



Processing and manufacturing of next generation lithium-based all solid-state batteries

Wahid Zaman ^{a,c}, Kelsey B. Hatzell ^{a,b,*}

^a Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08540, USA

^b Andlinger Center for Energy and Environment, Princeton University, Princeton, NJ 37240, USA

^c Mechanical Engineering Department, Vanderbilt University, Nashville, TN 37240, USA



ARTICLE INFO

Keywords:

Solid state battery
Manufacturing
Solid electrolyte

ABSTRACT

All solid-state batteries are safe and potentially energy dense alternatives to conventional lithium ion batteries. However, current solid-state batteries are projected to costs well over \$100/kWh. The high cost of solid-state batteries is attributed to both materials processing costs and low throughput manufacturing. Currently there are a range of solid electrolytes being examined and each material requires vastly different working environments and processing conditions. The processing environment (pressure and temperature) and cell operating conditions (pressure and temperature) influence costs. The need for high pressure during manufacturing and/or cell operation will ultimately increase plant footprint, costs, and machine operating times. Long term, for solid state batteries to become economical, conventional manufacturing approaches need to be adapted. In this perspective we discuss how material selection, processing approach, and system architecture will influence lithium-based solid state battery manufacturing.

1. Introduction

Decreasing carbon emissions to address climate change challenges is dependent on the growth of low, zero or negative emission technologies. Transportation accounts for nearly 25% of CO₂ emissions worldwide. [1] Thus, electrifying transportation systems is important for disentangling this sector from fossil fuels. Electric cars accounted for 2.6% of global car sales in 2020 and 9% in 2021, a substantial increase from 2010 where only 0.2% of global sales were electric vehicles. Rapid EV adoption is due to coupled materials innovation and policy. Commercialization of energy dense cathodes LiNiMnCoO₂ (NMC) and LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) has dramatically increased battery pack specific energy (~220 Wh/kg) and vehicle range. [2] Despite these promising cathodes, there is continued interest in engineering batteries with energy densities exceeding 500 Wh/kg to meet future driving range requirements (>300 miles per charge). [3] Conventional Li-ion battery systems that utilize graphite anodes (specific capacity 350 mAh/g) cannot achieve these energy density requirements. Replacing graphite anodes with Li metal (specific capacity 3860 mAh/g) is one potential path toward energy dense batteries. However, Li metal is highly reactive and prone to active material loss during cycling (e.g. dead lithium). Lithium can also form dendritic structures which short an electrochemical cell upon cycling.

[4] Li metal batteries based on liquid electrolytes also pose considerable safety challenges due to coupled gas evolution and flammability challenges. [5].

Recently, there has been renewed interest in all solid-state batteries to address these challenges. Ions move through a solid electrolyte rather than a liquid electrolyte in all solid-state batteries. [6–8] Many solid electrolyte materials are incompatible with high voltage cathodes and/or energy dense anodes (Li metal) and suffer from poor rate performance (< 2C). In addition, many solid electrolytes require inert manufacturing infrastructure which increases cell costs. Currently small scale electronic and radio-frequency identification applications utilize low power (2 Ah) solid-state batteries. [9–11] EVs and consumer electronics will require larger format cells with substantially higher energy densities. Furthermore, scalability remains a major hurdle for the adoption of all solid-state batteries in applications like electric vehicles which have demands exceeding 150 GWh. [12–14] This scale is expected to grow by 3 × to 450 GWh by 2024. [15] Widespread implementation of SSBs is reliant on establishing low-cost manufacturing pathways. Currently, time and technology-based forecasts have suggested that the minimum cost achievable for a solid-state battery based on an oxide and sulfide types of solid electrolyte are \$157/kWh and \$113/kWh. [16–17] These estimates exceed conventional LIBs costs (\$101/kWh). [18] Closing the

* Corresponding author.

E-mail address: kelsey.hatzell@princeton.edu (K.B. Hatzell).

cost-gap between conventional and SSBs is critical for adoption.

The environmental footprint and technoeconomics of SSB manufacturing rely heavily on material supply chain, recycling, and repurposing opportunities. Simultaneous development of materials processing, cell design, and recycling strategies is important for rapid integration of solid-state batteries. There is growing attention on recycling conventional LIBs where materials (mostly cathodes) are recovered from several extractive metallurgical approaches (pyrometallurgy, hydrometallurgy) and direct recycling [19–21]. Direct recycling approaches may be adopted in SSB because individual components can be directly separated. Supply chain (mining, processing, refining, shipping) for solid state batteries is anticipated to be more challenging than conventional LIBs, due to the use of critical elements (e.g.; Ge, Ta) and increases in lithium content (Fig. 1a,b). Both resource availability and materials processing costs will be critical for identification of key battery chemistries and architectures for adoption of next generation all solid-state batteries.

1.1. Solid-state battery architectures

Overcoming degradation processes at buried solid interfaces is necessary for realization of high rate, high-capacity solid state batteries (350 Wh/kg). This requires engineering architectures that can adequately address chemo-mechanical phenomena (dendrites, physical voids, chemically unstable interfaces, sluggish transport kinetics) and manufacturing challenges. [14,22–23] Stress gradients can occur during

materials assembly and operations which impact degradation modes. [24] In addition, potential gradients can arise at interfacial inhomogeneities and drive dendrite formation and subsequent failure. [25–27] Chemo-mechanical degradation and material transformations are also exacerbated in solid state batteries that contain dense electrodes and electrolytes with high stiffness. This can lead to material fracture during dynamic operating conditions. [28] Composite solid-state cathodes experience repeated expansion/contraction which contribute to loss of interfacial contact and cracking during cycling. [29] It is desirable to have a composite cathode with a high density to ensure efficient ion transport. [30] Novel solid-state battery architectures are needed to address stress and potential gradients that arise due to chemo-mechanical dynamics within a solid-state battery. [12,31].

Cold-pressed powder processing produces thin film pellets (0.5–2 mm diameter) and is widely used with research and development laboratories (Fig. 1b-i). [25,32–33] Pellet-based solid electrolytes typically operate under pressure which leads to further densification. [34] Full cells can be assembled via stacking the anode, solid electrolyte, and cathode on top of each other (Fig. 1c-ii). Stack pressure can impact full cell performance and has been shown to be an effective strategy for preventing unwanted void formation and delamination at the anode. [35–36] This approach is unlikely to scale for industrial production because thick solid electrolyte result in low energy densities. [37] Composite cathodes account for <7% of total cell weight in pellet-based architectures (Fig. 1b- i). Decreasing the solid electrolyte by an order of magnitude (<10 μ m) and increasing the cathode content by 8 \times is

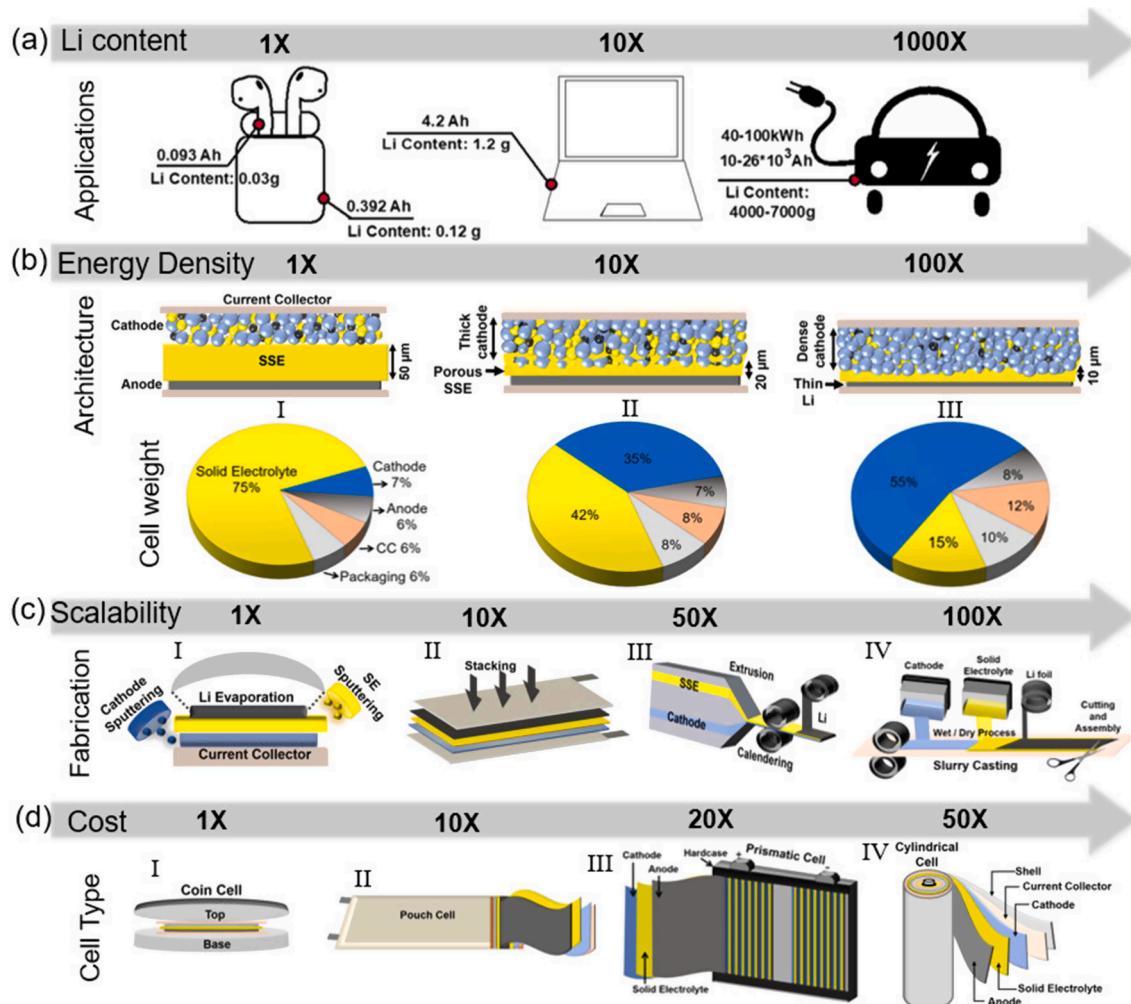


Fig. 1. Schematic of (a) battery-driven applications, (b) battery architecture from low to high energy density, corresponding weights of battery components (c) manufacturing processes of ASSBs with respect to scalability and (d) cell type with respect to production cost.

ultimately necessary for solid state batteries to compete with conventional batteries.

