery components were investigated by laser diffraction (ISO 13320) methods. The analyses were carried out in aqueous or isopropanol dispersions. The measuring device used was the SYNC analyzer from Microtrac, which has a measuring range of 10 nm to 4 mm and is suitable for all types of powders and dispersions. The camera, which is available as standard, allows dynamic image analysis (ISO 13322-2) to be performed in addition to laser diffraction, thus providing information on the particle shape. Likewise, the sensitivity for small amounts of oversize particles is significantly increased by the image analysis.

Laser Diffraction (LD) and Dynamic Image (DIA) Measurement

With the SYNC, Microtrac MRB extends its established Tri-Laser technology with a powerful image analysis that offers users a new, unique measurement experience. Particle size measurement by laser diffraction (LD) is the most widely used technology in research and industry and is considered the standard for quality control. The measurement is based on the interaction of laser light with particles in a dispersion. This produces a scattered light pattern that is recorded over an angular range of 0.02 - 163° using Microtrac MRB technology, allowing the size distribution to be calculated. The SYNC uses two detector arrays and three lasers. The analyzer can be equipped with red lasers or a combination of red and blue lasers (Figure 3).

Small particles scatter light to large angles, while large particles scatter light to small angles. The evaluation is performed using Microtrac MRB's innovative modified Mie scattering theory. This algorithm provides accurate particle size distributions for both round and non-spherical particles as well as for transparent, reflective, and absorbing materials.

Modern particle analyzers are often expected to do more than simple size analysis. Dynamic Image Analysis (DIA) provides important insights into particle shape and thus detailed information on physical material properties. While laser diffraction only provides an equivalent diameter based on the assumption of spherical particles, image analysis can separately evaluate length and width of the particles in addition to shape parameters. A particle stream illuminated by stroboscopic light source is photographed by a high-resolution digital camera, and a video file of the particle stream is created from the images.

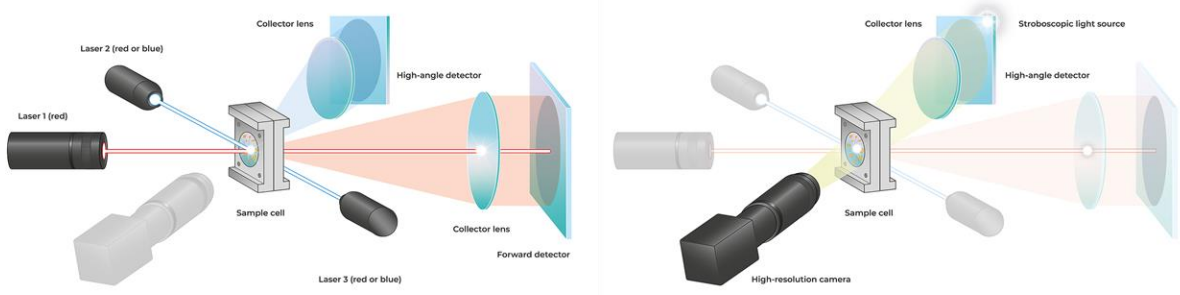


Figure 4: *Optical design of the SYNC analyzer. For laser diffraction (left), three red or blue lasers and two detector arrays are used. Dynamic image analysis (right) is performed in the same measurement cell using a stroboscopic light source and a camera. The particles are detected as shadow projections.*

Samples

Anode material:

- spherical graphite anode material measured in isopropanol (IEP)
- Synthetic Graphite and milled Coke were measured in IEP, water with Triton X and dry shown in Figure 5.

