

Challenges in speeding up solid-state battery development

Jürgen Janek   & Wolfgang G. Zeier  

Recent worldwide efforts to establish solid-state batteries as a potentially safe and stable high-energy and high-rate electrochemical storage technology still face issues with long-term performance, specific power and economic viability. Here, we review key challenges that still involve the need for fast-conducting solid electrolytes to provide sufficient transport in composite cathodes. In addition, we show that high-performance anodes together with protection concepts are paramount to establish dense high-energy solid-state batteries and that lithium-based solid-state batteries as well as metal anodes may not be the ultimate solution. We further discuss that diversity in terms of materials, research teams and approaches is key to establish long-term solid-state batteries. About ten years after the first ground-breaking publication of lithium solid electrolytes with an ionic conductivity higher than that of liquid electrolytes, it is time to realistically address the remaining key challenges for full-scale commercialization, cell performance and implementation.

Lithium-ion batteries (LIBs) are so far the undisputed technology when it comes to electrochemical energy storage, due to their high energy and power density, excellent cyclability and reliability. The recent push for vehicle electrification would not be possible without the cost-effective mass production of LIB cells in parallel with their yet ever-growing performance. As the performance of LIBs will nevertheless approach a limit, potential follow-up cell concepts are being researched intensively. As one of the more realistic advancements, the solid-state battery (SSB) recently emerged as a potential follow-up technology with higher energy and power densities being expected, due to the possibility of bipolar stacking, the potential usage of the lithium metal or silicon anode and projected higher device safety. In addition, solid electrolytes (SEs) can prevent electrode cross-talk, that is, the unwanted chemical interaction of dissolved active materials, which would eliminate one cause of the long-term instability of LIBs. Further, the high lithium-ion transference number of inorganic SEs of around unity allows very fast charging capabilities without electrolyte polarization, which indeed leads to the high projected power densities.

However, any commercial feasibility strongly depends on a variety of parameters, such as the storage performance in terms of specific

capacity and power, safety and ultimately cost and materials resources. Recent calculations¹ demonstrated that even at the cell level—which not only includes all internal battery components, such as materials, binders and current collectors, but also the housing, poles and gaskets—the SSB can potentially replace the LIB. For instance, a LIB based on NCA ($\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$) versus graphite reaches a specific energy and an energy density of 265 Wh kg⁻¹ and 635 Wh l⁻¹, respectively. In contrast, a SSB based on NCA versus lithium metal may theoretically reach 393 Wh kg⁻¹ and 1,143 Wh l⁻¹, respectively¹. The potential for SSB technology is attractive and serious progress has been reported by companies such as Samsung, Solid Power, QuantumScape and Toyota, just to name a few. However, the LIB is a moving target, and engineering issues beyond mere electrochemical considerations, as well as costs, will surely dominate any commercial development.

The recent and fast research worldwide² has led to a much better understanding of the key challenges for the solidification of batteries over the past decade³. First, these include the understanding, design and preparation of solid-state composite electrodes (in particular cathodes) that require a minimum stack pressure for stable long-term operation. Ideally this pressure is below 0.1 MPa, but a few megapascals

¹Institute of Physical Chemistry & Center for Materials Research (ZfM/LaMa), Justus Liebig University, Giessen, Germany. ²Batteries and Electrochemistry Laboratory (BELLA), Institute of Nanotechnology, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany. ³Institute of Inorganic and Analytical Chemistry, University of Münster, Münster, Germany. ⁴Institut für Energie- und Klimateforschung (IEK), IEK-12 Helmholtz-Institut Münster, Forschungszentrum Jülich, Münster, Germany.  e-mail: juergen.janek@phys.chemie.uni-giessen.de; wzeier@uni-muenster.de

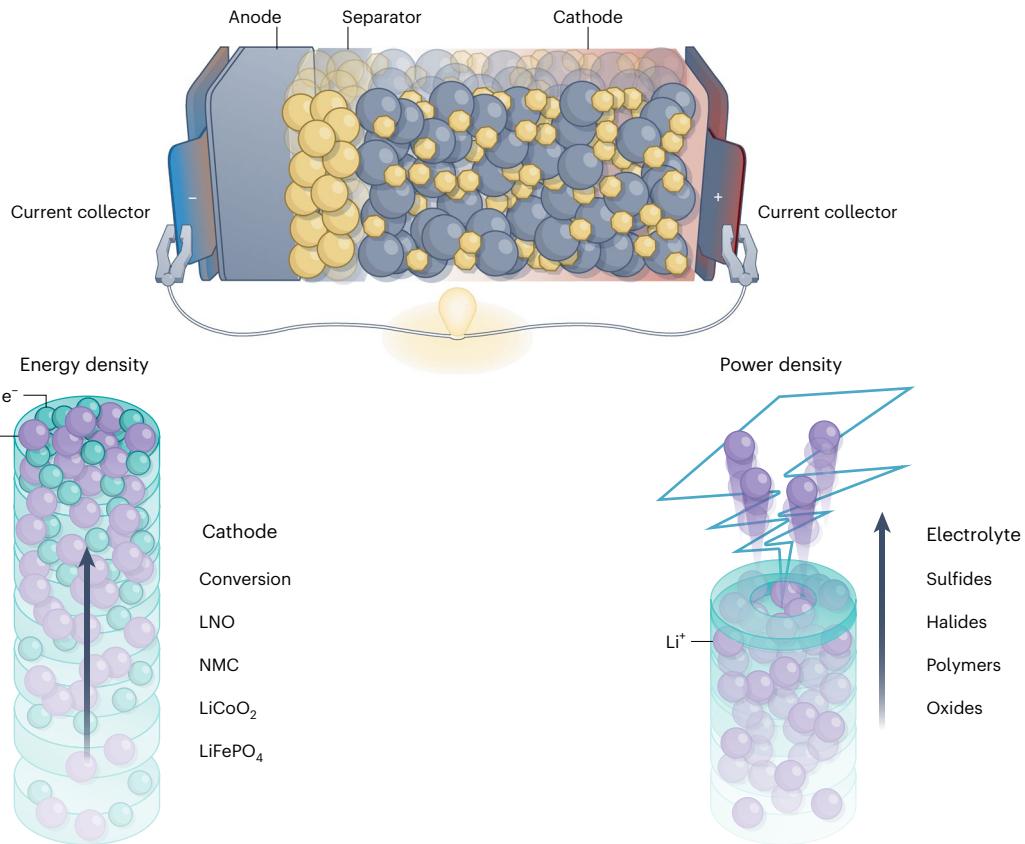


Fig. 1 | Generalized lithium SSB cell concept. The most relevant materials today for the anode, SE and cathode, indicating their major impact on cell performance in terms of energy density and power density. Credit: Elisa Monte/JLU Giessen.

may also be technically acceptable. Second, the development of stable high-rate and high-capacity anodes, for example, on the basis of lithium metal or silicon. Third, the design of SEs that offer very high (effective) ionic conductivities in thick and optimized cathode architectures, as well as sufficient stability and low costs. Fourth, long-term stable and low-resistance interfaces between the active materials and the SE. Fifth, potentially more sustainable approaches, such as Na-based and sulfur conversion-based SSBs. In addition, the rise of 'hybrid' concepts that combine solid and liquid or gel-polymer electrolytes becomes important, as does the need to allow scale-up and low-cost production.

Here, we provide views on the most relevant question of how to realistically attain SSBs as a potential mass market product. Although we summarized some of these issues qualitatively about six years ago⁴, since then a variety of promising possible cell concepts and configurations have arisen and the rapid development of the field calls for an update in a more quantitative manner, with the goal to provide new directions in SSB research.

Composites transport and chemomechanics are key

A generalized scheme of a typical SSB is shown in Fig. 1, which summarizes the various potential materials that are used for the most relevant cell configurations. We assume—in line with previous analyses^{5,6}—that the cathode will be decisive for the areal capacity and specific energy (as well as energy density). The separator needs to be as thin as possible, as long as it still keeps its function. Once a high-capacity anode can be applied, the anode will also be comparably thin, and the cathode will dominate the cell design. The proper function of solid electrode composites is key to the success of the SSB concept. Active materials

expand and contract during battery cycling as lithium is extracted and incorporated, together with the reduction and oxidation of (mostly) transition metal ions. Even small volume changes can lead to a substantial strain and corresponding local stress between particles of the active materials and the SE particles⁷. Although the volume changes may be less problematic in oxide-based SSBs⁸, in the well-performing sulfide-based SSBs, the requirement for particle contact between the ionic conductor and the active material needs to be considered as any chemomechanical volume change will have severe local repercussions⁹. Indeed, the contact loss and microstructural cracking due to the volume changes of the active material is the major reason for the required external pressure (stack pressure) to ensure the continuous operation of a SSB with ceramic SE¹⁰. Battery packs provide serious upper limits for the cell stack pressure, and this is one of the most critical constraints for the successful design of SSB cells¹¹.

These chemomechanical challenges add additional complexity to the design of cathode composites. First and foremost, the effective ionic and effective electronic conductivities of the cathode composites need to be high¹². Given that multiple solid phases are at play, composites that have high loadings of active materials will result in a highly tortuous pathway for ions. Indeed, recent work shows that by decreasing the volume fraction of the SE in the composite, the effective ionic conductivity of inorganic SEs is significantly lowered compared with the bulk conductivity of the SE¹³, which lowers the overall attainable charge rates and capacities (Fig. 2).

