Particle size and zeta potential of electrode materials: better characterization, better performance

Relevant for: particle size distribution, particle size, zeta potential

Nowadays the power efficiency of many portable devices such as mobile phones, tablets or speakers is extremely related to the use of rechargeable lithium-ion batteries, which have a high working voltage and a high energy density. In recent years, their application has expanded in various fields such as electric bicycles, electric vehicles, and hybrid vehicles. For this reason, the particle characterization of electrode materials and possible additives is very important for the quality control as well as for the optimization of manufacturing processes in order to produce safe and long lasting batteries.

1 Introduction

One of the most common types of rechargeable batteries are lithium-ion batteries. The main components of lithium-ion batteries are a cathode (positive electrode), an anode (negative electrode) and an electrolyte. The electrolyte provides a medium for the exchange of ions which produces the electricity (1). Most Li-ion batteries have a positive electrode (cathode) made of lithium metal oxides coated onto an aluminium foil and a negative electrode (anode) consisting of carbon (e.g. graphite) coated onto a copper foil (Figure 1).

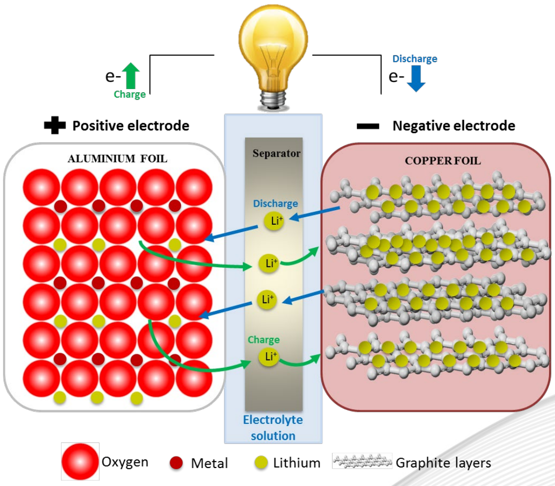

Figure 1: Internal structure of a lithium ion battery

The aluminium and the copper represent the current collectors which transfer the energy to the device (cell phone, computer, car). The lithium ions travel between the anode and the cathode through an electrolyte solution composed of a lithium salt (e.g. LiPF6) dissolved in an organic solvent (e.g. diethyl carbonate), which covers the separator membrane. The latter is responsible for prevention of internal short circuits caused by the flow of electrons inside the battery.

In a typical rechargeable lithium-ion battery (Figure 1), lithium ions move from the negative electrode to the positive electrode during discharge and in the opposite direction when charging (2).

There are different existing types of lithium ion batteries. The choice of electrode materials determines the performance and the uniqueness of the battery.

1.1 Role of the particle size and particle size distribution

Information regarding particle size is relevant not only to ensure the quality of electrode materials over the course of the production process, but also in the design of experiment (DoE) studies for developing new batteries with high performance using simulation processes.

The particle size and size distribution of electrode materials affect the lithium ions diffusion thus changing the power density (current released, loading capability) and the energy density (stored energy, battery capacity) of the produced battery. In Table 1 the main differences related to the particle size are presented.

Table 1: Main differences related to the particle size

	Small particles	Big particles
Diffusion of lithium-ions in the electrode material	Faster because the diffusion path is shorter (3)	Slow because Li ions hardly leave the bulk
Charge/ Discharge time	Short due to the short diffusion path	Long
Degradation due to interaction of the	High due to the higher surface area	Poor

electrolyte at the surface		
Volume changes upon cycling	Small	Large
Resistance to fracture	High	Low
Cycling ability, battery life	Poor, short	Good, long
Power density (current released)	High due to the higher ionic mobility	Low
Energy density (stored energy)	Low: • reduction of void size • reduction of the overall electrolyte volume	High

The particle size distribution (PSD) is also relevant and gives additional information.

Electrode materials with a monodisperse (narrow) particle size distribution of small irregular shaped particles are characterized by a high interaction with electrolyte solution thanks to the higher surface area (4). This determines high energy release (high power) in short time.

A broad PSD with a mixture of big and small particles has a high packing density (Figure 2) and allows to produce high-loading electrode materials (thick electrodes) which contributes to an increase of the energy density (stored energy) (5) (6).