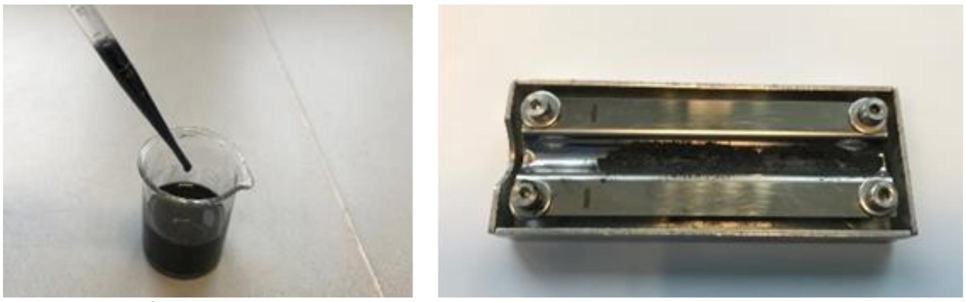


Figure 5: *wet and dry sample preparation of milled Coke*

- Silicon Anode Material

Cathode material:

- Some cathode material

Separator:

- Some separator material

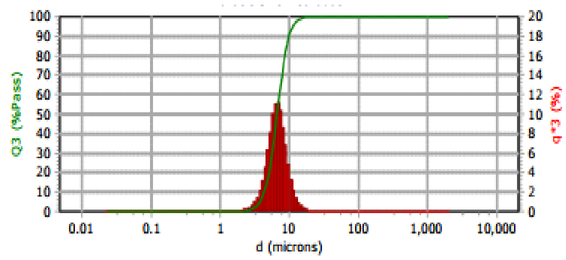
Electrolyte:

- Solid State Electrolyte

Results

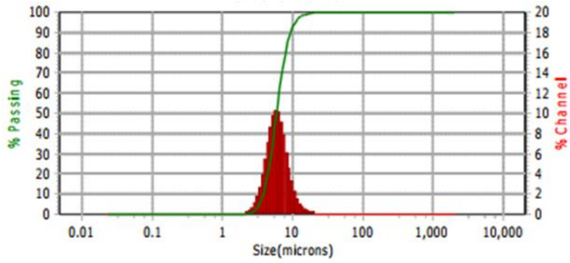
The first results shown in Figure 6 are particle size distributions of a) a silicon anode material, b) a cathode material, c) solid state electrolyte and d) a separator material.

A silicon anode material



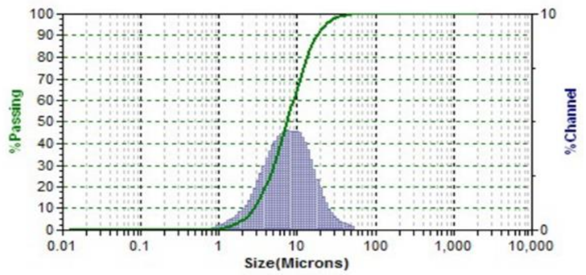
X_{50} = 6.57 µm

B cathode material



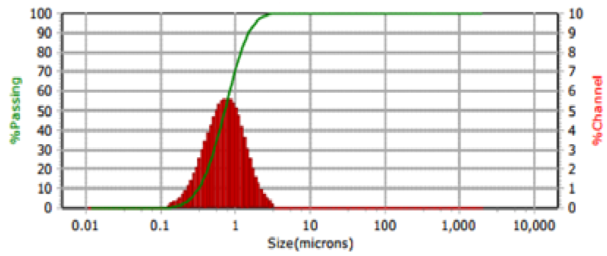
X_{50} = 5.89 µm

C solid state electrolyte



X_{50} = 7.45 µm

D separator



X_{50} = 0.72 µm

Figure 6: *different battery materials*

In the next measurements performed with Sync some synthetic graphite and milled coke were measured in isopropanol, water with Triton X as a dispersant and the original powder was measured in the dry mode with our TurboSync. In table 1 can be clearly seen that we have a very good reproducibility between all three different types of measurement.

