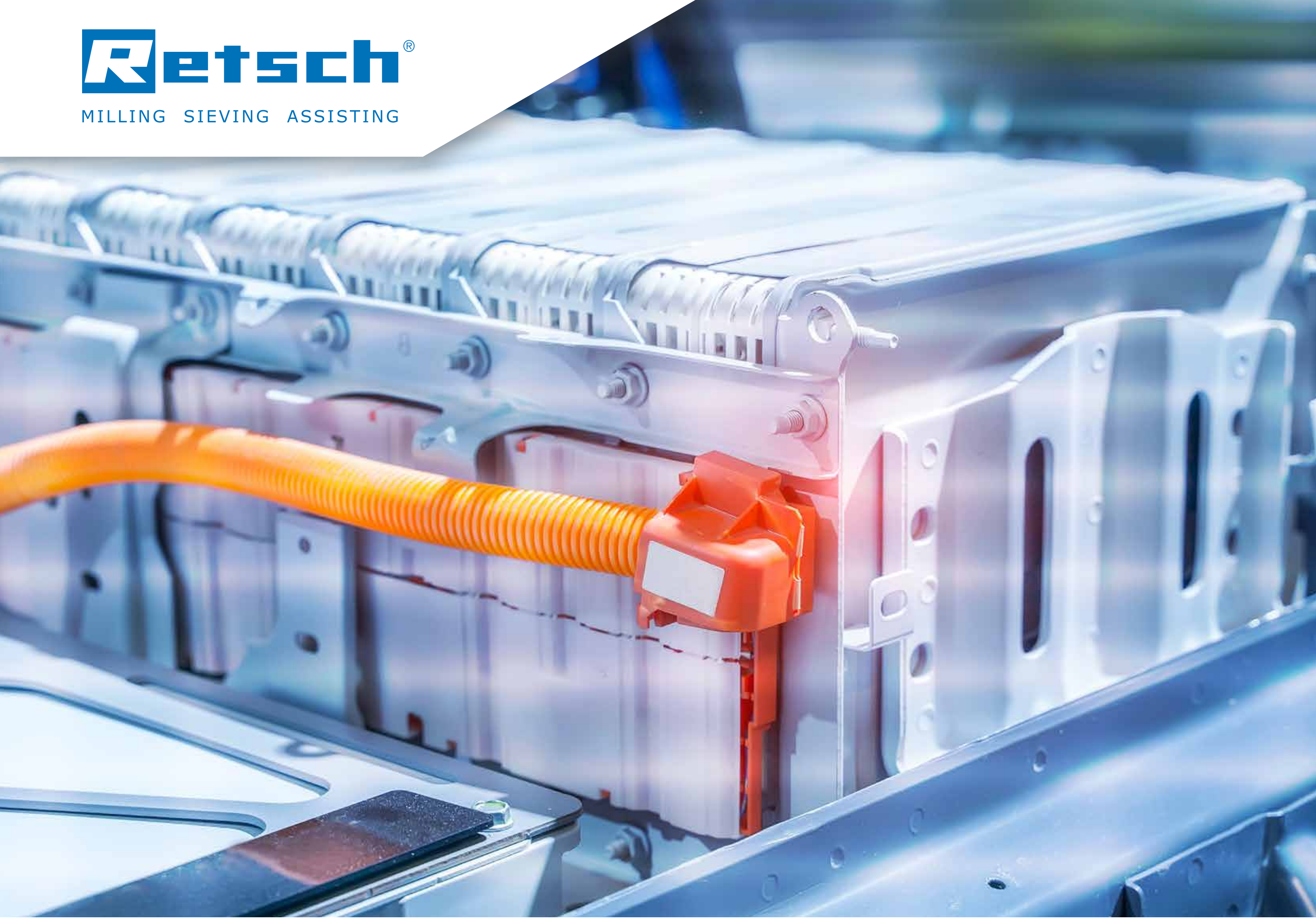

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UNLOCKING THE POTENTIAL: THE ROLE OF BALL MILLS IN BATTERY TECHNOLOGY

From research to manufacturing and quality control, laboratory ball mills play an essential role along the value chain in battery production. First and foremost, the various types of ball mills are used in research and development. Provided they can accommodate the required amount of material to be processed, laboratory mills are also used in pilot plants for small-scale battery production. When it comes to large-scale production processes, agitator bead mills, vibrating bead mills or continuous horizontal axis bead mills are the standard machines. But laboratory ball mills are also indispensable in these Giga factories and recycling plants; they are used for quality control to prepare samples for analysis.

In this white paper, the four main application areas of Retsch laboratory ball mills in battery technology will be discussed. Each area is illustrated by specific application examples:

- **Section 1** **Reducing the particle size of battery materials**
- **Section 2** **Mixing and particle coating**
- **Section 3** **Synthesis of new battery materials**
- **Section 4** **Sample preparation for analysis**

The introductory section focuses on a basic understanding of the functional principle and provides handling guidelines for laboratory ball mills. Additional information on Retsch and other Verder Scientific products is given in the form of side notes - completing the picture that Verder Scientific offers to enable progress in battery technology.

Figure 1: In planetary ball mills, mixer mills and drum mills the jars follow different patterns of movement.

ONE BALL MILL IS NOT LIKE THE OTHER

What makes one ball mill better suited for a specific purpose than another? To understand the factors that differentiate ball mill types, we will first look at their common characteristics. Basically, the working principle of each ball mill is the same: it is based on the concept that the sample material is moved potentially together with grinding balls inside a closed jar. This movement results in strong mixing and crushing effects of the material. The apparent difference, which can be seen immediately, lies in the different way the jars move. The classification of ball mills according to their movement is typically reflected in their names. In a planetary ball mill, for example, a jar rotates on a circular path similar like a planet rotates around the sun, in a mixer mill a jar performs an oscillating shaking movement in a horizontal position and in a drum mill the jar simply rotates around its central axis (see Figure 1).

Ball mills are furthermore characterized by significant differences in the sizes of available grinding jars. Retsch offers mills with jar capacities from 1.5 ml up to 150 l and balls are available from 0.1 mm to 40 mm, see Figure 2.

A third and very important characteristic of a ball mill, which also has a great influence on the result of a milling process, is the power of a mill. Depending on the application, jars should be moved either slowly for gentle material processing or, most commonly, at high speed for effective grinding effects. Here, the maximum speed, which is given as maximum frequency or maximum revolutions per minute (rpm), is often used as a synonym for performance. A more meaningful physical quantity than speed is the acceleration force "g", which is induced by the kinetic energy of a ball mill. In the High-Energy Ball Mill Emax for example, an unrivalled acceleration of 76 g can be obtained, if running at its maximum speed of 2000 rpm.

Figure 2: Examples of different jar and ball sizes used in laboratory ball mills: (a) small metal cups of 2 ml capacity used in Retsch mixer mills and (b) EasyFit jar with a capacity of 500 ml used in a Retsch planetary ball mills and (c) grinding balls of different size.

SELECTING THE MOST SUITABLE BALL MILL

To identify the most suitable ball mill for a particular application, the task and required outcome need to be defined. Sample size, batch volume, process time, available materials of grinding tools and final fineness are the keywords here. Once the application requirements are clear, a suitable mill can be selected. To facilitate this process, Retsch displays the strength and efficiency of each ball mill model in a spider-net diagram, see Figure 3.

A planetary ball mill, for example, offers a big jar volume compared to a mixer mill and shows a high value on this diagonal. A mixer mill in contrast offers various possibilities for temperature control and has a high value in this field. Considering that a single ball mill is most often used for a variety of applications, a good compromise must be found to ensure that all application requirements can be optimally met.

