Energy Storage Materials for Solid-State Batteries: Design by Mechanochemistry

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Commercialization of solid-state batteries requires the upscaling of the material syntheses as well as the mixing of electrode composites containing the solid electrolyte, cathode active materials, binders, and conductive additives. Inspired by recent literature about the tremendous influence of the employed milling and dispersing procedure on the resulting ionic transport properties of solid ionic conductors and the general performance of all-solid-state batteries, in this review, the underlying physical and mechanochemical processes that influence this processing are discussed. By discussing and combining the theoretical backgrounds of mechanical milling with regard to mechanochemical synthesis and dispersing of particles together with a wide range of examples, a better understanding of the critical parameters attached to mechanical milling of solid electrolytes and solid-state battery components is provided.

1. Introduction

The development of new types of batteries has mainly transitioned to solid-state battery based concepts (Figure 1a) that are thought to better address the demand of higher energy densities, exceeding commercial lithium-ion batteries using liquid electrolytes.[1–3] In addition, solid-state batteries with their inorganic solid electrolytes are expected to be safer,[4,5] however this still remains to be seen. Furthermore, the chemical and mechanical instabilities between the solid electrolyte and lithium,[6–10] the partially low electrochemical stability windows of the solid electrolytes,[11–13] that go hand in hand with decomposition reactions on the anodes[14,15] and cathodes[16–19] respectively, are still issues that have to be addressed.[20]

These fundamental issues are likely to be solved in the coming years; nevertheless, it will require additional effort to commercialize of solid-state batteries. While liquid-based cells are commercially well developed and the manufacturing of the active and passive materials as well as the battery cells have been refined over the years, the processing and especially upscaling of solid-state electrolytes and solid-state battery cells is still challenging.

The aspects of processing and upscaling are essential because large amounts of solid electrolyte need to be available to produce solid-state batteries on a Gigafactory scale. Classic solid-state syntheses of solid electrolytes pose a problem regarding the aspect of scalability, as those are usually performed inside quartz ampoules in small quantities. The direct scalability in these syntheses is questionable[21,22] and energy-intensive processes with high temperatures are economically not viable. By contrast, in liquid-based syntheses the upscaling of these electrolytes may be possible,[23,24] however, the potential environmental impact based on solvents remains unclear especially as possibly remaining solvent may contaminate the electrolyte.[21,22]

In addition to the upscaling of the electrolyte manufacturing process, particle processing for solid electrolyte–active material composites needs to be developed and upscaled to generate optimized composite materials for mass-producing electrode sheets. An alternative to solvent-based processes and classic solid-state syntheses is the mechanical mixing/milling techniques that allow the mechanochemical synthesis of solid electrolytes (see Figure 1b) and processing of cathode composites even...
Indeed, in recent years the usage of mechanical (ball) milling of solid electrolytes and solid-state battery composites has significantly increased. However, the process of milling itself has so far been treated rather phenomenologically, purely as a trial-and-error approach to solid electrolyte formation and composite production. Yet, recent work in the field shows the tremendous influence of the milling parameters as well as mechanochemical syntheses themselves on the structure and transport of these ionic conductors and composite electrodes, as well as the performance resulting performance of solid-state batteries.

In this review, we attempt to provide the reader with a better understanding of the fundamentals of mechanochemical milling by showing for instance which milling parameters affect the power and stressing energy input into the system. In addition, we will show selected examples of how milling parameters can influence phase formation, structure formation and the resulting transport properties as well as the solid-state battery performance. We hope that by better understanding the critical parameters attached to mechanical milling, the design of future studies for mechanical milling of solid electrolytes and solid-state batteries can be simplified and future upscaling can be improved.

2. Processing Considerations Using Mechanical Milling

As with any synthetic reaction or synthetic process, when using mechanochemical or mechanofusion processes, several parameters can be varied to achieve the resulting product, being it a single-phase material or a composite electrode. It is immensely important to understand how the milling parameters and with that the stressing conditions affect the energy transfer to the solids and the reactions or the microprocesses in general.

2.1. Stressing Conditions and Energy Input

For grinding as well as mechanochemical reactions the stressing conditions within the different ball mills are decisive. As generally accepted and defined by Kwade and co-workers in detail, the stressing conditions in mills are defined by following mechanisms.

I) Stressing type: Arrangement of particles during stressing (single particles, layer of particles, bed of particles) as well as the kind of energy input to particles that comprises of the compression and shear between two surfaces, the impact at one surface, and within a fluid.

II) Stressing energy/stressing intensity: Energy that is transferred to the particles during one stressing event (mill-related characteristic parameter) and with that, focusing on the product particles, the intensity of a stressing event. The intensity is the energy transferred to the particles related to the volume or mass of the stressed particles. Therefore, it is a specific energy input at one stressing event and a product-related characteristic parameter.

III) Collision frequency: The frequency of media collisions within the mill chamber, which determine the number of stressing events per product volume (for example, a feed particle) during the entire process.

The stressing type, stressing intensity, and stressing number influence the product quality, for instance, the product fineness or yield.
2.1.1. Detailed Description of Stressing Condition

Due to the large number of different mechanisms that occur simultaneously in the reaction chamber, i.e., the mill, it is important to describe the conditions of energy dissipation and stressing in detail. In regard to the stressing conditions, the power input $P$, either total or in normal direction, is determined by the product of the collision frequency $CF$ and mean stressing energy $SE$ (either in total or in normal direction, see Equations (1) and (2)), which are mill-related conditions

$$ P_{\text{normal}} = CF \cdot SE_{\text{normal}} $$  \hspace{1cm} (1)

$$ P_{\text{total}} = CF \cdot SE_{\text{total}} $$  \hspace{1cm} (2)

The values of stressing energy and collision frequency\[34–37\] are accessible via simulations based on the discrete-element-method (DEM).\[38\] However, the total power $P_{\text{total}}$ (Equation (3)) can also directly be determined by the rotational speed $n_{\text{SUN}}$ of the sun wheel (Figure 2a) and the torque $M$, which is experimentally measured by a torque sensor or extracted from the respective DEM simulation\[34\]

$$ P_{\text{total}} = 2\pi \cdot n_{\text{SUN}} \cdot M $$ \hspace{1cm} (3)

The power describes the energy that is available per unit time for the total amount of reagents and thus, can directly limit the process rate.

Figure 2. Schematic of the work principle of a planetary ball mill. a) Two oppositely located jars are attached to a rotating disk (sun wheel) with the radius $R$ from the center of the disk to the center of one of the jars. b) The jars rotate around their own axis in normal direction to the disk. The most influential factors of the synthesis route are the powder filling ratio (b) also called the filling of the jars, c) the sun wheel rotation speed $n_{\text{SUN}}$ and d) jar rotation speed $n_{j}$.

Considering the stressing energy, a distinction needs to be made between normal fractions transferred by head-on collisions and total dissipation of the entire collision. With the total power input and the collision frequency a mean value for the total energy dissipation $SE_{\text{total}}$ (Equation (4)) can be obtained\[36\]

$$ SE_{\text{total}} = \frac{P_{\text{total}}}{CF} $$ \hspace{1cm} (4)

The normal stressing energy, $SE_{\text{normal}}$ (Equation (5)) transferred by head-on collisions was identified in several studies as breakage relevant.\[34,39\] It is a function of the relative collision velocity $v_{\text{rel,n}}$ in normal direction and the masses $m_{1}$ and $m_{2}$ of the colliding media\[40,41\] as well as the coefficient of restitution, COR.

$$ SE_{\text{normal}} = \frac{m_{1}m_{2}}{2(m_{1} + m_{2})} v_{\text{rel,n}}^2 \cdot (1 - \text{COR}^2) $$ \hspace{1cm} (5)

The equation is based on contact physics and derived by energy and momentum conservation and it incorporates all transferred energy to the particles along the mostly unspecified dissipation pathways of fracture, amorphization, conversion, and heat. The coefficient of restitution is a dimensionless number and reflects the plastic-elastic behavior of the collision. For a totally elastic impact COR equals one with no energy dissipation. For a totally plastic impact COR equals zero and the maximum fraction is converted into stressing energy.\[41–44\] Several factors and microprocesses within the stressed particle bed affect the COR: for instance, the material itself as well the particle size and the cohesiveness of the powder determine the beds deformation behavior. Additionally, the thickness of the bed influences how much energy is dissipated for breakage and conversion, and thus, the COR. Often, with increasing bed thickness, the COR decreases, as more powder is compressed and refined or converted and more energy is dissipated.\[44,45,46\]

Equation (5) demonstrates that the stressing energy can be much lower than the kinetic energy of the milling media, as only part of it is actually dissipated. This is especially the case if the relative velocity between the colliding milling media is low or the coefficient of restitution is close to unity due to a high-collision elasticity. However, if a bed of relatively soft particles as thiophosphate particles is stressed, the majority of the kinetic energy is transferred into the particle bed. Additionally, it already shows that the energy input into the system scales with the mass of milling media.