Not only does one need a SE with a sufficiently high conductivity to compensate the tortuosity and residual void issues, especially in thick electrodes¹⁴, it is additionally paramount to establish the usage of polymer binders¹⁵ or optimize the particle size distribution¹⁶ to mitigate

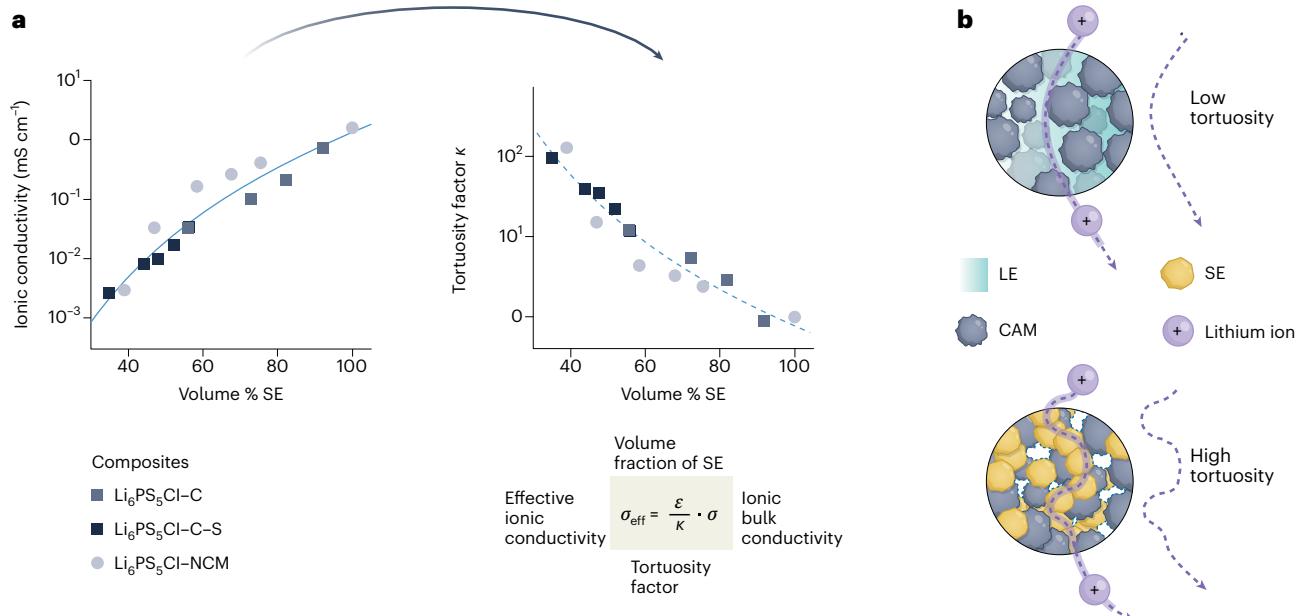


Fig. 2 | Tortuosity effects in solid-state cathode composites. **a**, Measured partial lithium-ion conductivity σ_{eff} and evaluated tortuosity factor κ as function of the weight fraction of the SE, which ultimately relates to the volume fraction ε . Values of the conductivity and tortuosity factors of Li-S- and NCM-based SSBs

are taken from Ohno et al.¹² and Minnmann et al.¹³, respectively. **b**, Schematic explanation of the higher tortuosity in SSB cathode composites compared with that in LIB cathodes with LEs. Credit: Elisa Monte/JLU Giessen.

the volume changes and create a beneficial ionic transport, as well as to establish hybrid composite architecture concepts entirely (see below). To design an optimized cathode composite includes challenges such as which binder to use and how to retain a high conductivity with the binder, all of which needs to be optimized towards the long-term (electro)chemical stability of the SE–binder–additive mixture. The design of an ideal cathode composite represents a multidimensional optimization problem in which a large fraction of the inherent interfacial issues is not well understood yet. Nevertheless, it is clear that a future SSB must have either a fully designed electrode micro- and macrostructure¹⁷, together with tailored cathode active material (CAM) particles¹⁸, contain SEs with a much faster ionic conduction, or ideally both. Despite being relatively simple descriptors¹⁹ that still require a proper theoretical treatment for the solid-state environment, the partial ionic and electronic tortuosity may provide the right metric to optimize cathode composites.

The need for designed high-performance solid electrolytes

Current LIBs use liquid electrolytes (LEs) with lithium-ion conductivities in the order of a few millisiemens per centimetre, and the strong increase in interest and research focus on SSBs stems from the recent achievements to push the ionic conductivity of SEs even beyond this limit. The development of sulfide fast ionic conductors, such as Li₁₀GeP₂S₁₂ (LGPS) and its derivatives, as well as the lithium argyrodites Li₆(P,Sb)₈X (X = halogen), all show ionic conductivities greater than 1 mS cm⁻¹. Oxide-based lithium SEs are often limited to conductivities below 1 mS cm⁻¹, and the mechanical stiffness and need for sintering to achieve good contact remain their major drawbacks. Therefore, hybrid concepts that involve oxides and liquid–polymer electrolytes seem to be one possible direction. In addition, disperse polymer-based electrolytes that contain low levels of liquids may also be a reasonable alternative²⁰. The very high ionic conductivity of lithium thiophosphates together with their low mechanical moduli are the predominant reasons why sulfide-based composites play a dominant role in the development of SSBs for room-temperature operation.

Clearly, the current generation of lithium-conducting inorganic SEs has led to a dawn of SSB research. However, is a conductivity of a few millisiemens per centimetre really enough, just because it is comparable to that of a LE? Considering LEs, 8–10 mS cm⁻¹ are typical total conductivities found²¹ and correspond at best to 4–5 mS cm⁻¹ of lithium-ion conductivity even if one assumes a rather high lithium transference number of 0.5. The aim of a comparable conductivity of the electrolytes seems fundamentally flawed, when considering the microstructures of the electrodes. The three-dimensional microstructure of CAMs in a porous electrode with a LE is intrinsically connected to a lower tortuosity compared with that in a solid-state composite that contains a physical mixture of SE, CAM particles and remaining pores. As a higher tortuosity reflects a longer pathway for ions in the solid state, a faster ionic transport is needed just to be comparable to the lithium-ion transport in LE-based cathodes^{13,22}. This effect is shown in Fig. 2b. Whereas the LE percolates well in a porous electrode structure, in the microstructure of a solid composite the active material, SE, binder, conductive additives and remaining pores all serve as additional components. These handicap the formation of a percolating ion conduction network, especially at low SE fractions, and include resistive heterogeneities like grain boundaries^{23,24}. An important point may even be that changing the different components also affects the pore size and pore distributions, which in turn severely affects the porous microstructure. Therefore, percolation thresholds and influences, such as tortuosity and particle size distributions, exert a major influence on performance—which is increasingly addressed^{13,19}. For a commercial device implementation with high energy density cells, thick electrode configurations are needed. For instance, assuming a high areal loading greater than 7 mAh cm⁻², which corresponds to an electrode thickness of over 100 μ m, current loads of 7 mA cm⁻² are only realistic with a minimum of an effective ionic conductivity of 10 mS cm⁻¹ (ref. ¹⁴). Assuming a lithium metal anode of 30 μ m, a separator of 20 μ m and a CAM volume fraction of 70%, this cell then corresponds to an energy density of 1,443 Wh l⁻¹ and a specific energy of 435 Wh kg⁻¹.

To this day, only a handful of lithium SEs reach an ionic conductivity of 10 mS cm⁻¹ at room temperature, that is, the highly substituted

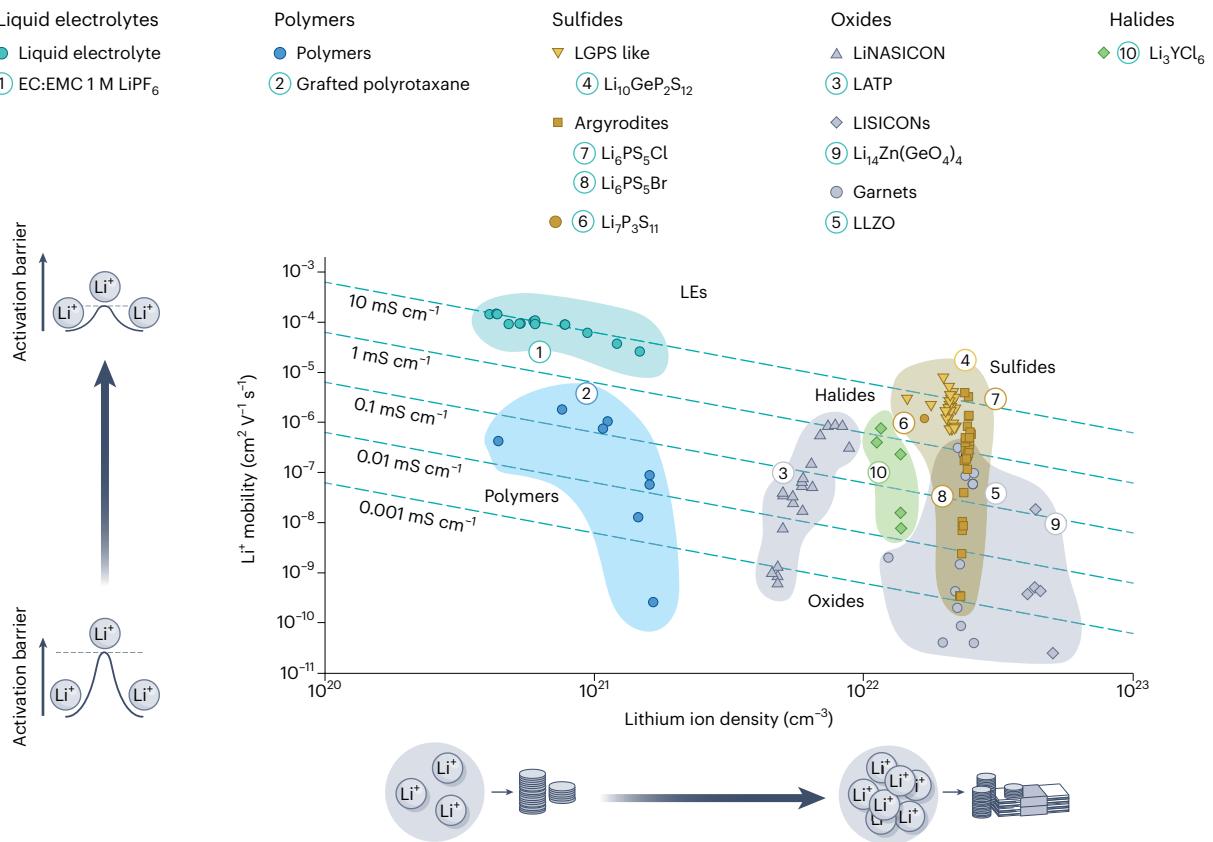


Fig. 3 | Classification of SEs based on lithium content. Lithium-ion conductivity as a product of ion mobility, charge (constant, not shown) and ion concentration (as ion carrier density). SEs with equal conductivity lie on dotted isoconductivity lines. The diffuse clouds indicate different groups of SEs. The mobilities and carrier densities for the sulfides (LGPS^{27,28,83–98}, argyrodite^{25,26,99–101} and Li₇P₃S₁₁

