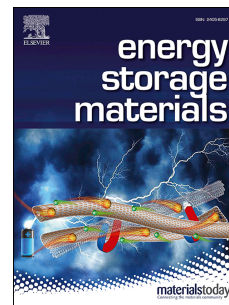


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Towards rationally mechanical design of inorganic solid electrolytes for all-solid-state lithium ion batteries

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Abstract

All-solid-state lithium ion batteries are being actively considered as promising candidates for next-generation energy storage applications. Compared with conventional lithium ion batteries using organic liquid electrolytes, all-solid-state lithium ion batteries using inorganic solid electrolytes demonstrate various distinct advantages, such as better safety without flammable explosions, more eco-friendliness without volatilization, higher stability without liquid leakage, wider cell voltage window and higher energy density. Extensive efforts have been focused on material, chemistry and electrochemistry of new solid-state electrolytes to enhance the capacity and long-term stability of solid-state lithium ion batteries. However, mechanical properties of solid electrolytes and multi-scale modeling of all-solid-state lithium ion batteries are less discussed. As a matter of fact, mechanical properties of solid electrolytes play a significant role in suppressing the growth of lithium dendrites, reducing electrode-electrolyte interfacial resistances and avoiding the propagation of fractures or cracks. In this review effort, we will discuss the mechanical properties, i.e. bulk, Young's and shear modulus, hardness, fracture toughness and elastic anisotropy of solid electrolytes, density functional theory modeling of elasticity, engineering discussions on interfacial resistances between solid electrolytes and electrodes, and electrochemical-mechanical modeling of all-solid-state lithium ion batteries. It is hoped that this review will contribute to the rationally mechanical design of solid electrolytes and further the development of advanced all-solid-state lithium ion batteries for energy storage.

Keywords: All-solid-state lithium ion batteries; solid electrolytes; mechanical properties; interfacial compatibility; multiphysics modeling

1. Introduction

Electricity demand, i.e. flexible electronic devices, electric vehicles and power stations, drives a rapid development of various energy storage devices ranging from a small-scale (miniwatt-hours) to a medium and even a large-scale (megawatt-hours). Energy storage systems include electric double layer capacitors (EDLCs) or supercapacitors (SCs) [1-4], lithium-ion batteries (LIBs) [5-10], sodium-ion batteries (SIBs) [11-13], magnesium-ion batteries (MIBs) [14,15], potassium-ion batteries (PIBs) [16-18], calcium-ion batteries (CIBs) [19,20], aluminum-ion batteries (AIBs) [21-23] and redox flow batteries (RFBs) [24-28].

In recent years, all-solid-state lithium ion batteries (ASSLIBs) [29-35] are being actively explored among researchers and engineers within the energy storage community. All-solid state batteries are being considered as alternative and promising candidates for the next-generation clean energy storage. Extensive research efforts on ASSLIBs are being carried out, and the relationship between the number of published articles associated with the keyword of solid electrolyte, and year based on the 'Web of Science' database for the past fifty years is shown in Figure 1 (a). In particular, it is clear to see that efforts on batteries with solid electrolytes receive exponentially increased attentions after 2010. Compared with the organic liquid electrolytes, several main advantages have been demonstrated for the inorganic solid electrolytes [29,30]: non-flammable, non-volatile, no liquid leakage, wider cell voltage window and higher energy density. Consequently, ASSLIBs should be more stable, safer and more benign to the working environment with respect to the battery operation conditions. Especially, the use of solid electrolytes (SEs) can effectively avoid the notable "shuttle" effect in solid-state lithium-sulfur batteries [37-39]. In the SEs, there lacks of organic liquid electrolytes as required medium to

support the “shuttle” transport. For the liquid electrolytes with the “shuttle” effect, the dissolved short- and long-chain lithium

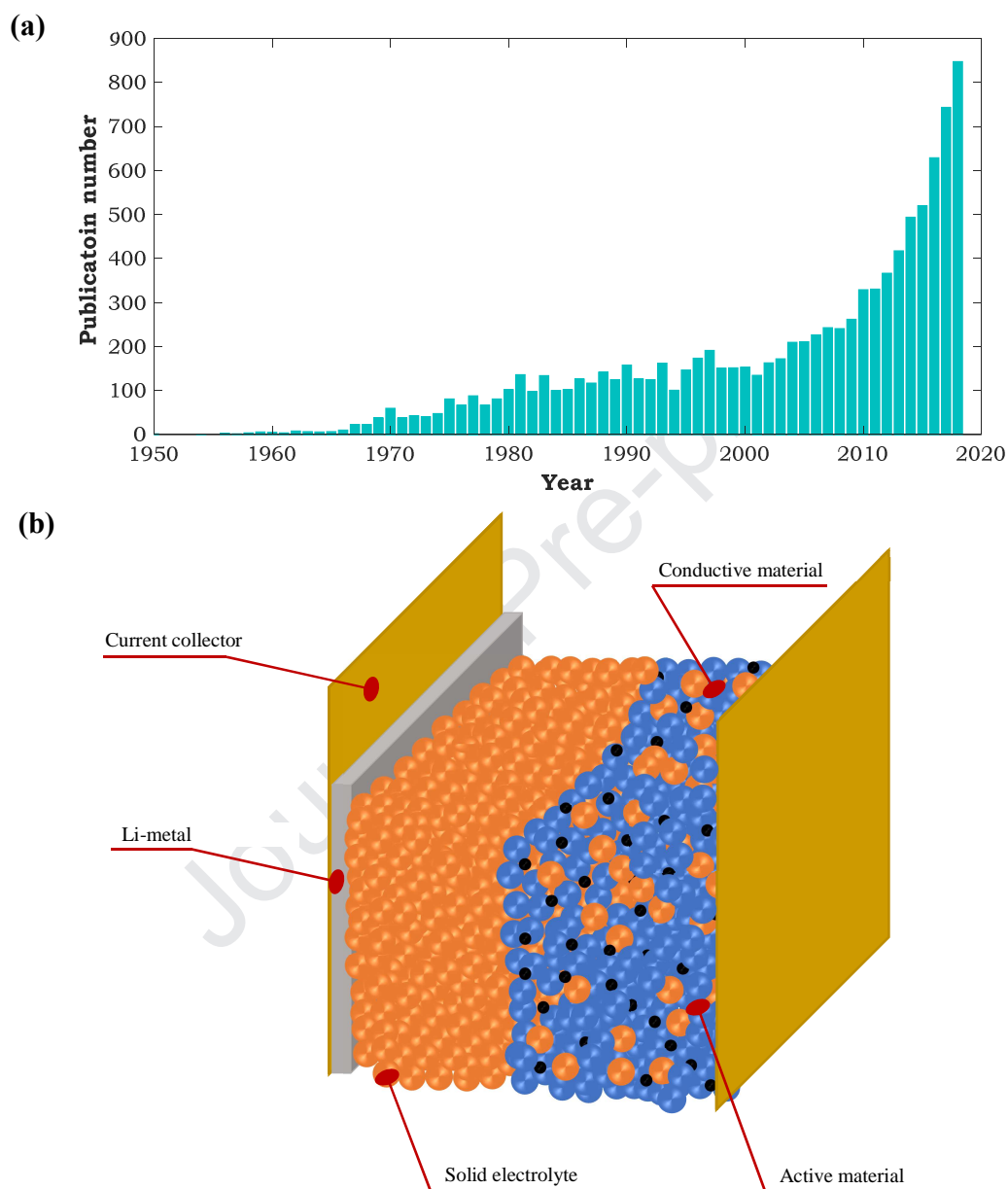


Figure 1:(a) The trend of publication number with year by using the keyword of the solid electrolyte based on the ‘Web of Science’ database, adapted from Ref. [36], Sakuda, *Journal of the Ceramic Society of Japan*, 2018; (b) schematic of a typical all-solid-state lithium ion battery, which includes current collectors, Li-metal anode, solid electrolyte and cathode (solid electrolyte, active and conductive materials), adapted from Ref. [69], Zhang et al., *Energy & Environmental Science*, 2018.

polysulfides are interactively formed at the both anode and cathode during the charge-discharge process, and leads to consumptions of extra lithium and sulfur [40]. By completely avoid this “shuttle” phenomena through using SEs in lithium-sulfur batteries, cell efficiencies, capacity and cycling ability are enhanced in contrast to the organic liquid electrolytes [38]. Advantages of ASSLIBs with inorganic solid electrolytes over the classic batteries with organic liquid electrolytes are gradually discovered and carefully examined among battery researchers. To date, various types of inorganic solid electrolytes have been reported: LISICON-like i.e. Li_4GeO_4 [41], thio-LISICON, i.e. $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [42], Argyrodite, i.e. Li_7PS_6 [43] and $\text{Li}_6\text{PS}_5\text{Cl}$ [44], Garnet, i.e. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [45], NASICON-like, i.e. $\text{LiTi}_2(\text{PO}_4)_3$ [46], Li-Nitride, i.e. Li_7PN_4 [47], Li-Hydride, i.e. LiBH_4 [48], Perovskite, i.e. $\text{Li}_{0.38}\text{Sr}_{0.44}\text{Ta}_{0.7}\text{Hf}_{0.3}\text{O}_{2.95}\text{F}_{0.05}$ [49], and Li-Halide, i.e. Li_3YCl_6 [50], etc. In general, the ionic conductivity of LISICON-like (can be up to 25 mS/cm, [51]) solid electrolytes is always higher than the other types of SEs. However, low ionic conductivity of the SEs has been considered as a main issue for hindering the development of advanced ASSLIBs [32,33,52]. Schematic of a typical all-solid-state lithium ion battery is shown in Figure 1 (b). The cell component includes anode, solid electrolyte, cathode and current collectors. During intercalation and de-intercalation, the Li^+ transport through the anode, interface between solid electrolyte and anode, solid electrolyte, interface between solid electrolyte and cathode.