Scalable SSB designs should mimic conventional LIBs where ions flow continuously between the anode and cathode via well percolated pores filled with a liquid electrolyte. Solid state batteries employ percolated regions of solid electrolyte materials instead of percolating pores. Thus, cathodes that contain both active material (cathode) and solid electrolyte materials are known as composite cathodes (Fig. 1b). Solid state cathodes can be processed by either direct mixing approaches or multi-step infiltration processes. The latter process requires infiltration of the solid electrolyte either via solvent or melting directly onto a preformed cathode sheet. [38–39] Infiltrating cathode material into a porous framework has been widely explored within the solid oxide fuel cell community and utilizes facile processing approaches (tape casting) which enables high densities (>98%) and rigid electrolytes. Porous frame-works are known as bi-layer or tri-layer cells which are promising for large-format ASSB production (Fig. 1b-ii). [40–41] Bi/tri-layer architectures require the use of a colloidal precursor or slurry which combines a binder and pore former (Fig. 1c-iv). When the film is sintered the pore former will burn away leaving behind a porous structure. [42–43] Recent reports have shown that composite architectures with thin dense solid electrolytes can demonstrate higher energy densities (195 Wh kg⁻¹) with 99% coulombic efficiency. [43] Higher active material density (>95%) and thicker electrodes (>5 mAh cm⁻²) can further increase the cell-level energy density [44] (Fig. 1b-iii). However, thick cathodes can be challenging to implement in practice because of mechanical failure (cracking) and transport limitations. [45] Ineffective ion and electron transport within thicker electrodes can contribute to low-material utilization and poor rate performance. [30] Therefore, identifying cost-effective manufacturing processes which provide exquisite control over multi-material processing is critical for thick electrodes to be realized. [46].

1.2. Manufacturing approaches for solid-state batteries

Materials selection and processing approach will dictate strategies for manufacturing large-format solid-state batteries. Currently available solid-state batteries are thin film and have low (<1 mAh) nominal capacities. Most thin film architectures employ vacuum deposition methods which are difficult to scale-up for EV applications. In addition, many solid-state battery materials are air/moisture sensitive and require inert environments for processing. All of these considerations are critical for engineering low-cost solid state batteries (Fig. 1c,d).

Recently, there have been promising commercial demonstrations which utilize roll-to- roll manufacturing to produce multi-layered solid-state batteries with 20 Ah cell capacity. Despite this progress there are three key manufacturing challenges to overcome: (1) thin defect-free solid electrolyte processing, (2) dense composite cathode fabrication and (3) thin lithium metal processing. A host of approaches are being considered to address these challenges including and not limited to tape casting, screen printing, extrusion, and aerosol deposition. Tape casting or screen-printing methods are widely examined for composite cathodes and solid electrolytes because it can enable high-throughput and scalable production volumes. However, high-throughput coating processes may require an additional calendaring step to alter part density. Extrusion or melt processing is being examined for lithium metal and alloy materials. Processing of lithium metal is a significant challenge because any contamination can drastically impact performance. Furthermore, a lot is unknown regarding how shear- and stress- experienced during processing can influence lithium metal properties. Finally, three-dimensional printing approaches are also being examined because they enable solid-state batteries with controlled meso- and microstructures. All 3D printed batteries can offer a wide range of form factors and low manufacturing cost with increased scalability. [47] Recently, Sakuu Inc. successfully employed their multi-material 3D printing technology to manufacture solid-state batteries in their 2.5

MWh pilot facility. Three-dimensional printing strategies (e.g., inkjet printing) need to be further explored but are unlikely for large capacity applications.

1.3. Manufacturing of solid electrolytes

A wide range of inorganic (ceramic) and organic (polymer) Li-ion conductors are being examined for solid-state batteries. Technoeconomic analyses suggest that the solid electrolyte should be <35% of the total manufacturing cost. [14,48] Unfortunately, current solid electrolyte processing is estimated to be nearly 70% of the cost associated with manufacturing a solid-state battery. One kilogram of LLZO, LGPS and Li₆PS₅Cl costs \$2000, \$69,500 and \$36,000. [14,49] The cost of solid polymers such as PEO and Li-salt is \$700/kg and \$1,980/kg. Processing cost of polymer or polymer-composite electrolytes (e.g., PEO-LLZO, PEO-LGPS) can therefore vary from \$7,000–50,000/kg. Due to simpler and cost-efficient processing, polymer or hybrid electrolyte based SSB manufacturing is anticipated to cost less than oxides or sulfides (\approx \$110/kWh). Material selection and manufacturing choice will dictate this end cost.

Garnet oxides (LLZO) are known for outstanding mechanical rigidity ($E_{modulus} = 129$ GPa), satisfactory ionic conductivity (10^{-4} S.cm⁻¹) and good electrochemical stability. [31] While other inorganic electrolytes are known to form reactive interphases at the interfaces, LLZO only forms a slightly less ion-conducting (tetragonal) but stable interphase. Synthesis of LLZO requires mechanochemical milling (e.g., ball milling) and high temperature sintering. The sintering step generally requires additional sacrificial LLZO as “mother-powder” to prevent Li loss. [50] High temperature processing is critical for grain growth and densification of polycrystalline LLZO. High densities of LLZO (>90%) are attained through pelletization via external isostatic pressure (>300 MPa). Rapid induction hot pressing (RIHP) has been shown to be an effective strategy for achieving higher densities (>98%). [32] These processing strategies, when transferred to the plant scale, require large footprints and high production costs. Freeze tape casting of porous 3D LLZO scaffolds (<100 μ m) is one of the “pressure- free” scalable approaches which can be implemented directly in solid-state batteries. [51–52] The 3D scaffolds were also featured in bi/tri-layer SSE architectures, which can be scaled up via tape casting. [42] Another pathway for alleviating pressure during processing is to utilize aerosol and vacuum-based deposition processes. Pulsed layer deposition (PLD), magnetron sputtering and atomic layer deposition (ALD) are also effective in producing ultra-thin (<10 μ m) solid electrolytes without stack pressure and at lower temperatures (\leq 650°C) [53–58]. Processing conditions (e.g., temperature, gas flow rates and deposition rates) all influence material properties. [59–60] Currently, a significant gap still exists between thin film and bulk solid electrolytes in terms of transport properties (e.g. ionic conductivity). Loss of lithium during processing is a considerable challenge for developing resilient processing chains.

Glassy amorphous sulfides (LPS, LGPS) and argyrodites (Li₆PS₅Cl) electrolytes display narrower voltage window but superior room temperature ionic conductivity when compared to oxides. Soft amorphous sulfide electrolytes offer several advantages including good inter- facial contact and low grain boundary resistance. [61–63] Sulfide solid electrolytes are typically synthesized using mechanochemical milling (>40 h) and can be compressed into thin pellets (<200 μ m) [64–66]. There are several on-going efforts to synthesize sulfide solid electrolyte via solution-processing approaches. [67–68] Solution-processing synthesis may enable high volume materials production and low costs. However, solution-processing conditions can have a significant impact on transport properties. [69] Stack pressure and heat treatment influences the densification, crystallinity, and ionic conductivity of both electrolytes (2 mS.cm⁻¹ for LPS, 5 mS.cm⁻¹ for LGPS and 1 mS.cm⁻¹ for Li₆PS₅Br) (Fig. 3a). [70–72] Halide based electrolytes (e.g., Li_{3-x}M_{1-x}Zr_xCl₆) are also an attractive class of superionic conductors (>1.4 mS.cm⁻¹) and demonstrate better electrochemical stability (>4V) due to incorporation

of halogens as anions (Fig. 3a) [73–74, 75–77]. Unlike garnet oxides, sulfide solid electrolytes cannot be processed via vapor deposition approaches and thus require hot-, warm-, or room temperature isostatic pressing to achieve viable thicknesses and densities. Furthermore, sulfide solid electrolytes cannot form porous scaffolds and thus are incorporated directly with the cathode material in composites.