Table1: *Results of the comparison of different methods to measure the particle size*

percentile	**Graphite IPA**	**Graphite water**	**Graphite dry**	**Milled coke IPA**	**Milled coke water**	**Milled coke dry**
X_{10} / µm	7.16	6.93	7.15	1.89	1.98	2.22
X_{50} / µm	12.22	11.95	12.38	9.26	9.93	8.71
X_{90} / µm	24.82	22.44	27.30	22.46	21.41	23.73

Figure 7 shows the corresponding passing curves of the measurements detailing the repeatability attained from the different measurement methods. The left side shows the graphite sample and the right side the milled coke.

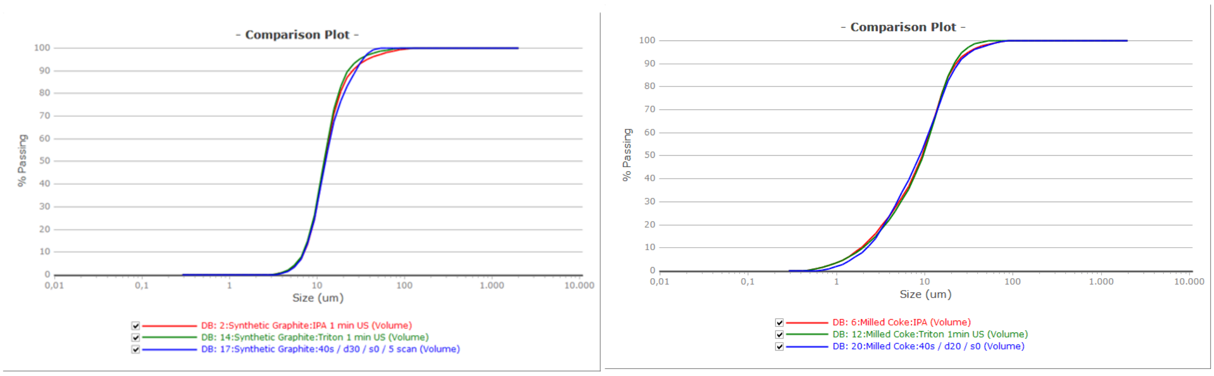


Figure 7: passing curve of graphite (left) and milled coke (right). Red was measured in IPA green in water and blue was the dry measurement.

As well as a laser diffraction measurement the SYNC also made a dynamic image analysis (DIA) - at the same time, in the same flow path, in the same sample cell, with the same software. Here can be seen the strength of the combination of both methods and the benefit of Microtrac's patented blend algorithm which shows both results in one graph. For example, it can be used for detection of oversized particles like shown in Figure 8 and 9.