Extensive efforts have been focused on increasing the ionic conductivity of SEs by elemental substitution or doping [33,53-58], and structure tuning [59-62]. For example, Ceder’s group has been using density functional theory (DFT) computations to fundamentally elucidate the Li^+ conduction mechanisms, and design new SEs with higher ionic conductivities [42,62]. Wang et al. found that the body-centered cubic-like anion framework is able to allow a direct Li^+

conduction path among adjacent tetrahedral sites, and thus it is considered as a preferred crystal structure for achieving a high ionic conductivity [62].

Several comprehensive reviews on properties of solid electrolytes, i.e. ionic conductivity, and their crystal structures [30,32,33,63], conduction mechanisms [33,52], stability of interface between SEs and anode or cathode [64,65], have been reported. Most current studies on SEs are heavily focused on the enhancement of ionic conductivity through the aspect of new materials, chemistries and electrochemistry. However, less efforts have concerned the mechanical properties of SEs, which play a significant role in suppressing the growth of lithium dendrites [66-71], enhancing compatibility between the electrode and electrolyte, i.e. reducing interfacial resistances and increasing the interfacial stability [29,30,72-76], and even avoiding the propagations of cracks [76-78]. More specifically, Li dendrites consume excessive lithium ions, and accelerate depletions of the active lithium ions utilized for reduced-oxidized reactions, and can even result in internal short-circuits within the cell if Li dendrites formed are long enough to penetrate through the whole cell [69]. The interfacial resistance is another critical issue that may play a significant role in limiting the performance of ASSLIBs [73]. Most reported SEs have a low wettability with the Li-metal anode, and thus the electrode-electrolyte interfacial resistance always cannot be ignored and even be very large for some cases [30]. The importance of minimizing interfacial resistances between SEs and Li-metal anode are being paid attention among battery researchers. For example, Hu's group has focused on adding an interlayer, i.e. Al_2O_3 [81], between the SEs and Li-metal to increase the wettability and reduce the interfacial resistance from $1710 \Omega \text{ cm}^2$ to $1 \Omega \text{ cm}^2$ to improve the cycling performance of ASSLIBs. The minimization of the interfacial resistances and a better understanding of the interfacial mechanisms are desired to enhance the performance and contribute to the optimization of

interface designs for ASSLIBs. Also, Kerman et al. [29] pointed out that the occurrence of “cracking” within the SEs is strongly detrimental to the performance of ASSLIBs. The “cracking” may be related to the mechanical properties of SEs, such as shear modulus, hardness, fracture toughness, etc. However, mechanisms on the “cracking” of SEs are not well understood. Therefore, understanding the fundamental mechanism of mechanical properties of SEs on affecting the electrochemical performance should be crucial to the performance optimization of ASSLIBs.

Wolfenstine et al. [82] first reported a short summary on mechanical properties of oxide-based garnet solid electrolytes. However, mechanical properties of the other solid electrolytes, i.e. Pervoskite and sulfide solid electrolytes, and other important aspects, i.e. interfacial resistance issues, DFT modeling of mechanical properties for solid electrolytes and multiphysics modeling of all-solid-state batteries were not discussed by them. In this effort, we will present a more comprehensive review and in-depth discussion on mechanical properties, i.e. bulk, Young’s and shear modulus, hardness, fracture toughness and elastic anisotropy of all possible types of solid electrolytes, density functional theory (DFT) modeling of elasticity, interfacial resistances between solid electrolytes and Li metal anode/cathode, and electrochemical-mechanical modeling of ASSLIBs. It is hoped that this review can contribute to the rationally mechanical design of solid electrolytes and further the development of advanced ASSLIBs.

2. Mechanical properties of solid electrolytes

2.1 Bulk, Young’s, shear, hardness and fracture toughness of solid electrolytes

A typical approach to measure the mechanical properties of solid electrolytes is by the indentation technique, i.e. Vickers and Berkovich indentations. McGrogan et al. [77] carried out Vickers indentation tests for the $\text{Li}_2\text{S-P}_2\text{S}_5$ (LPS) sulfide-based solid electrolyte, which was

prepared by a melt-quenching method, in the mineral oil. Because the sulfide electrolytes are sensitive to the air and moisture, and can be greatly deteriorated when they are exposed to them. Thus, the mineral oil may be a good choice for the mechanical tests of sulfide-based solid electrolytes. It was found that the corresponding bulk modulus and hardness of LPS was 18.5 ± 0.9 GPa and 1.9 ± 0.2 GPa. The fracture toughness for the annealed sample was measured to be 0.23 ± 0.04 MPa m^{1/2} based on the crack trajectories after the Vickers indentation as shown in Figure 2 (a). Allu et al. [83] found that the hardness of NASICON type glassy $\text{Na}_{2.8}\text{Ca}_{0.1}\text{Al}_2\text{Ga}_{0.5}\text{P}_{2.7}\text{O}_{12}$ (NCAGPO) ranges from 3.19 GPa to 3.34 GPa through the Vickers indentation. It was also pointed out that the enhanced hardness can be achieved through the ion-exchange treatment by introducing compressive stress on the surface of the NCAGPO glass. The optical microscope image of NCAGPO glass after the Vickers indentation is shown in Figure 2 (b). The mechanical properties of Al-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) was measured by using a micro-pillar indentation splitting method [84], which was previously developed by Sebastinatti et al. [85]. The Young's modulus, hardness and fracture toughness was measured to be 145.6 ± 7.3 GPa, 8.5 ± 0.4 GPa and 0.99 ± 0.05 MPa m^{0.5}, respectively. The spectroscopy electron microscopy (SEM)-focus ion beam (FIB) images of Al-LLZO after the micro-pillar indentation is shown in Figure 2 (c) and (d). It can be seen that some extra “secondary” cracks were generated during the indentation process. However, it was emphasized that those “secondary” cracks only have a trivial effect on the estimation of the fracture toughness, because the micro-pillar indentation only accounts the required load and energy to initiate the occurrence of cracking [84]. The measurements for the mechanical properties of solid electrolytes provide necessary database for modeling strain and stress distributions, and understanding cracking

conditions in ASSLIBs. A summary of mechanical properties of solid electrolytes by experiments in the literature is shown in Table 1. Most experimental studies on mechanical