The last class of solid electrolytes being examined are organic solid polymer electrolytes (SPEs). These electrolytes combine a binary lithium salt with a bulk polymer material [78–81]. Lithium ions motion is governed by the polymer chain segmental mobility. The room-temperature ionic conductivity and mechanical stiffness of SPE are lower than most inorganic solid electrolytes ($< 10^{-4}$ mS.cm⁻¹, 2 MPa). [82] Hybrid solid electrolytes (HSEs) are a family of solid electrolytes which combine a polymer and inorganic ion conductor. This hybrid or composite approach can lead to improved mechanical and transport properties. [83–85] Oxide-based HSEs demonstrate ionic conductivity up to 0.4 mS.cm⁻¹ and sulfide-based hybrid solid electrolytes demonstrated an ionic conductivity approaching 0.11 mS.cm⁻¹ (Fig. 3a). [86–87] Hybrid and all organic solid electrolytes can be processed under low temperature and pressure conditions using traditional coating approaches [88]. However, organic solid electrolytes can suffer from dendrite propagation, low ionic conductivity, mechanical and thermal stability. [89] High solid electrolyte market penetration is dependent on developing low temperature, low pressure, and low-cost manufacturing strategies. Traditional manufacturing steps include mixing, annealing, sintering, thinning/ and stacking. The quality of thin electrolytes processed via coating routes is highly dependent on coverage speed, viscosity, mixing parameters and volume flow (Fig. 2). Ultimately, there needs to be more work on understanding how processing conditions impact solid electrolyte performance before scaling up can be realized.

2. Manufacturing of cathodes

Composite cathodes contain an active material (CAM > 80 wt%), an electronic conductor (>10 wt%) and an ionic conductor (>10 wt%). Solid state cathodes are processed via traditional wet chemistry-based coating manufacturing approaches. There has been ongoing interest in highly viscous and dry processing of composite cathodes via extrusion and powder bed mixing in order to minimize solvent handling. [40] For further densification of composites, co-sintering approaches (>700°C) are often employed which can lead to unwanted side reactions at

interfaces due to cross-diffusion. [13,90] Composite cathodes rely on intimate contact between each constituent (e.g., cathode, electrolyte, and carbon). Many materials experience chemical decomposition at these triple points. [91] Active materials undergo frequent volume expansion/contraction during cycling, which causes gradual degradation and interfacial cracking. Both ionic and electronic percolation in composites are dependent on the cathode-solid electrolyte particle size ratio. Numerous theoretical studies have investigated the impact of particle size and composition on the composite cathode energy density. [92–93] In practice, transport limitations in thick electrodes and chemical decomposition need to be resolved to achieve similar performances with conventional cathodes. This may require advanced manufacturing approaches that enable precise control over electrode microstructure during processing. [94].

Similar to solid electrolytes, a range of vacuum deposition techniques are being explored for ASSB cathodes. Electrodeposition of additive and binder-free cathodes is a promising approach that allows 100% utilization of cathodes in solid-state batteries. [95] Pulsed layer deposition (PLD) and RF-magnetron sputtering can enable additive-free deposition of thin film cathodes (e.g., LCO, LFP) with precision control in nanoscale. [31,56] The fabricated battery architectures can potentially achieve highest relative fraction of active materials (>60% of cell weight) (Fig. 1b-iii). But due to slow processing speed and high maintenance cost, these techniques are challenging to scale up and replace conventional slot-die/tape-casting based manufacturing. [96] Aerosol deposition enables room temperature fabrication of dense cathode films (LFP, NMC) via ejecting cathode particles from a source material. [97–98] Despite the advantages, vacuum deposition techniques lack scalability to m²/min levels. These are also challenging to apply in sulfur-based cathodes. Therefore, facile slurry-based and sintering-free coating of dense composite cathodes are considered to be industrially adaptable for ASSBs. The slurry-based processing is comprised of conventional LIB coating strategies: wet/dry mixing of composites, layer formation, stacking and lamination [48] (Fig. 2). For EV-compatible operation, cathodes must deliver a specific capacity of 500 Wh/kg⁻¹ and areal capacity of > 5 mAh/cm², which requires a thicker (>100 µm) or denser cathode (>95% active loading). [99] Chemo-mechanical effects dominate at the cathode|SE interface and within the bulk cathode which currently limits the lifetime of these thick cathodes. [29,100–101] Therefore, the slurry-based method for ASSB may require higher stack pressure to achieve higher relative density. [102] Tape

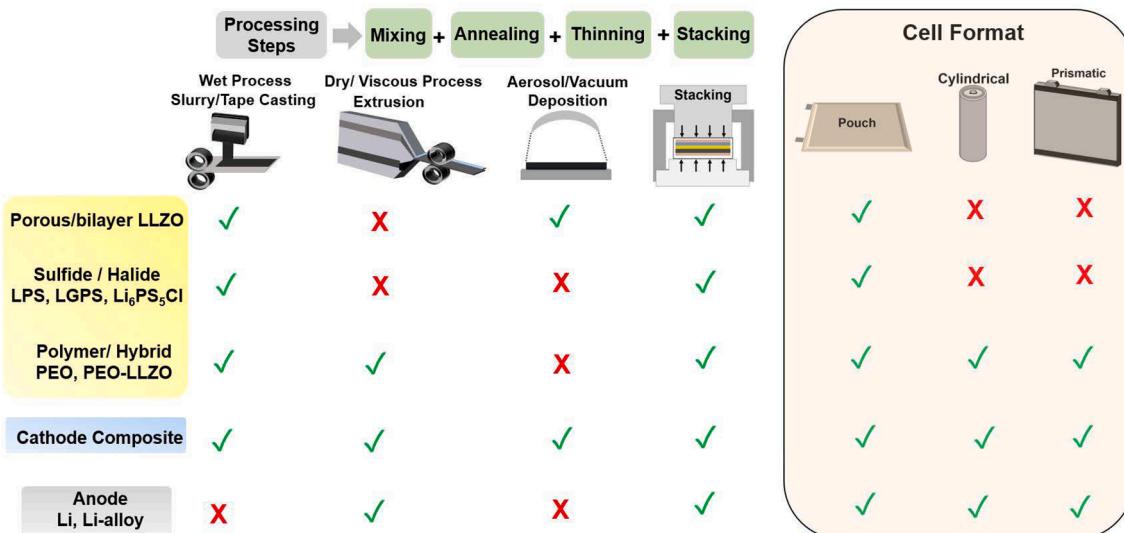


Fig. 2. Prospects of available scaled up technologies and cell formats for solid-state battery manufacturing. Each technology requires three key steps to check: mixing of materials, annealing and thinning/calendering, followed by stacking cell assembly. The figure shows better opportunity for slurry/tape casting manufacturing for solid-electrolytes and cathodes. For metal anode processing, extrusion/pressure-assisted lamination is preferred.

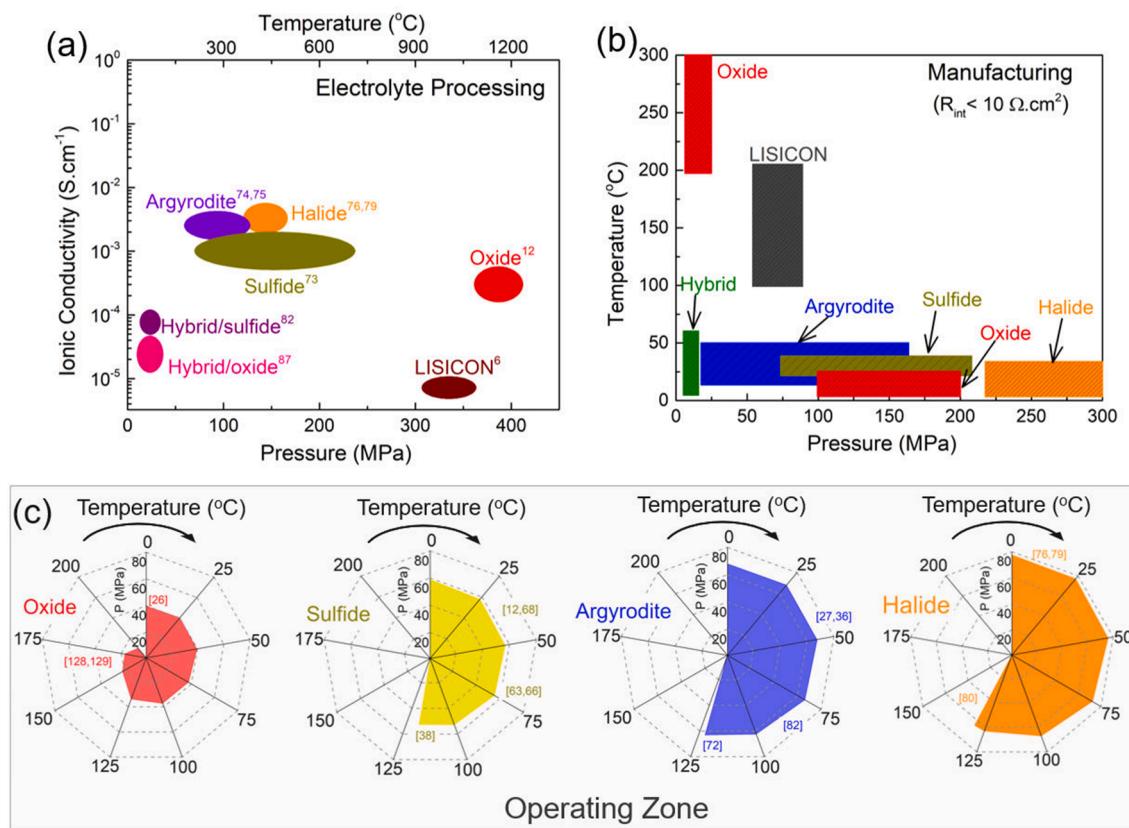


Fig. 3. Role of pressure and temperature in different steps of manufacturing solid-state batteries with solid electrolytes: (a) electrolyte processing (ionic conductivity as a function of processing pressure and temperature), (b) cell manufacturing for good interfacial contact ($< 10 \Omega \cdot \text{cm}^2$), (c) operating range for batteries with oxide, sulfide, argyrodite and halide electrolytes.

casting or screen printing, followed by a calendering step will be a suitable approach for scaled-up production.

