Challenges in Speeding up Solid State Battery Development

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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 in order to provide sufficient transport in composite cathodes. In addition, we will show that high-performance anodes together with protection concepts are paramount for establishing 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 will further discuss that diversity in terms of materials, research teams and approaches will be key to establish solid-state batteries long term. About ten years after the first ground-breaking publication of lithium solid electrolytes with an ionic conductivity higher than of liquid electrolytes it is time to realistically address the remaining key challenges for full-scale commercialization, cell performance and implementation.

Lithium-ion batteries (LIB) 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) has 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 (SE) can prevent electrode cross talk, i.e. the unwanted chemical interaction of dissolved active materials, which would eliminate one cause for long term instability of LIBs. Further, the high lithium ion transference number of inorganic SEs around unity allows very fast charging capabilities without electrolyte polarization, indeed leading 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 calculations[1] have 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 ($LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$) vs. graphite reaches specific energies and energy densities of 265 Wh/kg and 635 Wh/L, respectively. In contrast, an SSB based on NCA vs. lithium metal may theoretically reach 393

Wh/kg and 1143 Wh/L, respectively.[1] 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 worldwide[2] has led to a much better understanding of the key challenges for *solidification* of batteries over the last decade.[3] 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 MPa may also be technically acceptable. Second, the development of stable high-rate and high-capacity anodes, e.g. 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, potentially more sustainable approaches such as, fifth, Na-based and sulfur conversion-based SSB. In addition, the rise of “hybrid” concepts combining solid and liquid or gel-polymer electrolytes becomes important, and last 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. While we have summarized some of these issues qualitatively about six years ago,[4] 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 are key – Transport, storage and chemomechanics

A generalized scheme of a typical SSB is shown in Figure 1, summarizing 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 significant strain and corresponding local stress between active materials particles and the SE particles.[7] While the volume changes may be less problematic in oxide-based SSB,[8] in the well performing sulfide-based SSB, the need for particle contact between the ionic conductor and the active material needs to be considered as any chemomechanical volume change will have severe local repercussions.[9] 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 continuous operation of SSB.[10] 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 cells.[11]

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 high.[12] Considering 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 the effective ionic conductivity of inorganic SEs is significantly lowered compared to the bulk conductivity of the SE by decreasing the volume fraction of the SE in the composite,[13] which lowers the overall attainable charge rates and capacities (see Figure 2).

Not only does one need a SE with a sufficiently high conductivity to compensate tortuosity and residual void issues, especially in thick electrodes,[14] it is additionally paramount to establish the usage of polymer binders[15] or optimize particle size distribution[16] to mitigate volume changes and create beneficial ionic transport, as well as to establish hybrid composite architecture concepts entirely (see below). While designing an optimized cathode composite includes challenges such as which binder to use, how to retain a high conductivity with 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 multi-dimensional optimization problem in which a large fraction of the inherent interfacial issues is not well understood yet. Nevertheless, it is clear that a future solid-state battery must have either a fully designed electrode micro- and macrostructure,[17] together with tailored cathode active material (CAM) particles,[18] contain SEs with much faster ionic conduction, or ideally both. While only being relatively simple descriptors[19] that still require 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 LIB use liquid electrolytes (LE) with lithium-ion conductivities in the order of a few mS/cm, and the strong increase in interest and research focus on solid-state batteries stems from the recent achievements in pushing the ionic conductivity of SEs even beyond this limit. The development of sulfide fast ionic conductors such as $Li_{10}GeP_2S_{12}$ and its derivatives, as well as the lithium argyrodites $Li_6(P,Sb)S_5X$, all show ionic conductivities greater than 1 mS/cm. Oxide-based lithium SEs are often limited to conductivities below 1 mS/cm, 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 become one possible direction. In addition, disperse polymer-based electrolytes containing low levels of liquids may also be a reasonable alternative.[20] The very high ionic conductivity of lithium thiophosphates, taken together with their low mechanical moduli are the predominant reasons why sulfide-based composites play a dominant role in the development of SSB 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 mS/cm really enough, just because it is comparable to a LE? Considering LE, 8-10 mS/cm are typical total conductivities found[21] that correspond at best to 4-5 mS/cm of lithium-ion conductivity even if one would assume 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 cathode active materials in a porous electrode with a LE is intrinsically connected to a lower tortuosity than compared to 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, faster ionic transport is needed just to be comparable to lithium-ion transport in LE-based cathodes.[13,22] This effect is shown in Figure 2.b Whereas the LE percolates well in a porous electrode structure, the microstructure in a solid composite of 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 includes 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 of greater than 7 mAh/cm^2, corresponding to an electrode thickness of over 100 μm, current loads of 7 mA/cm^2 are only realistic with a minimum of an effective ionic conductivity of 10 mS/cm.[14] When assuming a lithium metal anode of 30 μm, a separator of 20 μm and a CAM volume fraction of 70 % this cell would then correspond to an energy density of 1443 Wh/L and a specific energy of 435 Wh/kg.