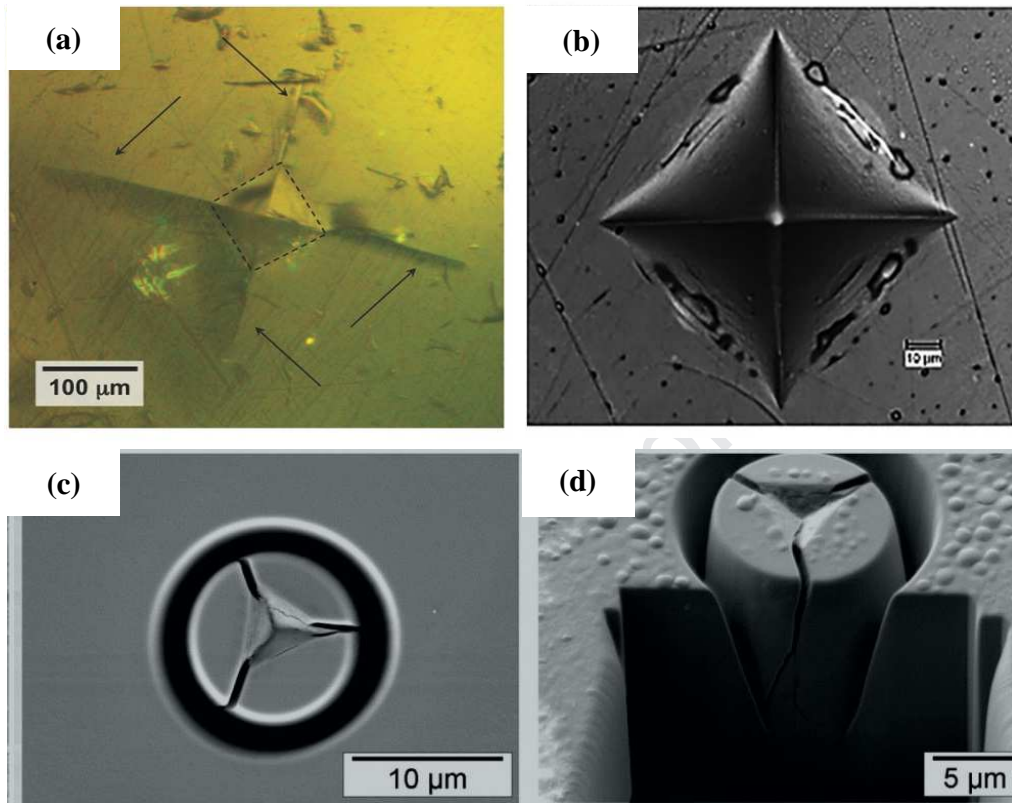


Figure 2: (a) Vickers indentation image of $\text{Li}_2\text{S-P}_2\text{S}_5$ (LPS) sulfide-based solid electrolytes, the arrows represent the cracks, **copyright permission is required**, McGrogan et al., *Advanced Energy Materials*, 2017, Ref. [93]; (b) Vickers indentation image of NASICON type glassy $\text{Na}_{2.8}\text{Ca}_{0.1}\text{Al}_2\text{Ga}_{0.5}\text{P}_{2.7}\text{O}_{12}$ (NCAGPO), **copyright permission is required**, Allu et al., *Journal of Non-Crystalline Solids*, 2018, Ref. [96]; (c) front views of micro-pillar indentation images of Al-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), **copyright permission is required**, Wang et al., *Journal of the European Ceramic Society*, 2018, Ref. [97] and (d) side views of micro-pillar indentation images of Al-substituted $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), **copyright permission is required**, Wang et al., *Journal of the European Ceramic Society*, 2018, Ref. [97].

properties of solid electrolytes are for the oxide-based garnet-type, perovskite and sulfide-based solid electrolytes. It can be concluded from Table 1 that the bulk, Young's and shear modulus, hardness, and fracture toughness of oxide-based garnet type/sulfide-based SEs is in the order magnitude of 95-105 GPa/15-25 GPa, 90-155 GPa/8-30 GPa, 30-65 GPa/3-10 GPa, 5-10 GPa/2 GPa and $0.8\text{-}1.0 \text{ MPa m}^{0.5}/0.2\text{-}0.35 \text{ MPa m}^{0.5}$, respectively. The perovskite SEs show a larger

Young's modulus and fracture toughness than the oxide-based garnet type SEs. It also can be seen that sulfide-based SEs have a much lower Young's modulus compared with the oxide-based garnet type SEs, and consequently the sulfide-based SEs should be remarkably less stiff due to a much smaller shear modulus than the oxide-based garnet type and perovskite SEs. The ratio of Li_2S over P_2S_5 also affects the mechanical properties of LPS [86]. It was pointed out that the Young's modulus might be related to the mean atomic volume, which is defined as the average volume per atom [95,96]. A smaller mean atomic volume brings a larger Young's modulus. Also, based on Monroe-Newman's rule [66,67] on Li-dendrite penetrations with respect to the shear modulus that a larger shear modulus is more beneficial to reduce Li-dendrites, and thus oxide-based garnet SEs are considered to be more capable to suppress the growth of Li-dendrites. However, some researchers concluded that sulfide-based SEs seem to have a superior stress-strain accommodation ability, which allows them to adjust the deformation at the interface [29,68,82,86]. Kato et al. [97] found that adding lithium halides into the Li_2S - P_2S_5 can decrease the Young's modulus of SEs to soften their stiffness, and consequently suppress the destruction of Li_xSi particles to improve the cell performance as shown in Figure 3. It can be seen that this all-solid-state battery using glass electrolytes mixed with lithium halides exhibits a less capacity degradation than the one without adding lithium halides.

Table 1: Mechanical properties, i.e. bulk, Young's and shear modulus, Poisson ratio, hardness and fracture toughness of solid electrolytes by experiments reported in literature, RUS-Resonant ultrasound spectroscopy; USVM-Ultrasonic sound velocity measurement; PUT: picosecond ultrasonic technology.

Type	Compound	Bulk Modulus (GPa)	Young's modulus (GPa)	Shear Modulus (GPa)	Poisson's ratio	Hardness (GPa)	Fracture Toughness (MPa m ^{0.5})	Processing method	Testing method	Sources
Garnet	Li _{6,24} La ₃ Zr ₂ Al _{0,24} O _{11,98}	102.8±0.3	149.8±0.4	59.6±0.1	0.257±0.002	6.3±0.3	-	Hot pressing	RUS+Vickers indentation	[87]
	Li _{6,24} La ₃ Zr ₂ Al _{0,24} O _{11,98}	97.7±0.2	132.6±0.2	52.1±0.04	0.274±0.001	5.2±0.4	-	Hot pressing	RUS+Vickers indentation	[87]
	Li _{6,19} Al _{0,27} La ₃ Zr ₂ O ₁₂	-	-	-	-	~ 8.1±0.8~ 9.0±0.4	0.97-2.37	Hot pressing	Vickers indentation	[89]
	Li _{6,91} La ₃ Zr _{1,98} Al _{0,13} O ₁₂	-	145.6±7.3	-	-	8.5±0.4	0.99±0.05	Sintering	Micro-pillar indentation	[84]
	Li _{6,17} Al _{0,28} La ₃ Zr ₂ O ₁₂	100.2±0.6	146.1±0.8	58.1±0.3	-	-	-	Hot pressing	Acoustic impulse excitation	[92]
		-	150.3±2.2	59.8±0.9	-	-	-	Hot pressing	Berkovich indentation	[92]
	Li _{6,5} La ₃ Ta _{0,5} Zr _{1,5} O ₁₂	96.0±1.4	139.9±2.1	55.7±0.8	-	-	-	Hot pressing	Acoustic impulse excitation	[92]
		-	153.8±2.7	61.2±1.1	-	-	-	Hot pressing	Berkovich indentation	[92]
Perovskite	Li ₇ La ₃ Zr ₂ O ₁₂	-	-	-	-	-	0.86-1.63	Hot pressing	Vickers indentation	[78]
	Li _{0,33} La _{0,567} TiO ₃	-	143-203	-	-	8.1±0.54- 9.5±0.63	1.08±0.20- 1.24±0.12	Sintering	USVM + Vickers indentation	[88]
	Li _{0,35} La _{0,55} TiO ₃	-	206.6- 244.2	-	0.257-0.261	7.08-7.27	-	Sintering	USVM+ Vickers indentation	[90]
	Li _{0,33} La _{0,57} TiO ₃	-	186±4- 200±3	-	-	9.2±0.2- 9.7±0.7	~ 1	Hot pressing	Vickers indentation	[91]
	Li _x La _{0,557} TiO ₃ (cubic)	-	~ 155-180	-	-	~ 11.8-12.3	~ 0.89-0.95	Hot pressing	Vickers indentation	[93]
	Li _x La _{0,557} TiO ₃ (tetragonal)	-	~ 148-180	-	-	~ 11.7-11.9	~ 0.83-0.94	Hot pressing	Vickers Indentation	[93]
Thio-phosphate	Li _{0,350} La _{0,557} TiO ₃	-	~ 155-185	-	-	~ 15-18	~ 0.8-1.0	Sintering	Vickers Indentation	[94]
	Li ₂ S-P ₂ S ₅	-	8.8-25	3.4-9.5	0.27-0.34	-	-	Hot pressing	USVM	[86]
	Li ₂ S-P ₂ S ₅	21	23	8.8	0.31	-	-	Hot pressing	USVM	[97]
	Li ₂ S-P ₂ S ₅	-	22-27	-	-	-	-	Hot pressing	USVM	[98]
	Li ₂ S-P ₂ S ₅	-	18.5±0.9	-	-	1.9±0.2	0.23±0.04	Annealing	Vickers indentation	[77]
							0.34±0.08	Non-annealing	Vickers indentation	[77]
Thio-phosphate	Li ₂ S-P ₂ S ₅ -LiI	15-19	17-21	6.3-8.1	0.31-0.32	-	-	Hot pressing	USVM	[97]