2.1. Manufacturing of anodes

There is a significant interest in using alkali metal-based anodes (e.g., Lithium) in solid state batteries because the absence of a liquid solvent can reduce irreversible active material loss. [103] Solid electrolytes, if engineered effectively with lithium metal, can regularize lithium deposition-dissolution dynamics, and enhance cycling efficiency of battery. Lab-scale and benchmarking studies typically employ an excess amount of Li metal ($>200 \mu\text{m}$) which is irrelevant for real applications. Li-metal thickness can be reduced to $10\text{--}20 \mu\text{m}$ by using stack pressure or extrusion [104–105]. However, excessive handling and processing of lithium can increase the probability of creep induced deformation and pulverization which greatly affects SSE|Li interfacial homogeneity. Surface defects and irregular morphologies in such at electrode interfaces can drive the formation of unwanted filaments and dendrites. [55] Lithium foil processing will require an energy-intensive purification process and an inert (Argon) working environment. Due to its adhesive nature, roll-to-roll processing for lithium is difficult to employ. Instead, a lamination process via extrusion can be implemented to secure the anode material on the current collectors or solid electrolytes (Fig. 2). [48] Surface passivation must be carried out in order to protect the anode during manufacturing steps that may occur in non-inert environments. [106] A lithiophilic solid electrolyte surface is important for contiguous contact with the anode. The solid electrolyte surface can be modified via chemical or physical treatment. [25,107] Artificial coatings/interlayers are widely used for solid electrolytes to avoid electrolyte decomposition when in contact with lithium metal. [77,108–109] These also improve lithium adhesion properties during battery cycling

and prevent volume changes. The interlayers are employed by forming stable ion-conducting interphases, either by an *in situ* reaction or the addition of a surface coating. Another approach to processing lithium metal is melt-induced stacking and vacuum-based deposition. [32,55,110–111] Melt-induced infusion is a convenient approach which allows plastic flow of lithium to achieve better contact with electrolyte. [112] Both techniques enable thin lithium layers but are too costly for high throughput production. In addition, these techniques are generally applicable for solid electrolytes with high yield strength and thermal stability (e.g., LLZO).

One of the most exciting and promising approaches is an anode-free architecture. [36] This approach can potentially eliminate the cost of anode manufacturing and increase gravimetric and volumetric energy density by 10%. [113] However, there are many challenges that need to be overcome until anode-less architectures are realized. A large volume change during the first charge coupled with rapid capacity loss are common with anode-free architectures. [114] Any lithium lost during discharging cannot be recovered (“dead Li”) which leads to low coulombic efficiencies. Interfacial chemo-mechanics within the anodic current collector and solid electrolyte becomes increasingly important as unstable charge transfer reactions can drive delamination. [115–117] Improper contact between the solid electrolyte and current collector can lead to failure via immediate shorting. [118] Electrodeposition (charging) and dissolution (discharging) can be altered via an applied pressure, controlled surface energy, controlled surface morphology, and variable temperatures. [119] While there are many technical challenges associated with attaining high performing anode-less geometries, there are significant gains in terms of manufacturing costs if achieved.

2.2. Effect of pressure and temperature on battery manufacturing and performance

External operating conditions during battery operating and battery manufacturing can play a large role on cell performance and plant design consideration. The conditions include working environment (e.g., inert or ambient conditions), stack pressure, and processing temperature. Pressure and temperature are two important cost and rate determining factors in all the aspects of SSB production (material synthesis, cell assembly and cycling). During cell assembly, stack pressure and heat treatment are frequently employed to improve interfacial contact. [107,109] Artificial coatings at the interfaces can also aid in improving interfacial resistances but result in an additional step in manufacturing line. [109] Overall, pressure and temperature can have significant impacts on the material properties. In particular, yield strength of both solid electrolyte and lithium is governed by the pressure dependent material density and calendaring. High temperatures can exacerbate chemical decomposition and lithium loss during processing but may increase packing density. Thus, processing pressure and temperature can have competing results in each component.

Mechanically robust oxide materials (e.g.; LLZO) typically can withstand high pressure (>200 MPa) and temperature (300°C). Operation under elevated pressure and temperature has been shown to be effective way to lower the interfacial resistance between lithium metal and solid electrolytes (1–10 Ω/cm^2) (Fig. 3b). [25,40] Thermal approaches to improve the wettability between lithium metal and sulfides and argyrodites-types solid electrolytes are challenging because many solid electrolytes exhibit chemical decomposition against Li metal, which is severe at high temperature. Therefore, stack pressure is the only mean to improve contact and prevent delamination. [25,120] Excessive stack pressure can cause electrolyte fracture and shorting (extrusion of lithium metal). [28,34].

Unwanted failure due to delamination, void formation, and/or dendrite propagation can occur in cells with low interfacial resistance. [121] Degradation mechanisms are driven by material properties, interfacial interactions, and operating conditions. These degradation processes lead to capacity decay and limits rate performance. It is estimated that SSB will require <15% capacity loss over 1000 cycles to compete with conventional batteries. Therefore, pressure and temperature during electrochemical cycling should be monitored to benchmark cell testing protocols. A recent report on a solid-state Li-S batteries (lab-scale) demonstrated good charge–discharge capacity (>3 mAh/cm² at 60°C) at an applied pressure of 30 MPa. [120] Solid state batteries require extensive pressure in material processing and operation. It is unclear how this pressure could be maintained in tradition battery geometries (e.g., pouch, jelly roll, etc.). Rigid external casing may be a pathway to control pressure without external pressure control. Garnet oxides have a wider temperature range (beyond the melting point of Li) but a small pressure range due to low ductility (<40 MPa) (Fig. 3c). [122–123] Argyrodites and sulfides are recommended to operate below 120°C but can withstand large stack pressure (>50 MPa) [26,124] (Fig. 3C). Overall, material selection for SSBs is critical to design battery architectures and predict manufacturing strategies. Technoeconomic analyses should precede development because variably operating and manufacturing conditions may drive up the cost of the battery.

2.3. Cell formats in battery manufacturing

Conventional lithium-ion batteries utilize cylindrical (jelly-roll), prismatic or pouch cell formats. Each of these formats present specific advantages and disadvantages when implemented with solid state battery materials. The most common form factor of currently produced SSBs is planar (prismatic or pouch cells). Planar cells retain the structural integrity of the solid electrolytes (Fig. 1d) [125–126]. For EV applications, this geometry offers a facile way for stacking batteries while maintaining uniform stress distributions on the cell. There is a

significant interest in combining structural elements in a car with the battery pack. Planar cells are envisioned to enable this functionality via vertical stacking or Z-stacking of cells. [46,127] Pouch cell are currently the most widely used format in solid-state battery manufacturing and can be integrated with all types of solid electrolytes (Fig. 3). It is also very important to adopt bipolar packing strategies for more effective material utilization. [23] Cylindrical cells offer higher capacity and output voltage via assembling in series and parallel connection. These contain safer and stronger battery housing with well-defined production parameters. The cells consist of hard casing, winding format which provide excellent shock resistance in a module. [7] However, most of the solid electrolytes lack mechanical flexibility and thus cylindrical formats are only envisioned for system with high polymer content. [127–128] Hybrid solid electrolytes are also promising because they can be integrated with a range of existing manufacturing approaches (roll-to-roll or extrusion based) (Fig. 3). High required stack pressure requirements will require the addition of stacking components (e.g., springs) into a battery housing which can dramatically increase the battery space and production cost. Therefore, it is desirable that cells operated at or below 5 MPa. Ultimately, the choice of architecture is going to depend on the application. There are range of applications from portable electronics to electric vehicles which use vastly different architectures and system design.

3. Conclusion

Scalable manufacturing and processing of solid-state batteries are an important component in decarbonizing transportation systems. There is considerable interest in solid electrolytes to integrate energy dense anode materials like lithium metal. Despite exciting progress in engineering solid materials with transport properties similar to liquid electrolytes, manufacturing at scale remains a looming challenge. The use of existing manufacturing infrastructure is necessary to meet cost goals (< \$80/kWh). Similar to conventional battery systems, solid-state batteries require processing and manufacturing approaches for anodes, cathodes, and electrolytes. Unlike conventional battery systems, solid state batteries require unique materials processing conditions (temperature and pressure). Commercially available Li-ion batteries typically operate at 0.1–1 MPa, whereas solid-state batteries require at least 10 MPa (or higher) of stack pressure to ensure stable cycling without contact losses or dendrites formation. This requires extensive modifications in product design and production line for Li-ion batteries, which will increase the overall costs. The manufacturing process of a solid-state battery depends on the type of solid electrolytes. Rigid or brittle solid electrolytes are challenging to employ in cylindrical or prismatic cells. More focus should be given to the development of compliant solid electrolytes. Meanwhile, it is also equally important to design composite cathode architecture with maximum packing density for improved volumetric energy density. Bi/tri-layer cell frameworks are promising approaches which can resolve these challenges, prevent delamination and material decomposition during battery cycling. Careful attention to system design and technoeconomic analyses are necessary to guide commercialization efforts and bridge lab-based research and development with technology adoption.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

W.Z. and K.B.H. acknowledge resources and support from the National Science Foundation under grant #1847029.