To this day, only a handful of lithium SEs reach an ionic conductivity of 10 mS/cm at room temperature, i.e. the highly substituted lithium argyrodites $Li_6(P/Sb)S_5(Cl/Br/I)$[25,26] and $Li_{10}GeP_2S_{12}$ and its derivatives.[27,28] It is yet unclear how many other materials classes can be pushed above this lower conductivity limit that is needed, especially considering that 10 mS/cm of effective conductivity and not ionic conductivity of the SE will be needed. Future efforts must focus on achieving several mS/cm effective ionic conductivity in the cell environment in order to obtain a solid-state battery that can perform with realistic loadings and current densities – or operation at elevated temperature has to be accepted.[13,22] These efforts should not only include trial and error but may need help in machine learning or high-throughput screening efforts to improve the current SEs while possibly identifying unknown or overlooked materials that may hold potential for the future. Overall, 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. While 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 have been achieved using Ge in the solid electrolyte, and efforts of using Li_3InCl_6 or Li_3ErCl_6 are questionable in regards to the price as a full substituent for thiophosphates 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 halides[29] especially as a bi-layer separator layout seems to be needed.[30] 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 to a LE.[31] Figure 3 shows pertinent electrolytes and their ionic mobility as a function of carrier density, i.e. lithium ion density, which has rarely been considered before. Whereas LE exhibit 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 conductivity.[31] Oxide-based SE lack mobility at too high carrier densities and polymer SE 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 SE and CAM 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 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 just 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 multi compositional space. In addition, finding novel materials with intrinsically higher ionic mobility – together with a low charge carrier density – seems a viable future option.

The need for high-performance anodes

While cathodes very much control the specific energy of SSBs due to their relatively low specific capacity and the corresponding need for thick cathodes, clearly one can only achieve specific energies comparable to 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 reversible high-rate operation. Remember that it is the graphite anode that limits the charge rate of LIBs.[32] The most obvious options are the lithium metal anode[10] 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 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 (see Figure 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, in order to meet the same stack pressure of LIBs. While it appears that $Li_7La_3Zr_2O_{12}$ (LLZO) can indeed operate dendrite-free at sufficiently high current densities and relatively low stack pressure,[39] there is still no open accessible proof for long term and large area operation available. Thiophosphate SEs suffer from SEI formation and dendrite growth.[40] While research on the laboratory scale suggests that the nature of the growing interphase can be self-limiting,[10] future work has still to show whether thiophosphates can be safely employed as separator material. Often, the so-called critical current density is used as a descriptor for long-term stable operation of the lithium metal anode. The critical current density (CCD) shall represent the upper limit for operation without danger of anode instability, yet it depends on a large number of materials properties and experimental variables, like e.g. the sequence of previous plating/stripping steps.[41] It is a process-dependent observable that hardly can be compared for different electrodes and experimental schemes. We conclude that it hardly can be used as a proper metric for 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 fast,[42] however at the cost of a reduced specific energy. Theoretical estimates for Li/LLZO composite anodes have recently been published and show that the capacity advantage is easily lost,[43] as LLZO has a high density. Microporous carbon or lithium/carbon composites may be an alternative,[44] yet no such anode concept has been proven to be superior. Alloying lithium and using a solid solution anode with wide solubility range for lithium is the second option that is particularly interesting in case of silicon where, 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 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 the 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 for LE.[45] 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 resulting in detrimentally resistive interphases,[46,47] that often seem to be redox-active themselves.[48] Recent work further showed that the thickness of the solid electrolyte interphase that is growing on the lithium metal anode in contact with sulfide SE has been severely underestimated (see Figure 4c for a general picture),[40] further challenging the need for protection concepts. However, while decomposition reactions are challenging for any technology, these hopefully can be mitigated by chemical design approaches of the interface or interphase.