	$\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiBr}$	22-23	22	8.1-8.2	0.33-0.34	-	-	Hot pressing	USVM	[97]
	$\text{Li}_2\text{S-P}_2\text{S}_5\text{-LiCl}$	20	21	7.8	0.33	-	-	Hot pressing	USVM	[97]
NASICON	$\text{Na}_{2.8}\text{Ca}_{0.1}\text{Al}_2\text{Ga}_{0.5}\text{P}_{2.7}\text{O}_{12}$	-	-	-	-	3.19-3.34	-	Hot pressing	Vickers indentation	[83]
LiPON thin film	LiPON	-	79±10	-	0.27±0.04	-	-	Magnetron sputtering	PUT	[99]
	LiPON	-	77	-	-	3.9-4.1	-	Magnetron sputtering	Nano-indentation	[100]
	LiPON	-	~ 85-141.3	-	-	~ 1.5-5.8	-	Ion beam assisted deposition	Nano-indentation	[101]
	LiPON	-	~ 6-147.2	-	-	~ 0.6-6.8	-	Ion beam assisted deposition	Nano-indentation	[102]

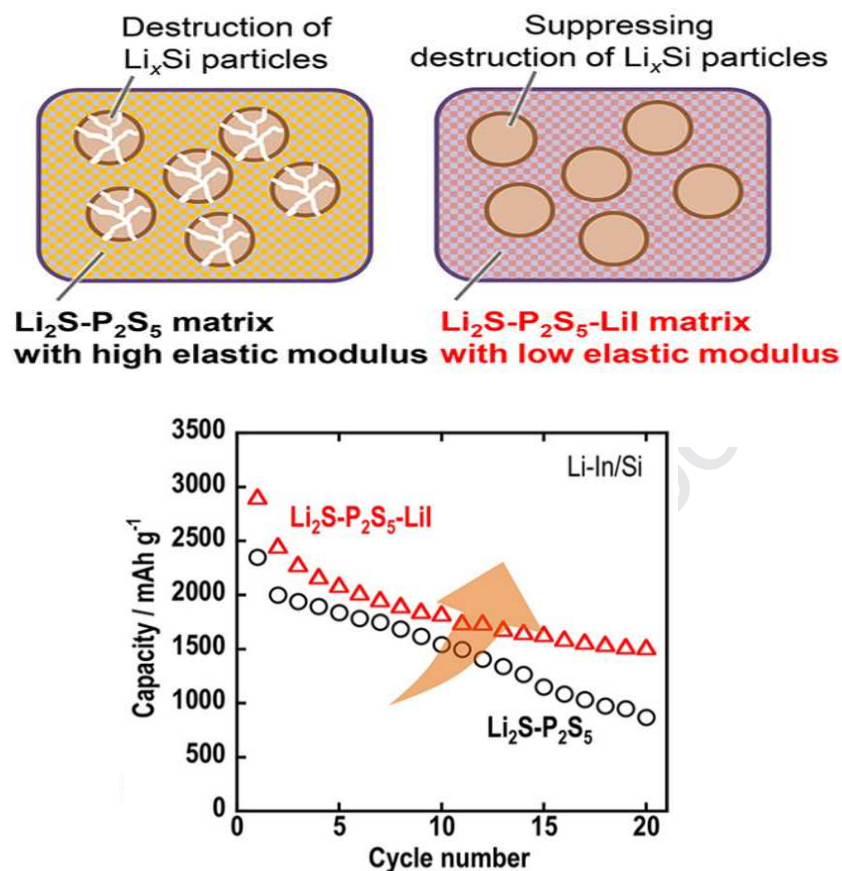


Figure 3: Enhancing cell performance in a sulfide-based all-solid-state battery by adding LiI with a low elastic modulus, copyright permission is required, Kato et al., *ACS Applied Energy Materials*, 2018, Ref. [97].

It is important to quantify whether the SEs belong to “brittle” or “ductile” property or not. In general, ductile SEs are better than brittle SEs in accommodating the strains and stresses induced at the interface between SEs and electrode active materials during lithium intercalation and de-intercalation [68]. Hence, less micro-cracks or fractures will be formed, and it will consequently lead to a more intimately interfacial contact for the ductile SEs [75,76]. Maintaining an intimate interface between SEs and electrode is critically desired for achieving stable and high performance ASSLIBs [29,103]. For example, Kato et al found that a smaller Young’s modulus, which always means more ductile, of sulfide SEs bring an improved cell performance [97]. They

concluded that SEs with a lower elastic modulus is more capable to relax large stress generated during cell operation than those SEs with a higher elastic modulus. To evaluate the “brittle” or “ductile” property, a theoretical relationship (see solid lines) between the bulk modulus (B) and the shear modulus (G) under a certain Young’s modulus (E) is shown in Figure 4. One possible rule to determine the “brittleness” and “ductility” of SEs can be referred to the “Pugh” criteria [104,68], which is based on the ratio of B/G values, with $B/G < 1.75$ for the “brittle” region, while $B/G > 1.75$ for the “ductile” region. Thus, the left-upper region with respect to the dash-line ($B/G=1.75$) is considered as the “brittle” domain and the other side region is considered as the “ductile” domain. Providing a fixed Young’s modulus and a shear modulus, a larger bulk modulus always results in a more “ductile” behavior. The experimental data [87,92,97] reported on the mechanical properties, i.e. shear and bulk modulus in the literature is summarized in Figure 4. It can be seen that the LPS SEs belong to the “ductile” region and the oxide-based garnet SEs are in the transition state between the “ductile” region and the “brittle” region. Although the “Pugh” rule might be slightly rough for capturing the critical transition from the “ductile” region to the “brittle” region, the ratio of B/G value might be considered as one criteria for describing the trend of “brittle” or “ductile” property. Thus, a more reliable and thorough theory or model should be developed to more accurately capture the transition line to separate the “ductile” region to “brittle” region for solid electrolytes. Separating the “ductile” or “brittle” property will be beneficial for ASSLIBs technology development by screening out the “ductile” solid electrolytes for high performance ASSLIBs batteries from the mechanical aspect. However, current experimental databases on bulk modulus and shear modulus of SEs are quite limited. There are still adequate rooms for examining mechanical properties of other SEs, i.e. LISICON, Thio-LISICON, NASICON, Perovskites, Li-Nitride, LiPON, etc. Filling the knowledge gap for

achieving a full database on mechanical properties of SEs is critical to design better SEs for use in future ASSLIBs.

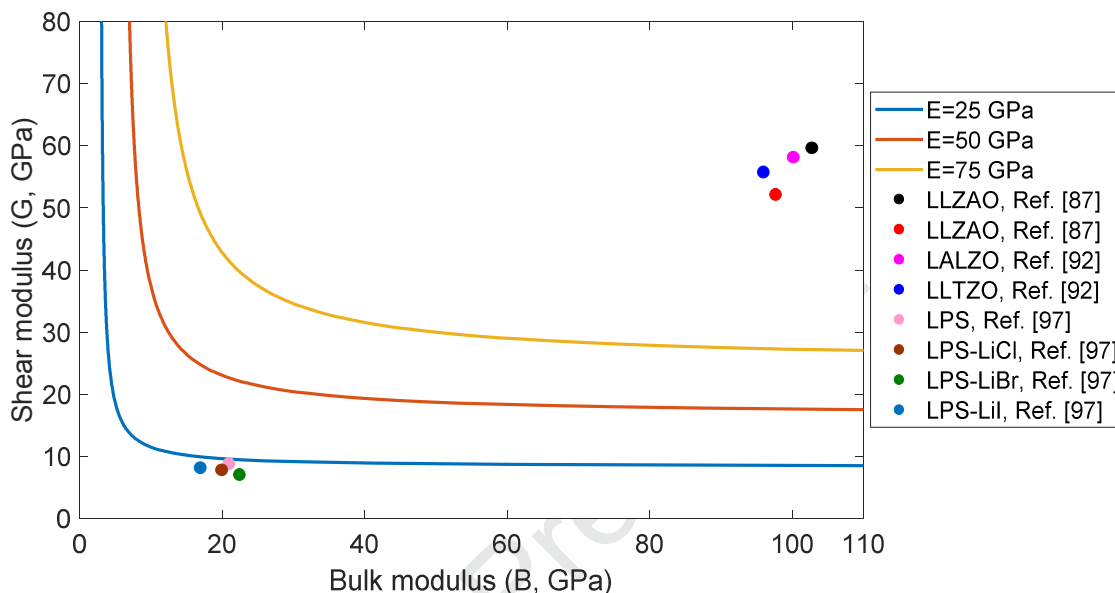


Figure 4: The relationship between the bulk modulus (B) and shear modulus (G) under different elastic modulus (E) based on the theoretical calculation, adapted from Ref. [68], and compared with experimental data reported in the literature [87,92,97], the scattered data for LPS-LiBr and LPS-LiI is an average value.