References

- [1] M. Tran, D. Banister, J.D. Bishop, M.D. McCulloch, Realizing the electric-vehicle revolution, *Nat. Clim. Change* 2 (2012) 328–333.
- [2] S. Hwang, S.M. Kim, S.M. Bak, K.Y. Chung, W. Chang, Investigating the Reversibility of Structural Modifications of $\text{Li}_{x}\text{Ni}_{y}\text{Mn}_{z}\text{Co}_{1-y-z}\text{O}_2$ Cathode Materials during Initial Charge/Discharge, at Multiple Length Scales, *Chem. Mater.* 27 (2015) 6044–6052.
- [3] Y. Ding, Z.P. Cano, A. Yu, J. Lu, Z. Chen, Automotive Li-Ion Batteries: Current Status and Future Perspectives, *Electrochemical Energy Reviews* 2 (2019) 1–28.
- [4] F. Shen, M.B. Dixit, X. Xiao, K.B. Hatzell, Effect of pore connectivity on Li dendrite propagation within LLZO electrolytes observed with synchrotron X-ray tomography, *ACS Energy Lett.* 3 (2018) 1056–1061.
- [5] M.M. Thackeray, C. Wolverton, E.D. Isaacs, Electrical energy storage for transportation - Approaching the limits of, and going beyond, lithium-ion batteries, *Energy Environ. Sci.* 5 (2012) 7854–7863.
- [6] X. Yang, K.R. Adair, X. Gao, X. Sun, Recent advances and perspectives on thin electrolytes for high-energy-density solid-state lithium batteries, *Energy Environ. Sci.* 14 (2021) 643–671.
- [7] H. Chen, et al., Free-standing ultrathin lithium metal–graphene oxide host foils with controllable thickness for lithium batteries, *Nature Energy* 6 (2021).
- [8] R. Schlem, C.F. Burmeister, P. Michalowski, S. Ohno, G.F. Dewald, A. Kwade, W.G. Zeier, Energy Storage Materials for Solid-State Batteries: Design by Mechanochemistry, *Adv. Energy Mater.* (2021).
- [9] Song, J.; West, W. *Handbook of Solid State Batteries*; Chapter Chapter 17, pp 593–625.
- [10] W. Greatbatch, J.H. Lee, W. Mathias, M. Eldridge, J.R. Moser, A.A. Schneider, The Solid-State Lithium Battery: A New Improved Chemical Power Source for Implantable Cardiac Pacemakers, *IEEE Trans. Biomed. Eng. BME-18* (1971) 317–324.
- [11] B.B. Owens, The role of solid electrolytes in lithium pacemaker batteries, *Solid State Ionics* 3–4 (1981) 273–275.
- [12] K.J. Kim, M. Balaish, M. Wadaguchi, L. Kong, J.L. Rupp, Solid-State Li-Metal Batteries: Challenges and Horizons of Oxide and Sulfide Solid Electrolytes and Their Interfaces, *Adv. Energy Mater.* 11 (2021) 1–63.
- [13] S. Kim, C. Jung, H. Kim, K.E. Thomas-Alyea, G. Yoon, B. Kim, M.E. Badding, Z. Song, J.M. Chang, J. Kim, D. Im, K. Kang, The Role of Interlayer Chemistry in Li-Metal Growth through a Garnet-Type Solid Electrolyte, *Adv. Energy Mater.* 10 (2020) 1–11.
- [14] M. Balaish, J.C. Gonzalez-Rosillo, K.J. Kim, Y. Zhu, Z.D. Hood, J.L. Rupp, Processing thin but robust electrolytes for solid-state batteries, *Nat. Energy* 6 (2021) 227–239.
- [15] Z.P. Cano, D. Banham, S. Ye, A. Hintennach, J. Lu, M. Fowler, Z. Chen, Batteries and fuel cells for emerging electric vehicle markets, *Nat. Energy* 3 (2018) 279–289.
- [16] J. Schnell, F. Tietz, C. Singer, A. Hofer, N. Billot, G. Reinhart, Prospects of production technologies and manufacturing costs of oxide-based all-solid-state lithium batteries, *Energy Environ. Sci.* 12 (2019) 1818–1833.
- [17] L. Maufer, F. Duffner, W.G. Zeier, J. Leker, Battery cost forecasting: A review of methods and results with an outlook to 2050, *Energy Environ. Sci.* 14 (2021) 4712–4739.
- [18] Edelstein, S. Green Car Reports. https://www.greencarreports.com/news/1134307_report-ev-battery-costs-might-rise-in-2022, 2021.
- [19] D.H. Tan, P. Xu, H. Yang, M.-C. Kim, H. Nguyen, E.A. Wu, J.-M. Doux, A. Banerjee, Y.S. Meng, Z. Chen, Sustainable design of fully recyclable all solid-state batteries, *MRS Energy & Sustainability* 7 (2020).
- [20] P. Xu, Q. Dai, H. Gao, H. Liu, M. Zhang, M. Li, Y. Chen, K. An, Y.S. Meng, P. Liu, et al., Efficient Direct Recycling of Lithium-Ion Battery Cathodes by Targeted Heating, *Joule* 4 (2020) 2609–2626.
- [21] L. Azhari, S. Bong, X. Ma, Y. Wang, Recycling for All Solid-State Lithium-Ion Batteries, *Matter* 3 (2020) 1845–1861.
- [22] P. Albertus, S. Babinec, S. Litelman, A. Newman, Status and challenges in enabling the lithium metal electrode for high-energy and low-cost rechargeable batteries, *Nat. Energy* 3 (2018) 16–21.
- [23] Schnell, J.; Krieger, H.; Imbsweiler, A. J.; Reinhart, G. Solid versus Liquid—A Bottom-Up Calculation Model to Analyze the Manufacturing Cost of Future High-Energy Batteries, *Energy Technology* 2020, 8.
- [24] T. Bartsch, F. Strauss, T. Hatsukade, A. Schiele, A.Y. Kim, P. Hartmann, J. Janek, T. Brezesinski, Gas Evolution in All-Solid-State Battery Cells, *ACS Energy Lett.* 3 (2018) 2539–2543.
- [25] T. Krauskopf, H. Hartmann, W.G. Zeier, J. Janek, Toward a Fundamental Understanding of the Lithium Metal Anode in Solid-State Batteries - An Electrochemo-Mechanical Study on the Garnet-Type Solid Electrolyte $\text{Li}_{0.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, *ACS Appl. Mater. Interfaces* 11 (2019) 14463–14477.
- [26] J. Kasemchainan, S. Zekoll, D. Spencer Jolly, Z. Ning, G.O. Hartley, J. Marrow, P. G. Bruce, Critical stripping current leads to dendrite formation on plating in lithium anode solid electrolyte cells, *Nat. Mater.* 18 (2019) 1105–1111.
- [27] A. Mistry, P.P. Mukherjee, Molar volume mismatch: A malefactor for irregular metal-lic electrodeposition with solid electrolytes, *J. Electrochem. Soc.* 167 (2020), 082510.
- [28] M.B. Dixit, W. Zaman, N. Hortance, S. Vujic, B. Harkey, F. Shen, W.Y. Tsai, V. De Andrade, X.C. Chen, N. Balke, K.B. Hatzell, Nanoscale Mapping of Extrinsic Interfaces in Hybrid Solid Electrolytes, *Joule* 4 (2020) 207–221.
- [29] T. Shi, Y.-Q. Zhang, Q. Tu, Y. Wang, M. Scott, G. Ceder, Characterization of mechanical degradation in an all-solid-state battery cathode, *J. Mater. Chem. A* 8 (2020) 17399–17404.
- [30] D. Hlushkou, A.E. Reising, N. Kaiser, S. Spannenberger, S. Schlabach, Y. Kato, B. Roling, U. Tallarek, The influence of void space on ion transport in a composite cathode for all-solid-state batteries, *J. Power Sources* 396 (2018) 363–370.
- [31] Delluva, A. A.; Delluva, A. A.; Dudoff, J.; Dudoff, J.; Teeter, G.; Holewin-ski, A.; Holewinski, A.; Holewinski, A. Cathode Interface Compatibility of Amorphous LiMn_2O_4 (LMO) and $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) Characterized with Thin-Film Solid-State Electrochemical Cells. *ACS Applied Materials and Interfaces* 2020, 12, 24992–24999.
- [32] A. Sharafi, H.M. Meyer, J. Nanda, J. Wolfenstine, J. Sakamoto, Characterizing the $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ interface stability and kinetics as a function of temperature and current density, *J. Power Sources* 302 (2016) 135–139.
- [33] S.P. Culver, R. Koever, W.G. Zeier, J. Janek, On the Functionality of Coatings for Cathode Active Materials in Thiophosphate-Based All-Solid-State Batteries, *Adv. Energy Mater.* 1900626 (2019) 1–14.
- [34] J.M. Doux, H. Nguyen, D.H. Tan, A. Banerjee, X. Wang, E.A. Wu, C. Jo, H. Yang, Y.S. Meng, Stack Pressure Considerations for Room-Temperature All-Solid-State Lithium Metal Batteries, *Adv. Energy Mater.* 10 (2020).
- [35] J.M. Doux, Y. Yang, D.H. Tan, H. Nguyen, E.A. Wu, X. Wang, A. Banerjee, Y. S. Meng, Pressure effects on sulfide electrolytes for all solid-state batteries, *J. Mater. Chem. A* 8 (2020) 5049–5055.
- [36] M.J. Wang, E. Carmona, A. Gupta, P. Albertus, J. Sakamoto, Enabling “lithium-free” manufacturing of pure lithium metal solid-state batteries through in situ plating, *Nat. Commun.* 11 (2020) 1–9.
- [37] D.Y. Oh, D.H. Kim, S.H. Jung, J.G. Han, N.S. Choi, Y.S. Jung, Single-step wet-chemical fabrication of sheet-type electrodes from solid-electrolyte precursors for all-solid-state lithium-ion batteries, *J. Mater. Chem. A* 5 (2017) 20771–20779.
- [38] X. Chen, P.M. Vereecken, Solid and Solid-Like Composite Electrolyte for Lithium-Ion Batteries: Engineering the Ion Conductivity at Interfaces, *Adv. Mater. Interfaces* 6 (2019) 1–31.
- [39] Y. Xiao, K. Turcheniuk, A. Narla, A.Y. Song, X. Ren, A. Magasinski, A. Jain, S. Huang, H. Lee, G. Yushin, Electrolyte melt infiltration for scalable manufacturing of inorganic all-solid-state lithium-ion batteries, *Nat. Mater.* (2021).
- [40] Z. Zhang, S. Chen, X. Yao, P. Cui, J. Duan, W. Luo, Y. Huang, X. Xu, Enabling high-areal-capacity all-solid-state lithium-metal batteries by tri-layer electrolyte architectures, *Energy Storage Mater.* 24 (2020) 714–718.
- [41] C. Zhao, Q. Sun, J. Luo, J. Liang, Y. Liu, L. Zhang, J. Wang, S. Deng, X. Lin, X. Yang, H. Huang, S. Zhao, L. Zhang, S. Lu, X. Sun, 3D Porous Garnet/Gel Polymer Hybrid Electrolyte for Safe Solid-State Li-O₂Batteries with Long Lifetimes, *Chem. Mater.* 32 (2020) 10113–10119.
- [42] G.T. Hitz, D.W. McOwen, L. Zhang, Z. Ma, Z. Fu, Y. Wen, Y. Gong, J. Dai, T. R. Hamann, L. Hu, E.D. Wachsman, High-rate lithium cycling in a scalable trilayer Li-garnet-electrolyte architecture, *Mater. Today* 22 (2019) 50–57.
- [43] B. Liu, L. Zhang, S. Xu, D.W. McOwen, Y. Gong, C. Yang, G.R. Pastel, H. Xie, K. Fu, J. Dai, C. Chen, E.D. Wachsman, L. Hu, 3D lithium metal anodes hosted in asymmetric garnet frameworks toward high energy density batteries, *Energy Storage Mater.* 14 (2018) 376–382.
- [44] X. Judez, G.G. Eshetu, C. Li, L.M. Rodriguez-Martinez, H. Zhang, M. Armand, Opportunities for Rechargeable Solid-State Batteries Based on Li-Intercalation Cathodes, *Joule* 2 (2018) 2208–2224.
- [45] Y. Kato, S. Shiotani, K. Morita, K. Suzuki, M. Hirayama, R. Kanno, All-Solid-State Batteries with Thick Electrode Configurations, *J. Phys. Chem. Lett.* 9 (2018) 607–613.
- [46] L. Xu, Y. Lu, C.Z. Zhao, H. Yuan, G.L. Zhu, L.P. Hou, Q. Zhang, J.Q. Huang, Toward the Scale-Up of Solid-State Lithium Metal Batteries: The Gaps between Lab- Level Cells and Practical Large-Format Batteries, *Adv. Energy Mater.* 11 (2021).
- [47] D.B. Ahn, K.H. Lee, S.Y. Lee, Printed solid-state electrolytes for form factor-free Li-metal batteries, *Curr. Opin. Electrochem.* 32 (2022), 100889.
- [48] Schnell, J.; Günther, T.; Knoche, T.; Vieider, C.; Köhler, L.; Just, A.; Keller, M.; Passerini, S.; Reinhart, G. All-solid-state lithium-ion and lithium metal batteries – paving the way to large-scale production, *Journal of Power Sources* 2018, 382, 160–175.
- [49] D. Karabelli, K.P. Birke, Weeber M, Race between polymer electrolytes and inorganic sulfide electrolytes. Batteries, A performance and cost overview of selected solid-state electrolytes, 2021, p. 7.
- [50] L. Yang, X. Tao, X. Huang, C. Zou, L. Yi, X. Chen, Z. Zang, Z. Luo, X. Wang, Efficient Mutual-Compensating Li-Loss Strategy toward Highly Conductive Garnet Ceramics for Li-Metal Solid-State Batteries, *ACS Appl. Mater. Interfaces* 13 (2021) 56054–56063.
- [51] Buannic, L.; Naviroj, M.; Miller, S. M.; Zagorski, J.; Faber, K. T.; Llordes, A. Dense freeze-cast $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolytes with oriented open porosity and contiguous ceramic scaffold. *Journal of the American Ceramic Society* 2019, 102, 1021–1029.
- [52] F. Shen, W. Guo, D. Zeng, Z. Sun, J. Gao, J. Li, B. Zhao, B. He, X. Han, A Simple and Highly Efficient Method toward High-Density Garnet-Type LLZTO Solid-State Electrolyte, *ACS applied materials interfaces* 12 (2020) 30313–30319.
- [53] C. Lohr, R. Djenadic, M. Bruns, O. Clemens, H. Hahn, Garnet-Type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte Thin Films Grown by CO₂-Laser Assisted CVD for All-Solid-State Batteries, *J. Electrochem. Soc.* 164 (2017) A6131–A6139.
- [54] M. Saccoccia, J. Yu, Z. Lu, S.C. Kwok, J. Wang, K.K. Yeung, M.M. Yuen, F. Ciucci, Low temperature pulsed laser deposition of garnet $\text{Li}_6.4\text{La}_3\text{Zr}_1.4\text{Ta}_0.6\text{O}_{12}$ films as all solid-state lithium battery electrolytes, *J. Power Sources* 365 (2017) 43–52.
- [55] E. Kazyak, M. Shin, W.S. Lepage, T.H. Cho, N.P. Dasgupta, Molecular layer deposition of Li-ion conducting “Lithicone” solid electrolytes, *Chem. Commun.* 56 (2020) 15537–15540.