In the mill, the milled particles tend to form a layer on the milling media surface, so that they are stressed as a particle bed.\[45,47\] Inside this particle bed the particles are subjected to several microprocesses of rearrangement, deformation, structural changes, and fracture.\[48,49\] Although these can hardly be characterized individually and change with layer thickness, COR also includes this energy absorption.\[50\] Eventually, a low COR indicates a good energy transition so that thicker layers initially appear beneficial. However, layer formation caused by cohesive states and firmly attached particles can negatively affect the activation process (both conversion and grinding) due to a lack of mixing and limited material transport.

The layer formation and flowability of particles affect the active mass ($m_{a}$) of particles that are stressed within a collision.
By that, also the stressing intensity SI (Equation (6)), i.e., the ratio of stressing energy to active mass as specific energy available per particle, is affected as each particle does only receive a part of the dissipated energy.[34,36,31-34]

\[
SI = \frac{SE}{m_A}
\] (6)

The product of the number of collisions (CF · t, where t is the process time) and intensity of stressing events provides a specific energy \( E_m \) (Equation (6)) that is transferred to the milled powder with a mass of \( m_{\text{powder}} \)

\[
E_m = \frac{CFSE}{m_{\text{powder}}} \cdot t
\] (7)

Thus, instead of using a stressing number, a specific energy that is transferred to the product particles, can be used as characteristic parameter to evaluate the process efficiency.

### 2.1.2. Stressing Conditions in regard to the Grinding Process

For grinding processes the stressing intensity (Equation (6)) is decisive to the breakage and can be regarded as the specific energy demand of the different microprocesses in the collision area.[34,55] The layer formation as well as the ability of the powder to flow around the media, and by that the active mass in the local process can be affected by suitable grinding additives.[43,54,56] in dry or liquid form.[57] In some cases, the reaction or the overall process itself needs a higher amount of liquid additive, for instance in the synthesis of cocrystals.[58,59] By using more liquid, the reagents and additives form a slurry state, leading to a lower active mass \( m_A \) and, thus, a higher stressing intensity, which is then called liquid-assisted-grinding. Due to the increasing stressing intensity, often smaller milling media are used for wet operation. The liquid assisted grinding can favor an increased crystallinity and higher product yields due to this increased stressing intensity.[60] or even control the selectivity to enable the formation of a specific product.[61–63]

In a grinding process with the mere aim of particle refinement, an optimum stressing intensity exists, resulting in a minimum of energy demand while intensity values below or above the optimum increase the energy demand of the process itself.[34,55,64] The fundamental physical phenomena of mixing, loading and energy dissipation are the same for all mechanical activation processes in ball mills.[65] and, similar to chemical kinetics, the process of size reduction and reaction is a rate phenomenon.[39]

#### 2.1.3. Ball Mills for Mechanochemical Milling

Several types of ball mills exist, which can be applied for mechanochemical syntheses and mechanofusion of solid materials. The different types can be classified according to how the milling media (also called beads or balls) are stimulated to move, i.e., how the energy is transferred into the milling chamber and to the bulk of material that needs to be processed. In principal four different types can be distinguished.[66,67]

- Tumbling ball mills:[68] Milling media are moved by the rotating mill chamber.
- Planetary ball mills:[37] Milling media are moved by the rotating mill chamber which rotates within a centrifugal field.
- Vibrating ball mills:[69] Milling media are moved by a vibrating mill chamber, whereas the vibration can be of very different nature (linear, circular, elliptical).
- Agitator ball mills/stirred media mills:[70] Milling media are moved by a rotating agitator/stirrer in a usually stationary chamber.

Depending on the type of milling approach, the energy transfer to the milling media is different resulting in different ball accelerations and thereby inertia forces that are being applied to the milling media. An overview is given in Table 1.

As almost all of the mechanical energy that is transferred into the milling chamber is eventually dissipated into heat. Also the part of the mechanical energy consumed for particle fracture and reactions is to a high percentage converted into heat. Therefore, the higher the power density within the milling chamber (power input divided by chamber volume) the more important adequate cooling becomes. However, a rotating drum is very hard to cool as it is very difficult to insert and remove the cooling liquid in a rotating jacket. The cooling of a moving chamber without rotation (vibrating chamber) is easier and more practical for a stationary chamber like in agitator mills.

The possibility for scale-up from laboratory scale to large production scale is another important topic to address. Tumbling ball mills and stirred media mills are realized at very large scales with drive powers in the MW scale. Vibrating mills are realized up to the 100 kW scale, whereas planetary ball mills are restricted to the low kW scale. So far, attempts to scale

| Name                  | Movement of balls             | Possibility of cooling | Ability of large scale | Maximum acceleration | Collision frequency[a] | Stressing energy[a] |
|----------------------|--------------------------------|------------------------|------------------------|----------------------|------------------------|---------------------|
| Tumbling ball mill   | Rotating drum                  | Very poor              | Very good              | \( 1 \times g \)      | Low                    | High                |
| Planetary ball mill  | Rotating drum in centrifugal field | Usually very poor     | Very poor              | \(<150 \times g\)    | Moderate               | Very high           |
| Vibrating ball mill  | Vibrating mill chamber         | Moderate               | Moderate               | \(<30 \times g\)     | High                   | High                |
| Agitator ball mill   | Rotating agitator/stirrer in stationary chamber | Moderate               | Very good              | \(<Several 100 \times g\) | Very high             | High                |

[a]Evaluation based on typically applied milling media sizes (g = gravitational acceleration).
these mills to larger sizes and to operate these mills continuously were not successful. Therefore, for an industrial application research results achieved in planetary ball mills have to be transferred to other mill types.

The above mentioned stressing conditions have been described for several milling types\cite{34,36,55} and can even be modeled by simulations using discrete element methods.\cite{34–37} An indication for the values of the stressing energy and the collision frequency as mill related characteristic parameters for the different ball mills is given in Table 1. As the product of collision frequency and stressing energy is a measure for the power input of a certain mill, a tumbling ball mill has the lowest power density (power input per mill volume) followed by the vibrating mill. The highest power densities are achieved by the stirred media mill followed by the planetary ball mills. However, new constructions of vibrating mills exist that achieve power densities comparable to planetary ball mills.\cite{71,72}

From a general point of view, planetary ball mills, vibrating ball mills, and stirred media mills are all suitable for mechanochemical syntheses of solid electrolytes and their further mechanical treatment to form composite materials. However, until now almost always planetary ball mills have been used due to their high availability, cost efficiency, simple handling, as well as the possibility to handle up to four processes at the same time in the mill. Therefore, in this review we will continue with a focus on the planetary ball mill. However, due to restrictions regarding cooling and scalability, the use of vibrating ball mills and agitated ball mills must surely increase and pave the way to large-scale application of this technology as further discussed in Section 5.

### 2.2. Solid-Phase Reactions by Mechanical Milling

Heterogeneous solid-phase reactions can be performed in ball mills in which mechanical energy is used to initiate the reactions as well as to create new reactive surfaces and new particle arrangements. Many reactions can proceed via solvent-free routes or with less toxic solvents, resulting in a more sustainable process at fewer risks.\cite{61,73} The direct reaction of solids in ball mills is often faster and does not require a subsequent recrystallization.\cite{61,73,74} so that these routes are regarded as very energy-efficient.\cite{75,76} Additionally, unique products can be obtained that are not accessible via solid state syntheses, solvent-based routes or only at insufficient purity.\cite{74,77–79} as even thermodynamically less stable products are attainable.

The energy required for the chemical conversion is provided mechanically by the milling media. At each collision, the milling media capture the mixture of particulate reagents and fractions of the milling media’s kinetic energy are dissipated initially into product conversion, microstructural fracturing, and generation of new surface, structural changes and heat dissipation, respectively.\cite{80,81} Even more so, the mechanical loading ensures the mass transfer at the contact zones exceeds transport limitations, which is particularly helpful to overcome solid-state diffusion limitations.