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. While it seems that these electronically insulating coatings lead to a potential drop and partially protect the solid electrolyte, interdiffusion and chemical decomposition is still observed.[49] 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 beneficial transport properties of a kinetically stabilized, *i.e.* 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? Second, can there be a theory-guided exploration of materials with reasonably kinetic stability windows? Current work explores the thermodynamic instability, however, the question if the decomposition products can kinetically lead to a stable decomposition interphase is rarely answered.[51]

Is lithium really needed?

Reducing the amount of Li in the SE seems important, but ultimately will only deliver a minor contribution to overall Li criticality as cathode and anode materials are still needed. And indeed, the same potential benefits that drive the development of sodium ion batteries, namely replacement of lithium and transition metals such as cobalt and nickel, justify the research on sodium-based solid-state batteries.[52] Various efforts are reported in understanding and pushing sodium ionic transport in solid electrolytes and indeed, much higher ionic conductivities can be achieved with the less polarizing Na^+ ion compared to Li^+.[53,54] Nevertheless, the oxide solid electrolytes retain their challenge of sintering and the thiophosphate classes show much faster decomposition at the Na metal anode compared to the lithium analogues.[55] The upcoming sodium halides so far are not competitive in ionic transport,[56] nevertheless, cell operation is possible.[57] Furthermore, strong decomposition reactions proceed between the CAM and the catholyte, which has limited most reports to the use of $NaCrO_2$, and better CAM for the usage in Na-SSB are still needed. Promising steps are being made in the development and understanding of hydroborate electrolytes, such as $Na_2B_{10}H_{10}$ and derivates. Fast ionic conductivities have been reported together with excellent electrochemical stability against the electrodes.[58–60] Overall, while providing many benefits, the development of sodium solid-state batteries needs to be intensified in terms of protecting the solid electrolyte with coatings of the CAM, as well as finding and enabling high-performance anodes in order to truly provide a competitive alternative. And indeed, finding the ideal composition is needed to achieve a quantitative analysis of potential energy and power densities for comparison with lithium-ionic SSB in the first place.

Alternative cathode materials

To date, the majority of experimental reports is focusing on NCM-type CAM in SSB. However, spinel-type or even Li-rich CAM offer higher potentials in cells and need to be considered as cell components.[61] Severe chemical reactions with the SE will occur, but as coatings need to be developed anyways, it may be worth to directly push the energy density by advanced cathode materials. On the other hand, CAM such as $LiFePO_4$ are rarely being used in sulfide SSB and are mostly found in polymer SSB. A fact that may very well change considering 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 $LiFePO_4$. Truly promising cell performance has been achieved by using conversion redox materials in SSB, such as sulfur. The lower charging potentials are of course one limitation, however, lower charging potentials prevent the electrochemical decomposition of the solid electrolyte and cycling capacities close to the theoretical capacity of S to Li_2S conversion have been obtained.[12] Yet, very similar challenges exist in Li-S solid state batteries that limit their current applicability. First, cathode composites are composed of not only solid electrolyte and active material, but significant volume fractions of carbon are needed to provide sufficient electronic conductivity. As the electrochemical reaction will occur at 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 SSB as otherwise sluggish reaction kinetics limit the performance.[12] Second, chemomechanical challenges are much more severe when S converts to Li_2S as the volume changes are significant. Nevertheless, for optimized Li-S solid state batteries projected gravimetric energy densities of over 800 Wh/kg seem reachable.[62] Potentially impactful cathode materials can be extended to copper sulfides[23] or iron sulfides[65], or the use of transition metal additives,[64] all of which seem promising so far. However, while their limitations have not been fully explored yet, companies such as Solid Power are pursuing the approach of more sustainable pyrite-based SSB.[66] Recently the possibility to employ sodium in the conversion of sulfur has attracted attention,[53,67] as a complete conversion reaction of S to Na_2S is possible with a theoretical capacity of 1675 mAh/g that lies above the theoretical capacity of 558 mAh/g 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 SSB.