Fracture toughness is a critical property that evaluates the capability to resist fracture or crack, and can be determined by the indentation technique [105,106]. It is considered that “ductile” fracture instead of “brittle” fracture always occurs in the materials with a high fracture toughness [107]. Extensive studies [108-114] on fracture toughness of electrodes for lithium ion batteries have been carried out. Those work tried to elucidate the fracture mechanism of electrodes, and the fracture effect on electrochemical performance, i.e. capacity degradation of lithium ion batteries. To date, a few studies [77,78,84,88,89,91,93,94] on determining the fracture toughness of SEs used in ASSLIBs by integrating experimental measurements and models have been reported. As shown in Table 1, the fracture toughness of garnet-type SEs is always much higher than that of LISICON-like, NASICON-like and LiPON thin films. However, the experimental

data on fracture toughness of solid electrolytes is quite limited, and more efforts on quantifying fracture toughness of solid electrolytes are desired. Achieving the mechanical property data can help multiphysics modeling of ASSLIBs by coupling electrochemical, thermo and mechanical aspects together.

2.2 Density functional theory calculations on elasticity of solid electrolytes

Density functional theory (DFT) can be considered as an alternative method integrating with experimental techniques for examining the mechanical properties of solid electrolytes. Few studies have been reported recently [68,115-120] on estimating intrinsically mechanical properties of solid electrolytes, which are based on elastic tensors or matrix computed from first-principles DFT methods. Wang et al. reported a theoretical work on predicting the elastic properties of $\text{Li}_{10}\text{Ge}_2\text{PS}_{12}$ (LGPS) and $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolytes by DFT [115], which shows that the LGPS is ductile and in favor of the mechanical processing. Deng et al. carried out a high-throughput and comprehensive study on predicting elastic properties of more than twenty SEs including both lithium and sodium SEs [68]. The theoretically elastic moduli of NASICON, garnet, LISICON, thio-LISICON, perovskite, and anti-perovskite SEs were calculated and compared with limited experimental data. The elastic properties were found to be strongly affected by the types of the anion species and crystal structures. The predicted modulus also shows that the Na-based SEs are always softer than the Li-based SEs. Yu et al. also calculated the shear modulus of LLZO by DFT modeling, and they evaluated the capability of LLZO for suppressing the growth of Li dendrites [92]. It was found that the stiffness of Li_3OCl is smaller than the one of LLTO and LLZO, but larger than the one of LGPS through DFT calculations. Based on the Pugh's ratio as calculated through its bulk modulus over the shear modulus, Li_3OCl seems to exhibit a mechanically brittle behavior [119]. Ahmad et al. [120] reported a new

computational method to evaluate the uncertainty bounds of mechanical properties for SEs. This approach is capable to isolate the numerical error caused by employing various exchange-correlation functionals in DFT calculations. Exploring mechanical properties of the solid electrolytes by the DFT modeling is still at an early stage, and more DFT work should be carried out to provide the design guidance for synthesizing compatible solid electrolytes.

2.3 Mechanical stability and elastic anisotropy behaviors of solid electrolytes

A stable mechanical property is a basic requirement for designing compatible SEs with the anode or cathode. For different crystal structures, i.e. triclinic, monoclinic, orthorhombic, rhombohedral, hexagonal, tetragonal and cubic, elastic rules for determining their mechanical stabilities are different. Discussions on rules based on Hill's work [121] for evaluating mechanical stabilities of various crystal structures were previously reported by Zeng et al. [122], Wu et al. [123], and Mouhat et al. [124]. For a higher symmetric crystal structure, requirements are more flexible, vice versa more rigid. For example, if $C_{11} > C_{12}$, $(C_{11} + 2C_{12}) > 0$ and $C_{44} > 0$ are satisfied, then SEs with a cubic crystal structure are stable, or else are unstable [124]. For a highly un-symmetric crystal structure, i.e. triclinic, expressions on elastic rules for mechanical stability are rather complex. Studies on elastic anisotropic analysis should be important for achieving a full understanding of mechanical properties along various directions. Equations for controlling the elastic anisotropic properties for the bulk modulus (B) and Young's modulus (E) for cubic, tetragonal, hexagonal and orthorhombic crystal structures can be found in the references [125-128].

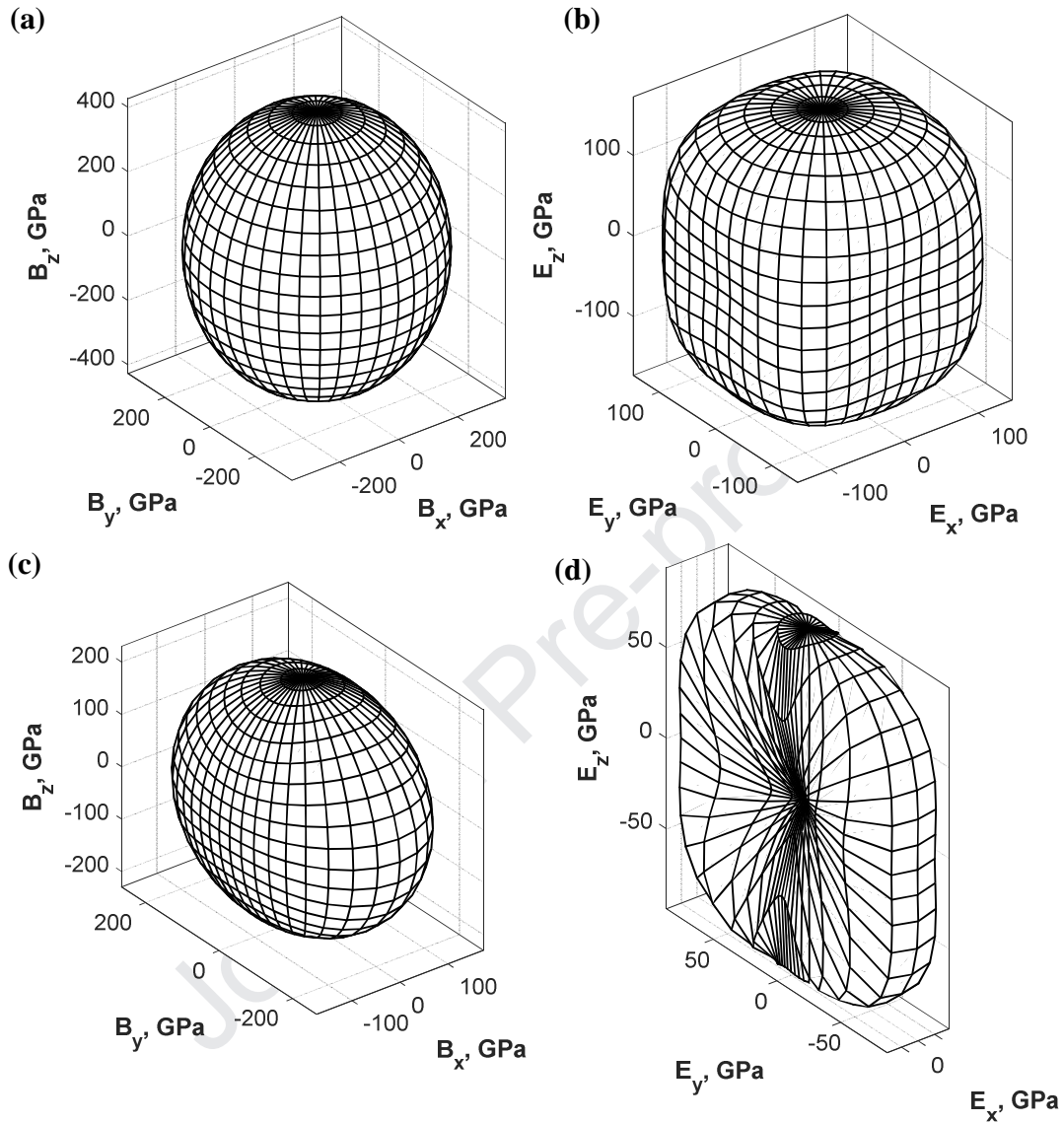


Figure 5: Elastic anisotropic analysis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$: (a) Bulk modulus and (b) Young's modulus, which is based on the reported elastic matrix computed by the density functional theory (DFT), Deng et al., *Journal of The Electrochemical Society*, 2016, Ref. [68]. Elastic anisotropic analysis of Li_3PO_4 : (c) Bulk modulus and (d) Young's modulus, which is based on the reported elastic matrix computed by the density functional theory (DFT), Deng et al., *Journal of The Electrochemical Society*, 2016, Ref. [68].