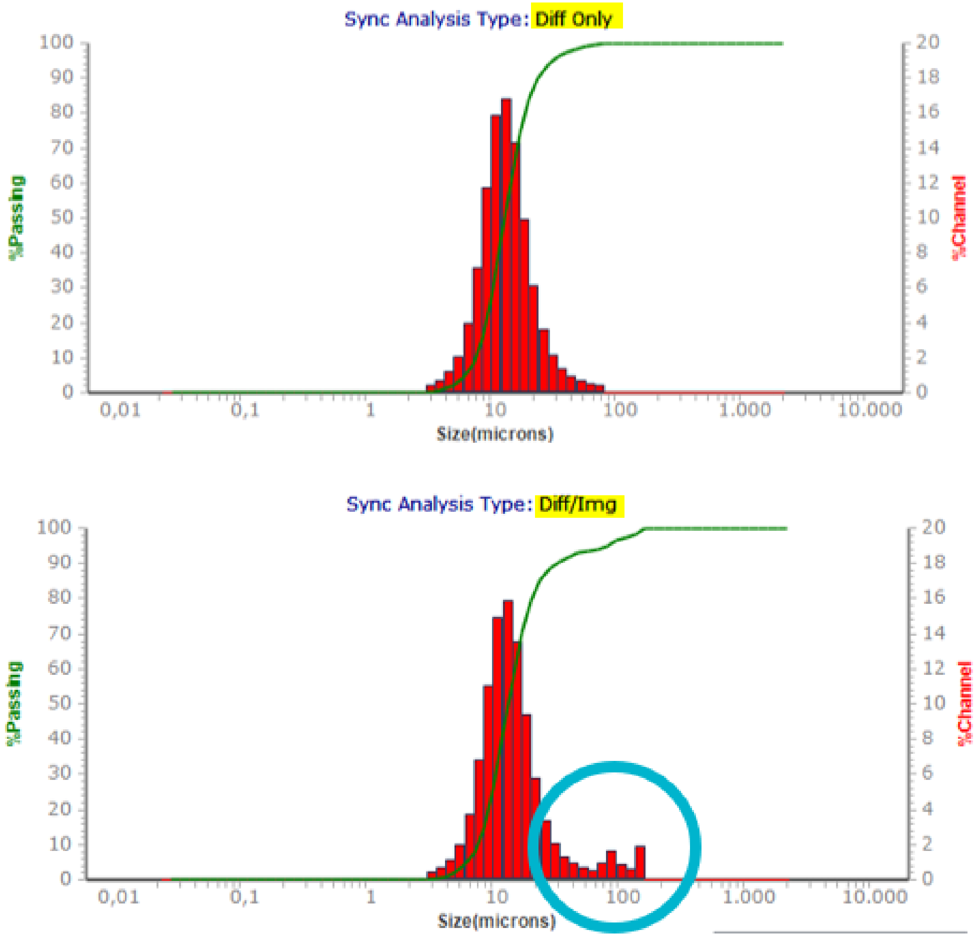


Figure 8: *Compare of a Laser Diffraction only and blend result of synthetic graphite*

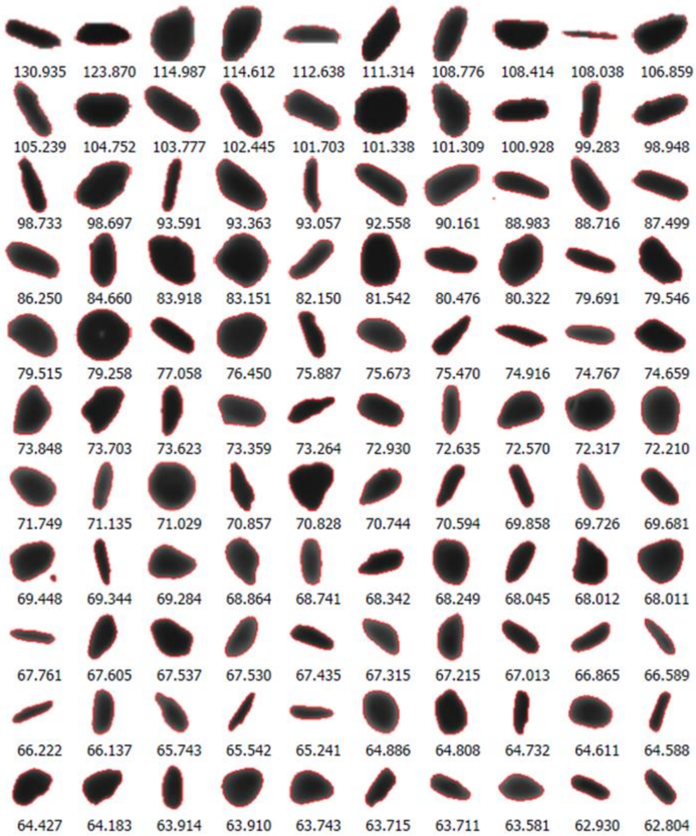


Figure 9: *Image of some oversized particles in synthetic graphite sample*

A similar result was also obtained for the milled Coke.

Also, a spherical graphite anode material was analyzed with the Sync. Here the sample was dispersed in isopropanol. In the laser diffraction result shown in Figure 10 a X_{50} was reported of 8.2 µm.