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/interphases at both 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 concept.[68] Aiming for low and room temperature operation, it appears that thiophosphate SEs need to be utilized as catholyte in a true SSB cell. Once dendrite formation at the lithium metal anode cannot be suppressed by the same SE as separator material, then either a polymer or an oxide SE has to be employed as separator.

These considerations show that there is a wide range of intermediate concepts on the route from LIB to true SSB in which different options of combining sulfide with polymers or oxides exist, leading to a layered-like hybridization concept[69] or even true three-dimensional mixing.[70] And it may well be that the chemomechanical issues of volume exchanges and contact losses at solid/solid interfaces requires a small fraction of liquid electrolyte to act as local contact “agent” and potentially even interphase former.[71] In fact, an SSB cell exclusively containing 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 reducing 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 long-term stable is an open question, as well as whether hybridization compromises safety. In view of the difficulties in processing e.g. sulfide SEs in liquids solvents, hybrid systems may at the end suffer from chemical instabilities. In-depth studies are definitely needed in order 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 needed.[72] Whereas academic research on SSB still focusses on pressed pellet-type cells that require high stack pressures to mitigate the above-mentioned chemo-mechanical 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 existing processing approaches will be used in order to generate a smoother transition away from lithium-ion batteries. Hence, composite cathodes need dry or wet processing in slurries, and solvent and binder interactions need to be considered.[73] 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 consider.[74] Here halide SE 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 drawback[75] and interfacial decomposition still seem to occur.[76] An upscaling of SE syntheses is a further requirement and milling or solution routes may be the best approach, criticality and prices of the precursors still need to be realistically established. Full SSB may bring cost advantages as expensive steps such as electrolyte infiltration and formation are not needed. Overall, the cost advantage of SSB needs to be explored and directed. In this respect, bipolar stacking is often considered a major cell construction advantage of future SSB,[77] as it appears to offer a simpler internal cell design and less current-leading connections outside the cell stack. – leading too 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, leading to a necessary control of all 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, recycling of solid-state batteries needs to be developed in full. Innovative recycling routes have been developed for various types of solid electrolytes,[78] however, large scale implementation is so far questionable, especially considering 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 could design solid electrolyte compositions for a later recycling process.

Diversity is key

Solid-state battery research and development has seen a tremendous growth and pace in the last few years, and a deeper understanding of the current limitations of SSB has been established. While this better fundamental understanding has helped to advance potentially successful cell concepts, still some old but also new questions and challenges for future large-scale production of SSB cells have to be answered and solved.[79] Figure 5 shows these now-known issues and potential mitigation strategies.

First, thick cathode architectures with low SE fraction are needed for reasonably high energy density. SEs with effective conductivities in the composite greater than 10 mS/cm are required to achieve fast rates in cathode composites with complex microstructures containing also 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 liquid electrolyte may be employed as catholyte. Once kinetics will not be sufficient at room temperature, operation at 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 solid electrolyte remain key challenges for high current densities and fast charge – discharge applications. While 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 finding compositions with lower element criticality, together with chemical approaches for composite route preparation, are needed to have SSB realistically replace LIB in the coming years. While these challenges may appear as critical, one should not forget that SBB cells may allow a more effective battery pack construction. Recent developments show that $LiFePO_4$ based LIB can be packed much denser in a pack up to 90 % of pack volume, while 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 of SSB cells.

Fourth, SSB are often regarded as being safer than LIB. However, whether increased safety exists still needs to be unequivocally proven as short circuits, the use of toxic solid electrolytes or even percolation of a liquid fraction of electrolyte to the anode may provide additional safety risks.[80] Even more, recent work shows the self-ignition and thermal runaway of Li_6PS_5Cl – NCM composites above 150°C.[81] It seems that the already favored chemical decomposition pathway becomes strongly favored at elevated temperatures, which cannot be seen when using $LiFePO_4$ as the CAM. Clearly, thermal battery management and associated safety risks of thermal runaways need to be more intensively investigated. Safety concerns may be different than for LIB, but without developing safety test standards for SSB, final conclusions cannot be made.