(ref. ¹⁰²), oxides (garnets^{103–111}, lithium superionic conductors (LISICON^{112–115} and LiNASICON^{116,117}), halides^{118–120}, polymers (polyethylene oxide-based^{121–125} and grafted polyrotaxane¹²¹) and LEs^{21,126–128} were calculated from their reported conductivities and compositions and can all be found in the Source Data. Credit: Elisa Monte/JLU Giessen.

lithium argyrodites Li₆(P/Sb)S₅(Cl/Br/I) (refs. ^{25,26}) and Li₁₀GeP₂S₁₂ and its derivatives^{27,28}. It is as yet unclear how many other material classes can be pushed above this needed lower conductivity limit, especially given that 10 mS cm⁻¹ of effective conductivity and not ionic conductivity of the SE will be needed. Future efforts must focus on achieving several millisiemens per centimetre of effective ionic conductivity in the cell environment to obtain a SSB that can perform with realistic loadings and current densities—or the operation at an elevated temperature has to be accepted^{13,22}. These efforts should not only include trial and error but may need help from machine learning or high-throughput screening efforts to improve the current SEs and possibly identify unknown or overlooked materials that may hold potential for the future. Overall, the effective ionic transport needs to be measured when novel or altered composite concepts are introduced.

Besides achieving the ionic conductivity limit, researchers need to consider also the cost of a material when it comes to potential application. Although it is often difficult to gauge the final price of a material as supply and demand, synthesis and production and other factors are involved, using resource-critical elements will surely be a cost risk. Recently, most improvements were achieved using Ge in the SE, and efforts of using Li₃InCl₆ or Li₃ErCl₆ are questionable in regards to the price as a full substituent for thiophosphate catholytes due to indium and the rare earth elements. In addition, the instability against reduction may rule out the general suitability of these lithium metal halides²⁹, especially as a bilayer separator layout seems to be needed³⁰. In general, the high molar concentration of lithium in inorganic SEs, and to a lesser extent in polymer SEs, will have a cost impact compared

with LEs³¹. Figure 3 shows pertinent electrolytes and their ionic mobility as a function of carrier density, that is, lithium-ion density, which has rarely been considered before. Whereas LEs exhibit a high lithium-ion mobility and a low amount of lithium per unit volume, sulfide SEs need up to two orders of magnitude more lithium for their high ionic conductivity³¹. Oxide-based SEs lack mobility at too high carrier densities and polymer SEs may just become a good compromise candidate for using less lithium, if the ionic mobility can be further improved by two orders of magnitude. Lowering the lithium content hence becomes important as inorganic SEs and CAMs have quite similar lithium-ion densities, and therefore the fraction of lithium in the SE scales well with the volume fraction of the SE. This means that an inorganic SE requires roughly 25% of the Li in the cathode composite. As the SE will also be required as a separator material, in total about 40% of the lithium in a SSB is being used up for the SE. A change in paradigm may be to design ionic conductors not by increasing the concentration of lithium, but rather tailoring known materials. This can, for instance, be performed based on structure–transport correlations, changing bonding and polarizability of the anion framework or simply by tailoring the processing conditions or working a multicompositional space. In addition, finding novel materials with an intrinsically higher ionic mobility—together with a low charge-carrier density—seems a viable future option.

The need for high-performance anodes

Although cathodes very much control the specific energy of SSBs due to their relatively low specific capacity and the corresponding need for thick

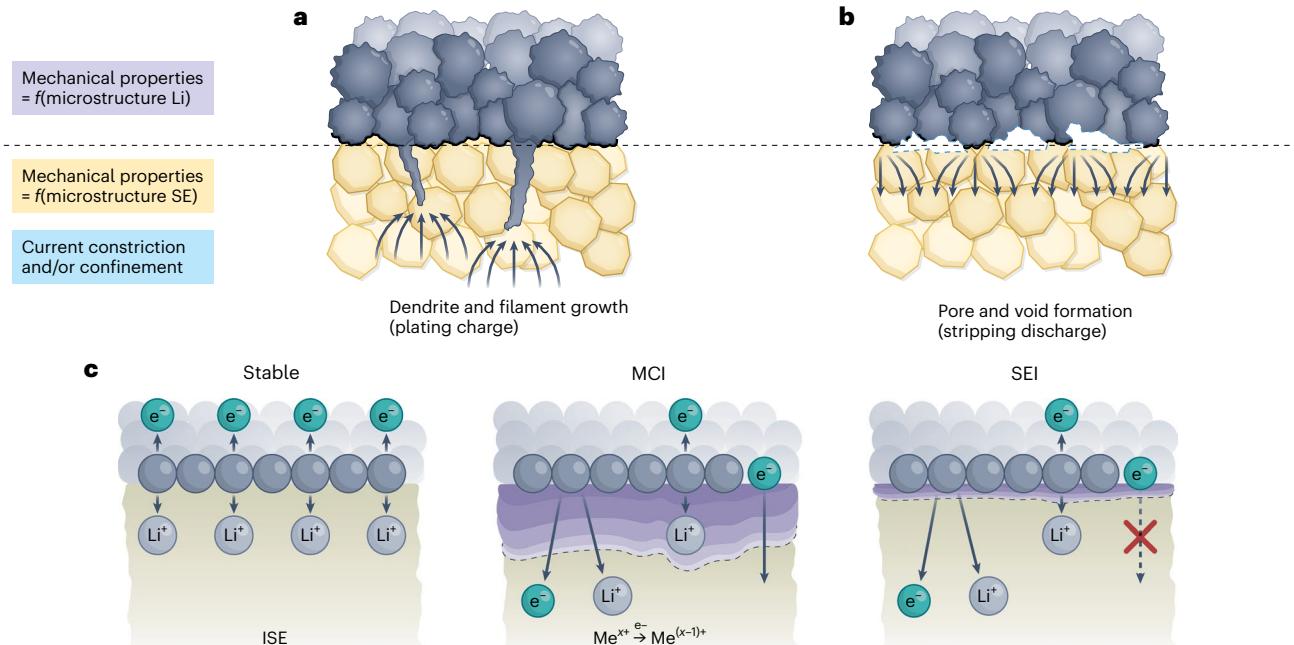


Fig. 4 | Critical issues of the lithium metal anode. **a**, Filament and dendrite formation causing short circuits during charging and current focusing. **b**, Pore and void formation during discharging causing constriction resistance and dendrite growth during subsequent plating. **c**, Interphase growth between the lithium metal and different SEs, showing a thermodynamically stable operation.

for example, with LLZO (left), kinetically unstable operation (middle) and kinetically stable operation (right). MCI, mixed-conducting interphase. ISE, inorganic solid electrolyte Credit: Elisa Monte/JLU Giessen. Panel Panel c inspired by ref. inspired by ref.¹⁰.

cathodes, clearly one can only achieve specific energies comparable with those of LIBs if high-capacity anodes with low potentials are used. The demand for fast charging with minor capacity fading requires additionally that these anodes allow a reversible high-rate operation. Remember that it is the graphite anode that limits the charge rate of LIBs³². The most obvious options are the lithium metal anode¹⁰ or a silicon-based anode^{33,34}. Both show massive volume changes during charging/discharging, so that their use obviously depends on the solution of critical mechanical issues—along with a number of other issues.

Reliable, reversible and safe operation of the lithium metal anode requires us to overcome potential issues caused by the inherent morphological instability during plating and stripping of lithium metal at the SE separator interface^{35,36}. Recent work helped to gain much deeper understanding of both dendrite formation and growth as well as of pore formation during stripping (Fig. 4)^{37,38}. Still, the stack pressure in most of these studies is too high, and the targeted pressure has to be below 0.1 MPa to meet the same stack pressure as that of LIBs. Although it appears that $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) can, indeed, operate dendrite free at sufficiently high current densities and relatively low stack pressure³⁹, there is still no open accessible proof of the long-term and large-area operation available. Thiophosphate SEs suffer from solid electrolyte interphase (SEI) formation and dendrite growth⁴⁰. Although research on the laboratory scale suggests that the nature of the growing interphase can be self-limiting¹⁰, future work has still to show whether thiophosphates can be safely employed as a separator material. Often, the so-called critical current density is used as a descriptor for the long-term stable operation of a lithium metal anode. The critical current density should represent the upper limit for operation without the danger of anode instability, yet it depends on a large number of material properties and experimental variables, for example, the sequence of previous plating–stripping steps⁴¹. It is a process-dependent observable that can rarely be compared for different electrodes and experimental schemes. We conclude that it can hardly be used as a proper metric for the reliable comparison of different anode concepts, and better reporting still has to be developed.