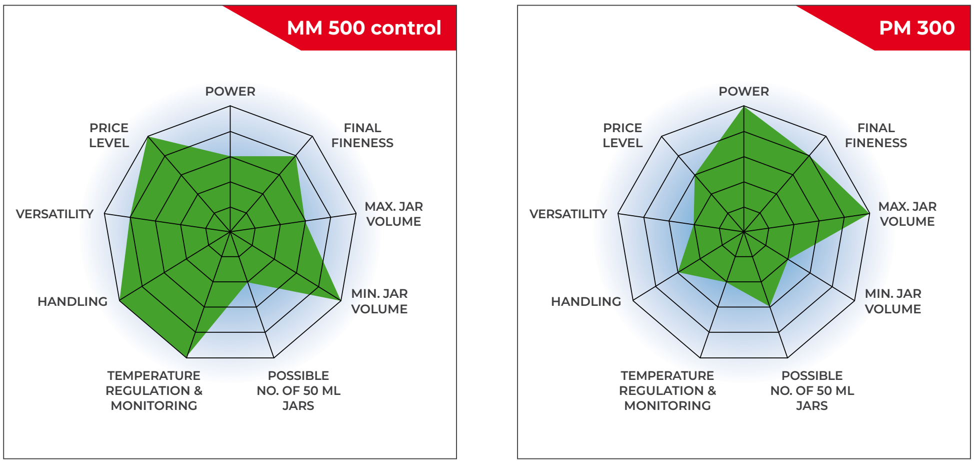


Figure 3: Retsch visualises the features and strengths of each ball bill model in a diagram to help finding the right model for a specific application. In the example shown it is easy to see that the Planetary Ball Mill PM 300 offers advantages in terms of power, final fineness and maximum jar volume compared to the Mixer Mill MM 500 control. The latter in terms offers easier handling, versatility and the ability to control the temperature during the process.

THREE RULES FOR THE OPTIMUM BALL MILL SETUP

In addition to selecting the right mill model, the success of a ball milling application also depends on the correct selection of accessories and process parameters. This includes jar sizes, jar materials, ball sizes, number of balls, material fill level, speed and time or cycle programs. Finding the optimum setup is a challenging task because the result depends on the motion of the balls inside the jar, which is inherently statistical and chaotic in nature.

A simple calculation of their movement is simply not possible and computational simulations are used to derive information about impact and friction effects, which are responsible for the ball milling result, see Figure 4.

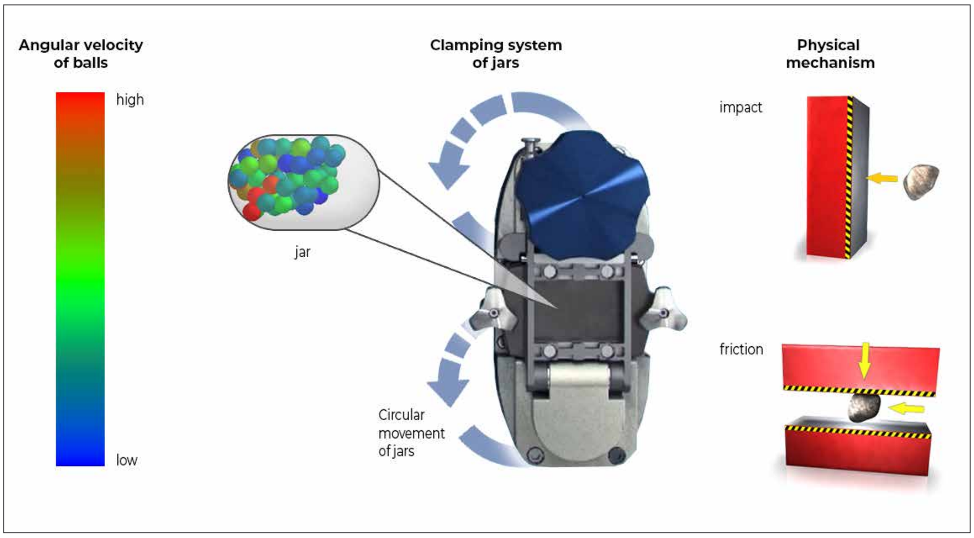


Figure 4: Schematic representation of the statistical ball movement for a specific setup of a High-Energy Ball Mill Emax. The colour of the balls illustrates their different angular velocities. Impact effects and friction are responsible for the ball milling result.

However, a basic understanding, combined with experience and experimentation, also helps to find the optimum accessories and milling parameters. Retsch calls this knowledge the "art of milling". A well-functioning ball milling process can be established by following three basic rules:

Rule 1: Select an appropriate grinding tool material
Grinding tools are generally offered in a variety of materials. The material of the grinding tools should be harder than the sample material and the abrasion of grinding tools should not affect the sample.

Rule 2: Follow the advice for optimal jar filling
The jar filling situation describes the number and size of balls and the amount of sample material. This optimum situation depends on what the mill is used for.

Dry grinding:	In a dry grinding process, the balls should be at least a factor of 3 larger than the largest particle of the sample material. The jar filling situation should follow the 1/3 rule, to protect the grinding equipment and allow for an effective particle size reduction: I 1/3 of the jar volume is filled with material. I 1/3 of the jar volume is filled with balls. I 1/3 of the jar volume is left free space to allow for movement.
Mechanochemistry:	In mechanochemistry, the ball-to-material weight ratio is often higher than 1, accepting the resulting increase in wear and material abrasion of the grinding tools.

SIDE NOTE
PARTICLE SIZE CHARACTERISATION

To characterize the particle size of a powder, sieve analysis can be performed. Retsch offers a wide range of sieve shakers, test sieves and evaluation software for an easy, rapid, reproducible and, above all, accurate analysis. Microtrac MRB, also part of Verder Scientific, offers a wide range of solutions for the characterization of particle size, morphology and porosity. These include various analytical techniques such as dynamic image analysis, laser diffraction, and gas adsorption.

Wet grinding: For final sizes < 5 µm wet grinding is the only option, also called colloidal grinding. In these wet grinding processes, a liquid, e.g. water, alcohol or buffer, is added to the sample to neutralize the surface charges and reduce the attraction of the particles to each other to prevent agglomeration effects. In a wet grinding process, ultra-fine particles are mainly produced by friction. The size of the balls should be at least a factor of three larger than the largest particle of the sample material and a fineness of 1/ 1000 times of ball size can be obtained. For wet grinding

- 2/3 of the jar volume should be filled with the balls.
- The dry sample material is then added in the jar and dispersed manually. Typically, sample material is added as long as it fills the spaces between the balls. Depending on the particle size of the material, sample volume can be as much as 1/3 of the jar volume.
- Finally, liquid is added and dispersed manually until the viscosity is like oil.

Mixing: Mixing can be carried out with any jar filling situation. For mixing, only the sample material/s are inserted in the jar or also balls can be added to the jar together with the sample material. The motion pattern of a mixer mill is particularly suitable for mixing purposes because accelerations are numerous and high. In any mixing process, it is essential to carefully select the jar filling to prevent any undesired reduction in particle size.

Rule 3: Select speed and process-time carefully
High speed produces powerful mixing and crushing effects. This may be necessary, for example, to break up large particles. The horizontal shaking motion in mixer mills generally tends to create more impact effects than in planetary ball mills, which tend to show more friction-dominated processes. However, the intensity of the impacts depends not only on the speed and the movement of the jars, but also on the specific jar filling situation.

Friction is also the main reason why heat is generated in a ball milling process. Heat generation is therefore usually higher in planetary ball mills than in mixer mills. Regardless of the type of ball mill used, if the temperature becomes too high, it may be necessary to reduce the speed, insert grinding breaks or select a set-up with active temperature control.

The longer the process time, the finer the particle size. This is particularly true unless particle size reduction did not yet reach the saturation point, where the particle size does not decrease any more. By increasing the energy input to the maximum speed, process time can often be reduced. However, the fastest processing may not always result in the finest particles due to other effects such as material baking problems or increasing grinding temperatures that in turn may prolong the grinding process due to necessary breaks.

1. BALL MILLING FOR REDUCING THE PARTICLE SIZE OF BATTERY MATERIALS

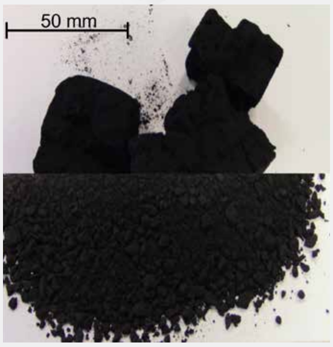
Battery technology uses raw materials such as nickel, manganese, cobalt, lithium or graphite. These materials need to be pulverized for further processing into battery active materials. Even the produced active electrode materials sometimes need to be pulverized and homogenized, e.g. NMC powder after sintering to be used as an electrode. The adjusted particle size and particle size distribution of the active materials significantly define the overall battery performance, like capacity, power density, rate capability, energy density, life cycle stability, and safety.