Fifth, for a field such as solid-state batteries that is comprised of microstructural issues, chemical issues, electrochemical questions, processing deliveries and still to some extent unknown underlying transport physics, it is important to bring in the principles of other disciplines into the field and welcome entering researchers. To truly unfold the potential of SSB, 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 in standardizing experimental cell setups[82] and procedures closer to practical conditions.[3]

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.

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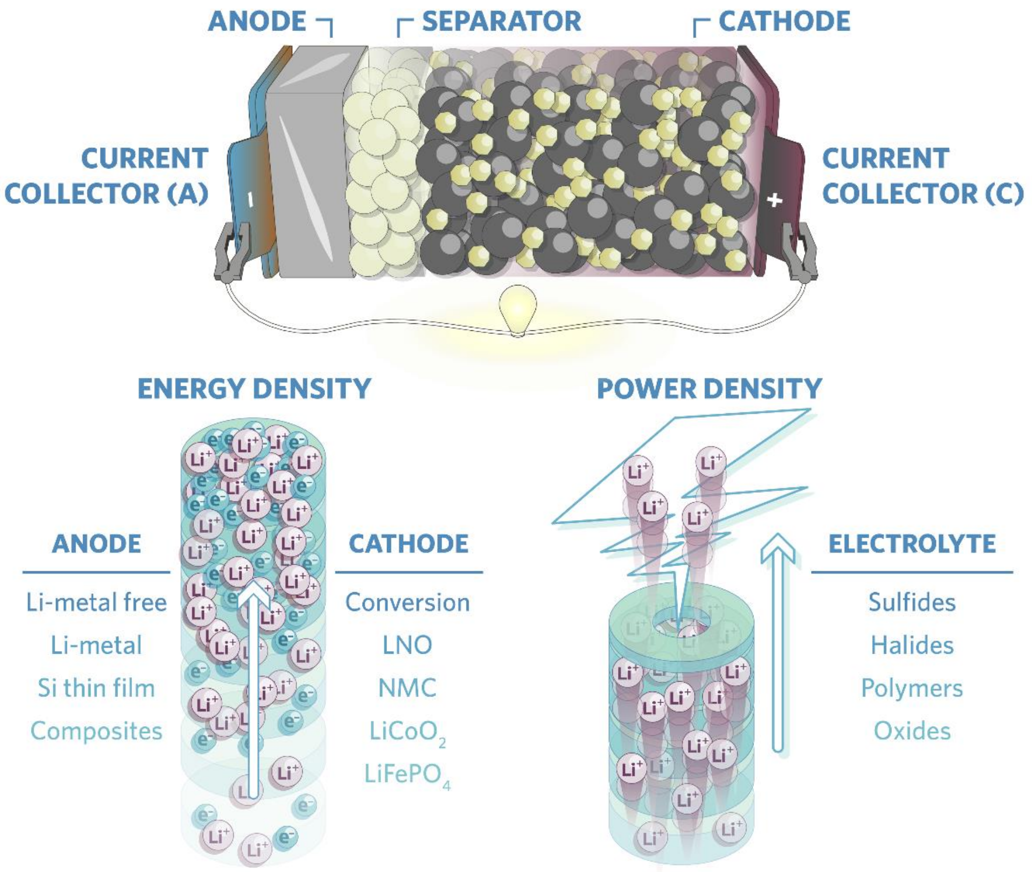

Figure 1: ***Generalized lithium solid-state battery cell concept***. *The most relevant materials today for anode, solid electrolyte and cathode, indicating their major impact on cell performance in terms of energy density and power density.*