A sufficient particle refinement ensures the mixing of reagents on the microscale,\cite{82} thus an inadequate refinement can lead to only a partial conversion in near-surface areas.\cite{36} in turn results in low homogeneity of the synthetic process. The process rate is considered as the overall rate of product conversion of a mechanochemical reaction. Besides the power input, the reaction rate affects the overall process performance, considering that the product batch is subsequently synthesized, depending on the availability and distribution of energy.

Altogether, the mechanochemical process is subject to a number of simultaneously occurring effects. The intensity of stressing may be rate determining, if it is below the activation threshold to induce a successful conversion. However, only rarely an effect of stressing intensity on the process rate can be demonstrated.\cite{83} While for example the stressing intensity of a ball milling process was always sufficient to overcome the activation threshold of the organic Knoevenagel condensation, making the power the decisive parameter,\cite{36} this is not always the case for solid-state reactions. Here, sometimes only local crystalline domains are formed that require a subsequent temperature treatment to yield the desired compound.\cite{28,84} In most cases, the influence of the stressing conditions is not clearly identified or the process parameters themselves are not described in detail. However, the influence of stressing intensity should not be neglected and it is therefore important to test and report the different process parameters when using ball-milling in solid-state syntheses to establish how much these affect product formation and crystallization. Therefore, the interpretation of data by these well understood effects of input parameters on the stressing conditions as well as a carefully designed parameter setting are essential. In addition to the required mechanical energy input to proceed the solid-state reaction, the generated heat can be distributed differently in the chamber and may accelerate the reaction, depending on its temperature level, and is further discussed in the next section.

### 2.3. Heat Generation

Although many mechanochemical reactions are characterized by negative reaction enthalpies, i.e., endothermic reactions, heat generation is always observed in ball mills.\cite{39,65,85,86} In contrast to grinding processes, this may affect the reaction kinetics.\cite{36} A solid-state reaction takes place at the interfaces of the reactants, so that an increased diffusion due to the increase in temperature accelerates the chemical conversion.\cite{87} The temperature increase was found to be connected to the power input,\cite{36,88} independent of whether the energy is dissipated via head-on collision or tangential stressing like rolling or friction.\cite{36} By milling media contacting, via collision and/or frictional contact, a large share of energy is dissipated into heat.\cite{39} In the contact area, locally high temperatures are reached by short duration\cite{89} and contribute to a rise up to media temperatures of 200 °C.\cite{39,90}

The temperature development, and especially temperature distribution, does not only depend on the power input, and with it the amount of energy available for heat dissipation,\cite{90} but also on the location of the powdery material either as free-flowing bulk material or in the form of layers on the milling media and the container wall. The temperature difference between the chamber and milling media can
be significant and depends on the heat dissipation via the media surfaces.\textsuperscript{[88]} Consequently, large milling media with a lower surface-to-volume ratio and thus, poorer heat dissipation, reach higher temperatures at their surface in comparison. Likewise, an increased layer formation on the milling media surfaces leads to increased milling media surface temperatures, since the layer confines the heat transfer.\textsuperscript{[88,90]} The product properties can hence be significantly influenced by the local temperature,\textsuperscript{[88]} such as the formation of a predominantly crystalline product at high temperatures compared to an amorphous product at lower local temperatures. Therefore, if the mill is not sufficiently cooled the processing has to be interrupted by operating pauses to cool down the chamber content.\textsuperscript{[28]}

2.4. Processing of Solid-State Electrolytes in Planetary Ball Mills

Planetary ball mills are most often used for laboratory synthesis of solid electrolytes, which may be attributed to the simplicity of the experimental set-up, the high suitability for lab operation as well as the wide-spread use of this technological device.\textsuperscript{[80,91]} Figure 2 depicts the parts and operation of a planetary ball mill. The horizontally orientated rotating milling chambers (in this case jars) are mounted on a so-called sun wheel, which rotates usually in the opposite direction to the jars and provides the centrifugal field for the rotating jars. The speed ratio k of the angular velocity of the jars, n_j, and the sun-wheel, n_{SUN}, can affect the motion of the balls within the jar.\textsuperscript{[17]} Depending on the ratio and the friction between the milling media a catteracting (milling media fly inside the jar) or a cascading motion (milling media roll on each other) of the balls is achieved. Besides the angular velocities, the size and density of the milling media as well as the powder to milling media ratio are decisive for the process performance and achieved product quality.

2.5. Influence of Operation Parameters

The effect of the different operational parameters on mechanochemical reactions is often discussed in detail, but separated from one another.\textsuperscript{[92]} However, each parameter affects the stressing conditions, i.e., the collision number and transferred stressing energies, and with it, the amount and distribution of dissipated energy. The stressing conditions then influence the reaction mechanism (especially stressing intensity) as well as the reaction rate (both collision frequency and stressing intensity), and the influence of the operation procedures is clearly convoluted. The suitable selection of operation parameters for setting defined conditions enables control of the process and helps reach the desired yield, but it can also help to understand the underlaying mechanism. The adjustable process parameters are 1) size and material of milling media, 2) the amounts of milling media, considered as media filling ratio, to ensure the comparability for various media sizes, and 3) the powder filling ratio. Beside that also the rotational speed of the sun wheel can be varied but very often this parameter is kept constant.

2.5.1. Milling Media Size and Material

The milling media size should provide a sufficient intensity to induce fracture or a successful conversion, but at a preferably high number of collision events. As the collisions are discrete events, where the energy is initially dissipated into the captured and stressed powder, a high collision number at sufficient stressing intensity is preferable to a small number of collisions with very high intensities. Coarser milling media lead to higher stressing energies and by that to increased intensities (cf. Equations (5) and (6)) due to their larger mass, at a cost of a lower collision frequency,\textsuperscript{[14]} whereas smaller milling media may need higher rotational speeds to achieve a certain stressing energy.

Some publications use only few but large milling media (>10 mm),\textsuperscript{[93,94]} which is often not recommended from the perspective of process engineering, especially not for milling media sizes that are large in comparison to the jar volume. The media motion is hindered due to limited space, accompanied by abrasion, leading to contamination (see below). Furthermore, the low number of media results in a very low collision frequency, hindering good mixing and fast processing. The high stressing energy may not be transferred homogeneously to the particles, which makes the process even less efficient. A stressing intensity that is higher than the one required for fracture or conversion, leads to poor energy utilization.\textsuperscript{[86,53]} In addition, the distribution of heat is impeded due to the surface ratio of milling media and inhomogeneous temperatures are expected.

As known in comminution processes the use of smaller milling media at higher speeds leads to a faster reduction in particle size when the stressing intensity is sufficient for an effective breakage due to the higher collision frequency in comparison to coarser media.\textsuperscript{[39]} In contrast to the local energy dissipation, the media size does not strongly affect the power, provided that the filling ratio or the total mass of media is kept constant. When discussing results, the total power input can be assumed to remain almost unchanged when solely the media size is varied.\textsuperscript{[14]}

Besides the size, the stressing energy is also directly affected by the density of the milling media. In a first approximation the stressing energy increases linearly with the milling media solids density. The milling media material is also of importance due to possible abrasion,\textsuperscript{[95]} which can lead to a contamination of the product or act as a beneficial reaction auxiliary.\textsuperscript{[96]} For instance, copper milling media has been used in the catalysis for solvent-free Sonogashira coupling,\textsuperscript{[97]} and when using steel milling media and mills, Fe contamination can often be found.

A suitable selection of the milling media is consequently subject to various requirements and recommendations: whereas a simple approach for high energy would be a higher mass and with it size of the milling media, the poor distribution of energy, and poor mixing as well as high energy generation should in the first approach lead to favoring smaller milling media at higher rotation speeds. Under solvent-free conditions the layer formation leads to a larger active mass and cushioning effects on the impact that can negatively affect the stressing intensity.\textsuperscript{[39,47]} Therefore, milling media in sizes larger than 1 mm should be used for dry processes, while for wet milling experiments even smaller sizes are recommended.\textsuperscript{[93,64]} Moreover, the
higher the density of the milling media, the smaller the media size can be chosen.

A large surface area of the milling media may lead to a higher total amount of material that sticks to the milling media and the jar surface. If low powder fillings are used, for instance, due to the low availability or high costs of educts, the issue of product loss due to strong adhesion needs to be addressed. Furthermore, smaller milling media also result in more stressing by rolling and friction,\textsuperscript{[34]} which can even intensify the adhesion behavior.