[56] Sastre, J.; Priebe, A.; Dobeli, M.; Michler, J.; Tiwari, A. N.; Romanyuk, Y. E. Lithium Garnet Li7La3Zr2O12 Electrolyte for All-Solid-State Batteries: Closing the Gap be- tween Bulk and Thin Film Li-Ion Conductivities. *Advanced Materials Interfaces* **2020**.

[57] R. Pfenninger, M. Struzik, I. Garbayo, E. Stilp, J.L. Rupp, A low ride on processing temperature for fast lithium conduction in garnet solid-state battery films, *Nat. Energy* **4** (2019) 475–483.

[58] A. Ohashi, M. Kodama, S. Xueying, S. Hori, K. Suzuki, R. Kanno, S. Hirai, Stress distribution in the composite electrodes of sulfide all-solid-state lithium-ion batteries, *J. Power Sources* **470** (2020), 228437.

[59] Sastre, J.; Lin, T. Y.; Filippin, A. N.; Priebe, A.; Avancini, E.; Michler, J.; Ti- wari, A. N.; Romanyuk, Y. E.; Buecheler, S. Aluminum-Assisted Densification of Co- sputtered Lithium Garnet Electrolyte Films for Solid-State Batteries. *ACS Applied Energy Materials* **2019**, *2*, 8511–8524.

[60] S. Lobe, A. Bauer, S. Uhlenbruck, D. Fattakhova-Rohlfing, Physical Vapor Deposition in Solid-State Battery Development: From Materials to Devices, *Adv. Sci.* **8** (2021) 1–33.

[61] Z. Liu, W. Fu, E.A. Payzant, X. Yu, Z. Wu, N.J. Dudney, J. Kiggans, K. Hong, A. J. Rondinone, C. Liang, Anomalous high ionic conductivity of nanoporous β -Li 3PS4, *J. Am. Chem. Soc.* **135** (2013) 975–978.

[62] S. Ohno, et al., How Certain Are the Reported Ionic Conductivities of Thiophosphate-Based Solid Electrolytes? An Interlaboratory Study. *ACS Energy Letters* **5** (2020) 910–915.

[63] K. Kerman, A. Luntz, V. Viswanathan, Y.-M. Chiang, Z. Chen, Review—Practical Challenges Hindering the Development of Solid-State Li Ion Batteries, *J. Electrochem. Soc.* **164** (2017) A1731–A1744.

[64] Kudu, Ö. U.; Famprikis, T.; Fleutot, B.; Braida, M. D.; Le Mercier, T.; Islam, M. S.; Masquelier, C. A review of structural properties and synthesis methods of solid elec- trolyte materials in the Li2S P2S5 binary system. *Journal of Power Sources* **2018**, *407*, 31–43.