The morphological (pore and dendrite) issues of the pure lithium anode can be overcome if a morphologically stable host structure or scaffold is used that can take up and give off lithium sufficiently fast⁴², but this is at the cost of a reduced specific energy. Theoretical estimates for Li–LLZO composite anodes were recently published and show that the capacity advantage is easily lost⁴³, as LLZO has a high density. Microporous carbon or lithium–carbon composites may be an alternative⁴⁴, yet no such anode concept has been proved to be superior so far. Alloying lithium and using a solid–solution anode with a wide solubility range for lithium is the second option, and is particularly interesting in the case of silicon for which, despite morphological changes, high current densities of up to 5 mA cm^{-2} seem to be possible at room temperature^{33,34}.

Aiming for SSBs that can compete with LIBs with respect to specific energy and power, the development of a high-rate lithium or silicon anode with a high specific and absolute capacity—ideally, reservoir-free metal anodes as such—will be decisive. Recent claims by industry promise that this target has already been achieved, which would, indeed, be a major game changer on the route to SSBs with superior performance.

Stable interfaces, interphases and coatings

The wide potential range of advanced anode and cathode materials provides similar issues for the stability of SEs as those for LEs⁴⁵. For instance, the chemical and electrochemical instability of lithium thiophosphates at the CAM, as well as the anode, remains a major factor in performance fading over time. Chemically, the SE easily reacts with active materials and at high or low potentials it decomposes, which results in detrimentally resistive interphases^{46,47}, which often seem to be redox-active themselves⁴⁸. Recent work further showed that the thickness of the SEI that is growing on the lithium metal anode in contact with the sulfide SE has been severely underestimated (see Fig. 4c for a general picture)⁴⁰, which further challenges the need for protection concepts. However, although decomposition reactions are challenging for any technology, these hopefully can be mitigated by chemical design approaches of the interface or interphase.

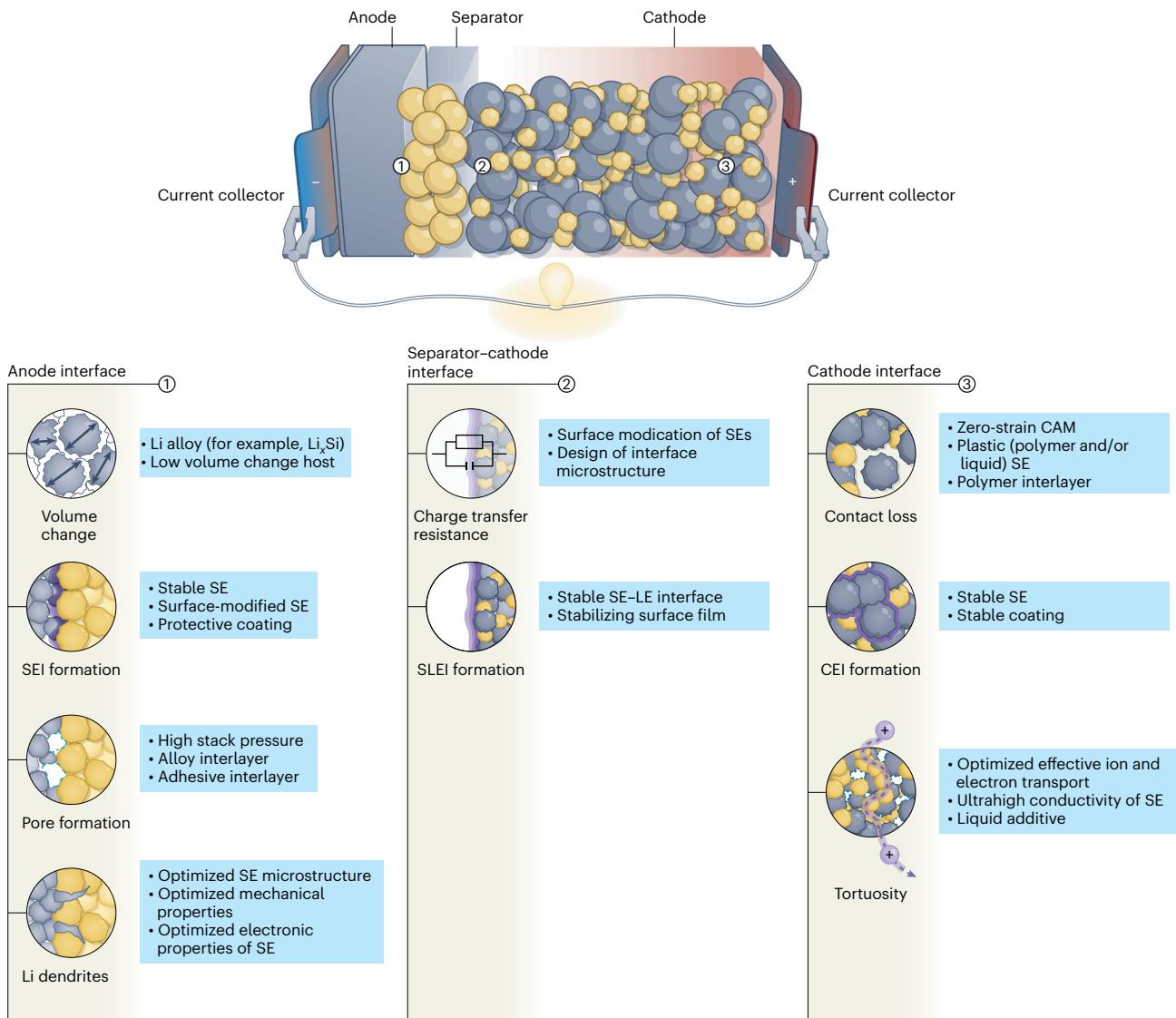


Fig. 5 | Known interface-related issues in SSBs and potential solutions. From the left: anode interface, separator-cathode hetero-ionic interface, cathode interface and potential mitigation strategies. SLEI, solid liquid electrolyte interphase. CEI, cathode electrolyte interphase. Credit: Elisa Monte/JLU Giessen.

Most recent work uses coatings on the CAM to prevent or at least slow down decomposition reactions^{49,50}. Coatings, such as LiNbO_3 or Li_2ZrO_3 , have been quite successful in recent years. Although it seems that these electronically insulating coatings lead to a potential drop and partially protect the SE, interdiffusion and chemical decomposition is still observed⁴⁹. A mechanistic understanding of the coating functionality, the coating materials properties, ideal coating procedure and, in the end, long-term stability are lacking. In particular, the introduction of new interfaces between the electrolyte and the coating as well as the coating and the active material adds additional complexity. Resistive coatings may make conductivity additives necessary, despite their currently detrimental influences. Coatings are needed as protective concepts and particular attention needs to be on gaining a better fundamental understanding during the development stage.

Further options to improve the long-term stability at the cathode/SE or anode/SE interface is the design of the forming interphase, with the following questions in mind. First, is it possible to design a SE or additives in such a way that the forming interphase exhibits the beneficial transport properties of a kinetically stabilized, that is, not growing, interphase layer together with a low interfacial impedance? And will liquid additives that may mitigate ionic tortuosity issues otherwise

compromise the long-term stability? Also, can there be a theory-guided exploration of materials with windows of reasonable kinetic stability? Current work explores the thermodynamic instability, but the question if the decomposition products can kinetically lead to a stable decomposition interphase is rarely answered⁵¹.

Is lithium really needed?

Reducing the amount of Li in the SE seems important, but ultimately will only deliver a minor contribution to the overall Li criticality as cathode and anode materials are still needed. Indeed, the same potential benefits that drive the development of sodium-ion batteries, namely the replacement of lithium and transition metals, such as cobalt and nickel, justify the research on sodium-based SSBs⁵². Various efforts are reported to understand and develop sodium ionic transport in SEs and, indeed, much higher ionic conductivities can be achieved with the less polarizing Na^+ ion compared with that of Li^+ (refs. ^{53,54}). Nevertheless, the oxide SEs retain their challenge of sintering and the thiophosphate classes show a much faster decomposition at the Na metal anode compared with that of the lithium analogues⁵⁵. So far, the upcoming sodium halides are not competitive in ionic transport⁵⁶; nevertheless, cell operation is possible⁵⁷. Furthermore, strong decomposition reactions proceed

between the CAM and the catholyte, which has limited most reports to the use of NaCrO_2 , and better CAMs for usage in the sodium SSBs are still needed. Promising steps are being made in the development and understanding of hydroborate electrolytes, such as $\text{Na}_2\text{B}_{10}\text{H}_{10}$ and its derivates. Fast ionic conductivities were reported together with an excellent electrochemical stability against the electrodes^{58–60}. Overall, although they provide many benefits, the development of sodium SSBs needs to be intensified in terms of protecting the SE with coatings of the CAM, as well as finding and enabling high-performance anodes to truly provide a competitive alternative. Indeed, finding the ideal composition is needed to achieve a quantitative analysis of the potential energy and power densities for comparison with lithium-ionic SSBs in the first place.