2.5.2. Rotational Speed

The rotational speed of the sun disk $n_{\text{SUN}}$ is an easily adjustable operation parameter. The speed ratio $k$ of the angular velocity of the jars, $n_j$, and $n_{\text{SUN}}$, can affect the motion of the balls within the jar.\textsuperscript{[37]} The chamber wall follows a motion path, in which the path depends on the speed ratio between sun disk and milling chamber. This means that for a ratio $k = -1$ follows a closed circle, for a ratio $k = -2$ a closed ellipse or even noninteger speed ratios are possible that result more complex paths. The chamber wall speed changes depending on its position, but the mean chamber rotational speed equals the one of the sun disk. However, most planetary ball mills have a fixed speed ratio due to the mechanical transmission, and only special machines allow this ratio to be selectable. The direction of the rotation of the sun wheel and milling media should be in each other’s opposite, to obtain higher collision frequencies and higher power input,\textsuperscript{[98,99]} resulting in a negative speed ratio. Different speed ratios can favor different motion patterns of the media charge and result in different stressing conditions.\textsuperscript{[8,100]} An optimum speed ratio can be investigated in regards to the highest stressing energies. However, this optimum increases with sun disk radius, and chamber diameter, as well as friction. This is why no generally valid value can be given, and the manufacturers often state that they use the best possible ratio.\textsuperscript{[101–103]}

In principle, the stressing energy and collision frequency, and with that the power input, increase with the rotational speed of the sun disk and with that also of the milling chamber (due to fixed speed ratio). However, the increase is not linear, since the milling media charge is subject to a complex motion pattern. This is due to the fact that the milling media are accelerated more strongly in contact with the wall, while simultaneously the time interval between the impacts on the chamber wall is shortened.\textsuperscript{[103]} All of this leads to a higher energy dissipation in particular, yet only to a slight increase of collision frequency. The effect of the rotational speed is superimposed by a multitude of other factors. The dependencies below (Equations (8)–(10)) are intended to serve as a rough estimation. The effect of the rotational speed on the stressing energy and power (both total and in normal direction) is amplified by larger media filling ratios, so that the corresponding exponent takes on larger values depending on the specified range.\textsuperscript{[14,100,101,104]}

\begin{align*}
\text{CF} & \propto n_{\text{SUN}}^3 \alpha = 0.4 - 0.6 \\
\text{SE} & \propto n_{\text{SUN}}^b = 2.4 - 3.1 \\
\text{P} & \propto n_{\text{SUN}}^c = 2.9 - 3.5
\end{align*}

These numbers can be used to interpret experimental results and to estimate the change of power, and thus, of the energy transferred into the product.

2.5.3. Media Filling Ratio

The filling ratio of milling media $\varphi_{\text{media}}$ (Equation (11)) is defined as ratio of media bulk volume, $V_{\text{media, bulk}}$, to the chamber volume, $V_{\text{chamber}}$. This definition is reasonable, as a filling higher than 1 is not possible, although free pore volume in the media bulk is still available.

\begin{equation}
\varphi_{\text{media}} = \frac{V_{\text{media, bulk}}}{V_{\text{chamber}}} = \frac{m_{\text{media}}}{(1 - \epsilon) \rho_{\text{media}} V_{\text{chamber}}} \tag{11}
\end{equation}

The bulk volume of media can be calculated based on the mass, $m_{\text{media}}$, and density, $\rho_{\text{media}}$, of media and by taking the bulk porosity, $\epsilon$, into account (Figure 3a). The media filling ratio mainly determines the power input into the milling chamber. With higher fillings, the collision frequency and, thus, the power input increases and allows for more powder while keeping the same powder-filling ratio (Figure 3b,d). Above a filling ratio of $0.5$–$0.6$ the power input starts to decrease, as the free path of the milling media is limited and the stressing

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{a,c) Media- and b,d) powder-filling ratios. In (b) the pore volume refers to the yellow area, representing the free space for powder, created by the milling media voids. A larger media-filling ratio allows for a larger powder filling due to an increased void-volume. This also allows for a precise powder-filling ratio adjustment (d). e,f) The motion of milling media can be hindered either by increasing the media size or by a high powder-filling ratio.}
\end{figure}
energy is significantly decreased. This holds true in absolute values; in relative values, i.e., when the powder filling ratio is kept constant and the mass of reagents is linearly increased with the media filling, the maximum relative powder can also be reached at fillings of 0.3. Therefore, filling ratios of 0.3 to 0.5 are recommended to be initially chosen, as higher fillings can limit the free movement of the milling media, while lower fillings with a low number of milling media induce a low collision frequency. However, the motion of the milling media can contribute to the deagglomeration of particulate layers, thus even smaller fillings may be favorable in some cases.

In contrast to the power input, the effects of the filling ratio on the stressing energy is more complex, as no general rule can be derived in dependence on the filling ratio. In a first approximation it could be assumed that there is no effect. But an increasing filling ratio and, thus, a decreasing free movement space for each milling medium negatively affect the media velocity, lower filling ratios tend to lead to higher stressing energies. However, at large milling media sizes the stressing energy can also decrease when the filling ratio is very small. Thus, the stressing energy is recommended to be controlled by an adequate selection of milling media size and density.

### 2.5.4. Powder Filling Ratio

Based on the media filling ratio, the powder filling ratio is defined as the portion of the free volume within the bulk of milling media filled with product powder. Often in literature the milling media-to-powder-ratio is used which describes a similar relation and is also often easier to calculate. However, the powder filling ratio considers that the active mass and also the damping behavior of the collisions depend on layer thickness and geometrical effects, which makes it reasonable to design the process in regard to the powder volume. Typical values for filling ratios are in the range of 0.5 to 1.

The powder filling ratio \( \phi_{\text{powder}} \) (Equation (12)) is determined by the bulk volume of powder, \( V_{\text{p,bulk}} \), in relation to the volume of pores of milling media bulk, \( V_{\text{media,bulk}} \cdot \varepsilon \) (Figure 3b). To consider the porosity of the powder, its bulk density \( \rho_{\text{P,bulk}} \) is measured experimentally.

\[
\phi_{\text{powder}} = \frac{V_{\text{p,bulk}}}{V_{\text{media,bulk}} \cdot \varepsilon} = \frac{V_{\text{p,bulk}}}{\phi_{\text{med}} \cdot \varepsilon \cdot V_{\text{chamber}}} = \frac{m_{\text{p}}}{\rho_{\text{med}} \cdot \varepsilon \cdot V_{\text{chamber}} \cdot \rho_{\text{P,bulk}}} \quad (12)
\]

The powder filling ratio can be varied in a wide range, and depends highly on the fracture behavior and the reaction itself. It has to be noted that the volume of the bulk powder can be quite high at the beginning of the milling process, e.g., for graphite powders as used in sulfur cathode composites within Li–S batteries. A large powder filling may impede the movement of the milling media, however, powder fillings ratios up to unity are common. Reducing the powder filling is often accompanied by shorter process times, but not necessarily by a linear dependency. Low powder fillings can be less efficient due to a reduced probability for the particles to be captured as well as a smaller active mass during collision. It is important to mention that the powder particles in the chamber dampen the collisions, which indicate the transference of energy into the powder. Therefore, it is highly recommended, if intensities occur that seem to be too low for the reaction to occur, to not reduce the powder filling, but rather to initially increase the stressing energy by larger milling media or higher rotational speeds.

### 2.6. Process Design and Practical Considerations

In comminution processes, the efficiency and size reduction are characterized in regard to the energy input. The goal is to identify the most efficient parameter setting, which does not necessarily correspond to the fastest processing. However, most publications on mechanochemical routes consider the effect of processing parameters and conditions on the conversion time, as the determination of energy input by power draw requires specific measurement systems (e.g., a torque sensor) or simulations which are in most cases not easily accessible.

However, considering the conversion as a function of time makes it hard to identify the mechanism, as it is difficult to distinguish between effects of energy dissipation and activation thresholds, and just faster mechanical processing. A faster process can be achieved by stressing larger amounts of reagents per time unit and thus, by the increased number of reaction sites, which would not necessarily accelerate the reaction rate.

While time intensive, it is recommended to investigate mechanochemical processes in regards to stressing intensity and energy demand. However, the determination of active mass to assess the stressing intensity can be difficult due to the strong adhesion of very thin powder layers and is associated with a large experimental effort. It not only changes with milling media size, but is also dependent on the layer formation, which has not been systematically described for different systems with varied operational parameters. Nevertheless, by testing varied milling media sizes, the effects of stressing intensity and collision frequency can be characterized in a rather straightforward manner.