In this section, three examples are presented out of numerous applications to show how particle size of battery materials can be reduced in laboratory ball mills. Silicon is given as an example of a standard ball milling application, milling of graphite is presented as a challenging milling task and grinding of a solid electrolyte shows an advanced ball milling application that requires the control of temperature and atmosphere.

SIDE NOTE

PRE-CRUSHING OF ELECTRODE MATERIAL IN A JAW CRUSHER

The Jaw Crusher BB 50 can be used to pre-crush brittle battery materials such as NMC material from 40 mm to < 1 mm.



Application example 1: Particle size reduction of silicon

Silicon can store up to ten times more lithium ions than graphite and is therefore used as the basic material for anodes or as an additive to graphite-based anodes in the form of a carbon-silicon composite. With the High-Energy Ball Mill Emax and the Mixer Mill MM 500 nano the particle sizes of silicon can be reduced to d_{90} = 500 µm, see Figure 5. Both mills are characterized by an extremely high energy input of 35 Hz and 2000 rpm, respectively. As shown in the figure, the resulting final fineness and particle size distribution depend on the chosen ball mill setup.

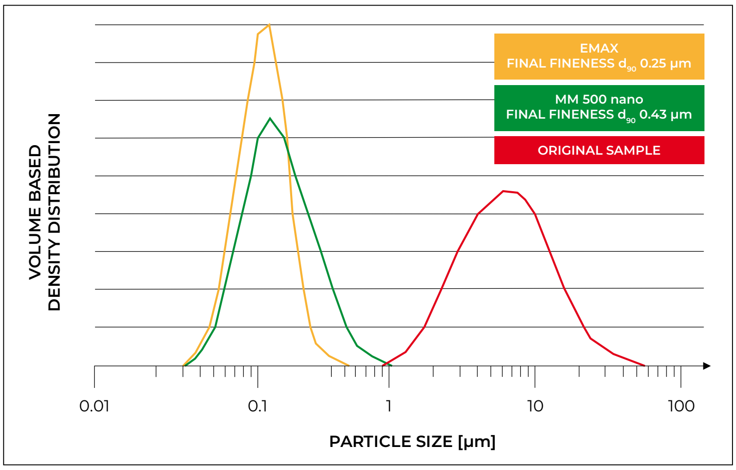


Figure 5: Volume-based particle size distribution of the original sample and after 60 min of grinding in the High-Energy Ball Mill Emax and Mixer Mill MM 500 nano.

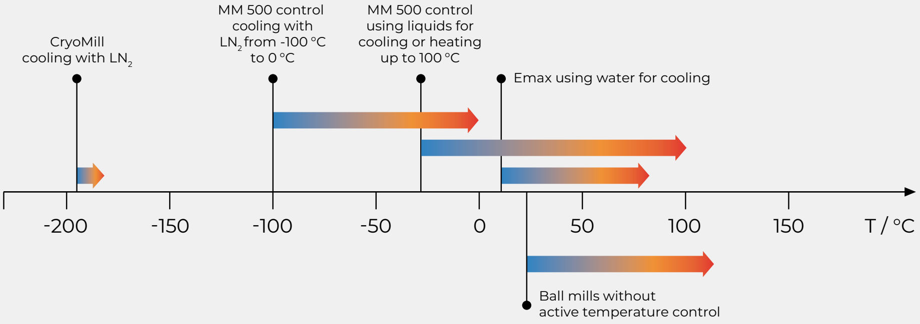
Grinding Details: *Grinding is carried out for 60 min. No further size reduction is achieved after that time. In both machines a comparable setup of 125 ml zirconium oxide jars and 275 g of grinding balls with a diameter of 0.5 mm is used. For the wet grinding process, 20 g silicon powder and approximately 30 ml of isopropanol are added to the jars and mixed until the slurry has a viscosity like oil. After 30 minutes of grinding at full speed of 35 Hz or 2000 rpm, respectively, 5 ml of liquid was added to maintain the viscosity.*

SIDE NOTE

LABORATORY BALL MILLS WITH ACTIVE TEMPERATURE CONTROL

High temperatures, for example above 80 °C, are not unusual for grinding processes in ball mills. The temperature development mainly arises from friction and depends on the ability of the mill to transfer heat from the jar to the environment and thus on the ball mill design. Retsch offers several ball mills with active temperature control to keep the jar temperature low during the grinding process. The Emax is equipped with an internal cooling circuit and additionally offers a software function to set a maximum jar temperature so that the mill automatically includes cooling breaks in the process. The MM 500 control continuously cools the jars during the process by using thermal fluids, like water, glycol or liquid nitrogen. In this way, a minimum temperature of - 100 °C can be achieved and also heating of the jars is possible. In the CryoMill, the jar is directly flushed with liquid nitrogen for maximum cooling down to -196 °C.

RETSCH BALL MILLS FOR ACTIVE TEMPERATURE CONTROL



SIDE NOTE

THERMAL TREATMENT OF BATTERY MATERIAL AND COMPONENTS

Thermal treatments are essential in battery manufacturing and are needed in electrode preparation, for example, in the sintering process of cathode materials or to control the degree of graphitization of the anode materials, as well as in coating technology or to extract reusable elements from recycled battery materials. Carbolite Gero, also a part of Verder Scientific, offer solutions for thermal processing of battery materials up to 3000 °C and under inert atmospheres.

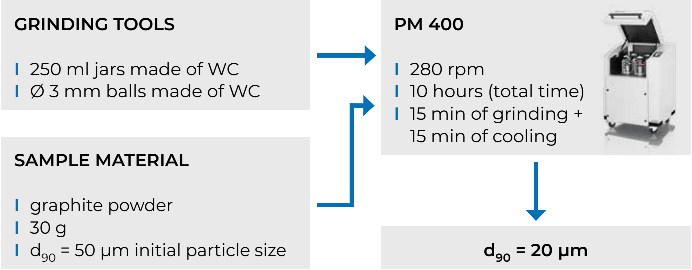
In a third experiment, which is not shown in the figure, grinding was carried out in a PM 100 Planetary Ball Mill for comparison. Similar particle sizes are achieved in this mill, but the jar temperature gets significantly higher than in the Emax and MM 500 nano. As a result, grinding breaks prolong the process. Also, handling is more complex, as a safety lid must be used to transfer the jar to a water-cooling bath to reduce temperature and pressure before opening. The heat generation during a ball milling process should be considered when choosing a grinding set-up, especially when working with temperature-sensitive materials. For such applications, laboratory ball mills with active temperature control are available.

Application example 2: Different approaches for grinding graphite

Graphite is commonly used as an electrode material in batteries, particularly in lithium-ion batteries, but also in other types of batteries such as alkaline and zinc-carbon batteries, as well as in fuel cells and capacitors. The particle size and particle size distribution of the graphite powder is an important feature in the electrode design as it affects the overall performance of the battery. The peculiarity here is that graphite is a solid lubricant and grinding of this material is not a trivial task. Due to its low frictional properties, the sample material induces high acceleration of the balls inside the jar and only low comminution. However, laboratory ball mills are still suitable to grind graphite powder. Two solutions are presented for grinding graphite in a planetary ball mill.

The first solution is a dry grinding process, see Figure 6. The maximum fineness achieved is d_{90} = 20 µm. In a second approach, a wet grinding process is carried out, see Figure 7. In this approach, a minimum particle size of d_{90} = 13 µm is achieved. However, if the wet grinding process is carried out in another mill, the High-Energy Ball Mill Emax, an even higher fineness of d_{90} = 1.7 µm is achieved. In the Emax, after only 1 hour of grinding, particles are already smaller than the minimum particle size that is achieved in the planetary ball mill after 8 h of grinding, see comparison of results in Figure 7. Thus, grinding of graphite in the Emax is much more efficient. This is due to the powerful impact effects produced by the unique movement of the balls inside the oval-shaped jars. Furthermore, thanks to its water-cooling system and the automatic setting of cooling breaks, the Emax can be operated continuously and comfortably without overheating.