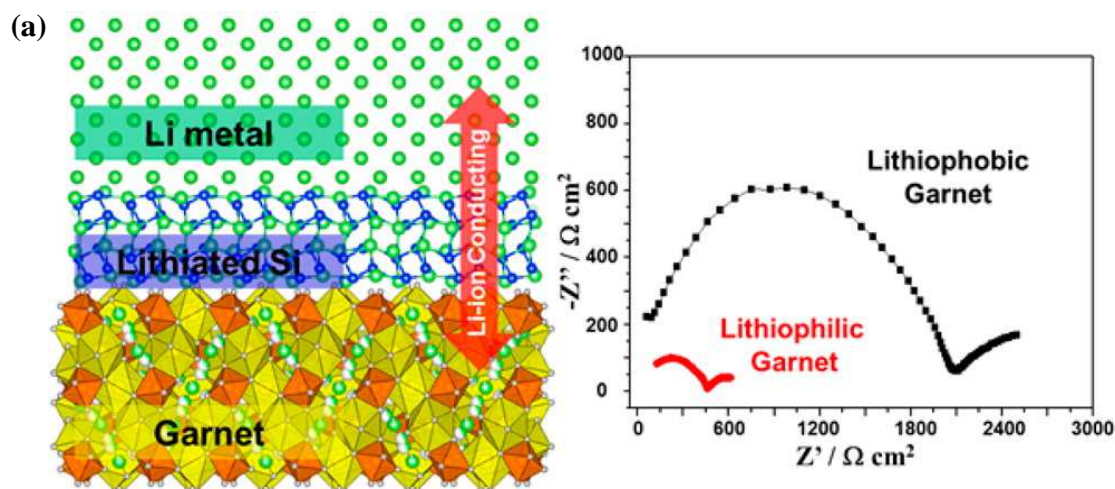
To date, no studies on elastic anisotropic analysis of SEs has been reported. Thus, there are adequate rooms for further quantifying the directionally mechanical properties of SEs. Examples on anisotropic analysis of bulk modulus and Young's modulus based on the reported elastic constants computed by density functional theory (DFT) [68] are shown in Figure 5. It can be seen that the bulk and Young's modulus for both $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and Li_3PO_4 as shown in Figure 5 (a)-(d) are not ideally isotropic. The bulk modulus of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ as shown in Figure 5 (a) along the [001] direction is larger than the other directions, i.e. [100] and [010]. The Young's modulus of Li_3PO_4 as shown in Figure 5 (d) exhibits extremely anisotropic behavior along the [100] direction. For an ideal isotropic bulk or Young's modulus, the shape should be spherical. The ideally spherical distributions of mechanical properties for SEs are desired. Dissecting and understanding the anisotropic behaviors of SEs will be beneficial to the rational design of SEs and useful guidance for the installation of the battery cell. Thus, exploring the isotropic SEs is desired for further efforts in ASSLIBs.

3. Engineering discussions on interface between solid electrolytes and electrodes

3.1 Interfacial resistance and wettability between solid electrolytes and Li-metal anode

Li metal is the anode popularly used for ASSLIBs, and the interfaces between the solid electrolytes and Li-metal have been considered as a critical issue for controlling the cell performance [7,64,65]. Wenzel et al. [129] early proposed three possible type of interfaces between the solid electrolytes and Li-metal: (1) "thermodynamically stable" without involving any reactions; (2) "thermodynamically unstable" allowing both electronic and ionic conductions and (3) "thermodynamically unstable" only allowing ionic conduction. The second type of interface allows the growth of Li dendrites, and even brings internal short-circuits for some extreme cases, i.e. LGPS [130] and LLTO [131]. However, poor mechanical compatibility of

those interfaces can contribute to large interfacial resistances and eventually greatly degrade the battery performance. Thus, it is critically important to obtain an intimate and stable interface between the solid electrolytes and Li-metal anode. To date, adding an interlayer between the solid electrolytes and Li-metal is being considered as the most popular and effective approach to enhance the mechanical compatibility to reduce the interfacial resistance. The reported interlayers include lithium thin film [132], indium [133], Au [134-136], SiO₂ [137], Si [138], Al [139], Al₂O₃ [80], ZnO [140], Ge [73], gel electrolyte [141], Li₃PO₄ [142], etc. For example, the resistance at the interface between the Ta-substituted Li₇La₃Zr₂O₁₂ solid electrolyte and the Li metal electrode can be reduced from $\sim 1,500 \Omega \text{ cm}^2$ to $\sim 380 \Omega \text{ cm}^2$ by inserting a thin layer of Au [134]. Moreover, the insertion of the Au thin layer contributes to suppress the growth of the Li dendrites, and consequently a homogenous interface between LLZO and Li-metal can be formed. The utilization of Li metal and uniformity of Li stripping/plating reactions can be also improved by inserting the Au layer [135]. It is worthy to mention that Hu's group [138-141,143-145] have contributed extensive efforts to reduce the interfacial resistances between the Li-metal anode and the solid electrolytes. In 2016, Hu et al. [138] first introduced a concept of 'superlithiophobicity-to-superlithiophilicity' for the interface between the solid electrolytes and the Li-metal as shown in Figure 6. It was found that the ultrathin Si alloy coated on the garnet-structured SE by the plasma-enhanced chemical vapor deposition (PECVD) could dramatically reduce the interfacial resistance between the Li-metal and the SE from $925 \Omega \text{ cm}^2$ to $127 \Omega \text{ cm}^2$. The electrochemical impedance spectroscopy (EIS) result as shown in Figure 6 demonstrates that the "lithiophilic" condition enables a much smaller interfacial resistance. This work leads further studies on how to form a "superlithiophilic" interface between the Li-metal and solid electrolytes



Transition from Super-lithiophobicity to Super-lithiophilicity of Garnet leads to a much smaller interfacial resistance

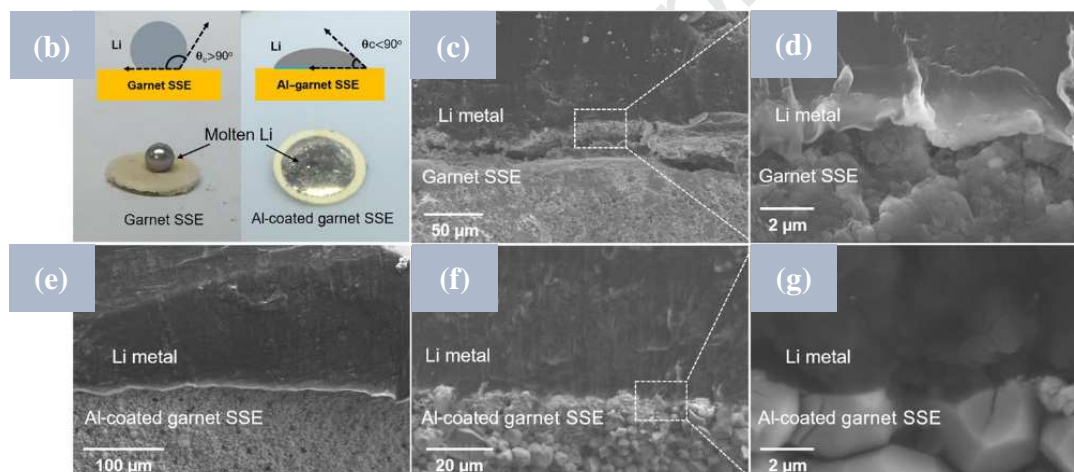


Figure 6: (a) A concept of transition from “superliophobicity” to “superlithiophilicity” for the garnet-structured solid electrolyte, copyright permission is required, Luo et al., *Journal of the American Chemical Society*, 2016, Ref. [138]; (b) Wettability tests for the garnet SE with Li and the Al-coated garnet SE with Li, contact angles are measured; (c) and (d) SEM images of interfacial morphology for the interface between Li-metal and garnet SE; (e), (f) and (g) SEM images of interfacial morphology for the interface between Li-metal and Al-coated garnet SE, copyright permission is required, Fu et al., *Science Advance*, 2017, Ref. [139].

by inserting a coating layer. The role of wettability on reducing the interfacial resistance has been emphasized since then. Other interfacial modifications through coating electrolytes, i.e., polymer electrolytes [146,147], etc., were also reported. The minimization of the interfacial resistance between the SEs and Li-metal can be achieved by improving the wetting condition at the interface. An example of an enhanced wetting surface between the Li-metal and garnet SE

obtained by inserting an Al layer is shown in Figure 6 [139]. The Al-coated garnet SE gets a better wettability with the Li-metal. Interfacial morphologies demonstrate that the Al coating layer is beneficial for the interfacial contact, and consequently reduce the resistance between the garnet SE and Li-metal. Enhanced cell performance, i.e. rate capability, discharge capacity, cycling stability, etc., can be achieved through modifying the interfaces between the SEs and Li-metal anode. Further work on designing interfaces with minimized resistances and superior wettability from the engineering aspect is strongly desired.