Different milling media sizes lead to changes in stressing energy that are more significant than the change in active mass, so that the highest intensity can be correlated to the largest milling media. To compare the results even without data on the corresponding energy, it is essential that the power input is comparable, ensured by the use of the same milling media filling ratio, or same total mass of milling media filling and a constant rotational speed. Then it can be identified whether and what effect the intensity has on the reaction (see Burmeister et al.).

For instance, it was reported that the use of coarser milling media at a constant number of media consequently results in a higher powder input, which reduces the reaction time. This is a direct result of the larger amount of material stressed per collision due to the larger total contact area and higher milling media filling ratio. The time reduction can then be attributed to different mechanisms, such as to the larger amount of reagents that are stressed and processed, to the higher amount of energy available for conversion per time unit, the accompanied higher temperatures, or the effect of higher local energy dissipation and, thus, stressing intensity. When the reaction...
time is reduced for heavier milling media while maintaining the same total mass this is due to the threshold energy of the pre-reaction process.\cite{83}

From a practical point of view, mechanical milling offers the possibility for a variety of tuning knobs for process optimization. Factors such as size and density of the milling media, filling ratio, and rotational speeds can be understood. Therefore, for comparable results it is important to report all these parameters. Second, knowing the required total formation energy to transform the precursors to the final product, the ideal process parameters can be chosen or at least investigated. However, multiple factors as morphology changes that are potentially not favorable need to be considered as well. For instance, whereas certain reactions for the syntheses of crystalline solid electrolytes may require a high stressing energy and high local heat generation for crystallinity, processing of solid-state battery composites will require softer milling approaches to not amorphize the materials employed. Overall, mechanical milling offers a variety of synthesis and processing conditions and can be rather regarded as a toolbox for solid-state syntheses, rather than a black box of unknown synthetic influences.

3. The Beneficial or Detrimental Influence of Mechanochemistry in Solid Electrolytes

3.1. General Comments

Before discussing a few cases in which mechanochemical processing affects the material properties and solid-state batteries, some general comments will be helpful for an understanding of the differences in applicable synthesis methods and the underlying possibilities to tune them. First of all, it is important to be able to determine the chemical structure that results from synthesis. The method of X-ray diffraction has long been the standard technique to investigate the average bonding environment within solid electrolytes. This however, requires crystalline compounds with a certain coherence length.\cite{108} Typically, high temperature or solvent-based syntheses yield highly (poly)crystalline or even single crystalline samples.\cite{28,84,109} The mechanochemical synthesis, however, has been shown to possibly result in a strong amorphization or not fully crystallized materials with low coherence, making any diffraction analysis difficult. Here, pair-distribution function analyses or nuclear magnetic resonance can be helpful to investigate the local structure of low-coherence materials.\cite{28,109–111} For instance, Figure 4 shows three different materials as an example of how milling itself leads to rather amorphous less coherent materials structures, compared to the more crystalline structures obtained after a subsequent annealing step. Remarkably, for Li$_3$ErCl$_6$ and Li$_6$PS$_5$Br it has been shown that a rapid crystallization within a minute with subsequent quenching results in apparently fully crystalline compounds,\cite{28,84} suggesting that the final material is already being formed locally during the mechanochemical syntheses albeit not fully crystallized.

Mechanochemical synthesis enables the formation of unique compounds, which cannot be obtained by a classic solid-state synthesis or only with unsatisfactory purity. Those compounds are often amorphous variations or metastable polymorphs of known compounds that can be stabilized by the kinetic energy

![Figure 4. Comparison of a mechanochemical preparation and classic high temperature processing or syntheses for different materials classes. Whereas mechanochemical synthesis leads to partially amorphous (low coherence) materials with prevalent crystalline domains, rapid crystallization can occur within a minute when annealing, eventually leading to growth and an ordering of those domains with a resulting long-range coherence. Data digitized from Schlem et al.,\cite{28} Gautam et al.,\cite{84} and Krauskopf et al.,\cite{109}](image-url)
transfer, contrary to equilibrium-formation during the classic solid-state approach. In the following case studies, we will address a few selected examples on how mechanochemical processing affects the structure and with it the transport properties of solid ionic conductors.

### 3.2. Lithium Conducting Halides

An interesting example of the severe influence of the preparation method on the local structure is some of the lithium halides. Mechanochemical synthesis offers the possibility of kinetic control, in contrast to a classic, thermodynamically controlled high temperature solid-state synthesis and hence enables the formation of thermodynamically less stable materials. In the case of Li₂ZnCl₄, for example, one has to carefully choose the synthesis parameters, as two polymorphs exist that are difficult to obtain separately from one another. The high temperature solid-state synthesis mainly yields a metastable olivine-type structure, while a low-temperature spinel-type structure coexists. A possibility to obtain the pure spinel is to anneal the mixture for a few weeks at a low temperatures. By contrast, preparation by a mechanochemical route results in the formation of solely the low temperature spinel-type modification within a fraction of synthetic time. Clearly, the reaction processes by heating in the ampoule and by momentum transfer in the mill are fundamentally different and can result in different polymorphs of materials. With the changing structure, the electrochemical performance of both structures differs significantly. Lutz et al. have shown that the high-temperature olivine-type structure has a significantly lower activation energy, governed by a higher ionic conductivity up until a temperature of around 200 °C where both polymorphs can coexist.

A material-class that is currently investigated for application in solid-state batteries is the ternary halide class Li₃MX₆ (M = Y, Er, In; X = Cl, Br, I). A multitude of compounds with various cation–anion combinations have been shown to have significantly different ionic transport properties achieved by different preparation methods. A detailed study on the comparison of a mechanochemical synthesis to a high temperature solid-state synthesis for Li₃(Y/Er)Cl₆ has shed light on less pronounced, but not less important changes that occur within the structure when comparing an ampoule synthesis to a mechanochemical synthesis with a subsequent rapid crystallization step. As an example for those compounds, Li₃ErCl₆ exhibits an erbium disorder between different positions (schematically shown in Figure 5a). Schlem et al. have shown that this exchange is not only influenced by the employed synthesis method, but can actually be tailored. Here, the mechanochemical synthesis leads to a significant disorder of up to 88.1%, while the ampoule synthesis only results in a disorder of only around 2.3% (Figure 5b). A variation of the annealing time for the mechanochemically synthesized compound reduces the disorder (Figure 5b). The disorder in this case can be understood as a variant of the thermodynamically most stable structure (ampoule synthesis), with a slight amount of disorder always found, likely due to entropic reasons, which is reversed in the mechanochemically synthesized compound by a thermic treatment. Moreover, the resulting transport properties change and have been directly correlated to the observed erbium disorder. The decreasing disorder with increased annealing time results in a decrease of the conductivity by over one order of magnitude, governed by an increase of the activation energy (Figure 5b). In other words, mechanochemically prepared materials of this class exhibit higher ionic conductivities.

However, a mechanochemical synthesis by itself is not always favorable. By comparing an as-prepared and subsequently annealed sample of Li₃InCl₆ and Li₃YBr₆, respectively, Li et al. and Schlem et al. have shown that the subsequently annealed sample exhibits an increased ionic conductivity, which is contrary to the observation in Li₃ErCl₆. In the case of Li₃YBr₆, the yttrium disorder is also larger in the mechanochemically synthesized sample and neutron diffraction studies suggest that here the disorder is detrimental due
to the structural differences, rather than beneficial on the ionic conductivity. This suggests that the local structural disorder introduced by mechanical milling can have a negative effect on the resulting ionic conductivity in some structures. Overall, these examples impressively show the impact the employed synthesis routes can have on the properties of lithium conducting halides and that processing is just as important as the structural chemistry aspect itself.