Grinding details: *The initial particle size of the graphite sample material is 50 µm. If graphite is present in a coarse-grained form, the material must be pre-crushed, for example in a rotor mill or jaw crusher, prior to processing in the laboratory ball mill. In the dry grinding process, 30 g of the sample material is processed in the Planetary Ball Mill PM 400 in a 250 ml grinding jar of tungsten carbide and with 600 g of grinding balls with a diameter of 3 mm. The mill is stopped every 15 minutes for 15 minutes to allow the sample cool down. After a total grinding time of 10 hours the particle size is reduced to* d_{90} *= 20 µm. In the wet grinding process 50 g of graphite powder is ground in the PM 100 Planetary ball in a 500 ml zirconium oxide jar together with 300 ml of grinding balls with 1 mm in diameter. Approximately 130 ml of isopropanol is used for the dissolution. After 8 hours of grinding at a speed of 450 rpm, the particle size was reduced to* d_{90} *= 13 µm. Also here, the planetary ball mill is stopped during the process to allow the sample to cool down. In a second experiment, 5 g of graphite powder with an initial particle size of 50 µm is ground in the Emax. In this setup, a 50 ml zirconium oxide jar is filled with the sample material, together with 110 g balls with 1 mm in diameter and approximately 13 ml of isopropanol. The grinding speed is 2,000 rpm and particle size is reduced to* d_{90} *= 1.7 µm.*



GRINDING TOOLS

- 250 ml jars made of WC
- Ø 3 mm balls made of WC

SAMPLE MATERIAL

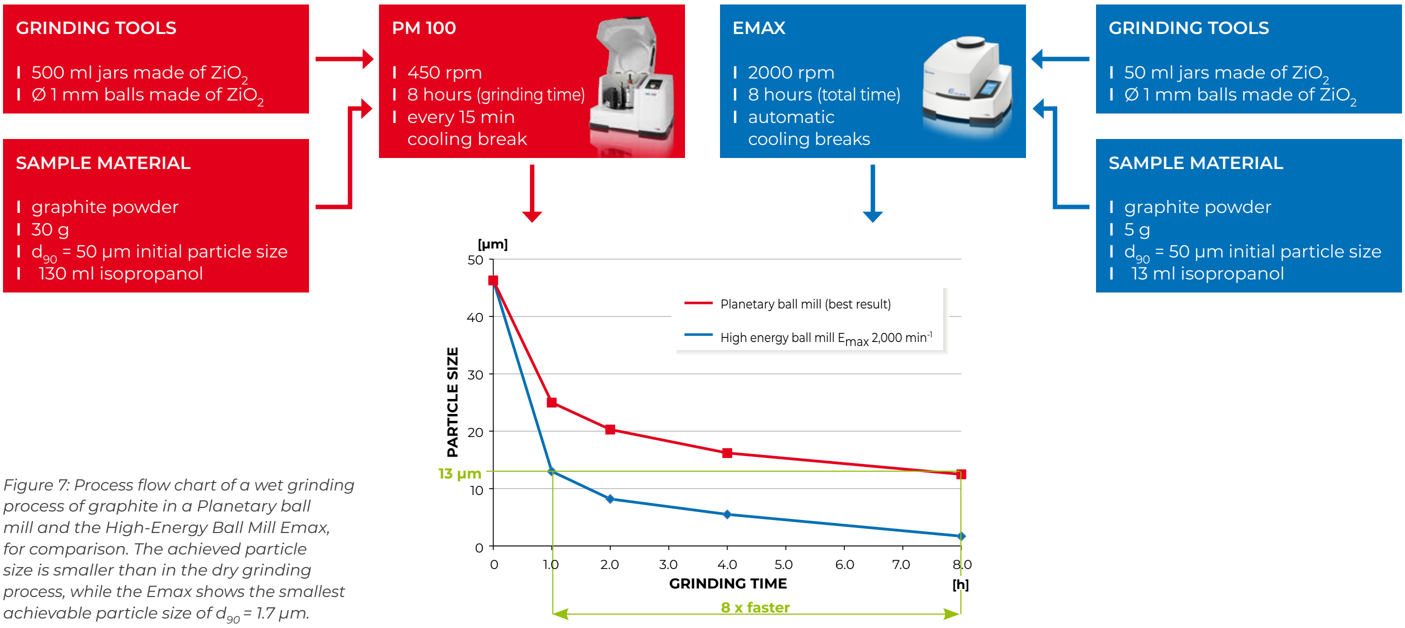
- graphite powder
- 30 g
- d_{90} = 50 µm initial particle size

PM 400

- 280 rpm
- 10 hours (total time)
- 15 min of grinding + 15 min of cooling

d_{90} = 20 µm

Figure 6: Process flow chart of a dry grinding process of graphite in a planetary ball mill.
The minimal achieves particle size is d90 = 20 µm.



GRINDING TOOLS
- 500 ml jars made of ZiO_2
- Ø 1 mm balls made of ZiO_2

SAMPLE MATERIAL
- graphite powder
- 30 g
- d_{90} = 50 µm initial particle size
- 130 ml isopropanol

PM 100
- 450 rpm
- 8 hours (grinding time)
- every 15 min cooling break

EMAX
- 2000 rpm
- 8 hours (total time)
- automatic cooling breaks

GRINDING TOOLS
- 50 ml jars made of ZiO_2
- Ø 1 mm balls made of ZiO_2

SAMPLE MATERIAL
- graphite powder
- 5 g
- d_{90} = 50 µm initial particle size
- 13 ml isopropanol

Figure 7: Process flow chart of a wet grinding process of graphite in a Planetary ball mill and the High-Energy Ball Mill Emax, for comparison. The achieved particle size is smaller than in the dry grinding process, while the Emax shows the smallest achievable particle size of d_{90} = 1.7 µm.

Application example 3: Temperature- and atmosphere-controlled grinding of a solid electrolyte

Some battery active materials require enhanced grinding conditions because they cannot tolerate increased temperatures or air contact. Lithium-phosphorus sulphide (LPS), for example, is used as a solid electrolyte in solid-state batteries. To enable a dense packing of the electrode materials, which is required for mechanical integrity, short ion paths and high energy densities, this electrolyte needs to be reduced to a defined particle size distribution. As LPS degrades if exposed to air, the jars must be filled in a glove box and the closed jars are then transferred to the mill. A pressure-tight jar sealing up to 5 bar is guaranteed for all Retsch Screw-Lock and Screw-Top jars, as well as for EasyFit jars, if used with safety lid, see Figure 8.

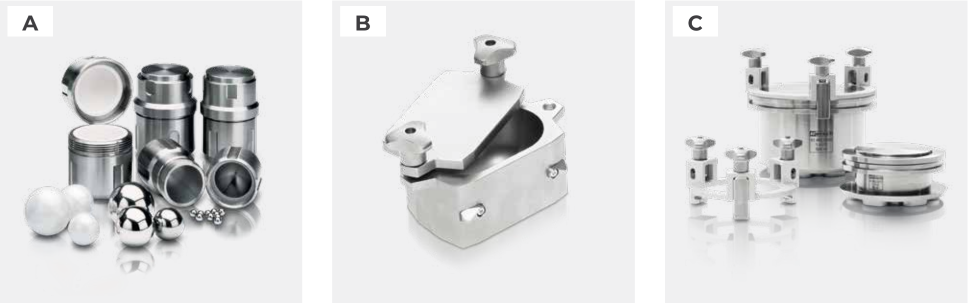


Figure 8: Picture of a Screw-Lock jar (a), a Screw-Top jar (b) and of a EasyFit jar (c) which is equipped with a safety closure device. These lids allow for a safe handling of battery material.

The second challenge in milling this solid electrolyte is that it tends to stick to the grinding jar walls after milling. Sticking of sample material to the grinding tools, also known as caking effect, is a common problem in ball milling processes that can have a negative impact on size reduction, homogenization, and material recovery. Sometimes, this problem can be solved by adding a few drops of alcohol to the jar.