4. Electrochemical-mechanical modeling of all-solid-state batteries

Extensive studies on transport phenomena and degradation of lithium batteries with organic liquid electrolytes by macro- (cell-level) [148-154] and meso-scale (particle-level) [155-157] modeling have been reported. Battery degradations and even failures in the liquid electrolytes due to the electrochemical, thermo and mechanical aspects were comprehensively quantified [158]. Loss of active materials [159], growth of solid electrolyte interphase (SEI) layer [160,161], thermal runaway [162] and microstructural cracking [163,164] have been considered as the major causes to the capacity fade. Understanding fundamentals on safety and failure mechanisms plays a crucial role in performance optimization and advanced design of lithium ion batteries.

However, there is quite limited work [75,76,165-167] on macro- and meso-scale modeling of lithium ion batteries with solid electrolytes that have been reported so far. Both computational modeling frameworks for lithium ion batteries and all-solid-state lithium ion batteries are similar, and they are typically based on the finite element, finite volume and finite difference methods [75,168]. However, there are some differences from the aspect of physics-based modeling: for the classic lithium ion batteries, the active particles are immersed in the organic liquid electrolytes while for all-solid-state lithium ion batteries, the active particles are embedded in the

inorganic solid electrolytes. The organic liquid electrolytes do not have any intrinsically mechanical properties, such as bulk modulus, Young's modulus and shear modulus, etc. While for the inorganic solid electrolytes, those are their intrinsically mechanical properties. Thus, the solid mechanics of the inorganic solid electrolytes need to be considered in modeling ASSLIBs. Bucci et al. [76] developed the first electrochemical-mechanical model by incorporating localized stress [169] and damage evolution [170] to predict the degradation of all-solid-state lithium ion batteries, especially focusing on elucidating the mechanical degradation due to the microstructure evolutions of the solid electrolytes. Fracture propagations caused by the volume expansion of electrode particles during intercalation, and the mechanical reliability of all-solid-state batteries were quantitatively assessed. The multiphysical model introduced by Bucci et al. [76] was shown in Figure 8. A 2D scheme was simplified for the 3D geometry based an assumption of a much thinner layer along the third direction. The components considered in the model include solid electrolytes, electrode particles and active materials. Swelling of electrode particles generated mechanical stress and fracture during Li-intercalation. The fracture evolution with time and different averaged state of charge (SOC) under different conditions, i.e. Young's modulus and fracture energy are shown in Figure 9. The calculated fracture propagation rate decreases with both increased Young's modulus and fracture energy of solid electrolytes. It was concluded that the fracture can be effectively avoided if the following two conditions can be satisfied: volume expansion of electrode particle is smaller than 7.5 %, and fracture energy of SEs is higher than 4 J m^{-2} . However, there could be still room for improvement on this model: (1) some assumptions are fairly justified, for example, both solid electrolytes and electrodes were ideally assumed to be linear elastically and diffusively isotropic. In fact, most materials are non-linear and non-isotropic; (2) Structures of electrode particles modeled are ideally simplified to be

square, which is far different from the actual structures of the electrodes; (3) The dense assumption for the composite cathode is ideal for considering the fracture generations by excessive stresses involved in the composite cathode for all-solid-state lithium ion batteries. In fact, a porosity of 5 % is common for a real composite cathode used in the laboratory experiments, and it should be capable to accommodate a 7.5 % volume expansion without generating significant stresses for inducing fractures and their propagations. Thus, the dense assumption should be carefully examined prior to carrying out the battery simulations.

(4) 2D geometry only limits the case in which the third-dimensional effect can be ignored. But, 3D geometry is desired to capture full physics for most battery structures. Following efforts on the role of micro-cracking in the effective conductivity of the composite electrode mixed with the solid electrolytes [165] and mechanical instability at the interface between the electrode and solid electrolytes [75] were also carried out. Very recently, Grazioli et al. [167] reported an electrochemical-mechanical model for the lithium ion batteries with solid polymer electrolytes (SPEs) and examined the effect of mechanical stress within the SPEs on battery performance. It was found that stress is able to either foster or reduce the depletion of salt concentration at the interface between electrode and SPEs. Knowledge of localized and globalized mechanical properties distributions of solid electrolytes will help to design better ASSLIBs for achieving a long-term stable operation. Further work on minimizing the “fracture” or “crack” propagation of SEs and enhancing the mechanical compatibility of electrode-electrolyte interface is desired for developing advanced ASSLIBs.

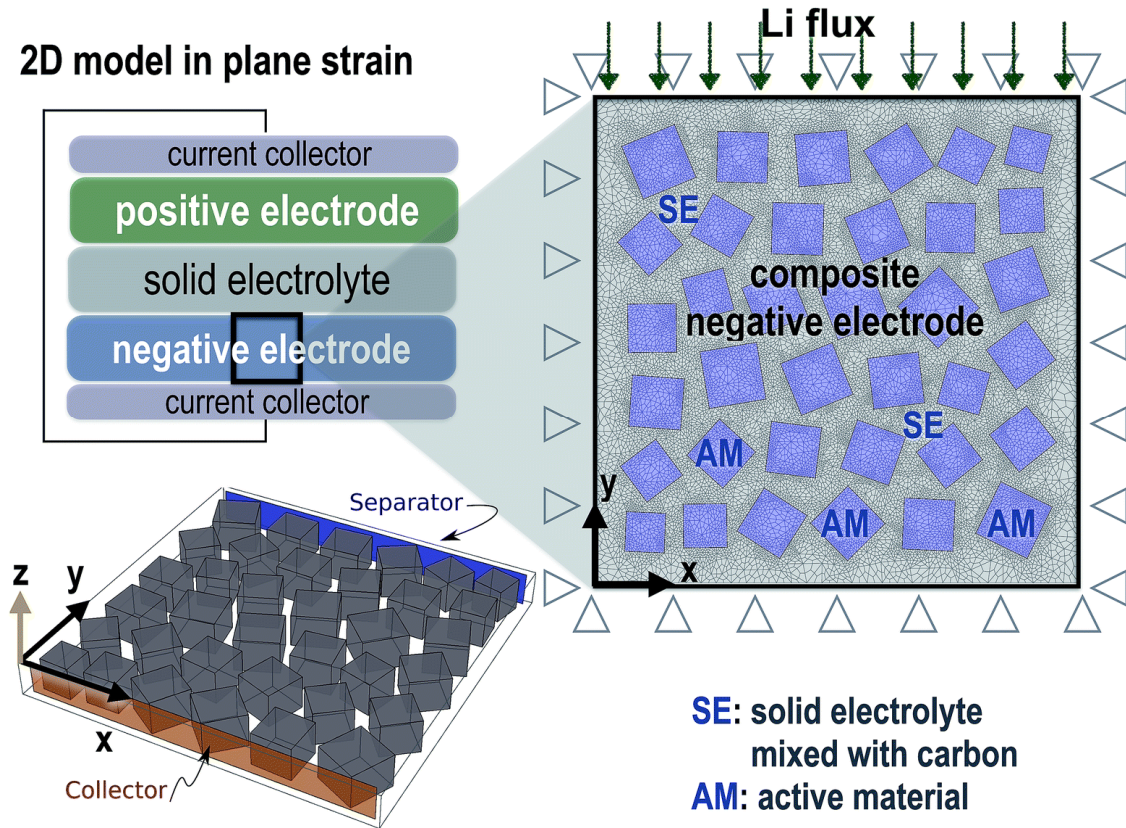


Figure 8: Geometry, discretization elements and boundary conditions of a finite element model of an all-solid-state lithium ion battery. The cell components include electronic particles, solid electrolytes and electronically conductive additives, copyright permission is required, Bucci et al., *Journal of Materials Chemistry A*, 2017, Ref. [76].