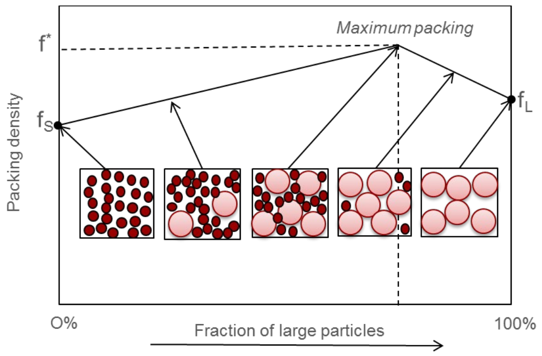

Figure 2: Packing density (f) of a bimodal particle mixture of small and large particles. Fundamentals of Refractory Technology; James P. Bennett & Jeffery D. Smith, Ceramic Transactions, Volume 25, 2001 (American Chemical Society)

1.2 Zeta potential to investigate electrode interactions with conductive additives

The major drawbacks of lithium oxide cathodes are the poor electronic and ionic conductivities (7).

Carbon based products such as carbon black and graphite help to increase the electric conductivity without being involved in the electrochemical redox process in lithium ion batteries. Carbon based products contribute to increased cathode cyclability (how many times a battery can undergo the process of complete charging and discharging until failure) by filling the free spaces in between the particles of the active material (8). By this action the electrode conductivity increases.

The carbon additives should form an homogenous mixture with the cathode material in order to get a stable electrode slurry and a uniform coating on the collectors. For this reason, the electrostatic interactions between different types of particulate material should be maximized by measuring the zeta potential. It is preferred that particles have opposite surface charges in order to initially promote the interaction. Of course, this interaction doesn´t have to prompt aggregation episodes (flocculation, coagulation) in the final mixture of carbon, cathode, binders (e.g. PVDF) and dispersant (e.g. water, organic solvents).

2 Experimental

Particle size analysis by laser diffraction

The particle size analyzer (PSA), based on laser diffraction, was used to conduct the measurements. The electrode materials which were tested for this report are listed in Table 2.

Table 2: Cathode and anode materials selected for the analysis

Cathode	**Anode**
Lithium cobalt oxide (LCO)	Natural graphite
Cobalt lithium manganese nickel oxide (NCM)	Synthetic graphite
Aluminium cobalt lithium nickel oxide (NCA)	

The measurements were performed in liquid dispersion mode and the Mie approximation was used to calculate the particle size distribution. For all lithium-oxide based cathode materials a refractive index of 1.54 with absorbance coefficient 0 was chosen. For the graphite samples, the used refractive index was 2.4 and absorbance coefficient 0.

The samples were dispersed in the liquid dispersion unit and a 0.2 % solution of sodium hexametaphosphate (SHMP) was used as dispersing medium in order to stabilize the dispersion.

Zeta potential by electrophoretic light scattering (ELS)

The pH has an important effect on the zeta potential because it changes the charge of surfaces and nanoparticles suspensions. The change of the zeta potential over pH was investigated to determine the possible interactions between the electrode material and the carbon conductive additives.

The study is focused on the LCO which has a high energy density but low charge and discharge rate which causes insufficient electronic and ionic conductivities and therefore low amount of power is produced (9). LCO can benefit from mixing with carbon based components because the conductivity improves (section 1.2).

The always present demand for green energy requires that materials and solvents used for the battery production are more eco-friendly. The replacement of organic solvents in the electrode slurry with water is the first step towards a high energy sustainability (10).

In this application report water instead of organic solvents (e.g. N-methyl-2-pyrrolidone, NMP) was used to prepare three suspensions:

- 0.05 % carbon black
- 0.05 % graphite
- 0.1 % LCO

For the LCO solution, 1 ml of a 0.01 % Triton X-100 was added to improve the wetting. In order to improve the dispersion of aggregates, the mixtures were homogenized by means of ultrasonic power.

The zeta potential measurements were conducted via electrophoretic light scattering (ELS) in the Litesizer 500 using the dosing unit accessory for automatic pH dependent titration.

3 Results and discussion

3.1 Particle size and size distribution of electrode materials

The median (D50) and the span (indicator of the broadness) were used to characterize the particle size distribution of electrode materials. The difference resulting from the investigated parameters allows defining the quality of the product and estimating the final battery performance.

The LCO shows the largest particle size and the highest span while NCM and NCA have a smaller mean size and a narrower distribution (Figure 3).

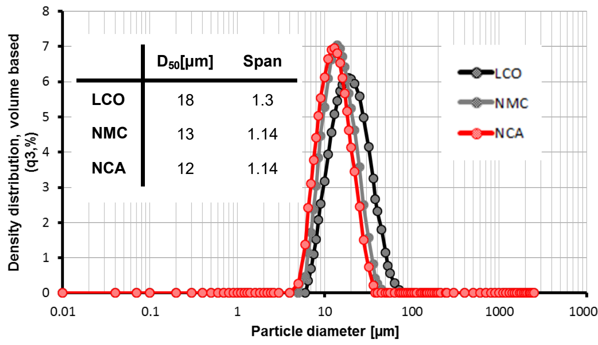

Figure 3: Particle size distribution of three different cathode materials

As discussed in the introductive paragraph, by decreasing the size and the broadness, the ability of the battery to store energy decreases. This happens because smaller particles increase the agglomeration tendency and decrease the void spaces (11). Due to this, the electrolyte volume and therefore the battery capacity will be also low (12).