Embrittling the material by freezing it to low temperatures may also help to prevent the caking effect. By freezing LPS to -100 °C and grinding at 15 Hz, the previous broad particle size distribution containing a fraction of large particles becomes narrow and monomodal, showing the required fineness. In addition, the material can be easily poured after the grinding process as caking effects are low, see Figure 9. Compared to grinding without cooling, the material yield is significantly increased in this process. Material recovery is an important consideration, especially when dealing with materials of low availability or high cost.

SIDE NOTE
WET GRINDING IN MM 400

Planetary ball mills, MM 500 nano, MM 500 control and Emax are typically used for wet grinding processes as the jar geometry is ideally suited to handling liquids. But wet grinding can also be performed with the MM 400, though the jar geometry of the MM 400 Screw-Top jars is not specifically designed for wet grinding. But the power of the MM 400 is sufficient and wet processes are manageable.
The particle size of a carbonaceous electrode material for example is reduced from d_{90} = 1 mm to d_{90} = 2 µm at 30 Hz in 1 hour.

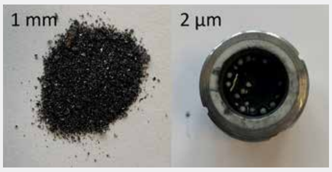


Figure 9: Sulphidic solid electrolyte (LPS) together with some balls in a 125 ml Screw-Lock jar of the MM 500 control, opened in a glove box.

Grinding details: *Grinding is performed in the Mixer Mill MM 500 control at – 100 °C in 125 ml stainless steel jars with 3 mm balls. The cooling is realized with liquid nitrogen. The sample material is pre-cooled for 15 minutes and the grinding is performed in 3 cycles, each of 10 minutes grinding at 15 Hz and 5 min cooling breaks at 3 Hz. The temperature of -100 °C is automatically and constantly maintained at the thermal plates throughout the entire process.*

2. BALL MILLING FOR MIXING AND PARTICLE COATING

There is a wide range of mixing and coating applications in battery technology. Various mixing devices can be employed, stirrers and vortex mixers are well-known, and ball mills are also widely used. Mixing is particularly important for several steps in the electrode production process, as illustrated in Figure 10. It should be noted, however, that laboratory-scale ball mills are primarily used in research and development, whereas large-scale production processes typically require mixing machines designed for high throughput and large batch sizes.

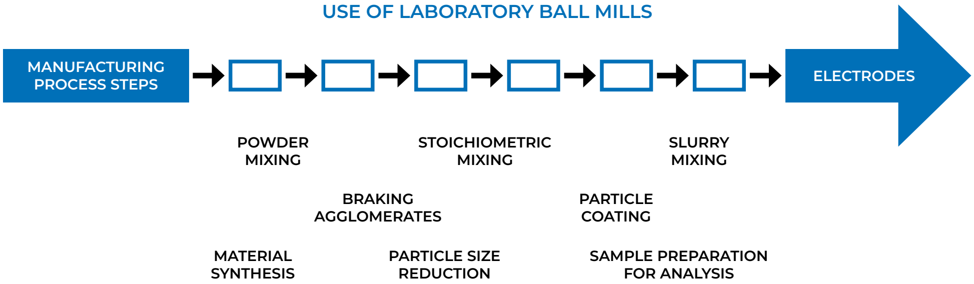


Figure 10: Process flow chart showing individual steps of electrode manufacturing including mixing and coating applications.

Ball mills can be considered for both, wet mixing of slurries and dry mixing of bulk solids. The constant material movement in the ball mill, whether at high or low energy input, with or without balls, yields excellent mixing results for a wide range of applications. Hereby, mixing in ball mills offers several advantages. The batch-wise operation of a ball mill allows for the convenient handling of powders and liquids, while also providing the flexibility to work under inert atmospheres. Additionally, the speed and processing time can be easily adjusted. Furthermore, Laboratory Mills typically offer a range of jar materials and jar volumes, which can be an important consideration for research questions. For instance, the Mixer Mill MM 500 nano can be operated with jars ranging from 1.5 ml to 125 ml, allowing different amounts of material to be processed, as shown in Figure 11. Moreover, extensive parameter variations are possible for experimental design, as most of the laboratory ball mills allow processing of multiple samples in one run. For example, the MM 500 nano can handle up to 36 samples in one operation. Detailed information on mixing battery materials in laboratory ball mills can be found in application example 4.

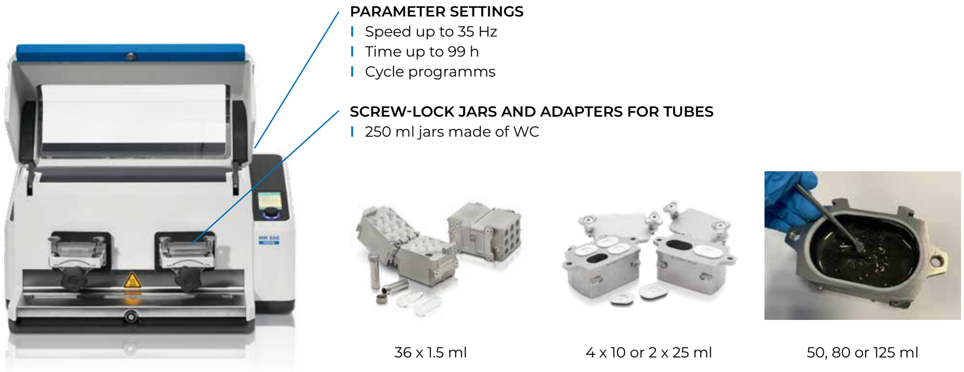


Figure 11: Mixer Mill MM 500 nano and its features for dry and wet mixing processes.

SIDE NOTE
ATMOSPHERE-CONTROLLED BALL MILLING

The usual process for handling atmosphere sensitive materials is to fill and open the jars in the glove box. Aeration lids can also be used to control or change the atmosphere in the closed jar. It is also possible to house a complete mill in a glove box.

SIDE NOTE

SLURRY STABILITY CHARACTERIZATION

Microtrac offers a unique technology for battery slurry characterization via a non-invasive optical technology. The Turbiscan static multiple light scattering is used to detect and quantify the homogeneity and stability of electrode slurries and their evolution over time.

Also, particle coating plays an important role for electrode materials and can be considered as a form of mixing process. In mixing and coating processes, size reduction should generally be avoided. The ball mill coating process operates on the principle of both, homogeneously mixing two materials and generating impact effects that facilitate the adhesion of the coating material to the particle surface. The process can be carried out in dry mode or in a slurry. Compared to other coating technologies, ball mills offer a simple, cost-effective and easily scalable method. However, the type of ball mill, as well as time and speed and the amount of material, should be chosen carefully to minimize the risk of unintended comminution and to ensure homogeneity.

There are several motivations for coating an electrode material in battery technology. A reason may be providing mechanical protection or increasing ion diffusion to improve the stability and longevity of a battery. But coating can also help to improve safety by preventing thermal runaway reactions, and to offer new opportunities for using environmentally-friendly and more scalable electrode materials. In Li-Ion technology, electrode surface coatings are actually seen as the most promising approach to improve material performance. Cathode materials, for example, are coated with a thin layer of conductive material, such as metal or carbon, to improve their electrochemical performance. Also, anode materials are coated, for example with a layer of carbon, to prevent them from degradation. In the field of solid-state-battery, material coatings represent a promising approach to bring electrode and electrolyte materials in close contact defined by a high mechanical strength and stability. Finally, several commercially available electrode materials already have surface coatings. A coating example is given with the application example 5.

Application example 4: Mixing of composite powders and slurries
The production of cathode materials typically involves stoichiometric mixing of raw material to create composite powders. For instance, to produce the well-known lithium nickel manganese cobalt oxide (NMC), a mixture of the starting materials including MnO_2, Co_3O_4, NiO, and Li_2Co_3 is required. Also, solid-state battery materials are based on composites, which consist of the active material and solid electrolytes and typically require a dry mixing process.

Wet mixing processes are required, for example, to prepare electrode slurries. Electrode slurries are complex systems with solid particles of different chemicals, sizes and shapes, dispersed in a viscous media. A cathode slurry generally contains the active material, conductive agent, binder and solvent. It is used to coat the battery active material onto the anode and cathode foils. A careful mixing is required as the properties of the slurry define the coating quality and thereby the conductivity, capacity and stability of the battery. Electrode slurry mixing in a laboratory ball mill allows for handling of organic solvents and to overcome agglomeration problems. They are also used to study the effect of different material compositions, intensity of mixing, temperature variations, viscosity variations or the order of adding chemicals to the slurry.