[65] C. Dietrich, D.A. Weber, S.J. Sedlmaier, S. Idris, S.P. Culver, D. Walter, J. Janek, W.G. Zeier, Lithium ion conductivity in Li2S-P2S5 glasses-building units and local structure evolution during the crystallization of superionic conductors Li3PS4, Li7P3S11 and Li4P2S7, *J. Mater. Chem. A* **5** (2017) 18111–18119.

[66] Stöffler, H.; Zinkevich, T.; Yavuz, M.; Hansen, A. L.; Knapp, M.; Bednarčík, J.; Randau, S.; Richter, F. H.; Janek, J.; Ehrenberg, H.; Idris, S. Amorphous versus Crystalline Li3PS4: Local Structural Changes during Synthesis and Li Ion Mobility. *Journal of Physical Chemistry C* **2019**, *123*, 10280–10290.

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

[68] Miura, A.; Rosero-Navarro, N. C.; Sakuda, A.; Tadanaga, K.; Phuc, N. H.; Matsuda, A.; Machida, N.; Hayashi, A.; Tatsumisago, M. Liquid-phase syntheses of sul- fide electrolytes for all-solid-state lithium battery. *Nature Reviews Chemistry* **2019**, *3*, 189–198.

[69] A.K. Hatz, R. Calaminus, J. Feijoo, F. Treber, J. Blahusch, T. Lenz, M. Reichel, K. Karaghiosoff, N.M. Vargas-Barbosa, B.V. Lotsch, Chemical Stability and Ionic Conductivity of LGPS-Type Solid Electrolyte Tetra-Li7SiPS8after Solvent Treatment, *ACS Applied Energy Materials* **4** (2021) 9932–9943.

[70] R. Garcia-Mendez, J.G. Smith, J.C. Neufeind, D.J. Siegel, J. Sakamoto, Cor- relating Macro and Atomic Structure with Elastic Properties and Ionic Transport of Glassy Li2S-P2S5 (LPS) Solid Electrolyte for Solid-State Li Metal Batteries, *Adv. Energy Mater.* **10** (2020).

[71] S. Wang, Y. Zhang, X. Zhang, T. Liu, Y.H. Lin, Y. Shen, L. Li, C.W. Nan, High- Conductivity Argyrodite Li 6 PS 5 Cl Solid Electrolytes Prepared via Opti- mized Sintering Processes for All-Solid-State Lithium-Sulfur Batteries, *ACS Appl. Mater. Interfaces* **10** (2018) 42279–42285.

[72] Cronau, M.; Szabo, M.; Konig, C.; Wassermann, T. B.; Roling, B. How to Measure a Reliable Ionic Conductivity? The Stack Pressure Dilemma of Microcrystalline Sulfide-Based Solid Electrolytes. *ACS Energy Letters* **2021**, 3072–3077.

[73] J. Liang, X. Li, K.R. Adair, X. Sun, Metal Halide Superionic Conductors for All- Solid-State Batteries, *Acc. Chem. Res.* **54** (2021) 1023–1033.

[74] A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes, *Nat. Rev. Mater.* **2** (2017) 1–16.

[75] H. Kwak, D. Han, J. Lyoo, J. Park, S.H. Jung, Y. Han, G. Kwon, H. Kim, S.T. Hong, K.W. Nam, Y.S. Jung, New Cost-Effective Halide Solid Electrolytes for All-Solid- State Batteries: Mechanochimically Prepared Fe3+-Substituted Li2ZrCl6, *Adv. Energy Mater.* **11** (2021) 1–10.

[76] T. Yu, J. Liang, L. Luo, L. Wang, F. Zhao, G. Xu, X. Bai, R. Yang, S. Zhao, J. Wang, J. Yu, X. Sun, Superionic Fluorinated Halide Solid Electrolytes for Highly Stable Li-Metal in All-Solid-State Li Batteries, *Adv. Energy Mater.* **11** (2021) 1–9.

[77] L.M. Rieger, R. Schlem, J. Sann, W.G. Zeier, J. Janek, Lithium-Metal Anode Instability of the Superionic Halide Solid Electrolytes and the Implications for Solid- State Batteries, *Angew. Chem.* **133** (2021) 6792–6797.

[78] D.T. Hallinan, N.P. Balsara, Polymer electrolytes, *Annu. Rev. Mater. Res.* **43** (2013) 503–525.

[79] M. Armand, Polymer solid electrolytes - an overview, *Solid State Ionics* **10** (1983) 745–754.

[80] J. Popovic, Dry Polymer Electrolyte Concepts for Solid-State Batteries, *Macromol. Chem. Phys.* **2100344** (2021) 1–11.

[81] W. Zaman, N. Hortance, M.B. Dixit, V. De Andrade, K.B. Hatzell, Visualizing percolation and ion transport in hybrid solid electrolytes for Li-metal batteries, *J. Mater. Chem. A* **7** (2019) 23914–23921.

[82] K.J. Harry, D.T. Hallinan, D.Y. Parkinson, A.A. MacDowell, N.P. Balsara, Detection of subsurface structures underneath dendrites formed on cycled lithium metal electrodes, *Nat. Mater.* **13** (2014) 69–73.

[83] J. Zheng, M. Tang, Y.Y. Hu, Lithium Ion Pathway within Li7La3Zr2O12- Polyethylene Oxide Composite Electrolytes, *Angewandte Chemie - International Edition* **55** (2016) 12538–12542.

[84] W. Liu, N. Liu, J. Sun, P.C. Hsu, Y. Li, H.W. Lee, Y. Cui, Ionic Conductivity Enhancement of Polymer Electrolytes with Ceramic Nanowire Fillers, *Nano Lett.* **15** (2015) 2740–2745.

[85] X. Zhang, T. Liu, S. Zhang, X. Huang, B. Xu, Y. Lin, B. Xu, L. Li, C.W. Nan, Y. Shen, Synergistic coupling between Li6.75La3Zr17Ta0.25O12 and poly(vinylidene fluoride) induces high ionic conductivity, mechanical strength, and thermal stability of solid composite electrolytes, *J. Am. Chem. Soc.* **139** (2017) 13779–13785.

[86] M.J. Lee, D.O. Shin, J.Y. Kim, J. Oh, S.H. Kang, J. Kim, K.M. Kim, Y.M. Lee, S. O. Kim, Y.G. Lee, Interfacial barrier free organic-inorganic hybrid electrolytes for solid state batteries, *Energy Storage Mater.* **37** (2021) 306–314.

[87] D.Y. Oh, K.T. Kim, S.H. Jung, D.H. Kim, S. Jun, S. Jeoung, H.R. Moon, Y.S. Jung, Tactical hybrids of Li+-conductive dry polymer electrolytes with sulfide solid electrolytes: Toward practical all-solid-state batteries with wider temperature operability, *Mater. Today xxx* (2021) 37–40.

[88] J. Popovic, D. Brandell, S. Ohno, K.B. Hatzell, J. Zheng, Y.Y. Hu, Polymer- based hybrid battery electrolytes: theoretical insights, recent advances and challenges, *J. Mater. Chem. A* **9** (2021) 6050–6069.

[89] F. Chen, D. Yang, W. Zha, B. Zhu, Y. Zhang, J. Li, Y. Gu, Q. Shen, L. Zhang, D. R. Sadoway, Solid polymer electrolytes incorporating cubic Li 7 La 3 Zr 2 O 12 for all-solid-state lithium rechargeable batteries, *Electrochim. Acta* **258** (2017) 1106–1114.

[90] K. Park, B.C. Yu, J.W. Jung, Y. Li, W. Zhou, H. Gao, S. Son, J.B. Goodenough, Electrochemical Nature of the Cathode Interface for a Solid-State Lithium-Ion Battery: Interface between LiCoO2 and Garnet-Li7La3Zr2O12, *Chem. Mater.* **28** (2016) 8051–8059.

[91] Miara, L.; Windmuller, A.; Tsai, C. L.; Richards, W. D.; Ma, Q.; Uhlenbruck, S.; Guillou, O.; Ceder, G. About the Compatibility between High Voltage Spinel Cathode Materials and Solid Oxide Electrolytes as a Function of Temperature. *ACS Applied Materials and Interfaces* **2016**, *8*, 26842–26850.

[92] K.J. Kim, J.L. Rupp, All ceramic cathode composite design and manufacturing towards low interfacial resistance for garnet-based solid-state lithium batteries, *Energy Environ. Sci.* **13** (2020) 4930–4945.

[93] T. Shi, Q. Tu, Y. Tian, Y. Xiao, L.J. Miara, O. Kononova, G. Ceder, High ac- tive material loading in all-solid-state battery electrode via particle size optimization, *Adv. Energy Mater.* **10** (2020) 1902881.

[94] M.B. Dixit, W. Zaman, Y. Bootwala, Y. Zheng, M.C. Hatzell, K.B. Hatzell, Scalable manufacturing of hybrid solid electrolytes with interface control, *ACS Appl. Mater. Interfaces* **11** (2019) 45087–45097.

[95] B. Zahiri, A. Patra, C. Kiggins, A.X.B. Yong, E. Ertekin, J.B. Cook, P.V. Braun, Revealing the role of the cathode–electrolyte interface on solid-state batteries, *Nat. Mater.* (2021).

[96] K.B. Hatzell, Y. Zheng, Prospects on large-scale manufacturing of solid state bat- teries, *MRS Energy Sustainability* (2021) 1–7.

[97] I. Kim, J. Park, T.H. Nama, K.W. Kim, J.H. Ahn, D.S. Park, C. Ahn, G. Wang, H. J. Ahn, Electrochemical properties of an as-deposited LiFePO4 thin film electrode prepared by aerosol deposition, *J. Power Sources* **244** (2013) 646–651.