### 3.3. Lithium Argyrodites

Some of the most researched thiophosphate-based solid electrolytes are the lithium argyrodites, with element-substituted compounds having a high conductivity up to 24 mS cm$^{-1}$.[126–131] Similar to the halides, these materials show varying degrees of disorder, here specifically an anion disorder in the form of a halide–sulfur crystallographic site exchange. As the exchange is often discussed to have a significant influence on the resulting transport properties,[84,132,133] many studies have attempted to influence this exchange by iso- and aliovalent substitutions.[126,134–139] However, changing the chemical environment also results in more convoluted influences on the resulting transport properties that can be difficult to separate.[134,138]

Brink et al.[111] have investigated the influence of the crystallite size on the resulting transport properties in Li$_6$PS$_5$I. While the classic solid-state synthesized compound has a poor ionic conductivity of around 10$^{-3}$ mS cm$^{-1}$,[111] a subsequent processing step of 120 min in the ball-mill can boost this value up to 0.5 mS cm$^{-1}$. Early on it was shown that a just milled (as prepared) Li$_6$PS$_5$I has a significantly better ionic conductivity compared to its annealed counterpart (Figure 6a), with reversed trends for Li$_6$PS$_5$Cl and Li$_6$PS$_5$Br.[113] A significant broadening of reflections observed in the diffraction pattern of the milled samples suggests an occurring amorphization during milling, as discussed for a multitude of different material classes.[28,122,140] Interestingly, although the $^6$Li MAS NMR spectrum does not change when comparing both samples (Figure 6b), the $^{31}$P spectrum changes notably (Figure 6c). The sharp peak in the $^{31}$P spectrum from the microcrystalline (ampoule synthesis) sample suggests a highly ordered arrangement within the PS$_4^{3-}$ tetrahedral units. A second contribution appears in the nanocrystalline sample (after the milling step) that is shifted toward smaller ppm values, indicating a larger amount of structural disorder of the PS$_4^{3-}$ tetrahedral units and a distribution of inequivalent P-sites with different P=S bond lengths and resulting local distortions. The remaining sharp peak with lower intensity compared to the ampoule synthesis that represents the highly symmetrical PS$_4^{3-}$ tetrahedral core with highly disordered, glassy like shell. An arrangement like this cannot be obtained by a classic solid-state synthesis, however, potentially by a solution-assisted synthesis.[21] The increased disorder and distortion leads to an enhancement of the ionic conductivity by two orders of magnitude from 10$^{-3}$ mS cm$^{-1}$ up to a value of 0.5 mS cm$^{-1}$, governed by an activation energy reduction from 0.47 to 0.36 eV.[111,141] Nevertheless, while milling of Li$_6$PS$_5$I leads to an increased ionic conductivity, milled Li$_6$PS$_5$Br, for instance, exhibits a lower ionic conductivity...

![Figure 6. a) Transport property comparison of a micro- (ampoule synthesized)- and nanocrystalline (subsequently ball-milled) sample of Li$_6$PS$_5$I. An increased ionic conductivity and decreased activation barrier can be observed for the nanocrystalline sample. b,c) Comparison of the $^6$Li and $^{31}$P nuclear magnetic resonance spectra for both differently prepared samples. Whereas no differences can be observed in the $^6$Li spectra, the $^{31}$P spectrum of the nanocrystalline (subsequently ball-milled) sample shows a larger spread of chemical shifts, indicating a greater structural distortion with a variety of different prevalent bond-lengths within the PS$_4^{3-}$ units. Adapted with permission.[111] Copyright 2020, American Chemical Society.](image-url)
3.4. Sodium Thiophosphate Na₃PS₄

Na₃PS₄ is one of the sodium-based compounds that has attracted significant interest in recent years due to having a good ionic conductivity of around 0.03 mS cm⁻¹.[109,142,143] Interestingly, Na₃PS₄ is known to crystallize in two polymorphs that are structurally close, but not identical, resulting from a minor PS³⁻ unit rotation that can be observed in the tetragonal modification.[109] It has been shown that a mechanochemical synthesis results in the formation of the cubic polymorph, while the high temperature ampoule synthesis yields the tetragonal polymorph.[144] Comparing this to the above-mentioned structures, this is highly surprising, as the mechanochemical synthesis usually results in a more distorted and disordered structure, which seems to be the opposite here. The direct comparison of a (tetragonal phase) solid-state synthesis and a (cubic phase) mechanochemical synthesis by Krauskopf et al.[109] shows that the cubic phase has significantly favorable transport properties. However, preparing the tetragonal phase by using a milling procedure followed by subsequent annealing, identical transport properties are found as for the mechanochemically prepared cubic phase. This suggests that the slight distortion from the cubic to the tetragonal phase is not the main driving force for the observation, but rather an aspect that has not yet been discussed for the previous compounds. Na₃PS₄ has only fully occupied sodium positions, which should result in a bad ionic conductivity.[109,145] However, introducing vacancies should result in a great enhancement,[109,143] as has been impressively shown by an antimony by tungsten substitution within Na₃SbS₄, where small amounts of vacancies and the stabilization of the cubic polymorph resulted in a conductivity increase of several orders of magnitude up to a value of 41 mS cm⁻¹.[147,148] When comparing solid-state synthetic approaches and ball milling, it was shown that Mo can be introduced in Na₃SbS₄ using mechanochemical milling, whereas a solid-state synthesis does not lead to a Mo incorporation, suggesting that milling does have an additional influence on the phase stability of these highly substituted materials.[147,149] A different type of disorder of sodium within the structure, where the compound still resembles the nominal composition, but has partially vacant sodium positions, with interstitial positions being slightly occupied by the missing sodium is discussed in a theoretical work by Zhu et al.[143] where it is shown that this type of disorder significantly boosts the electrochemical performance. This general idea of introducing disorder in the mobile species substructure might be the reason, why the mechanochemically synthesized compounds usually have a better ionic conductivity, as it has been previously reported for different materials. It is furthermore worth mentioning that the transport properties of every compound are not necessarily favored by a vacancy introduction.

Another important aspect when comparing a mechanochemical to classic solid-state synthesis is the occurring microstructural strain, which has been discussed in detail by Famprikis et al.[142] The peak width and systematic broadening in a diffraction pattern can give insight into the average grain size and microstrain. Here, a systematically increasing broadening of the diffraction peaks from the mechanochemical synthesis to the ampoule synthesis can be attributed to the increasing grain size and significantly decreasing microstrain. Moreover, the resulting ionic conductivity is heavily dependent on the micro- and macrostructure that is used for the transport property measurement (Figure 7a). The finer powder and smaller grain size of the mechanochemically milled sample result in an improved mechanical processing capability, facilitating the pellet-consolidation and potentially boosting the overall electrochemical performance by enhancing the contact behavior at the interfaces and decreasing the tortuosity for ionic diffusion (Figure 7b).[142]

An in-depth work by Nguyen et al. shows in great detail the influence of the disk-rotation speed (compare to Figure 1a,c) and milling-media size on the formation and ionic conductivity of Na₃PS₄.[150] Figure 8 shows the dependency of the conductivity respective to the total milling time for a) different rotations speeds and b) milling-media sizes. Strikingly, after a
certain amount of milling time, the different synthesis conditions result in compounds with the same conductivities, converging against a plateau of $10^{-4}$ S cm$^{-1}$. Valuable information can be obtained by comparing the different synthesis conditions. With increasing rotation speed (Figure 8a) a higher ionic conductivity can be achieved in a smaller amount of time, with the larger milling media (Figure 8b) resulting in the same observation. This is likely related to the necessary energy to transform the precursors to the final material. A higher rotation speed increases the power input, so that more energy is available to reach the conductivity plateau in a smaller amount of time. However, also the stressing energy is increased. To distinguish between the effect of power and stressing intensity, the influence of the size of media is considered. The larger milling media at a constant filling ratio, which corresponds to a constant total mass of media, lead to higher stressing energies, while the power input remains nearly unchanged. Here, the larger media is clearly favorable over the smaller media sizes, which indicates that the compound with high conductivity is achieved by high local energy dissipation.

Valuable information for upscaling can be obtained by the work of Nguyen et al.\cite{150} regarding the scalability of such synthesis procedures. While the required synthesis time is commercially of great interest in context of the financial feasibility, the safety aspect cannot be neglected. Large amounts of precursor powder and heavy milling-media can be dangerous when rotated at a high speed in giant jars. The above-shown data suggest that a compromise of milling media size and rotation speed can yield the same result, enabling the employment of milder preparation procedures when increasing the milling time (Figure 8a) by reducing the rotational speed.

### 3.5. Li$_3$S–P$_2$S$_5$ Glass–Ceramics and Hybrid Electrolytes

The lithium thiophosphate glass–ceramics have experienced significant attention in last decades, due to their interesting chemistry, including a wide range of possible stoichiometries, their mechanically soft nature and good electrochemical performance. However, the mostly amorphous nature makes these compounds difficult to study by classic X-ray diffraction techniques. Here, mainly the groups around Tatsumisago and co-workers,\cite{151-153} Dietrich et al.\cite{110} and Eckert et al.\cite{154} paved the way for a better understanding of the structural details within these compounds. Early discussions on the (Li$_2$S)$_x$–(P$_2$S$_5$)$_{1-x}$ glasses were reported by Tachez et al.\cite{155} with a maximum range of $(0.63 < x < 0.68)$ obtained by melt quenching, which was exceeded by Zhang and Kennedy\cite{156} up to a range of $0.5 < x < 0.7$. Employing a mechanochemical approach, Tatsumisago et al.\cite{153} were able to expand the glass-formation range up to $x = 0.8$, again showing the ability of the ball mill synthesis to exceed limitations of classic synthesis approaches.