Grinding details: *In a typical mixing process, the ingredients are filled into the jar in a specific order. If required, they can also be pre-stirred by hand. The mill is then operated until the required homogeneity is achieved. Mixer mills are especially suited for mixing processes, because of their horizontal oscillation movement. But also planetary ball mills and drum mills are used. Gentle mixing is achieved at low speed or frequency. Increasing the speed intensifies the mixing effect and herewith generally reduces the mixing time. Also grinding balls, for example light grinding balls made of steatite, can be added. However, the more energy is introduced into the system, the stronger the mechanical forces acting on the particles. It is important to note that a vigorous mixing in a ball mill can reduce the size of particles or damage an existing particle coating, so as with any mixing action, the time and speed of the mill must be carefully chosen.*

Application example 5: Coating of electrode particles
Ball milling, whether through wet or dry methods, is used as method to coat electrode particles. An example of a wet coating process in a ball mill is the polymer coating of silicon. Silicon is a promising anode material for Li-ion batteries but is also challenging due to large volume changes during cycling and poor electrical conductivity. The polymer layer improves cycling stability and reduces battery costs by minimizing required binder-to-polymer ratios. Another example for a dry coating process of electrode material using a ball mill is the

SIDE NOTE
THERMAL PROCESSING OF BATTERY MATERIAL

Thermal treatments are essential in battery technology and are needed in electrode preparation, for example, in the sintering process of cathode materials or to control the degree of graphitization of the anode materials, as well as in coating technology or to extract reusable elements from recycled materials. Carbolite Gero offers a wide range of solutions for thermal treatment in battery technology up to 3000 °C and under inert atmosphere.

application of ZrO_2 or SiO_2 to LiNi0.5Mn1.5O4 (LNMO) cathode material. LNMO is a high potential cathode material for Li-ion batteries and its coating reduces the interfacial charge transfer resistance to improve the battery charging rate.

Grinding details: *A Drum Mill is used for coating LNMO. However, a planetary ball mill or a mixer mill can also be considered. Small zirconium balls with a diameter between 3 mm to 5 mm can be used in this process. For the coating process, the LMNO is only partially calcined at low temperatures and then finalized at higher temperatures in a second step after the coating process, as this strategy results in a higher degree of homogeneity. A small amount of ethanol is added to the jar to improve the process. The coating process is carried out for up to 24 hours.*

3. BALL MILLING FOR THE SYNTHESIS OF NEW BATTERY MATERIALS

Mechanochemical synthesis is a powerful and innovative method in the field of materials science, offering a new approach to develop unique battery materials. In mechanochemistry, mechanical energy is employed to bring chemicals into close contact, create new surfaces and generate heat to initiate or accelerate chemical reactions. Compared to the solvent-based processes of classical synthesis routes, mechanochemistry is an environmentally friendly alternative and part of the so-called green chemistry. Ball mills are perfectly suited for mechanochemial applications because they allow for high energy input and a reproducible parameter setting.

Mechanochemical synthesis has become particularly popular in the field of solid-state batteries. Here, it is used to create innovative electrolytes, separators or multi-phase composites of high purity or to optimize their microstructure. As many chemicals under consideration are air-sensitive and expensive, batch-wise processing in small-cavity jars is beneficial. However, the major challenge in mechanochemistry is that it is still not fully understood how the milling parameters affect the chemical reaction mechanism. Altering the movement pattern, speed, ball size, chemical amount, ball filling ratio, or temperature can influence the atomic and microstructure of the resulting battery materials, which ultimately determine their stability and ionic transport properties. What is the effect of the type, intensity and number of mechanical events on the reaction? Are the same results obtained with lower energy input but longer process times? Answering these questions is crucial for scaling up a process to larger sample quantities. An example for a mechanochemical synthesis of solid electrolyte is given in the application example 6.

Application example 6: Synthesis of solid electrolytes
Lithium conducting halides, such as rare earth halides, are considered as solid electrolytes or composite materials to improve the performance and stability of solid-state batteries. Through mechanochemical synthesis followed by rapid crystallization, a disordered and distorted microstructure can be obtained, showing superior transport properties compared to materials derived by classical solid-state synthesis.

Grinding Details: *A Planetary ball mill is used for the synthesis of the nitride halide* Li_5NCl_2*. For the reaction, LiCl and* Li_3N *in stoichiometric amounts are added to a zirconium oxide jar. The mass ratio of spheres to precursors is 13:1. Balls of 10 mm in diameter are used. All preparation steps are carried out in an argon atmosphere. The ball mill runs at 600 rpm for 10 hours with cycles of 5 minutes milling and 5 minutes grinding breaks. If necessary, a manual homogenization for loosening baked powder can be done before continuing the process after a break.*

MM 400 with 4 x 5 ml adapter and steel tubes

SIDE NOTE
MM 400 - FOR MECHANOCHEMICAL APPLICATIONS

The Mixer Mill MM 400 is the first ball mill which enables calibration of time and speed. This ensures high accuracy and reproducibility, which are required for the investigation of mechanochemical applications. The mill allows for process times up to 99 hours and programmable cycles for long reaction times. Moreover, a wide range of jar sizes and materials is offered, including e. g. an adapter for 4 x 5 ml stainless steel grinding jars for 8 reactions in one run. In contrast to a planetary ball mill, the horizontal jar movement of a mixer mill enables performing in-situ spectroscopy and to investigate the kinetics and find the best yield of a mechanochemical reaction during the process. For spectroscopy, transparent jars are available, and the bottom plate of the device is removeable.

SIDE NOTE

METALLOGRAPHIC SAMPLE PREPARATION

Metallographic sample preparation is required in battery technology for the analysis of assembled components or batteries to enable visual inspection under the microscope, such as to ensure that the electrode coating has a uniform thickness, no cracks, optimum adhesion to the substrate and a geometric alignment. QATM, part of Verder Scientific, offers products for cutting, grinding, and polishing batteries.

4. BALL MILLING FOR PREPARING SAMPLES FOR ANALYSIS

Laboratory analysis plays a crucial role in the development, testing and quality control of materials used in battery technology. Especially the chemical composition and structure of materials are highly important aspects that are analyzed at numerous points along the battery value chain. Starting with raw materials such as ores, knowledge of their mineralogical composition and purity is required to define processing steps, market value and environmental compliance.

Also, battery component suppliers and battery manufacturers rigorously analyze the quality of their electrode powders, separator materials and solid electrolytes, sometimes even several times during the manufacturing process, as any contamination or moisture ingress during production or transport degrades quality. This especially applies to intermediate products such as the final sintered NMC cathode material, which is available on the market as a ready-to-use battery component. Moreover, also in the battery assembly process and in the battery testing stadium material properties are investigated. Electrode slurries, for example, are dried, ground and tested on impurities. Structural phase changes in electrodes are monitored over repeated charge-discharge cycles, for the investigation of battery degradation mechanisms. After all, material analysis is also of fundamental importance in the battery recycling industry. Here, it is used to assess the purity of recycled battery materials, qualify a recycling process, determine the market value of the recycling fractions and assess suitability for second life applications.

The list of applied analytical methods used is long. X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), inductively coupled plasma (ICP) and mass spectrometry, Fourier transform infrared spectroscopy (FTIR) and many more are used to gain knowledge about material properties. These methods require only a small amount of material to be analysed, ranging from a few grams to milligrams. However, if this amount is simply taken from the original sample, it may not accurately represent the whole sample. Inhomogeneities will lead to overrepresentation of components or missing components and even if the analysis is performed correctly, the results will not be meaningful.

To obtain a reliable result, the sample analysed must be truly representative, which means that its composition must reflect that of the total sample. The required analytical fineness is achieved by particle size reduction, homogenization and careful sample splitting. Required particle sizes typically range from 1 mm down to a few µm and ball milling technology is a commonly used method to achieve this.