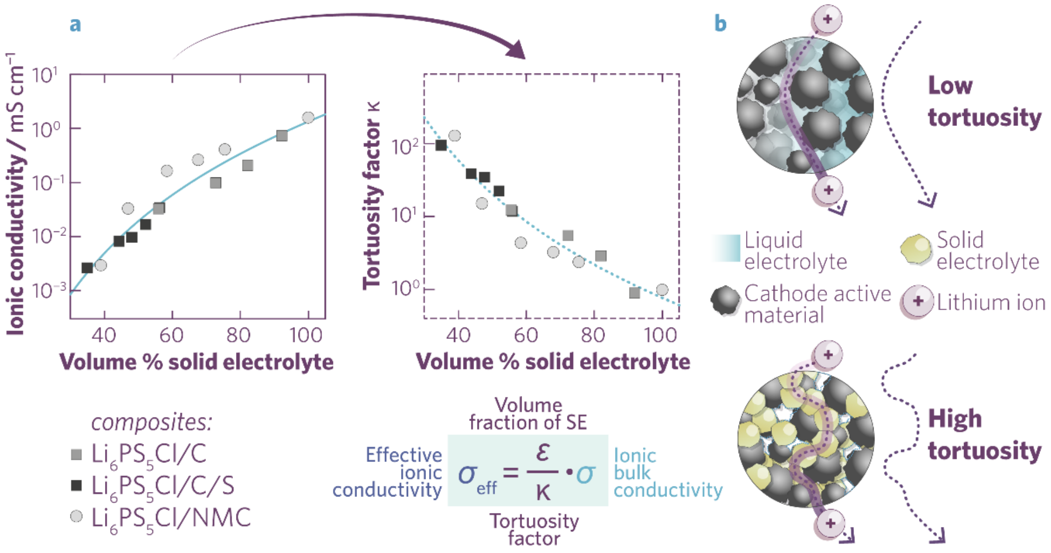

Figure 2: ***Tortuosity effects in solid-state cathode composites.*** *a) Measured partial lithium-ion conductivity* σ_{eff} *and evaluated tortuosity factor* κ *as function of weight fraction of solid electrolyte, which ultimately relates to the volume fraction* ε. *Values of conductivity and tortuosity factors of NCM- and Li-S- based solid-state batteries taken from references* 13 *and* 83, *respectively. b) Schematic*

explanation of higher tortuosity in SSB cathode composites compared to LIB cathodes with liquid electrolytes.