For instance, Li$_3$PS$_4$ exists in three different polymorphs, the $\gamma$, $\beta$, $\alpha$-phase representing the low-, medium-, and high-temperature modifications, respectively.\cite{157} A classic solid-state synthesis with a standard cooling step results in the formation of the low temperature $\gamma$-phase. It has been shown however that a solution based synthesis\cite{158,159} can yield nanocrystalline powder of $\beta$-Li$_3$PS$_4$ and a mechanochemical synthesis\cite{111} with a subsequent crystallization step can yield $\beta$-Li$_3$PS$_4$ with standard crystallite sizes, with both being stable at room temperature. Besides achieving different polymorphs, by synthesizing Li$_3$S–P$_2$S$_5$ glasses with different molar ratios, different possible polyhedral connectivity of the PS$_4^3$–tetrahedra within different compositions can be found that cannot be obtained by a classic solid-state synthesis.\cite{160} Liu et al.\cite{160} compare interesting different approaches to incorporate Zn$^{2+}$ into the Li$_3$PS$_4$ glass–ceramics to increase the charge-carrier density. The approach of adding ZnO to a final, amorphous mixture of Li$_3$PS$_4$, followed by an annealing step does not appear to result in a successful incorporation of Zn$^{2+}$ into the structure. Contrary to this, starting from a mixture of the precursors P$_2$S$_5$, Li$_3$S, and ZnO that are being pre-processed via milling and subsequent crystallization results in a successful co-incorporation of Zn$^{2+}$ and O$^{2-}$, doubling the ionic conductivity up to a value of 1.12 mS cm$^{-1}$ for Li$_{3.06}$P$_{0.98}$Zn$_{0.02}$S$_{3.98}$O$_{0.02}$, compared to the
pristine Li₃PS₄ glass–ceramic. The beneficial effect of an aliovalent substitution on Li₃PS₄ has recently been confirmed by Zhao et al. in a Li₃PₓS₉₋ₓTeₓS₉ glass–ceramic.[165] The usage of mechanochemical synthesis again demonstrates how the kinetic energy transfer enables the formation of metastable compounds and local structures that are not accessible via classic solid-state routes.

Aiming to combine the advantages of different electrolyte classes, interest in so-called hybrid electrolytes has recently increased. One goal is to unite the high conductivity at room temperature of sulfides with the flexibility and good processability of polymers. Hayashi et al.[162] prepared such inorganic–organic hybrid electrolytes by a mechanochemical reaction in a planetary ball mill. 70Li₂S·30P₂S₅ (mol%) and different −OH group terminated oligomers (diethylene glycol, polyethylene glycol with molecular weights of 400 and 1000, polyethylene glycol dimethyl ether, and 1,4-butanediol) were processed together with alumina milling media (10 mm in diameter) in alumina jars for 5 h at a rotation speed of 370 rpm. At a polymer mole fraction of 20% or less, fine powders were obtained that revealed the formation of P=O–C bonds for all samples except for the one prepared with polyethylene glycol dimethyl ether indicating a reaction of the P-S-P network with the −OH group. Interestingly, it was found that small amounts of the oligomers can enhance the ionic conductivity by reducing the glass transition temperature Tg of 70Li₂S·30P₂S₅. Oligoethers exhibited a decrease in ionic conductivity, which was attributed to ether oxygen atoms working as a weak trap for Li⁺. The same result was observed for longer chain lengths. Hence, the hybrid electrolyte with 2 mol% 1,4-butanediol showed the best performance with an ionic conductivity of 9.7 × 10⁻⁴ S cm⁻¹ at 25 °C compared to 6.3 × 10⁻⁴ S cm⁻¹ of the pristine 70Li₂S·30P₂S₅. Although, this work already demonstrates the potential of hybrid electrolytes, further improvement might be achieved by optimization of the ball milling process as well as application of solid electrolytes with a higher initial ionic conductivity.

### 4. The Influence of Mechanochemical Processing of Solid-State Batteries

#### 4.1. General Comments

The processing and upscaling of solid-state batteries is still challenging and although the mechanochemical synthesis can potentially enable such an upscaling, the effects on the different compounds are yet not fully understood. The processing of solid electrolytes for the use as separators to enhance the interface behavior respective to the anode and furthermore the processing of cathode composites are especially challenging as they potentially include multiple phases (cathode active material, SE, carbon additives or binders) that behave differently while processing. Furthermore, the mechanochemical milling procedure, being a solvent-free route could enable the processing of coatings while overcoming the risk of damaging the material due to a chemical instability. Moreover, the necessary drying process after a solvent-assisted coating can potentially change the microstructure, leading to cracks within secondary particles[167]

#### 3.6. Oxides-Based Solid Electrolytes

As the prominent oxide-based solid-electrolytes represent the mechanically hardest and most brittle compounds, a mechanochemical processing or synthesis is of great interest, especially because it can assist with the previously discussed necessary particle breakage for a successful reaction. To our best knowledge, no systematic study exists that directly compares the influences of the preparation method via milling on the transport properties of those prominent oxide-based solid electrolytes. Influences via different sol–gel approaches have been shown.[22] However, amorphization during milling and crystallization by annealing was still observed and some interesting approaches regarding the synthesis were suggested.[161,164] Nagao et al.[165] for example, show that the transport properties of xLiₓBO₃·(100-x) Li₂CO₃ glasses depend on their preparation method and resulting crystallinity. A complete amorphization can be observed during milling, with an occurring crystallization by annealing at 260 °C (metastable phase) or 450 °C (glass ceramic). The conductivity of the glass ceramic is doubled compared to the amorphous mixture (6.5 vs 3.0 × 10⁻⁴ mS cm⁻¹), and while this compound cannot be regarded as a good lithium-ion conductor, the investigation shows that the trends observed for the different material classes may hold for the oxides as well. An interesting aspect of the garnet solid-electrolyte preparation is the solvent-assisted approach during the processing in the ball mill. Song et al.[166] report the synthesis of Liₓ₆Aₓ₁₂₃₃LaₓZrₓ₉₅Caₓ₀₅Oₓ₁₄ by mechanochemically milling a mixture of Li₂CO₃, La₂O₃, and Zrₓ₉₅Caₓ₀₅Oₓ₃, in ethanol, with a subsequent crystallization step and a resulting high ionic conductivity of 0.52 mS cm⁻¹. The use of a liquid buffer layer during ball milling not only influences the microstructure, but moreover has a significant influence on the energy that is transferred onto the precursors. While solution-assisted milling may be difficult due to the limited chemical stability of solid-electrolytes in combination with some solvents,[23] it may pave ways for new and interesting synthesis approaches that have not been investigated yet.

#### 4.2. Detrimental Influences of Milling on the Electrolyte

As shown above, the synthesis of solid electrolytes via mechanochemical milling often leads to better ionic conductors, nevertheless, Dewald et al.[168] have shown for LiₓPSₓCl and Li₁₀GePₓS₁₂ that the ionic conductivity decreases if the ampoule synthesized compound is further processed in the ball mill (**Figure 9**). By investigating the compound by X-ray diffraction, it was shown that the observed trends by rapid annealing and quenching are reversed when a crystalline compound is processed in the ball mill, where a significant amorphization occurs. In the case of the argyrodite, it is difficult to gauge whether only an amorphization or also a partial decomposition into precursors or intermediates occurs.[84] This relates to the significantly broadened reflections with very low intensity, where it is difficult to distinguish different contributions. This observation raises the concern regarding the validity of a
mechanochemical route in upscaling solid state battery mixtures either for separators or in cathode composites. It may very well be that a subsequent mechanochemical processing step is beneficial for the transport properties in certain materials compositions, whereas it is detrimental in others. In addition, the process parameters will likely be important in which harsher milling may lead to faster amorphization when compared to wet or low energy milling.