The preparation process must ensure that the material properties under investigation are not altered. A particular concern is the introduction of unwanted material into the sample. Material contamination can be caused by abrasion from grinding tools. If, for example, heavy metals are to be analyzed, the use of ZiO_2 jars and balls instead of stainless steel grinding tools can be a solution. In addition, grinding tools must be thoroughly cleaned to avoid cross-contamination from previously processed materials. Also, the heat generated during the grinding process must be considered, especially when dealing with temperature sensitive materials.

Another important issue in this context is the use of grinding aids. Depending on the material being processed and the specific requirements of the result, different grinding aids can be used. Solid, liquid or gaseous grinding aids such as talcum, alcohol or argon can improve the grinding process. Drying or tempering of the sample material may also be considered, especially for wet, soft or elastic materials. For example, polymer battery components are frozen to very low temperatures to embrittle the material for effective crushing in the ball mill.

A particular challenge in ball milling is related to the presence of metals. Metals are present, for example, in recycling products, battery casings and electrodes, which typically contain materials such as aluminum and copper for conducting electricity. Laboratory ball mills usually do not crush, but rather tend to flatten them. Only very thin or ductile metallic parts can be pulverized up to a certain point. Macroscopic metal components generally should be extracted from the sample material prior to the ball milling process, possibly using magnetic forces, and independently analyzed if required.

SIDE NOTE
SAMPLE DIVIDING

Sample materials are often macroscopically heterogeneous and present in large quantities. Since most analytical methods can only analyze a small amount, it is necessary to split the original sample. Also, if a two-step grinding process is required, with a pre-crushing step prior to fine grinding, often only part of the total amount is processed. In any case, the splitting of the sample must ensure that the processed material is still representative and has the same properties as the original sample to obtain reliable analytical results. Sampling by hand can only be done if the sample is completely homogeneous in terms of material and particle size. Sample splitters can be used for more accurate splitting. Automatic sample dividers are also available for dry, free-flowing samples. The sample divider uses a vibratory feeder and rotating tube assembly to evenly divide the sample into sub-samples.

This section presents four examples of sample preparation that are highly relevant to battery technology. Application example 7 and 8 are related to the commonly used techniques of X-Ray fluorescence spectroscopy and X-ray diffraction and application example 9 and 10 include the sample preparation of electrode and polymeric materials as examples for challenging ball milling tasks for sample preparation.

Application example 7: Sample preparation for XRF Spectroscopy
X-Ray fluorescence (XRF) spectroscopy is an analytical technique that is widely used in battery technology to determine the chemical composition of materials. XRF spectroscopy is for example used to

- analyze the chemical composition of nickel laterite, as laterite ores provide a large percentage of the world's nickel production
- identify and quantify impurities such as aluminum and iron in silicon, as silicon is often sourced from recycled silicon wafers
- control the chemical composition of NMC materials, as this is a battery component that is commercially available
- identify precious metal residues in the recycled polymer fraction, as these are considered as lost material and may cause hazardous problems

Care must be taken when preparing samples for XRF spectroscopy, as the laboratory sample of a few grams often represents a total quantity of several tonnes. Particularly when dealing with inhomogeneous or coated materials, the sample must be thoroughly homogenized to ensure that each material fraction is measured. In addition, this method has a specific particle size requirement for operation. The size must be within the saturation depth of the X-rays to provide meaningful results. Typically, particle sizes smaller than 100 µm are required for XRF spectroscopy to ensure reliable results for elements lighter than potassium.

For improved processing, the prepared sample powders are usually pressed into pellets. A pellet forms a densely compacted material with a flat surface, containing a substantial amount of sample material, which increases the sensitivity and accuracy of X-ray fluorescence. Finally, the quality of sample preparation has a huge influence on the analytical results of XRF spectroscopy. For example, manganese dioxide, used as a cathode material for various types of batteries, already has a high fineness of 0.2 - 0.6 mm, is further homogenized in a Planetary Ball Mill PM 100 and pressed into a pellet for XRF spectroscopy, see grinding details and Figure 12.

Grinding details: *360 g of manganese oxide powder is placed together with approximately 200 zirconium oxide balls of 5 mm in diameter in a 500 ml EasyFit zirconium oxide grinding jar. The jar is equipped with a safety closure device for safe transport. Grinding is carried out in a PM 100 Planetary Ball Mill at a speed of 350 rpm for 30 minutes. Particle size is reduced to* $d_{90} = 50$ *µm. Higher speeds would accelerate the size reduction but there is a potential problem of material sticking to the wall of the jar and to the grinding balls at higher energy input. After grinding, the sample is divided and pressed into a pellet with the Retsch pellet press PP 40.*

Figure 12: Sample of manganese oxide before (a) and after the milling process in the PM 100 (b).
For XRF analysis the sample is pressed into a pellet (c).

SIDE NOTE
PRODUCTION OF PELLETS FOR X-RAY FLUORESCENCE SPECTROSCOPY

For XRF spectroscopy, utilizing pelletized sample material offers advantages. Unlike loose powder, a pellet has a high concentration of elements within the compacted sample material and smooth surface, making elements better detectable by X-rays. The pellet press PP 40 from Retsch is a benchtop model with high press forces up to 40 tons, which are built automatically in up to three steps.

Pellet Press

SIDE NOTE

ELEMENTAL ANALYSIS

Eltra, a part of Verder Scientific, offers a range of elemental analyzers for the determination of carbon, hydrogen, nitrogen, sulfur, and oxygen content in battery materials.

Application example 8: Sample preparation for X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis is a technique used to determine the atomic and molecular structure of crystalline materials. XRD is for example applied to

- control the crystallite size in silicon-based electrode materials, to understand how the lithium ions are accommodated during charging
- analyze the solid phase transition of NMC cathode material to understand its electrochemical behavior
- quantify the degree of graphitization in carbon materials to optimize the battery capacity
- study the crystalline structure of solid electrolytes to improve their ionic conductivity
- characterize electrode coatings to develop improved battery performance
- quantify phase purity of battery components for quality control

In XRD analysis, particle size and particle size distribution have a significant effect on the results. The particle size should be ideally less than 10 microns and a narrow particle size distribution is required to ensure accurate information about the crystal structure. Large particles can lead to an underestimation of the presence or concentration of certain ingredients with higher X-ray absorption.

But even if the required analytical fineness can be achieved, not every ball mill is suitable for XRD sample preparation. Mixer mills or planetary ball mills, for example, can introduce defects, dislocations, and grain boundary areas in the material as they work with high energy. The XRD-Mill McCrone, on the contrary, gently homogenizes the sample and preserves the crystal lattice structure. The XRD-Mill McCrone is equipped with a jar, which is almost completely filled with grinding cylinders and operates at minimal movements. This allows for a gentle form of grinding, purely based on frictional stress, which reduces the damage of the crystal structures. A typical grinding example is the XRD sample preparation of copper ore, see Figure 13. XRD is here used for mineral evaluation, for example, to assess the sustainability of raw materials for battery production.

Grinding Details: *A grinding jar for XRD-Mill McCrone with 125 ml capacity made of polypropylene is filled with an array of 48 identical cylindrical zirconium oxide grinding elements. 1 g of the sample material is added. Prior to fine grinding, the original rock was pre-crushed in a jar crusher to achieve a particle size of 500 µm. Additionally, 14 ml of ethanol is added to the jar to keep the sample in motion and avoid caking effects. The mill is run at maximum speed for 3 hours to obtain a final particle size of* d_{90} *= 5 µm with a narrow particle size distribution. As a result, the signals in the X-ray diffraction pattern are peak-shaped, with small half-widths, allowing for very good phase analysis.*