Alternative cathode materials

To date, the majority of experimental reports concerning CAM in SSB focus on nickel–cobalt–manganese oxides (NCM). However, spinel-type or even Li-rich CAM offer higher potentials in cells and need to be considered as cell components⁶¹. Severe chemical reactions with the SE will occur, but as coatings need to be developed anyway, it may be worthwhile to directly improve the energy density by advanced cathode materials. However, CAMs such as LiFePO_4 are rarely used in sulfide SSBs and are mostly found in polymer SSBs. A fact that may very well change given that the driving force for decomposition in NCM–sulfide SE composites is mainly the formation energy of the phosphate ion, which is already present in LiFePO_4 . A truly promising cell performance was achieved by using conversion redox materials in SSBs, such as sulfur. The lower charging potentials are, of course, one limitation; however, lower charging potentials prevent the electrochemical decomposition of the SE and cycling capacities close to the theoretical capacity of the S to Li_2S conversion were obtained¹². Yet, very similar challenges exist in Li–SSBs and limit their current applicability. First, cathode composites are composed of not only SE and an active material, but notable volume fractions of carbon are also needed to provide a sufficient electronic conductivity. As the electrochemical reaction will occur at the triple phase boundaries of SE, S and C, the microstructure and fast ionic transport within the composites becomes much more important than in intercalation-based SSBs as otherwise sluggish reaction kinetics limit the performance¹². Second, chemomechanical challenges are much more severe when S converts into Li_2S as the volume changes are substantial. Nevertheless, for optimized Li–S SSBs projected gravimetric energy densities of over 800 Wh kg^{-1} seem reachable⁶². Potentially impactful cathode materials can be extended to copper sulfides^{23,63} or iron sulfides⁶⁴, or the use of transition metal additives⁶⁵, all of which seem promising so far. However, although their limitations are not fully explored yet, companies such as Solid Power are pursuing the approach of a more sustainable pyrite-based SSB⁶⁶. Recently the possibility to employ sodium in the conversion of sulfur has attracted attention^{53,67}, as a complete conversion reaction of S into Na_2S is possible with a theoretical capacity of $1,675 \text{ mAh g}^{-1}$ that lies above the theoretical capacity of 558 mAh g^{-1} of high-temperature Na–S batteries. Surely more research and development can be expected in the coming years in the direction of conversion cathode chemistry for SSBs.

Hybrid cell concepts from all solid to almost solid

Obviously, LIBs can operate with a single optimized LE that is a mixture of compounds and contains additives that support the formation of stable interfaces and/or interphases at both the anode and cathode. It may well be that a successful solid-state cell concept relies on the combination or at least two SEs—or of a SE and a liquid or gel polymer electrolyte in a ‘hybrid’ cell concept⁶⁸. Aiming for a low- and room-temperature operation, it appears that thiophosphate SEs need to be utilized as the catholyte in a true SSB cell. Once dendrite formation at the lithium metal anode cannot be suppressed by the same SE as the separator material, then either a polymer or an oxide SE has to be employed as the separator.

These considerations show that there is a wide range of intermediate concepts on the route from LIBs to true SSBs in which different options of combining sulfides with polymers or oxides exist, which leads to a layered-like hybridization concept⁶⁹ or even true three-dimensional mixing⁷⁰. It may well be that the chemomechanical issues of volume changes and contact losses at solid/solid interfaces require a small fraction of the LE to act as local contact ‘agent’ and potentially even interphase former⁷¹. In fact, a SSB cell that exclusively contains solid components is not necessarily a reasonable target. If a small fraction of a low-viscosity additive helps to form better interfaces and interphases, as well as to reduce porosities and high tortuous pathways, the overall benefits of an almost-solid-state battery (from all solid to almost solid) are potentially up to par with, if not superior to, true all-solid-state batteries. However, whether the new interfaces in hybrid systems are stable long-term is an open question, as well as whether hybridization compromises safety. In view of the difficulties in processing, for example, sulfide SEs in liquid solvents, hybrid systems may in the end suffer from chemical instabilities. In-depth studies are definitely needed to provide a realistic assessment.

Production and cost

Together with the design of the SSB cell as such, cost-efficient industrial materials processing and cell fabrication is needed⁷². Whereas academic research on SSBs still focuses on pressed-pellet-type cells that require high stack pressures to mitigate the above-mentioned chemomechanical issues, pouch cells are needed for device implementation and provide the option of bipolar stacked cells. Stack pressures need to be minimized, which seems possible using hybrid solid–liquid approaches. For device production, ideally the existing processing approaches will be used to generate a smoother transition away from LIBs. Hence, composite cathodes need dry or wet processing in slurries, and solvent and binder interactions need to be considered⁷³. In addition, industrial concerns such as prices, waste, boiling points (removal of solvent) or viscosity (for conveyers or stirrers), as well as the toxicity, are important parameters to consider⁷⁴. Here, halide SEs may ultimately have an advantage as they seem to be water processible; nevertheless, the cost of the elements and so far low ionic conductivity remains a major drawback⁷⁵ and interfacial decomposition still seems to occur⁷⁶. An upscaling of the SE syntheses is a further requirement and milling or solution routes may be the best approach, but criticality and prices of the precursors still need to be realistically established. Full SSBs may bring cost advantages as expensive steps, such as electrolyte infiltration and formation, are not needed. Overall, the cost advantage of SSBs needs to be explored and directed. In this respect, bipolar stacking is often considered a major cell construction advantage of future SSBs⁷⁷, as it appears to offer a simpler internal cell design and less current-leading connections outside the cell stack, which leads to an increased energy density. However, in practice, this concept also has some drawbacks. The production of asymmetric electrode sheets (anode or cathode on each side) requires more effort. Even more critical, each single cell will age at a slightly different rate, which will lead to growing differences in cell voltage, and lead to a necessary control of all the individual cells. We believe that bipolar stacking requires a more careful and critical evaluation in the future, as it is currently considered too optimistic.

Finally, for long-term sustainability, the recycling of SSBs needs to be developed in full. Innovative recycling routes were developed for various types of SEs⁷⁸; however, large-scale implementation is so far questionable, especially given the unknowns in terms of target product costs, resulting performance degradation or even simpler issues such separating components as mixed solid-state electrolytes and hybrid cells. It will be necessary to target these efforts in depth. In addition, we need to keep recycling goals in mind so that we can design SE compositions for a later recycling process.

Diversity is key

SSB research and development has seen a tremendous growth and pace in the past few years, and a deeper understanding of the current limitations of SSBs has been established. Although this better fundamental understanding helps to advance potentially successful cell concepts, still some old but also new questions and challenges for the future large-scale production of SSB cells have to be answered and solved⁷⁹. Figure 5 shows these now-known issues and potential mitigation strategies.

First, thick cathode architectures with a low SE fraction are needed for a reasonably high energy density. SEs with effective conductivities in the composite greater than 10 mS cm^{-1} are required to achieve fast rates in cathode composites with complex microstructures that also contain binder, conductive agents and pores. Once a completely solid cathode cannot achieve the required performance or long-term operation, a hybrid electrolyte or even a LE may be employed as the catholyte. Once the kinetics are not sufficient at room temperature, operation at a slightly elevated temperature may be an option for some fields of application—probably not in electric vehicles.

Second, a high-performance anode is paramount. Dendrite growth, pore formation and decomposition reactions at the interface between a lithium metal anode and the SE remain key challenges for high current densities and fast charge–discharge applications. Although there are clear promises, the ultimate proof of long-term stable and large-area lithium metal anodes is yet missing. The lithium metal anode is no longer the sole contender, and the silicon electrode has entered the SSB stage, opening up a range of new problems such as the SE stability at the Si/SE interface.

Third, a concerted effort to lower the lithium content in SEs as well as to find compositions with a lower element criticality, together with chemical approaches for the composite route preparation, are needed to have SSBs realistically replace LIBs in the coming years. Although these challenges may appear as critical, one should not forget that SSB cells may allow a more effective battery pack construction. Recent developments show that LiFePO₄-based LIBs can be packed much more densely to take up to 90% of the pack volume, whereas NCM-based cells require better cooling and achieve less filling in the pack, which reduces the advantage of NCM materials with their high specific capacity. We expect that optimized SSB packs can also profit from a wider temperature window for the SSB cells.

Fourth, SSBs are often regarded as being safer than LIBs. However, whether increased safety exists or not still needs to be unequivocally proved, as short circuits, the use of toxic SEs or even percolation of a liquid fraction of the electrolyte to the anode may provide additional safety risks⁸⁰. Even more, recent work shows the self-ignition and thermal runaway of Li₆PS₅Cl–NCM composites above 150 °C (ref. ⁸¹). It seems that the already favoured chemical decomposition pathway becomes strongly favoured at elevated temperatures, which cannot be seen when using LiFePO₄ as the CAM. Clearly, thermal battery management and the associated safety risks of thermal runaways need to be more intensively investigated. Safety concerns may be different from those for LIBs, but without developing safety test standards for SSBs, final conclusions cannot be made.

Fifth, for a field such as SSBs that comprises microstructural issues, chemical issues, electrochemical questions, processing deliveries and still, to some extent, unknown underlying transport physics, it is important to bring the principles of other disciplines into the field and welcome entering researchers. To truly unfold the potential of SSBs, diversity in the approaches, not just the materials, is the key to full development. The field needs more researchers from physics, mathematics, computer science, chemistry and engineering. Overall, successful SSB development will require more efforts to standardize experimental cell set-ups⁸² and procedures closer to practical conditions³.

Finally, we are confident that SSBs will see commercial success, yet it is open whether this means success in specific niche applications or in the mass market.

