Lithium iron phosphate

New Insights with the PowMaster Particle Analysis System

Lithium iron phosphate (LFP) is widely used as a cathode material for lithium-ion batteries due to its stability and safety. However, LFP suffers from inherent challenges, including low tap density, poor electronic conductivity, and slow lithium-ion diffusion. These limitations can be mitigated by optimizing LFP morphology and applying a conductive carbon coating.

We used the innovative PowMaster system—a particle analyzer that simultaneously measures the mass and diameter of individual particles— to investigate a commercial LFP powder. Our results 1) reveal a **bimodal particle size distribution** due to the poor quality of the carbon coating, 2) offer **new insights into LFP particle structure** and 3) measured a **median LFP particle mass of 150 femtogram** (fg; femto – 10^{-15})

Analyzing LFP with the PowMaster

The PowMaster gives insight into the carbon coating and the structure of the LFP itself. In the diagram, such an exemplary data set is shown. The blue diamonds show the number-weighted distribution of the particle mass and diameter. The grey circles show the effective particle density calculated from the mass and diameter. The most striking observation is that the commercial LFP contains two very different types of particles. The heavy and large particles (m_{50}: 150 fg; d_{50}: 660 nm) are the LFP particles themselves. They only make up 41% of the particles by number, but since the individual particles are heavy, they contribute 99.4% of the total mass. The lighter particles (m_{50}: 1.1 fg; d_{50}: 120 nm) are isolated carbon particles that are not firmly attached to the LFP-core particles.

	LFP-core particles	Isolated carbon particles
Number - fraction	41 %	59%
Mass - fraction	99.4 %	0.6%
Particles per gram	$1.84 \cdot 10^{12}$ #/g	$2.60 \cdot 10^{12}$ #/g
preF / scaling factor	$4.48 \cdot 10^{-6}$	$2.26 \cdot 10^{-6}$
Df / structural index	2.77	2.58
Number-weighted distribution / median values		
m_{50}	150 fg	1.1 fg
d_{50}	660 nm	120 nm
ρ_{50}	1.00 g/cm³	1.14 g/cm³
Mass-weighted distribution / median values		
m_{50}	1960 fg	4.3 fg
d_{50}	1660 nm	210 nm
ρ_{50}	0.81 g/cm³	0.93 g/cm³

Table 1: Summary of characteristic data points derived from the PowMaster analysis