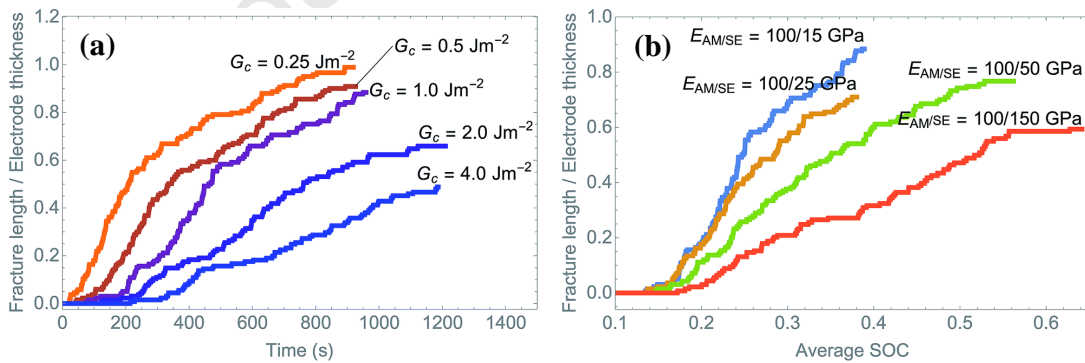


Figure 9: (a) The evolution of fracture length with respect to the electrode thickness within the solid electrolytes with time under several fracture energies ranging from 0.25 J m^{-2} to 4.0 J m^{-2} computed by a finite element model, copyright permission is required, Bucci et al., *Journal of Materials of Chemistry A*, 2017, Ref. [76]; (b) The trend of fracture length with respect to the electrode thickness with various Young's modulus ranging from 15 GPa to 150 GPa of solid electrolytes with a fixed Young's modulus (100 GPa) of the active materials, copyright permission is required, Bucci et al., *Journal of Materials of Chemistry A*, 2017, Ref. [76].

5. Discussions

This review paper attempts to provide a comprehensive literature summary and discussions on mechanical properties of solid electrolytes, and their potential effects on critical components that are closely related to the cell performance of ASSLIBs. It is believed that the mechanical properties of SEs should have significant influences on electrolyte and interface designs, which are critical to achieve high performance ASSLIBs. Several key considerations on the role of mechanical properties include suppressing Li-dendrite, reducing micro-crack generation and enhancing interfacial compatibility, as elaborated in the following:

(1) Suppressing Li-dendrite: For all-solid-state lithium ion batteries with the Li-metal anode, which enables a high theoretical capacity ($> 3800 \text{ mAh g}^{-1}$), how does effectively suppress the growth and propagation of Li-dendrite is one of the most significant challenges [171,172]. The Li-dendrite can eventually penetrate through the separator and cause short-circuits, and consequently lead to thermal runaway and failure of ASSLIBs [103]. From the mechanical design aspect, according to the model developed by Monroe and Newman [173,174], it is suggested the growth of Li-dendrite can be avoided if the shear modulus of solid electrolytes can be twice larger than the one of Li-metal (4.25 GPa) [84]. Based on the collected experimental data as shown in Table 1, it can be seen that the shear modulus of garnet-type SEs (LLZO) with a magnitude of 50-65 GPa should be more robust than the thio-phosphate SEs (LPS) with a magnitude of 3-10 GPa in suppressing the formation of the Li-dendrite. However, multiple recent reports [175,176] have found lithium dendrite growth even in the garnet SEs though interconnected pores and grain boundaries at high deposition rates. Whether this is due to the elasticity softened near grain boundaries [177] or the relatively high electronic conductivity of

solid electrolytes [34] is still under debate. A conclusive understanding for dendrite suppression in solid electrolyte remains elusive.

(2) Reducing micro-crack generation: Recent studies [75,76,178] have gradually realized the role of mechanical properties of solid electrolytes in affecting their microstructure evolutions, including micro-crack generation and propagation, which can increase the ion/electron tortuosity and cell resistance and consequently can facilitate degradation of cell performance [29,76,179]. Minimization of micro-crack is being considered as a critical factor for achieving a long-term and high electrochemical performance of ASSLIBs [29,82,103]. By determining the “brittleness” or “ductility” of solid electrolytes, it might be able to screen SEs that have a less tendency for cracking. Some studies point out that the ductile SEs are more capable to accommodate large stresses, which can cause micro-crack generation, during repeated intercalation and de-intercalation [68,115,116]. Based on the “Pugh” rule, Figure 4 shows that LPS SEs are more “ductile”, when compared with the oxide-based garnet SEs, which means LPS SEs have a less chance to generate micro-cracks. From the aspect of reducing the micro-crack generation, it is preferred to synthesize “ductile” solid electrolytes instead of “brittle” ones.

(3) Enhancing interfacial compatibility: Large interfacial resistance between the solid electrolytes and electrode is a critical issue for ASSLIBs, especially for ASSLIBs with Li-metal anode [30,180]. To enhance the interfacial compatibility, securing an intimate interface between the solid electrolytes and Li-metal anode is vital for achieving a long-term cycling performance [64,181]. The “ductile” SEs, i.e. thio-phosphate, as shown in Figure 4 have a deformable nature and are able to form an intimate interface with Li-metal. Apart from screening and synthesizing “ductile” SEs, surface modifications, i.e. adding an interlayer, are also effective to increase the wettability of solid electrolytes and reduce the interfacial resistance [73]. The interlayers can be

pure metal, oxide, and even other solid electrolytes [81,140,142]. Thus, the minimization of the interfacial resistance between the SEs and Li-metal can be achieved by both synthesizing “ductile” SEs and introducing interlayers for enhancing the interfacial compatibility.

Prior to carrying out experimental synthesis, DFT can be used as a useful tool for predicting the mechanical properties, i.e. elastic moduli and wettability, of SEs as the initial screening to save the labor efforts and capital costs. To date, the database of mechanical properties of SEs is still far away from sufficient for achieving a clear understanding of their roles in the battery fabrication, operation and cycling performance. Both extensive experimental investigations and DFT calculations on mechanical properties of SEs are critically desired.

Summary and outlook

All-solid-state lithium ion batteries are being developed for next-generation energy storage applications. Compared with conventional lithium ion batteries using organic liquid electrolytes, all-solid-state lithium ion batteries using inorganic solid electrolytes demonstrate various distinct advantages, such as better safety without flammable explosions, more eco-friendliness without volatilization, higher stability without liquid leakage, wider cell voltage window and higher energy density. In this review, we have focused to discuss mechanical properties, i.e. bulk, Young's and shear modulus, hardness, fracture toughness and elastic anisotropy of solid electrolytes, density functional theory (DFT) modeling of elasticity, interfacial resistance between the solid electrolytes and electrodes, and electrochemical-mechanical modeling of ASSLIBs from the engineering aspect. To develop next-generation all-solid-state batteries for various energy storage applications, the following several aspects of work are kindly suggested to be carried out through both experimental and modeling approaches:

(1) Experimental understanding of the relationship between mechanical properties of solid electrolytes and electrochemical performance of ASSLIBs is crucial to design better solid electrolytes. Although it was pointed out that a solid electrolyte with a higher shear modulus has a higher capability to suppress lithium dendrites, other studies also stated that a more rigid solid electrolyte tends to more easily crack and may cause electronic disconnects among active materials. Thus, a fully understanding of the role of mechanical properties of solid electrolytes on rate performance and capacity of ASSLIBs is strongly desired.

(2) Continually experimental efforts on examining the mechanical properties of solid electrolytes are needed. Currently only a limited number of research reports on mechanical properties are available on a few selected oxide-based and sulfide-based solid electrolytes. Also, it is necessary to develop well-controlled experimental designs for measuring mechanical properties of solid electrolytes. It was found that those experimental values are strongly related to various factors, such as moisture, etc. In particular, the sulfide-based solid electrolytes are extremely sensitive to the air and humidity. Thus, it is critical to design effective strategies to avoid undesired effects. Achieving a full picture of mechanical properties of all types of solid electrolytes associated with their chemical and electrochemical properties should be beneficial to an improved understanding of their performance in ASSLIBs.

(3) Experimental studies on microstructure evolutions within solid electrolytes during in-operando conditions of ASSLIBs. As it was discussed earlier, only few studies preliminarily demonstrated that extensive fractures of solid electrolytes occur during the intercalation and strongly affect the performance of all-solid-state batteries through the finite-element modeling. It is suggested that integrating advanced experimental characterization techniques, i.e. X-ray tomography and 3D reconstruction technique may achieve to capture dynamics of solid

electrolytes' microstructures, and correlate them with the performance of ASSLIBs. Quantifying the relationship between the microstructures of solid electrolytes and battery performance will benefit the mechanical design of solid electrolytes for ASSLIBs.

(4) Electrochemical-thermal-mechanical modeling of ASSLIBs. Multiphysics modeling integrated with the in-situ/in-operando experimental investigations are able to elucidate the capacity fading and even failure mechanism of ASSLIBs. Guidance on rational design of solid electrolytes towards minimizing the performance degradation of ASSLIBs may be suggested through the combination of the electrochemical-thermal-mechanical modeling and in-operando experimental techniques.

Conflicts of interest

There is no conflict to declare.

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