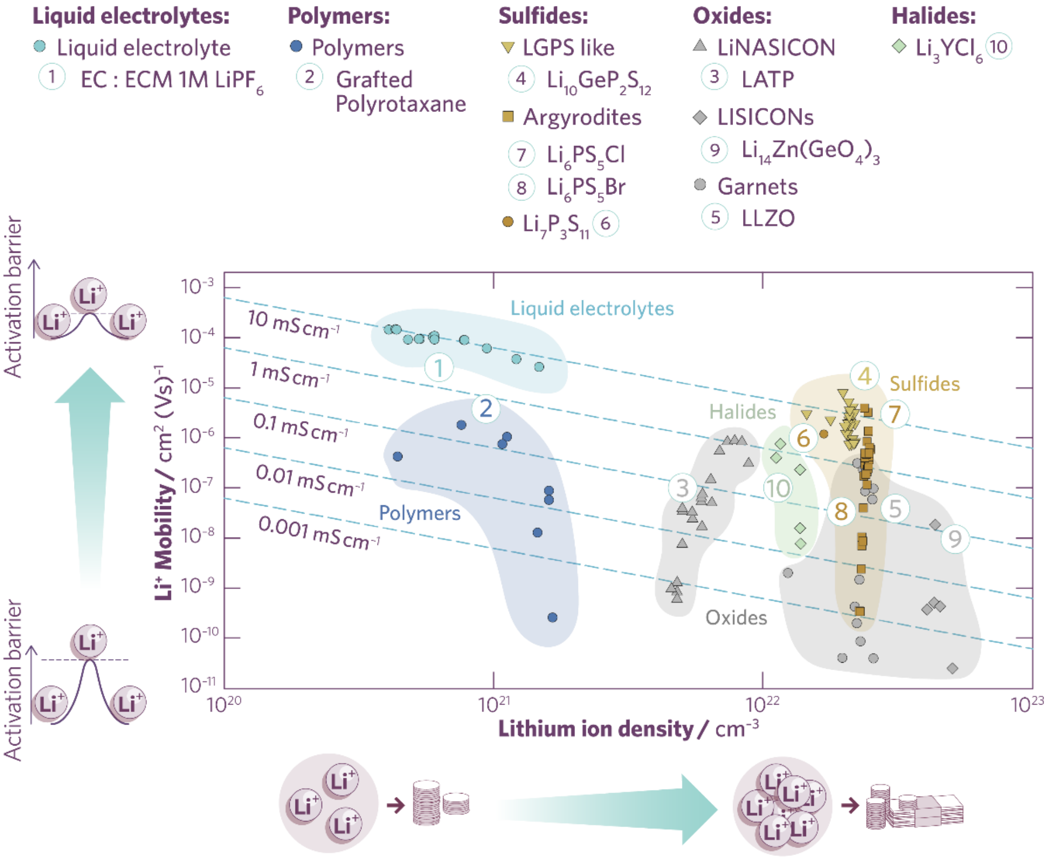

Figure 3: Classification of solid electrolytes based on lithium content. *Lithium-ion conductivity as product of ion mobility, charge (constant, not shown) and ion concentration (as ion carrier density). SEs with equal conductivity lie on dotted iso-conductivity lines. The diffuse clouds indicate different groups of SEs. The mobilities and carrier densities for the sulfides (LGPS,*[27,28,84–99] *argyrodite,*[25,26,100–102] *Li_7PS3_{11}*[103]*), oxides (garnets,*[104–112] *LISICON,*[113–116] *LiNASICON*[117,118]*), halides,*[119–121] *polymers (PEO-based*[122–126] *and grafted polyrotaxane*[122]*) and liquid electrolytes*[21,127–129] *were calculated from their reported conductivities and compositions and can all be found in the Source Data.*

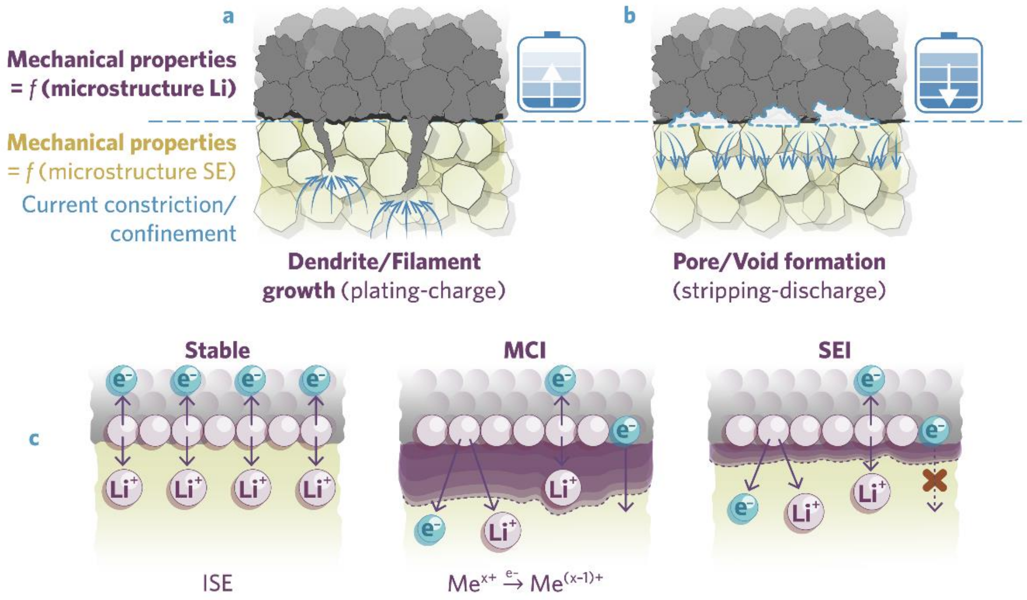

Figure 4: ***Critical issues of the lithium metal anode***. *a) Filament and dendrite formation causing short-circuits during charging and current focusing, b) pore/void formation during discharging causing constriction resistance and dendrite growth during subsequent plating, c) interphase growth between lithium metal and different SEs (modified graphs from reference [10]), showing thermodynamically stable operation (e.g. with LLZO, left), kinetically unstable operation (MCI = mixed-conducting interphase, middle) and kinetically stable operation (SEI = solid electrolyte interphase, right).*