References

1. Betz, J. et al. Theoretical versus practical energy: a plea for more transparency in the energy calculation of different rechargeable battery systems. *Adv. Energy Mater.* **9**, 1803170 (2019).
2. *Solid-State Battery Roadmap 2035+* (Fraunhofer ISI, 2022).
3. Randau, S. et al. Benchmarking the performance of all-solid-state lithium batteries. *Nat. Energy* **5**, 259–270 (2020).
A first benchmarking study that suggests quantitative research targets for solid-state battery development.
4. Janek, J. & Zeier, W. G. A solid future for battery development. *Nat. Energy* **1**, 16141 (2016).
5. Kerman, K., Luntz, A., Viswanathan, V., Chiang, Y.-M. & Chen, Z. Review—practical challenges hindering the development of solid state Li ion batteries. *J. Electrochem. Soc.* **164**, A1731–A1744 (2017).
6. Pasta, M. et al. Energy 2020 roadmap on solid-state batteries. *J. Phys. Energy* **2**, 32008 (2020).
7. Koerver, R. et al. Chemo-mechanical expansion of lithium electrode materials—on the route to mechanically optimized all-solid-state batteries. *Energy Environ. Sci.* **11**, 2142–2158 (2018).
8. Ihrig, M. et al. Study of LiCoO₂/Li₇La₃Zr₂O₁₂:Ta interface degradation in all-solid-state lithium batteries. *ACS Appl. Mater. Int.* **14**, 11288–11299 (2022).
9. Ren, Y. et al. Oxide-based solid-state batteries: a perspective on composite cathode architecture. *Adv. Energy Mater.* <https://doi.org/10.1002/aenm.202201939> (2023).
10. Krauskopf, T., Richter, F. H., Zeier, W. G. & Janek, J. Physico-chemical concepts of the lithium metal anode in solid-state batteries. *Chem. Rev.* **120**, 7745–7794 (2020).
A review on the properties and challenges of the lithium-metal anode in solid-state batteries.
11. Gao, X. et al. Solid-state lithium battery cathodes operating at low pressures. *Joule* **6**, 636–646 (2022).
A study highlighting the need and possibility to operate solid-state composites at low pressures.
12. Ohno, S., Rosenbach, C., Dewald, G. F., Janek, J. & Zeier, W. G. Linking solid electrolyte degradation to charge carrier transport in the thiophosphate-based composite cathode toward solid-state lithium–sulfur batteries. *Adv. Funct. Mater.* **31**, 2010620 (2021).
13. Minnmann, P., Quillman, L., Burkhardt, S., Richter, F. H. & Janek, J. Quantifying the impact of charge transport bottlenecks in composite cathodes of all-solid-state batteries. *J. Electrochem. Soc.* **168**, 040537 (2021).
This work highlights the challenges of ionic and electronic charge transport in composite electrodes and provides guidelines to characterize these.
14. Bielefeld, A., Weber, D. A. & Janek, J. Modeling effective ionic conductivity and binder influence in composite cathodes for all-solid-state batteries. *ACS Appl. Mater. Interfaces* **12**, 12821–12833 (2020).
15. Lee, Y. G. et al. High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes. *Nat. Energy* **5**, 299–308 (2020).
Seminal study showing that zero lithium-excess solid-state batteries are possible with high energy densities.
16. Cronau, M., Duchardt, M., Szabo, M. & Roling, B. Ionic conductivity versus particle size of ball-milled sulfide-based solid electrolytes: strategy towards optimized composite cathode performance in all-solid-state batteries. *Batter. Supercaps* **5**, e202200041 (2022).
17. Bielefeld, A., Weber, D. A., Rueß, R., Glavas, V. & Janek, J. Influence of lithium ion kinetics, particle morphology and voids on the electrochemical performance of composite cathodes for all-solid-state batteries. *J. Electrochem. Soc.* **169**, 20539 (2022).

18. Minnmann, P. et al. Designing cathodes and cathode active materials for solid-state batteries. *Adv. Energy Mater.* **12**, 2201425 (2022).

19. Nguyen, T. T. et al. The electrode tortuosity factor: why the conventional tortuosity factor is not well suited for quantifying transport in porous Li-ion battery electrodes and what to use instead. *npj Comput. Mater.* **6**, 123 (2020).

20. Imholt, L. et al. Supramolecular self-assembly of methylated rotaxanes for solid polymer electrolyte application. *ACS Macro Lett.* **7**, 881–885 (2018).

21. Dahbi, M., Ghamouss, F., Tran-Van, F., Lemordant, D. & Anouti, M. Comparative study of EC/DMC LiTFSI and LiPF₆ electrolytes for electrochemical storage. *J. Power Sources* **196**, 9743–9750 (2011).

22. Kato, Y. et al. All-solid-state batteries with thick electrode configurations. *J. Phys. Chem. Lett.* **9**, 607–613 (2018).

First study to highlight the need for faster solid electrolytes with conductivities over 10 mS cm⁻¹ when high electrode loading is desired.

23. Froboese, L., Sichel, J. F., Van Der, L. T. & Helmers, L. Effect of microstructure on the ionic conductivity of an all solid-state battery electrode. *J. Electrochem. Soc.* **166**, 318–328 (2019).

24. Bielefeld, A., Weber, D. A. & Janek, J. Microstructural modeling of composite cathodes for all-solid-state batteries. *J. Phys. Chem. C* **123**, 1626–1634 (2019).

25. Kraft, M. A. et al. Inducing high ionic conductivity in the lithium superionic argyrodites Li_{6+x}P_{1-x}Ge_xS₅I for all-solid-state batteries. *J. Am. Chem. Soc.* **140**, 16330–16339 (2018).

26. Zhou, L., Assoud, A., Zhang, Q., Wu, X. & Nazar, L. F. New family of argyrodite thioantimonate lithium superionic conductors. *J. Am. Chem. Soc.* **141**, 19002–19013 (2019).

27. Kato, Y. et al. High-power all-solid-state batteries using sulfide superionic conductors. *Nat. Energy* **1**, 16030 (2016).

28. Kamaya, N. et al. A lithium superionic conductor. *Nat. Mater.* **10**, 682–686 (2011).

29. Riegger, L. M., Schlem, R., Sann, J., Zeier, W. G. & Janek, J. Lithium-metal anode instability of the superionic halide solid electrolytes and the implications for solid-state batteries. *Angew. Chem. Int. Ed.* **60**, 6718–6723 (2021).

30. Wang, C. et al. A universal wet-chemistry synthesis of solid-state halide electrolytes for all-solid-state lithium-metal batteries. *Sci. Adv.* **7**, eab1896 (2022).

31. Nair, J. R., Imholt, L., Brunklaus, G. & Winter, M. Lithium metal polymer electrolyte batteries: opportunities and challenges. *Electrochem. Soc. Interface* **28**, 55–61 (2019).

32. Weiss, M. et al. Fast charging of lithium-ion batteries: a review of materials aspects. *Adv. Energy Mater.* **11**, 2101126 (2021).

33. Lewis, J. A., Cavallaro, K. A., Liu, Y. & McDowell, M. T. The promise of alloy anodes for solid-state batteries. *Joule* **6**, 1418–1430 (2022).

34. Tan, D. H. S. et al. Carbon-free high-loading silicon anodes enabled by sulfide solid electrolytes. *Science* **373**, 1494–1499 (2021).

Seminal study showing the usage of Si metal anodes to be potentially competitive to Li metal.

35. Krauskopf, T. et al. The fast charge transfer kinetics of the lithium metal anode on the garnet-type solid electrolyte Li_{6.25}Al_{0.25}La₃Zr₂O₁₂. *Adv. Energy Mater.* **10**, 2000945 (2020).

36. Liu, X. et al. Local electronic structure variation resulting in Li ‘filament’ formation within solid electrolytes. *Nat. Mater.* **20**, 1485–1490 (2021).

37. Krauskopf, T. et al. Lithium-metal growth kinetics on LLZO garnet-type solid electrolytes. *Joule* **3**, 2030–2049 (2019).

38. Ning, Z. et al. Visualizing plating-induced cracking in lithium-anode solid-electrolyte cells. *Nat. Mater.* **20**, 1121–1129 (2021).

39. Wang, M. J., Choudhury, R. & Sakamoto, J. Characterizing the Li-solid-electrolyte interface dynamics as a function of stack pressure and current density. *Joule* **3**, 2165–2178 (2019).

40. Otto, S. K. et al. In situ investigation of lithium metal–solid electrolyte anode interfaces with ToF-SIMS. *Adv. Mater. Interfaces* **9**, 2102387 (2022).

41. Lewis, J. A. et al. Role of areal capacity in determining short circuiting of sulfide-based solid-state batteries. *ACS Appl. Mater. Int.* **14**, 4051–4060 (2022).

Careful work highlighting the intrinsic challenges of using critical current densities as a metric.

42. Fuchs, T. et al. Increasing the pressure-free stripping capacity of the lithium metal anode in solid-state-batteries by carbon nanotubes. *Adv. Energy Mater.* **12**, 2201125 (2022).

43. Kravchyk, K. V., Zhang, H., Okur, F. & Kovalenko, M. V. Li-garnet solid-state batteries with LLZO scaffolds. *Acc. Mater. Res.* **3**, 411–415 (2022).

44. Bloi, L. M. et al. Mechanistic insights into the reversible lithium storage in an open porous carbon via metal cluster formation in all solid-state batteries. *Carbon* **188**, 325–335 (2022).

45. Schwietert, T. K. et al. Clarifying the relationship between redox activity and electrochemical stability in solid electrolytes. *Nat. Mater.* **19**, 428–435 (2020).

46. Auvergniot, J. et al. Interface stability of argyrodite Li₆PS₅Cl toward LiCoO₂, LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂, and LiMn₂O₄ in bulk all-solid-state batteries. *Chem. Mater.* **29**, 3883–3890 (2017).

47. Walther, F. et al. Visualization of the interfacial decomposition of composite cathodes in argyrodite-based all-solid-state batteries using time-of-flight secondary-ion mass spectrometry. *Chem. Mater.* **31**, 3745–3755 (2019).

48. Dewald, G. F. et al. Experimental assessment of the practical oxidative stability of lithium thiophosphate solid electrolytes. *Chem. Mater.* **31**, 8328–8337 (2019).

49. Culver, S. P., Koerver, R., Zeier, W. G. & Janek, J. On the functionality of coatings for cathode active materials in thiophosphate-based solid-state batteries. *Adv. Energy Mater.* **9**, 1900626 (2019).

50. Sun, N. et al. Surface-to-bulk synergistic modification of single crystal cathode enables stable cycling of sulfide-based all-solid-state batteries at 4.4 V. *Adv. Energy Mater.* **12**, 2200682 (2022).

This work shows the need for changing active material particle sizes for their use in solid-state batteries.