Summary		Percentiles		Size Percent		Peaks Summary		
Data	Value	%Tile	Size(um)	Size(um)	%Tile	Dia(um)	Vol%	Width
MV(um):	9.17	10.00	4.19			8.2	100	7.84
MN(um):	3.23	20.00	5.47					
MA(um):	6.92	30.00	6.44					
CS:	8.66e-1	40.00	7.32					
SD:	3.92	50.00	8.20					
		60.00	9.18					
Mz:	8.69	70.00	10.35					
si:	4.24	80.00	11.95					
Ski:	0.2621	90.00	14.85					
Kg:	1.212	95.00	18.27					

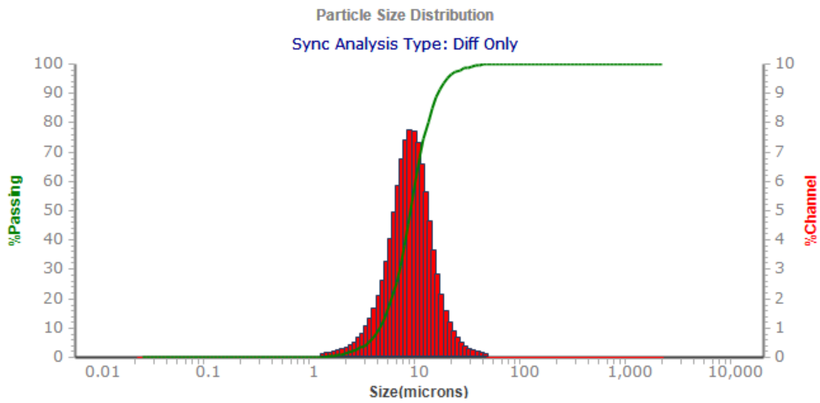


Figure 10: *Particle size distribution of the Laser Diffraction result from the Sync*

During this measurement also the DIA of the SYNC was used to measure the sphericity of the particles. In this case the benefit of the combination of LD and DIA is shown. Figure 11 shows the particle distribution in Da (Area equivalent diameter) and the sphericity. A value of 1 means a perfect spherical particle. From the scatter diagram it is seen that the most particles will be nearly spherical but also some non-spherical are present in the sample