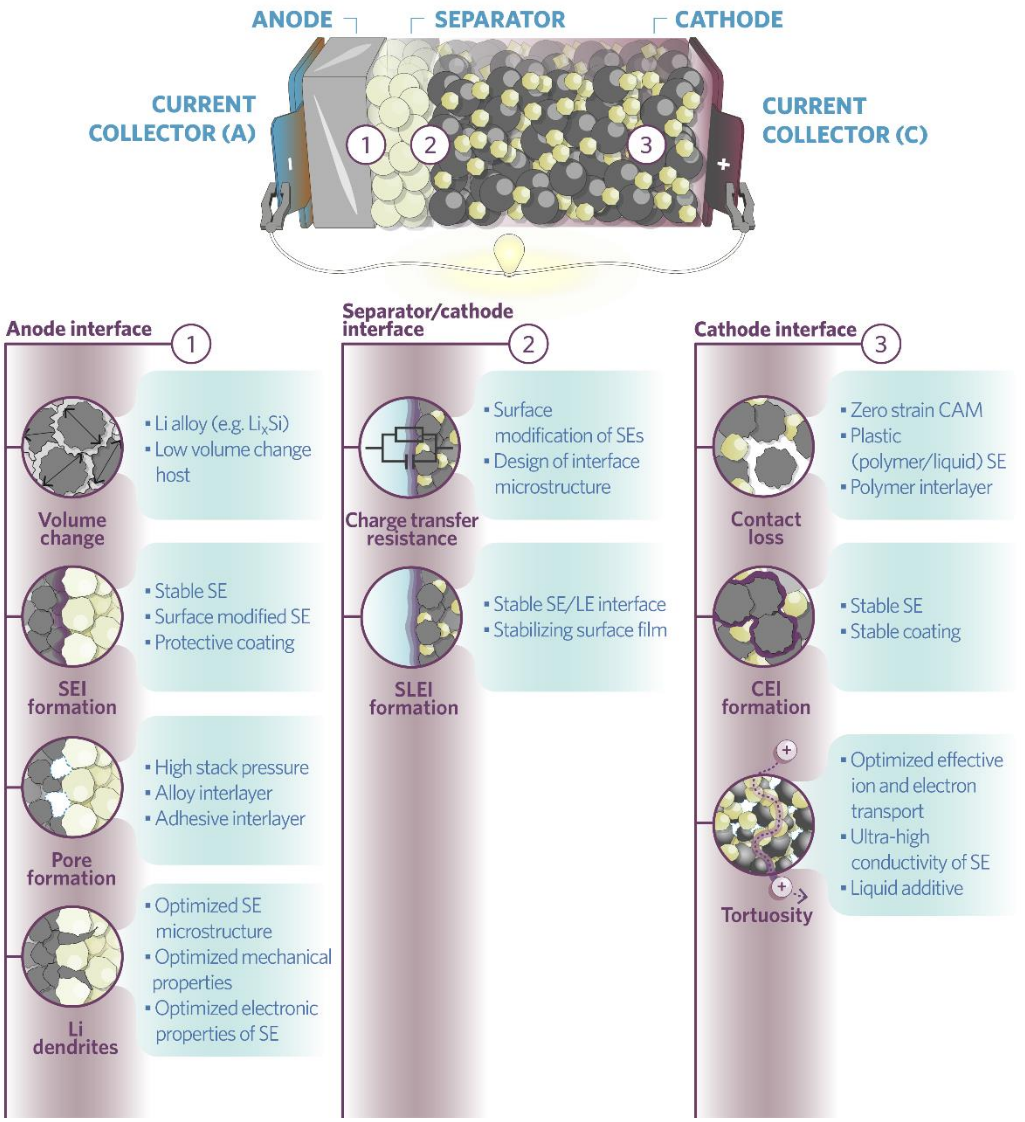

Figure 5: ***Known interface-related issues in solid-state batteries and potential solutions.*** *From left: anode interface, separator/cathode hetero-ionic interface, cathode interface and potential mitigation strategies.*

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