51. Sendek, A. D. et al. Combining superionic conduction and favorable decomposition Products in the crystalline lithium–boron–sulfur system: a new mechanism for stabilizing solid Li-ion electrolytes. *ACS Appl. Mater. Int.* **12**, 37957–37966 (2020).

52. Zhao, C. et al. Solid-state sodium batteries. *Adv. Energy Mater.* **8**, 1703012 (2018).

53. Hayashi, A. et al. A sodium-ion sulfide solid electrolyte with unprecedented conductivity at room temperature. *Nat. Commun.* **10**, 5266 (2019).

54. Fuchs, T., Culver, S. P., Till, P. & Zeier, W. G. Defect-mediated conductivity enhancements in Na_{3-x}Pn_{1-x}W_xS₄ (Pn=P, Sb) using aliovalent substitutions. *ACS Energy Lett.* **5**, 146–151 (2020).

55. Wenzel, S. et al. Interfacial reactivity benchmarking of the sodium ion conductors Na₃PS₄ and sodium β -alumina for protected sodium metal anodes and sodium all-solid-state batteries. *ACS Appl. Mater. Int.* **8**, 28216–28224 (2016).

56. Zeier, W. G., Schlem, R., Banik, A., Eckardt, M. & Zobel, M. Na_{3-x}Er_{1-x}Zr_xCl₆-A halide-based fast sodium-ion conductor with vacancy-driven ionic transport. *ACS Appl. Energy Mater.* **3**, 10164–10173 (2020).

57. Wu, E. A. et al. A stable cathode-solid electrolyte composite for high-voltage, long-cycle-life solid-state sodium-ion batteries. *Nat. Commun.* **12**, 1256 (2021).

58. Duchêne, L. et al. A highly stable sodium solid-state electrolyte based on a dodeca/deca-borate equimolar mixture. *Chem. Commun.* **53**, 4195–4198 (2017).

59. Duchêne, L. et al. A stable 3 V all-solid-state sodium-ion battery based on a closo-borate electrolyte. *Energy Environ. Sci.* **10**, 2609–2615 (2017).

60. Duchêne, L., Remhof, A., Hagemann, H. & Battaglia, C. Status and prospects of hydroborate electrolytes for all-solid-state batteries. *Energy Storage Mater.* **25**, 782–794 (2020).

61. Lee, H. J. et al. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode microstructure for all-solid-state batteries. *Nano Lett.* **22**, 7477–7483 (2022).

62. Ohno, S. & Zeier, W. G. Toward practical solid-state lithium–sulfur batteries: challenges and perspectives. *Acc. Mater. Res.* **2**, 869–880 (2021).

This perspective highlights the promising advances in Li–S-based solid-state batteries.

63. Santhosha, A. L. et al. Macroscopic displacement reaction of copper sulfide in lithium solid-state batteries. *Adv. Energy Mater.* **10**, 2002394 (2020).

64. Dewald, G. F., Liaqat, Z., Lange, M. A., Tremel, W. & Zeier, W. G. Influence of iron sulfide nanoparticle sizes in solid-state batteries. *Angew. Chem. Int. Ed.* **60**, 17952–17956 (2021).

65. Xu, S. et al. A high capacity all solid-state Li–sulfur battery enabled by conversion-intercalation hybrid cathode architecture. *Adv. Funct. Mater.* **31**, 2004239 (2021).

66. Bettenhausen, C. Solid Power wins \$12.5 million for FeS_2 cathodes *Chem. Eng. News* (1 October 2021).

67. Tanibata, N., Deguchi, M., Hayashi, A. & Tatsumisago, M. All-solid-state Na/S batteries with a Na_3PS_4 electrolyte operating at room temperature. *Chem. Mater.* **29**, 5232–5238 (2017).

68. Wang, C. et al. Boosting the performance of lithium batteries with solid–liquid hybrid electrolytes: interfacial properties and effects of liquid electrolytes. *Nano Energy* **48**, 35–43 (2018).

69. Simon, F. J., Hanauer, M., Richter, F. H. & Janek, J. Interphase formation of $\text{PEO20:LiTFSI-Li}_x\text{PS}_5\text{Cl}$ composite electrolytes with lithium metal. *ACS Appl. Mater. Int.* **12**, 11713–11723 (2020).

70. Li, Y. et al. Thin solid electrolyte layers enabled by nanoscopic polymer binding. *ACS Energy Lett.* **5**, 955–961 (2020).

71. Fuchs, T. et al. Working principle of an ionic liquid interlayer during pressureless lithium stripping on $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) garnet-type solid electrolyte. *Batter. Supercaps* **4**, 1145–1155 (2021).

72. Schnell, J. et al. All-solid-state lithium-ion and lithium metal batteries—paving the way to large-scale production. *J. Power Sources* **382**, 160–175 (2018).

73. Miura, A. et al. Liquid-phase syntheses of sulfide electrolytes for all-solid-state lithium battery. *Nat. Rev. Chem.* **3**, 189–198 (2019).

74. Ghidiu, M., Ruhl, J., Culver, S. P. & Zeier, W. G. Solution-based synthesis of lithium thiophosphate superionic conductors for solid-state batteries: a chemistry perspective. *J. Mater. Chem. A* **7**, 17735–17753 (2019).

75. Li, X. et al. Air-stable Li_3InCl_6 electrolyte with high voltage compatibility for all-solid-state batteries. *Energy Environ. Sci.* **12**, 2665–2671 (2019).

76. Rosenbach, C. et al. Visualizing the chemical incompatibility of halide and sulfide-based electrolytes in solid-state batteries. *Adv. Energy Mater.* <https://doi.org/10.1002/aenm.202203673> (2022).

77. Jung, K. N., Shin, H. S., Park, M. S. & Lee, J. W. Solid-state lithium batteries: bipolar design, fabrication, and electrochemistry. *ChemElectroChem* **6**, 3842–3859 (2019).

78. Azhari, L., Bong, S., Ma, X. & Wang, Y. Recycling for all solid-state lithium-ion. *Batter. Matter* **3**, 1845–1861 (2020).

79. Duffner, F. et al. Post-lithium-ion battery cell production and its compatibility with lithium-ion cell production infrastructure. *Nat. Energy* **6**, 123–134 (2021).

80. Bates, A. M. et al. Are solid-state batteries safer than lithium-ion batteries? *Joule* **6**, 742–755 (2022).

First study to approach the question of device safety concerns in solid-state batteries.

81. Kim, T. et al. Thermal runaway behavior of $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolytes for $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and LiFePO_4 in all-solid-state batteries. *Chem. Mater.* **34**, 9159–9171 (2022).

82. Ohno, S. et al. How certain are the reported ionic conductivities of thiophosphate-based solid electrolytes? An interlaboratory study. *ACS Energy Lett.* **5**, 910–915 (2020).

83. Kato, Y. et al. Synthesis, structure and lithium ionic conductivity of solid solutions of $\text{Li}_{10}(\text{Ge}_{1-x}\text{M}_x)\text{P}_2\text{S}_{12}$ ($\text{M}=\text{Si, Sn}$). *J. Power Sources* **271**, 60–64 (2014).

84. Hori, S. et al. Synthesis, structure, and ionic conductivity of solid solution, $\text{Li}_{10+\delta}\text{M}_{1+\delta}\text{P}_{2-\delta}\text{S}_{12}$ ($\text{M}=\text{Si, Sn}$). *Faraday Discuss.* **176**, 83–94 (2014).

85. Sun, Y., Suzuki, K., Hori, S., Hirayama, M. & Kanno, R. Superionic conductors: $\text{Li}_{10-\delta}[\text{Sn}_y\text{Si}_{1-y}]_{1+\delta}\text{P}_{2-\delta}\text{S}_{12}$ with a $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type structure in the $\text{Li}_3\text{PS}_4\text{--Li}_4\text{SnS}_4\text{--Li}_4\text{SiS}_4$ quasi-ternary system. *Chem. Mater.* **29**, 5858–5864 (2017).

86. Sun, Y. et al. Oxygen substitution effects in $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ solid electrolyte. *J. Power Sources* **324**, 798–803 (2016).

87. Kwon, O. et al. Synthesis, structure, and conduction mechanism of the lithium superionic conductor $\text{Li}_{10+\delta}\text{Ge}_{1+\delta}\text{P}_{2-\delta}\text{S}_{12}$. *J. Mater. Chem. A* **3**, 438–446 (2015).

88. Krauskopf, T., Culver, S. P. & Zeier, W. G. Bottleneck of diffusion and inductive effects in $\text{Li}_{10}\text{Ge}_{1-x}\text{Sn}_x\text{P}_2\text{S}_{12}$. *Chem. Mater.* **30**, 1791–1798 (2018).

89. Bron, P. et al. $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ —an affordable lithium superionic conductor. *J. Am. Chem. Soc.* **135**, 15694–15697 (2013).

90. Iwasaki, R. et al. Weak anisotropic lithium-ion conductivity in single crystals of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$. *Chem. Mater.* **31**, 3694–3699 (2019).

91. Suzuki, K. et al. Synthesis, structure, and electrochemical properties of crystalline Li–P–S–O solid electrolytes: novel lithium-conducting oxysulfides of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ family. *Solid State Ion.* **288**, 229–234 (2016).

92. Hori, S., Suzuki, K., Hirayama, M., Kato, Y. & Kanno, R. Lithium superionic conductor $\text{Li}_{9.42}\text{Si}_{102}\text{P}_{2.1}\text{S}_{9.96}\text{O}_{2.04}$ with $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type structure in the $\text{Li}_2\text{S}\text{--P}_2\text{S}_5\text{--SiO}_2$ pseudoternary system: synthesis, electrochemical properties, and structure–composition relationships. *Front. Energy Res.* **4**, 1–9 (2016).