4.3. Processing of Separators for Lithium Metal Anodes

Mechanical failure that manifests itself as cracks is still a challenging aspect of solid electrolyte application in all-solid-state batteries. The amorphous Li$_3$PS$_4$ glass is known to form a stable, albeit more resistive decomposition products at the interface (Li$_2$S and Li$_3$P formation) in contact with a lithium metal anode.\cite{169} An interfacial resistance can however be reduced by introducing LiI due to the resulting increased Li conductivity. The increased stability to Li metal anode has also been reported.\cite{170} To investigate the influence of density and microstructure on the resulting mechanochemical stability, Dixit et al.\cite{171} show a detailed study on different postprocessing techniques. They compare an as-prepared, milled sample of a Li$_3$PS$_4$–LiI mixture with a subsequently annealed sample. The milling step has the benefit of reducing the particle size, which allows for a higher packing density that is further increased by the subsequent annealing step. Comparing the ionic conductivities (Figure 10), the LiI addition and postprocessing both highly benefit the ionic transport, which is related to the densification of the lithium-diffusion matrix by additionally reducing the number of lithium-blocking pores. Overall, their work shows the importance of considering the influences of milling as well as additives on the performance of separators against lithium metal anodes.

4.4. Influences of Processing on the Cathode Active Material

A stable, high-capacity cathode that partially consists of a cathode active material is an important part of the battery. Redox active materials such as LiNi$_x$Co$_y$Mn$_{2-x}$O$_2$ or LiMn$_2$O$_4$ are mostly chosen.\cite{7,16,19,172–174} The particle size of the cathode active material and thereby resulting packing density, especially in combination with a (ion- or electron) conducting additive has a tremendous influence on the resulting electrochemical performance. It has been previously shown that smaller cathode particles generally exhibit a higher capacity and generally better cycling performance than their large-particle counterparts. Although smaller particles can be obtained by varying experimental methods,\cite{175–177} the easy to use milling procedure furthermore allows for a direct mixing of the cathode active material with carbon additives.

The coating of cathode active material particles is of particular interest, as uncoated particles can suffer from chemical-instabilities against additives, or in case of a solid-state
battery against the solid electrolyte, leading to a surface degradation and potential failure of the battery. Using a dry, soft milling approach, Hwang et al. have shown that a layer of Al₂O₃ can be applied as a coating on NaNi₀.₆Co₀.₂Mn₀.₂O₂ particles. While exhibiting the same charge and discharge capacity, the capacity retention is significantly enhanced for the NaNi₀.₆Co₀.₂Mn₀.₂O₂.

An example, which shows that milling is not always beneficial is represented by LiCoO₂, which is known to crystallize in three different structures. While the rhombohedral structure LiCoO₂ can be used as the known intercalation cathode active material, the spinel LiCoO₂ and distorted rock-salt structures suffer from a poor electrochemical performance and are therefore unfavorable. Obrovac et al. have shown that the rhombohedral LiCoO₂ undergoes a phase transition to the unfavorable LiCoO₂ phase during sufficiently long mechanochemical milling durations. Furthermore, Rodriguez et al. have observed the formation of Co₃O₄ during milling, which is possibly related to different milling conditions. However, no degradation is observed within 4 h of milling time, still allowing for a quick processing in a ball mill to enable the use of rhombohedral LiCoO₂ in a cathode composite. Overall, the influence if mechanical mixing of cathodes with coatings or solid electrolytes requires careful control of the process parameters and in-depth future studies.

**4.5. Influences of Processing on LiS Cathode Composites**

With the rise of highly lithium-conducting thiophosphates, lithium–sulfur solid-state batteries have garnered increasing interest. The importance of processing on the cathode composite has been shown by Ohno et al. during the investigation of different processing approaches on the charging-behavior of Li–S batteries. Cells were prepared with a sulfur–carbon and solid electrolyte (Li₆PS₅Cl) cathode composite mixture, either by hand-grinding or by ball-milling. Using the ball-milled cathode composite (Figure 11a) the initial discharge capacity is significantly increased, but furthermore the capacity retention after the first charge is significantly improved (100%) compared to the hand-milled sample (46%). By employing X-ray photoelectron spectroscopy analyses, it was shown that a lower fraction of the used S₈ sulfur is reduced to Li₂S in the hand-ground mixture (Figure 11c,d), explaining the lower discharge capacity. While almost all of the formed Li₂S is being oxidized to S₈ in the ball-milled sample (high-capacity retention) significant amounts of Li₂S still persist in the hand-ground sample (Figure 11e), showing incomplete charging. The mechanochemical milling reduces the S particles size to ensure they are small enough to prevent contact losses during the volume changes accompanied by cycling of Li–S solid state batteries. Clearly, mechanochemical processing of cathode composite microstructures is important for the performance of all solid-state batteries.

**4.6. Processing of Polymer Composite Powder for Solid-State Cathodes**

Solid electrolytes, as well as electrode materials can suffer from instability against moisture or solvents. A coating on such particles, however, can have a beneficial effect on the chemical stability against each other and against the atmosphere. The composite microstructure is of great importance regarding the electrochemical performance. Graebe et al. reported the use of a planetary ball mill for the preparation of a composite material for solvent-free manufacturing of polyethylene oxide (PEO) based solid-state electrodes. This
solvent-free process allows a reduction of the number of process steps, the processing time, the costs and environmental impact can be lowered. The dry mixing and mechanofusion process step is the key challenging step as it ensures a free-flowing powder necessary to produce a dense solid-state cathode or solid-state separator. Coatings of SiO$_2$ or C$_{65}$ on PEO secondary particles retain their microstructural integrity (Figure 12d,e). PEO forms a soft foam when being mixed with the conducting salt LiTFSI (Figure 12d). However, by mixing the PEO secondary particles with SiO$_2$, the further agglomeration of PEO particles is prevented by the formation of a SiO$_2$ layer (coating) on PEO (Figure 12b,c). As a result of the retained microscale structure of PEO, the ionic conductivity is significantly increased (Figure 12a). Interestingly, for the formation of a separator a speed mixer, which is in principle a planetary mill with inclined jars, turns out to be sufficient. By contrast, for the cathode preparation, milling media have to have been added to the speed mixer to achieve the demanded powder density and homogeneous distribution of active cathode particles.

5. Conclusion and Outlook

As shown in this review, we have attempted to provide a deeper look into the mechanical and physical nature of milling processes as well as their influence on the manufacturing of solid electrolytes, cathode composites, and solid-state battery materials in general. It was shown that a large number of parameters are important, such as the stressing energy, collision frequency, overall power as well as specific energy input, and processing time. These need to be well-understood and considered to enhance the achievable product quality and improve the manufacturing process. The selection of milling media size allows to control and investigate the effect of stressing energy: larger media lead to higher energy dissipation, while the power is hardly affected if the filling ratio remains constant. By contrast, increasing the rotation speed results in both, a higher stressing energy as well as a higher power input. The filling ratio is less significant in terms of stressing conditions and may therefore be selected in a range of 0.3–0.5, combining comparatively high stressing energies with high power inputs.

Although planetary mills are helpful in laboratory scale syntheses, the upscaling to manufacturing levels is difficult. A strength-related design of the mill due to the high accelerations of the cups, the need for continuous operation with continuous feeding of material, as well as cooling larger apparatuses and a general temperature control are still challenging. However, using vibrational mills and stirred media mills will ultimately overcome those obstacles.

Generally, although not applicable on every single solid electrolyte compound class, the introduction of defects and distortions during the mechanochemical milling preparation result in an enhanced electrochemical performance. To some extent this stems from the occurring breakage of particles, eventually resulting in better compressibility and consolidation behavior, or from the appearance of metastable products as well as very defective material structures. However, a significant amorphization can be observed when processing fast ionic conductors for composite or separator generation. As this effect can be detrimental for the electrochemical performance, the post-processing of fast conductors needs to be better investigated and evaluated.
Mechanical mixing poses a great opportunity for scalability; however, many questions are yet unanswered regarding the processing of multicomponent materials such as cathode composites that comprise of a solid electrolyte, a cathode active material as well as binders and conductive additives. The combination of different materials, which may behave differently mechanically, is a complex topic that needs to be studied in depth. Detailed studies on the influence of simple milling parameters, as the loading, filling-ratios, composition ratios, milling media, and milling times and even the use of liquid-milling assisted techniques will help the community to get a better insight into the occurring changes of cathode composites for a future upscaling of solid-state batteries.

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Conflict of Interest
The authors declare no conflict of interest.

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Figure 12. a) Conductivity comparison of the pristine PEO particles and the SiO2 coated particles with LiTFSI as conductive salt, showing the enhanced conductivity of the coated version. b–e) Schematic on the coating of the PEO particles (b) and LiTFSI agglomeration (c), with SEM images of the pristine and coated version in (d) and (e), respectively. The formation of the foam-like structure in (d) can be bypassed by applying the coating. Reproduced with permission.[187] Copyright 2017, IOP Science.
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