However, the large surface area given by small particles reduces the diffusion distance within electrodes and helps to facilitate ion exchange between the electrode and the electrolyte (13).

In fact, NMC and NCA samples are cathode materials with a low capacity but high energy density and fast charge (14).

As regards the results of anode materials, it can be seen in Figure 4 how the particle size distributions of natural and synthetic graphite are comparable.

The synthetic one shows a slightly smaller D50 and higher span. In this case, there is no indication for any significant difference in the performance. Nonetheless particle size analysis is a valid quality control tool to verify that the synthetized graphite has the same properties as the natural one.

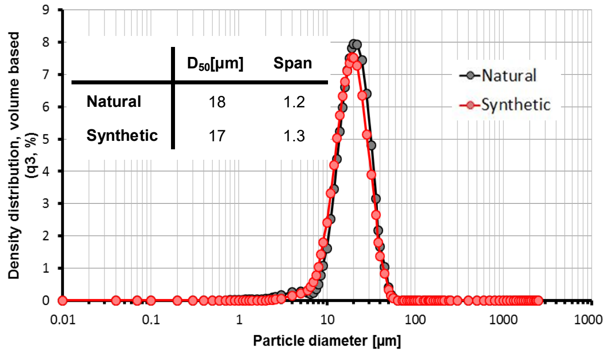

Figure 4: Particle size distribution of natural and synthetic graphite

The percentage of fine fraction was additionally measured in the PSA (Table 3). This information is helpful in the manufacturing phase to estimate the properties and stability of the final battery.

In fact the higher the fine fraction in a polydisperse electrode powder, the denser the packing will be. Therefore, fewer voids between large particles are available for the volume changes caused by lithium ions intercalation during charge/discharge cycles and at the same time the larger surface area favors the contact between electrode and electrolyte (15).

Table 3: Amount of the fine fraction in the electrode material measured by the PSA

Electrodes	Particles < 10 µm [%]
Cathode materials	
LCO	10.6
NMC	22.2
NCA	32.9
Anode materials	
Natural graphite	9
Synthetic graphite	12

The amount of fine fraction has to be controlled and monitored to determine the proper percentage which guarantees the functionality but also the safety. A high percentage of the fine fraction can cause rapid degradation of the battery, because the larger surface area makes it subjected to erosion by the electrolyte, which increases by cycling (surface degradation) (4). Moreover, the high fine fraction can cause problems during the coating process due to the increase of the slurry viscosity (16).

3.2 Zeta potential of LCO and conductive additives

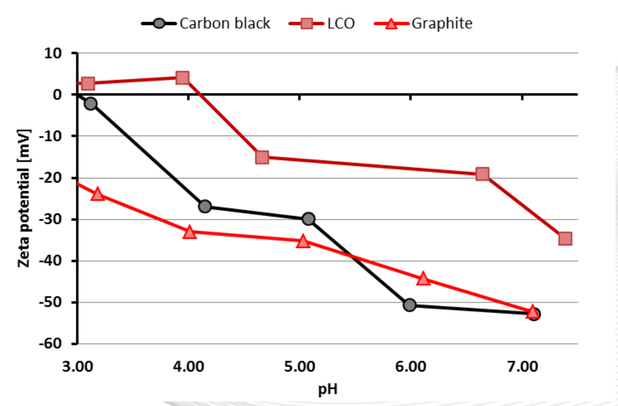

Figure 5: pH dependence of zeta potential for carbon black, graphite and LCO

Figure 5 shows that the carbon black and graphite particles have mostly a negative zeta potential, while the LCO particles have a positive zeta potential below pH 4. This means that in case of an electrode slurry with carbon additives, the pH of the mixture should be adjusted at pH 4 or lower in order to promote the electrostatic interactions between carbon additives and the electrode material.

4 Conclusions

Particle size and zeta potential can provide important information during the manufacturing and quality control phase of lithium ion batteries.

The investigation of electrode materials by laser diffraction allows determining parameters such as the median, the span and the amount of fine fraction.

Finding the right combination is the key to produce batteries with high efficiency and degradation stability.

Recently, the research focus moves towards new solutions to increase the conductivity of electrode materials. In most of them carbon based materials are used as conductive additives. The optimal mixing between different components in the final electrode slurry strictly depends on electrostatic interactions. Therefore, the zeta potential measurements are necessary to obtain a uniform coating with greater resistance to fracture.

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