93. Liang, J. et al. $\text{Li}_{10}\text{Ge}(\text{P}_{1-x}\text{Sb}_x)_2\text{S}_{12}$ lithium-ion conductors with enhanced atmospheric stability. *Chem. Mater.* **32**, 2664–2672 (2020).

94. Hori, S. et al. Structure–property relationships in lithium superionic conductors having a $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type structure. *Acta Crystallogr. B* **71**, 727–736 (2015).

95. Inagaki, M. et al. Conduction mechanism of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -type lithium superionic conductors in a Li–Sn–Si–P–S system. *Chem. Mater.* **31**, 3485–3490 (2019).

96. Kuhn, A., Doppel, V. & Lotsch, B. V. Tetragonal $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ and Li_7GePS_8 —exploring the Li ion dynamics in LGPS Li electrolytes. *Energy Environ. Sci.* **6**, 3548–3552 (2013).

97. Kuhn, A. et al. A new ultrafast superionic Li-conductor: ion dynamics in $\text{Li}_{11}\text{Si}_2\text{PS}_{12}$ and comparison with other tetragonal LGPS-type electrolytes. *Phys. Chem. Chem. Phys.* **16**, 14669–14674 (2014).

98. Kim, K. H. & Martin, S. W. Structures and properties of oxygen-substituted $\text{Li}_{10}\text{SiP}_2\text{S}_{12-x}\text{O}_x$ solid-state electrolytes. *Chem. Mater.* **31**, 3984–3991 (2019).

99. Kraft, M. A. et al. Influence of lattice polarizability on the ionic conductivity in the lithium superionic argyrodites $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X}=\text{Cl, Br, I}$). *J. Am. Chem. Soc.* **139**, 10909–10918 (2017).

100. Sakuda, A. et al. Mechanochemically prepared $\text{Li}_2\text{S}\text{--P}_2\text{S}_5\text{--LiBH}_4$ solid electrolytes with an argyrodite structure. *ACS Omega* **3**, 5453–5458 (2018).

101. Minafra, N., Culver, S. P., Krauskopf, T., Senyshyn, A. & Zeier, W. G. Effect of Si substitution on the structural and transport properties of superionic Li-argyrodites. *J. Mater. Chem. A* **6**, 645–651 (2018).

102. Mizuno, F., Hayashi, A., Tadanaga, K. & Tatsumisago, M. High lithium ion conducting glass-ceramics in the system $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$. *Solid State Ion.* **177**, 2721–2725 (2006).

103. Zeier, W. G., Zhou, S., Lopez-Bermudez, B., Page, K. & Melot, B. C. Dependence of the Li-ion conductivity and activation energies on the crystal structure and ionic radii in $\text{Li}_6\text{MLa}_2\text{Ta}_2\text{O}_{12}$. *ACS Appl. Mater. Interfaces* **6**, 10900–10907 (2014).

104. Cussen, E. J., O'Callaghan, M. P., Powell, A. S., Titman, J. J. & Chen, G. Z. Switching on fast lithium ion conductivity in garnets: the structure and transport properties of $\text{Li}_{3+x}\text{Nd}_3\text{Te}_{2-x}\text{Sb}_x\text{O}_{12}$. *Chem. Mater.* **20**, 2360–xO2369 (2008).

105. Wu, J. F. et al. Gallium-doped $\text{Li}_3\text{La}_3\text{Zr}_2\text{O}_{12}$ garnet-type electrolytes with high lithium-ion conductivity. *ACS Appl. Mater. Interfaces* **9**, 1542–1552 (2017).

106. Logéat, A. et al. From order to disorder: the structure of lithium-conducting garnets $\text{Li}_{7-x}\text{La}_3\text{Ta}_x\text{Zr}_{2-x}\text{O}_{12}$ ($x=0\text{--}2$). *Solid State Ion.* **206**, 33–38 (2012).

107. Ohta, S., Kobayashi, T. & Asaoka, T. High lithium ionic conductivity in the garnet-type oxide $\text{Li}_{7-x}\text{La}_3(\text{Zr}_{2-x}\text{Nb}_x)\text{O}_{12}$ ($x=0\text{--}2$). *J. Power Sources* **196**, 3342–3345 (2011).

108. Rettenwander, D. et al. Synthesis, crystal chemistry, and electrochemical properties of $\text{Li}_{7-2x}\text{La}_3\text{Zr}_{2-x}\text{Mo}_x\text{O}_{12}$ ($x=0.1\text{--}0.4$): stabilization of the cubic garnet polymorph via substitution of Zr^{4+} by Mo^{6+} . *Inorg. Chem.* **54**, 10440–10449 (2015).

109. Li, Y., Han, J. T., Wang, C. A., Xie, H. & Goodenough, J. B. Optimizing Li^+ conductivity in a garnet framework. *J. Mater. Chem. B* **22**, 15357–15361 (2012).

110. Awaka, J., Kijima, N., Hayakawa, H. & Akimoto, J. Synthesis and structure analysis of tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with the garnet-related type structure. *J. Solid State Chem.* **182**, 2046–2052 (2009).

111. Percival, J., Kendrick, E. & Slater, P. R. Synthesis and characterisation of the garnet-related Li ion conductor, $\text{Li}_5\text{Nd}_3\text{Sb}_2\text{O}_{12}$. *Mater. Res. Bull.* **43**, 765–770 (2008).

112. Zhao, G., Suzuki, K., Yonemura, M., Hirayama, M. & Kanno, R. Enhancing fast lithium ion conduction in $\text{Li}_4\text{GeO}_4-\text{Li}_3\text{PO}_4$ solid electrolytes. *ACS Appl. Energy Mater.* **2**, 6608–6615 (2019).

113. Deng, Y. et al. Enhancing the lithium ion conductivity in lithium superionic conductor (LISICON) solid electrolytes through a mixed polyanion effect. *ACS Appl. Mater. Interfaces* **9**, 7050–7058 (2017).

114. Deng, Y. et al. Structural and mechanistic insights into fast lithium-ion conduction in $\text{Li}_4\text{SiO}_4-\text{Li}_3\text{PO}_4$ solid electrolytes. *J. Am. Chem. Soc.* **137**, 9136–9145 (2015).

115. Hong, H. Y. P. Crystal structure and ionic conductivity of $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ and other new Li^+ superionic conductors. *Mater. Res. Bull.* **13**, 117–124 (1978).

116. Pérez-Estébanez, M., Isasi-Marín, J., Többens, D. M., Rivera-Calzada, A. & León, C. A systematic study of NASICON-type $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (M : Cr, Al, Fe) by neutron diffraction and impedance spectroscopy. *Solid State Ion.* **266**, 1–8 (2014).

117. Weiss, M., Weber, D. A., Senyshyn, A., Janek, J. & Zeier, W. G. Correlating transport and structural properties in $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) prepared from aqueous solution. *ACS Appl. Mater. Int.* **10**, 10939–10944 (2018).

118. Schlem, R. et al. Mechanochemical synthesis: a tool to tune cation site disorder and ionic transport properties of Li_3MCl_6 (M = Y, Er) superionic conductors. *Adv. Energy Mater.* **10**, 1903719 (2019).

119. Asano, T. et al. Solid halide electrolytes with high lithium-ion conductivity for application in 4 V class bulk-type all-solid-state batteries. *Adv. Mater.* **30**, 1803075 (2018).

120. Park, K. H. et al. High-voltage superionic halide solid electrolytes for all-solid-state Li-ion batteries. *ACS Energy Lett.* **5**, 533–539 (2020).

121. Imholt, L. et al. Grafted polyrotaxanes as highly conductive electrolytes for lithium metal batteries. *J. Power Sources* **409**, 148–158 (2019).

122. Butzelaar, A. J. et al. The power of architecture-cage-shaped PEO and its application as a polymer electrolyte. *Polym. Chem.* **12**, 4326–4331 (2021).

123. Wu, N. et al. Enhanced surface interactions enable fast Li^+ conduction in oxide/polymer composite electrolyte. *Angew. Chem. Int. Ed.* **59**, 4131–4137 (2020).

124. Wang, W., Yi, E., Fici, A. J., Laine, R. M. & Kieffer, J. Lithium ion conducting poly(ethylene oxide)-based solid electrolytes containing active or passive ceramic nanoparticles. *J. Phys. Chem. C* **121**, 2563–2573 (2017).

125. Chung, S. H. et al. Enhancement of ion transport in polymer electrolytes by addition of nanoscale inorganic oxides. *J. Power Sources* **97–98**, 644–648 (2001).

126. Ding, M. S. & Jow, T. R. Conductivity and viscosity of PC-DEC and PC-EC solutions of LiPF_6 . *J. Electrochem. Soc.* **150**, A620 (2003).

127. Kirillov, S. A., Gorobets, M. I., Tretyakov, D. O., Ataev, M. B. & Gafurov, M. M. Phase diagrams and conductivity of lithium salt systems in dimethyl sulfoxide, propylene carbonate and dimethyl carbonate. *J. Mol. Liq.* **205**, 78–84 (2015).

128. Nyman, A., Behm, M. & Lindbergh, G. Electrochemical characterisation and modelling of the mass transport phenomena in LiPF_6 -EC-EMC electrolyte. *Electrochim. Acta* **53**, 6356–6365 (2008).

Acknowledgements

We acknowledge financial support within the cluster of competence FESTBATT funded by Bundesministerium für Bildung und Forschung (BMBF; projects 03XP0431, 03XP0430A and 03XP0430F). We thank P. Till for support in data analyses.

Competing interests

The authors declare no competing interests.

Correspondence should be addressed to Jürgen Janek or Wolfgang G. Zeier.

Peer review information *Nature Energy* thanks Marm Dixit, Taro Hitosugi, Jennifer Rupp and Fan Wu for their contribution to the peer review of this work.