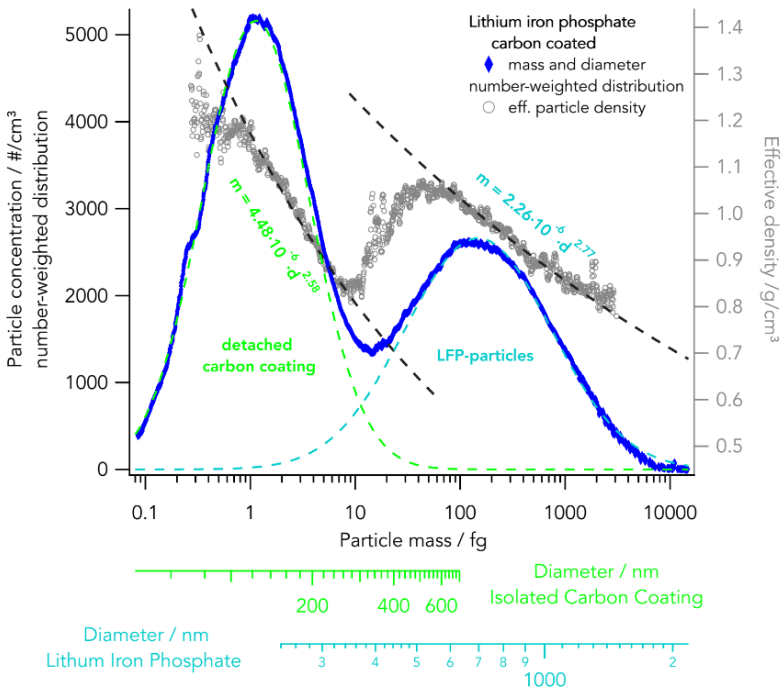

Figure 1: PowMaster analysis of a carbon-coated lithium iron phosphate

For both the carbon and LFP particles, the effective particle density is significantly below the respective material density ($\rho_{graphite}$: 2.2 g/cm³; ρ_{LFP}: 3.47 g/cm³) and declines as the particle becomes larger and heavier. This observation is typical for aggregated and structured particles.
The effective particle density can be understood as a particle packing density. For a particle to be large, more primary particles must be fused together, resulting in more branched-out and open-pore structures with lower densities.
The correlation between the particle mass and diameter can be expressed by a power-law (mass = preF ·dia^{Df}). For the case of perfect spheres, the pre-factor would be preF = π/6·ρ and the structural index (~fractal dimension) Df = 3.
The carbon particles' Df is 2.58, a typical value for carbon blacks, which also have similar particle masses and diameters (see already published application notes on femtoG.com). The Df for the LFP is 2.77, combined with an effective density (ρ_{50}: 1.00 g/cm³) far below the material density of 3.47 g/cm³, indicating that the LFP has a more sponge-like structure than aggregated. This result is typical for sintered primary particles.

Comparison with reference data

In the product data sheet, some information on the morphology and material composition is given and can be reinterpreted with the result presented here.

d_{50} by Laser diffraction size analysis	1.5µm
specific surface area (SSA) by N_2-BET	11 m²/g
Tap density	0.8 g/cm³
Material density / ρ_{LFP}	3.47 g/cm³
Carbon content by mass	1.4 %

Table 2: Reference data for the analyzed LFP

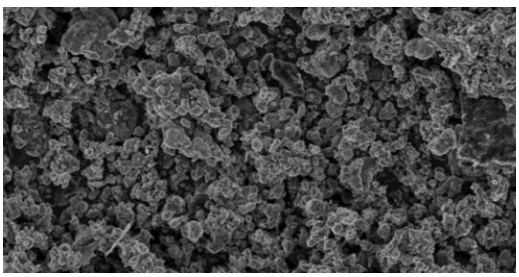

Figure 2: SEM-image of an LFP powder

Focus - LFP Morphology

Particle size and morphology determine the cell's rate performance, conductivity and capacity. Reducing the (primary) particle size is an effective way of increasing the surface area, which increases the total charge transfer rate. However, smaller particles tend to form larger and more open-structure aggregates and thus decrease the interconnectivity of the LFP. With an increase in aggregation level, the tap density increases, which lowers the volumetric energy storage capacity. Producing electrode materials with integrated porosity can provide high surface areas and reduced diffusion distances whilst maintaining superior particle connectivity.
Measuring those particles' true size and porosity (~density^{-1}) is challenging with established particle size analysis methods.

The PowMaster records a number-weighted distribution (q1) of the mobility diameter. Like all equivalent diameters, this is an approximation of the particle's geometric dimensions. Since the particle mass is also measured, a mass-weighted size distribution (q3) can be easily calculated, and a d_{50} of 1.66 µm is obtained. This compares very well with the reference value of d_{50}: 1.5 µm, even though laser diffraction records an optical particle diameter and light-intensity(~volume) weighted distribution. Due to effects like angular scattering overlap, the carbon particles cannot be detected by laser diffraction particle sizing.

Under the simplified assumption that the LFP primary particles are spherical, a PP-diameter of 150 nm can be calculated from its material density and specific surface area (d_{pp}= 6/(SSA·ρ_{LFP})). This diameter is significantly lower than the here-measured diameter of 660 nm (d_{50}, q1) since the LFP particles are aggregated and structured. This high degree of particle aggregation results in a low tap density and a comparatively low volumetric energy storage capacity. The SEM image (Figure 2) gives a visual impression of this observation.