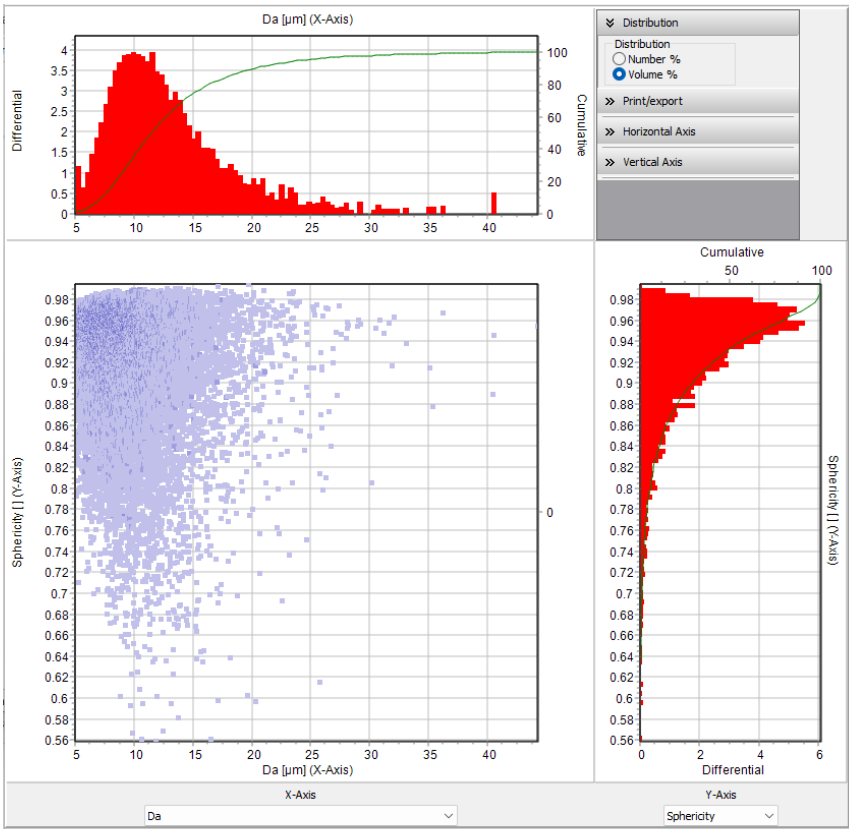


Figure 11: *Scatter diagram shown the area equivalent diameter vs. sphericity. The scatter diagram shows the location of each particle in the sample with respect to the value plotted on the top X-axis and the Y-axis on the right. Sphericity (scale of 0.56 to 1), 1 would be a perfect sphere.*

Also, images of the particles were taken and can be shown in figures 12a spherical and 12b non-spherical particles.

A **B**

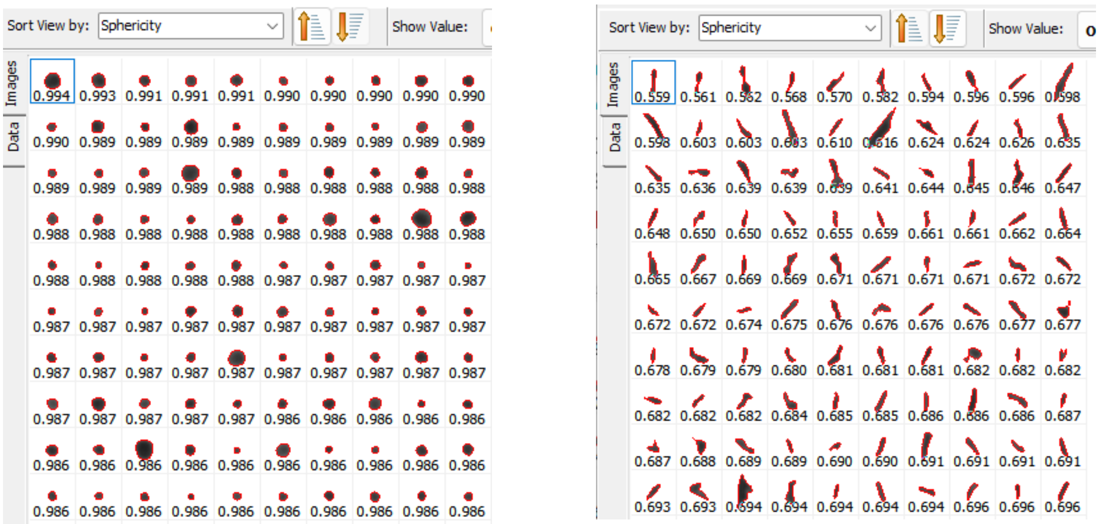


Figure12: *A few selected particles were shown as an example for a) spherical particles and b) non - spherical particles*

Summary

Laser diffraction is suitable for fast and easy characterization of battery materials with a measurement time of only a few seconds. Since the measuring device rinses and cleans itself automatically, sample run times of 1-2 minutes are realistic. Excellent reproducibility and flexible application possibilities characterize the method. Reliable evaluation algorithms for reflective particles provide reliable results.

The simultaneous use of image analysis significantly increases the probability of detecting small amounts of oversize particles.

Literature

{1} BLÄUBAUM, Lars, et al. Impact of Particle Size Distribution on Performance of Lithium-Ion Batteries. *ChemElectroChem*, 2020, 7. Jg., Nr. 23, S. 4755-4766.

[2] HASHIMOTO, Tsutomu, et al. Development of Grid-stabilization Power-storage Systems Using Lithium-ion Rechargeable Batteries. *Mitsubishi Heavy Industries Technical Review*, 2011, 48. Jg., Nr. 3, S. 48-55.