[98] S. Iwasaki, T. Hamanaka, T. Yamakawa, W.C. West, K. Yamamoto, M. Motoyama, T. Hirayama, Y. Iriyama, Preparation of thick-film LiNi1/3Co1/3Mn1/3O2 electrodes by aerosol deposition and its application to all-solid-state batteries, *J. Power Sources* **272** (2014) 1086–1090.

[99] Randau, S.; Weber, D. A.; Kotz, O.; Koerver, R.; Braun, P.; Weber, A.; Ivers- Tiffée, E.; Adermann, T.; Kulisch, J.; Zeier, W. G.; Richter, F. H.; Janek, J. Bench- marking the performance of all-solid-state lithium batteries. *Nature Energy* **2020**, *5*, 259–270.

[100] R. Koerver, W. Zhang, L. De Biasi, S. Schweidler, A.O. Kondrakov, S. Kolling, T. Brezesinski, P. Hartmann, W.G. Zeier, J. Janek, Chemo-mechanical expansion of lithium electrode materials-on the route to mechanically optimized all-solid- state batteries, *Energy Environ. Sci.* **11** (2018) 2142–2158.

[101] P. Minnmann, L. Quillman, S. Burkhardt, F.H. Richter, J. Janek, Editors' Choice—Quantifying the Impact of Charge Transport Bottlenecks in Composite Cath- odes of All-Solid-State Batteries, *J. Electrochem. Soc.* **168** (2021), 040537.

[102] M.J. Wang, E. Kazヤk, N.P. Dasgupta, J. Sakamoto, Transitioning solid-state batteries from lab to market: Linking electro-chemo-mechanics with practical consid- erations, *Joule* **5** (2021) 1371–1390.

[103] D. Lin, Y. Liu, Y. Cui, Reviving the lithium metal anode for high-energy batteries, *Nat. Nanotechnol.* **12** (2017) 194–206.

[104] A. Mauger, M. Armand, C.M. Julian, K. Zaghib, Challenges and issues facing lithium metal for solid-state rechargeable batteries, *J. Power Sources* **353** (2017) 333–342.

[105] J. Popovic, The importance of electrode interfaces and interphases for rechargeable metal batteries, *Nat. Commun.* **12** (2021) 8–12.

[106] Duffner, F.; Konometer, N.; Tubke, J.; Leker, J.; Winter, M.; Schmuck, R. Post- lithium-ion battery cell production and its compatibility with lithium-ion cell produc- tion infrastructure, *Nature Energy* **2021**, *6*, 123–134.

[107] A. Sharafi, C.G. Haslam, R.D. Kerns, J. Wolfenstein, J. Sakamoto, Controlling and correlating the effect of grain size with the mechanical and electrochemical properties of Li7La3Zr2O12 solid-state electrolyte, *J. Mater. Chem. A* **5** (2017) 21491–21504.

[108] X. Xu, G. Hou, X. Nie, Q. Ai, Y. Liu, J. Feng, L. Zhang, P. Si, S. Guo, L. Ci, Li7P3S11/poly(ethylene oxide) hybrid solid electrolytes with excellent interfacial compatibility for all-solid-state batteries, *J. Power Sources* **400** (2018) 212–217.

[109] X. Han, Y. Gong, K. Fu, X. He, G.T. Hitz, J. Dai, A. Pearse, B. Liu, H. Wang, G. Rubloff, Y. Mo, V. Thangadurai, E.D. Wachsman, L. Hu, Negating interfacial impedance in garnet-based solid-state Li metal batteries, *Nat. Mater.* 16 (2017) 572–579.

[110] J.G. Connell, T. Fuchs, H. Hartmann, T. Krauskopf, Y. Zhu, J. Sann, R. Garcia-Mendez, J. Sakamoto, S. Tepavcevic, J. Janek, Kinetic versus Thermodynamic Stability of LLZO in Contact with Lithium Metal, *Chem. Mater.* (2020).

[111] S. Chen, J. Zhang, L. Nie, X. Hu, Y. Huang, Y. Yu, W. Liu, All-Solid-StateBatteries with a Limited Lithium Metal Anode at Room Temperature using a Garnet- Based Electrolyte, *Adv. Mater.* 33 (2021) 1–10.

[112] C. Xu, Z. Ahmad, A. Aryanfar, V. Viswanathan, J.R. Greer, Enhanced strength and temperature dependence of mechanical properties of Li at small scales and its implications for Li metal anodes, *PNAS* 114 (2017) 57–61.

[113] R.V. Salvatierra, W. Chen, J.M. Tour, What Can be Expected from “Anode-Free” Lithium Metal Batteries? *Advanced Energy and Sustainability Research* 2 (2021) 2000110.

[114] Heubner, C.; Maletti, S.; Auer, H.; Hüttl, J.; Voigt, K.; Lohrberg, O.; Nikolowski, K.; Partsch, M.; Michaelis, A. From Lithium-Metal toward Anode-Free Solid-State Batteries: Current Developments, Issues, and Challenges. *Advanced Functional Materials* 2021, [2106608](#).

[115] A.L. Davis, E. Kazyak, D.W. Liao, K.N. Wood, N.P. Dasgupta, Operando Analysis of Interphase Dynamics in Anode-Free Solid-State Batteries with Sulfide Electrolytes, *J. Electrochem. Soc.* 168 (2021), 070557.

[116] S. Menkin, C.A. Okeefe, A.B. Gunnarsdottir, S. Dey, F.M. Pesci, Z. Shen, A. Aguadero, C.P. Grey, Toward an Understanding of SEI Formation and Lithium Plating on Copper in Anode-Free Batteries, *J. Phys. Chem. C* 125 (2021) 16719–16732.

[117] S. Chen, J. Zhang, L. Nie, X. Hu, Y. Huang, Y. Yu, W. Liu, All-Solid-State Batteries with a Limited Lithium Metal Anode at Room Temperature using a Garnet- Based Electrolyte, *Adv. Mater.* 33 (2021) 1–10.

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

[119] C. Fang, B. Lu, G. Pawar, M. Zhang, D. Cheng, S. Chen, M. Ceja, J.M. Doux, H. Musrock, M. Cai, B. Liaw, Y.S. Meng, Pressure-tailored lithium deposition and dissolution in lithium metal batteries, *Nat. Energy* 6 (2021) 987–994.

[120] P. Bonnick, K. Niitani, M. Nose, K. Suto, T.S. Arthur, J. Muldoon, A high performance all solid-state lithium sulfur battery with lithium thiophosphate solid electrolyte, *J. Mater. Chem. A* 7 (2019) 24173–24179.

[121] C.W. Wang, F.C. Ren, Y. Zhou, P.F. Yan, X.D. Zhou, S.J. Zhang, W. Liu, W. D. Zhang, M.H. Zou, L.Y. Zeng, X.Y. Yao, L. Huang, J.T. Li, S.G. Sun, Engineering the interface between LiCoO₂and Li₁₀GeP₂S₁₂solid electrolytes with an ultrathin Li₂CoTi₃O₈interlayer to boost the performance of all-solid-state batteries, *Energy Environ. Sci.* 14 (2021) 437–450.

[122] B. Kinzer, A.L. Davis, T. Krauskopf, H. Hartmann, W.S. LePage, E. Kazyak, J. Janek, N.P. Dasgupta, J. Sakamoto, Operando analysis of the molten Li-Li₂O interface: Understanding how the physical properties of Li affect the critical current density, *Matter* 4 (2021) 1947–1961.

[123] Y. Jin, K. Liu, J. Lang, D. Zhuo, Z. Huang, C. Wang, H. Wu, Y. Cui, An intermediate temperature garnet-type solid electrolyte-based molten lithium battery for grid energy storage, *Nat. Energy* 3 (2018) 732–738.

[124] D. Spencer Jolly, Z. Ning, G.O. Hartley, B. Liu, D.L.R. Melvin, P. Adamson, J. Marrow, P.G. Bruce, Temperature Dependence of Lithium Anode Voiding in Argyrodite Solid-State Batteries, *ACS Applied Materials Interfaces* 13 (2021) 22708–22716.

[125] P.H. Notten, F. Roozeboom, R.A. Niessen, L. Baggetto, 3-D integrated all-solid-state rechargeable batteries, *Adv. Mater.* 19 (2007) 4564–4567.

[126] D.S. Ashby, C.S. Choi, M.A. Edwards, A.A. Talin, H.S. White, B.S. Dunn, High-performance Solid-State Lithium-Ion Battery with Mixed 2D and 3D Electrodes, *ACS Applied Energy Materials* 3 (2020) 8402–8409.

[127] B. Wu, Y. Yang, D. Liu, C. Niu, M. Gross, L. Seymour, H. Lee, P.M.L. Le, T.D. Vo, Z. D. Deng, E.J. Dufek, M.S. Whittingham, J. Liu, J. Xiao, Good Practices for Rechargeable Lithium Metal Batteries, *J. Electrochem. Soc.* 166 (2020) A4141–A4149.

[128] Z. Li, H.M. Huang, J.K. Zhu, J.F. Wu, H. Yang, L. Wei, X. Guo, Ionic Conduction in Composite Polymer Electrolytes: Case of PEO:Ga-LLZO Composites, *ACS Appl. Mater. Interfaces* 11 (2019) 784–791.