Focus - Carbon Coating

The poor electrical conductivity of LFP has to be mitigated by applying a coating with a conductive carbon. The homogeneous dispersion of conductive carbon within the electrode matrix is crucial for establishing efficient electron pathways. There are different possibilities for distributing the carbon on the surface, ranging from a homogenous surface coating to interspersed carbon particles between the LFP particles. Either way, it is desired that the carbon is firmly attached to the LFP-core particle.
A non-uniform carbon distribution or detached particles result in 1) poor connectivity between active material particles and the conductive network, adversely affecting the electrode's overall conductivity. 2) increase the viscosity in the electrode slurry, and 3) increase the rate of side reactions.
Generally, there are trade-offs in the structures and performance of the carbon particles. Smaller carbon particles or layers tend to attach better to host particles, can enter smaller pores and prevent the LFP particles from unwanted aggregation, larger and aggregated carbon particles provide better electrical conductivity due to the longer continuous carbon chains/networks but can break off more easily.
The here-tested carbon-coated LFP was produced via a solid-state reaction method in which an organic substance was thermally decomposed and formed the elemental carbon that coats the LFP particles' surface. The producer provided no detailed information beyond the total carbon content, which is 1.4%. However, 0.6% of the total mass is made up of isolated carbon particles. This implies that 43% of added carbon is not firmly attached to the LFP particles. At the moment, it is unclear if this is the result of delamination of the carbon coating or if those isolated carbon particles result from unwanted side reactions during the production process.

Optimizing a carbon-coated LFP.

Based on the briefly summarized properties of an LFP, one can make assumptions about the particle structure for an ideal product. Independent of the question whether or not such ideal LFP particles can be produced, the PowMaster system can provide the necessary data to optimize the LFP production. In Figure 3, data for such an idealized LFP is plotted and compared to the product presented here.

1) Reduction of the amount of isolated carbon particles, as those particles contribute little to the increase in electrical conductivity
2) A narrower LFP-particle distribution would reflect a more homogenous LFP. Further, larger aggregates or structured particles would improve the interconnectivity within the cathode
3) A higher fractal index, ideally 3, would imply that the particle density and pore structure for all particles is the same independent of their size, resulting in a more homogenous powder. Based on the analysis of other materials, a fractal index close to 3 also correlates with a high tap density, which is beneficial for a high volumetric energy storage capacity
4) Whether or not an overall higher or lower particle density is ideal remains an open question.

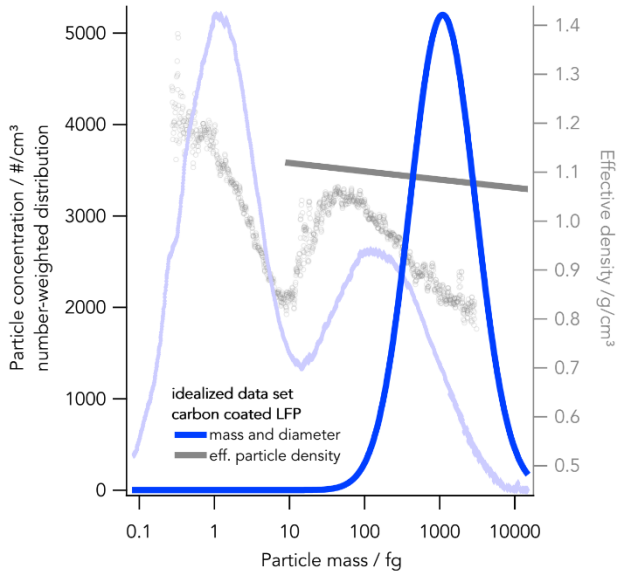

Figure 3 Data set for an LFP with an ideal particle size and structure

Using the PowMaster

If you want to improve the performance and consistency of your battery materials, femtoG can help. Our advanced particle analysis technology offers unprecedented insight into particle size, structure, and coating efficiency—critical parameters for optimizing cathode materials.

Contact us today:
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Find more information on PowMaster here.