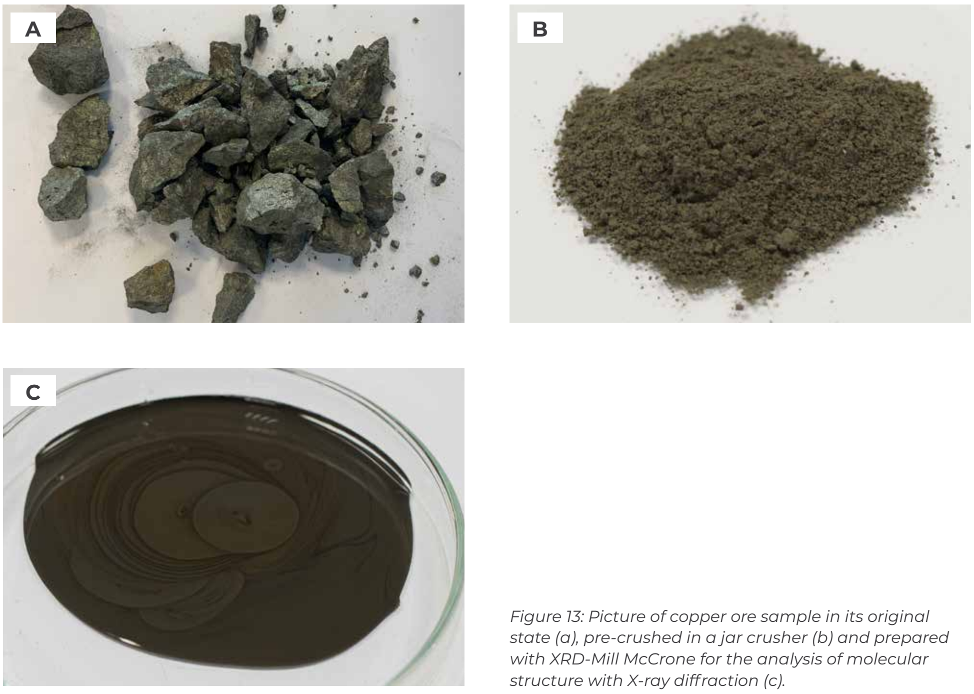


Figure 13: Picture of copper ore sample in its original state (a), pre-crushed in a jar crusher (b) and prepared with XRD-Mill McCrone for the analysis of molecular structure with X-ray diffraction (c).

Application example 9: Sample preparation of electrodes for analysis
The material analysis of anodes and cathodes is a fundamental element of quality control and research. Understanding the composition, structure, and properties of these key components is essential for optimizing battery performance, capacity, and longevity. In a lithium-ion battery an electrode is built from coating of active material, for example a metal oxide or a carbon-based compound, onto a current collector, typically on thin foils made of aluminum or copper which serves as electrical conductor. Due to its metal component, crushing of electrodes is challenging in a ball mill. However, homogenization of electrode sheets or electrodes from recycling processes may be possible to a limited extend. Figure 14 shows an example, where anode and cathode foils are milled in the Mixer Mill MM 400 to a particle size of d_{90} = 1 mm.

***Grinding Details:** Anode and cathode sheets are pulverized in the Mixer Mill MM 400, a bench-top ball mill model that can be placed in a fume cupboard to protect the operator from hazardous dust. The screw-top jars can be handled with gloves. A 35 ml jar made of zirconium oxide is filled with a 20 mm ball and 5 g of the electrode sample until the bottom part of the jar is full. Prior to ball milling, the electrode foils are manually pre-cut to 1 cm² pieces. Speed is set to 30 Hz and grinding is performed for 10 s before another 5 g of sample material is added to fill up the volume of the jar. Grinding then proceeds for 4 min. Increasing the grinding time does not result in smaller particles sizes.*

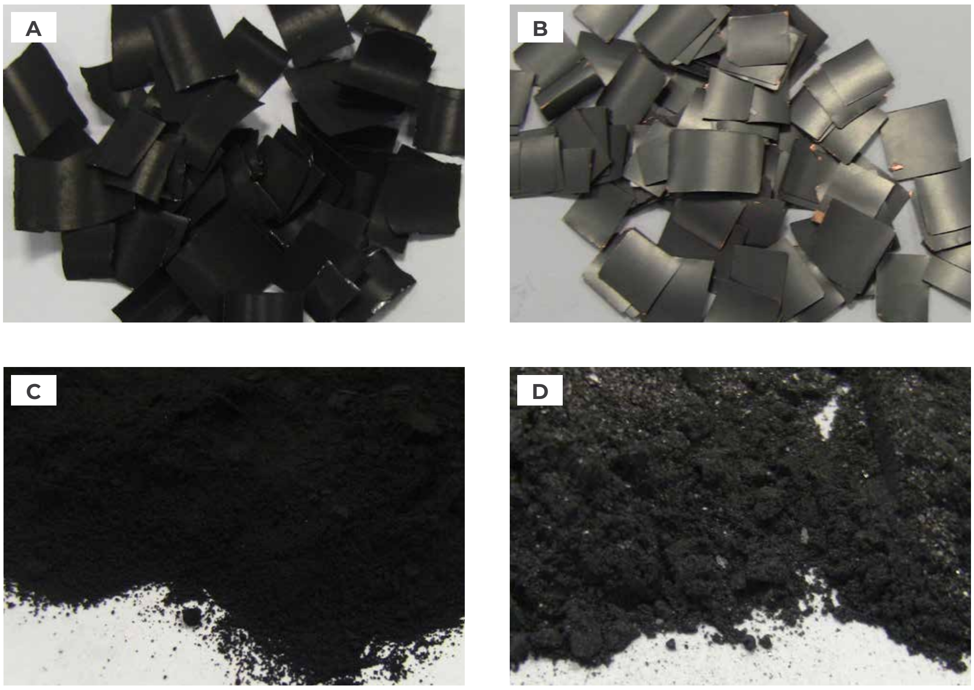


Figure 14: Picture of the cathode (left) and anode electrode foil (right) before and after the ball milling in the MM 400.

CryoMill with a 50 liter liquid nitrogen container

Application example 10: Sample preparation of polymeric recycling fraction
There are several ways to recycle batteries, including mechanical and chemical processes, as well as hydrometallurgical and pyrometallurgical methods. To qualify the process, minimize the environmental impact and maximize the recovery of valuable components, the amount of residues in the recycled fractions needs to be identified. The challenge here is that these fractions commonly have a heterogeneous appearance with a wide range of different materials and particle sizes. Depending on the specific process used, the solid fractions contain metals and polymers in the form of pieces or powders. The separation of materials can be accomplished using various processes, for instance through sieving.

As an application example, a recovered polymeric fraction from the recycling process of a lithium-ion battery is analyzed, see Figure 12. The sample primarily consist of the separator membrane, which is commonly made of polypropylene or polyethylene, however, may also contain electrode materials or parts of the battery casing.

Residues need to be analyzed for their elemental composition and quantity. The sample preparation of this fraction is not trivial because polymers have ductile properties and cannot be easily crushed in a ball mill. For this type of material, the CryoMill, a laboratory ball mill specially designed for grinding elastic materials, is used. In this cryogenic ball milling process the sample is frozen to very low temperatures by cooling with liquid nitrogen taken from a tank.

The mill has an integrated cooling system that continuously cools the grinding jar to a temperature of -196 °C prior to and during the grinding process. With this method of ball milling, the polymeric fraction can be homogenized, ready for example for microwave digestion and ICP-MS analysis, to quantify the residues of metals such as lithium, cobalt, nickel, manganese.

Grinding details: *For the homogenization of a polymer battery recycling fraction, zirconium oxide grinding tools are used to avoid contamination of the sample with iron. A jar of 25 ml volume is filled with 1 ball of 20 mm size and 1 g of the sample material. As the sample material consists mainly of thin foils up to 15 mm long, which lose volume during grinding to powder, the sample is squeezed into the jar but still meets the jar filling rules. For the CryoMill, larger jar sizes are only available in stainless steel. Alternatively, grinding can be carried out in the MM 500 control Mixer Mill which offers jar volumes of up to 125 ml and maximum jar cooling of -100 °C. In this example, the CryoMill is programmed for 13 minutes pre-cooling and 9 cycles of 2 minutes grinding and 1 minute break. The pre-cooling and grinding breaks allow the sample to cool to minimum temperatures for maximum embrittlement. In this application example most of the sample is ground to a particle size < 1 mm, however a few larger metal particles remain.*

SUMMARY

This paper provides a comprehensive overview of the general use of ball mills and their application in battery technology. It covers the wide range of ball mill applications throughout the battery manufacturing process, from raw materials to recycling. The benefits of using ball mills are illustrated by ten specific application examples taken from research and quality control. Specific information on the details of the grinding process is provided to give an in-depth understanding of ball mill technology.

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