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Perspective

Solid-state electrolytes for safe rechargeable lithium metal batteries: a strategic view

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Abstract

Despite the efforts devoted to the identification of new electrode materials with higher specific capacities and electrolyte additives to mitigate the well-known limitations of current lithium-ion batteries, this technology is believed to have almost reached its energy density limit. It suffers also of a severe safety concern ascribed to the use of flammable liquid-based electrolytes. In this regard, solid-state electrolytes (SSEs) enabling the use of lithium metal as anode in the so-called solid-state lithium metal batteries (SSLMBs) are considered as the most desirable solution to tackle the aforementioned limitations. This emerging technology has rapidly evolved in recent years thanks to the striking advances gained in the domain of electrolyte materials, where SSEs can be classified according to their core chemistry as organic, inorganic, and hybrid/composite electrolytes. This strategic review presents a critical analysis of the design strategies reported in the field of SSEs, summarizing their main advantages and disadvantages, and providing a future perspective toward the rapid development of SSLMB technology.

Keywords: solid-state electrolytes, lithium metal batteries, polymer electrolytes, safe batteries, inorganic solid electrolyte, hybrid electrolyte, composite electrolyte

1. Introduction

Global energy consumption is currently strongly dependent on the combustion of non-renewable fossil fuels, and this scenario is aggravated by the development of our society and a growing energy demand. Moreover, it is foreseen that energy consumption will increase nearly 50% by 2050, causing serious environmental risks such as global warming, pollution, and continuous depletion of energy resources [1]. All these facts together evince the urgency of finding an environmentally sustainable energy supply to replace the excessively used fossil fuels.

This need has tipped the balance in favor of electrochemical energy storage, among which lithium-ion batteries (LIBs) have been extensively investigated as the most suitable choice. Conventional LIBs are composed of a graphitized material as negative electrode, a Li transition metal oxide as positive electrode, and an organic carbonate-based liquid solution as electrolyte. However, this technology is believed to be close to reach its theoretical energy density limit [2],

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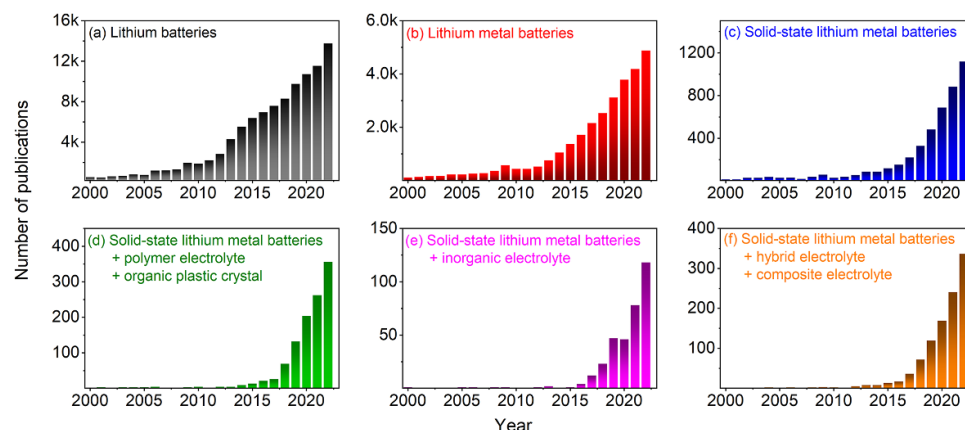


Figure 1. Research tendency [i.e. number of publications vs. year] in the field of SSLMBs: (a) Li batteries, (b) Li metal batteries, (c) SSLMBs, (d) SSLMBs utilizing either polymer or organic plastic crystal electrolytes, (e) SSLMBs utilizing inorganic electrolyte, and (f) SSLMBs utilizing either hybrid or composite electrolytes. The values were obtained via the keyword search in Scopus database on the 28 February 2023.

which is still not enough to meet the current demand, and at the same time arises a severe safety concern ascribed to the use of volatile organic solvents [3].

To go beyond LIB technology, Li metal (Li°) anode has emerged as the most promising alternative to graphite in current LIBs due to its ten times higher theoretical capacity [3860 mAh g^{-1} (Li°) vs. 372 mAh g^{-1} (graphite)] [4, 5]. Nevertheless, the extremely high reactivity of Li° implies severe security hazards, especially when combined with a highly flammable liquid electrolyte. For that reason, the deployment of Li° as an anode requires a complete concept shift approach towards safer electrolytes. In this context, solid-state electrolytes (SSEs) arise as the preferred replacement of alkyl carbonate-based liquid electrolytes due to their intrinsic safety and the foreseen higher energy density of solid-state Li metal batteries (SSLMBs) [6, 7]. SSEs can be classified as organic solid electrolytes (where the most widely used ones are solid polymer electrolytes, (SPEs)), inorganic solid electrolytes (ISEs), and the combination of both leading to hybrid or composite electrolytes.

SSEs have attracted much interest in recent years from both the scientific community and industry. As seen in figure 1, the number of publications per year related to solid-state batteries has been increasing drastically in the last decade. Moreover, recently, several companies dedicated to solid-state battery technologies have been announced or funded [e.g. Prologium, Automotive Cells Company, Welion, QuantumScape, etc.], and in particular solid-state Li metal polymer batteries (SSLMPBs) have been successfully implemented as power sources for electric vehicles by BlueSolutions demonstrating the potential application of these electrolytes [8].

In this review, we propose a critical analysis of current status of the different SSEs and their application in SSLMBs. Several recently published reviews have tackled the general comparison of SSEs by means of physicochemical and electrochemical properties, for that reason the present work aims to present the main challenges found nowadays and the future outlook for SSEs development [9, 10].

2. Features of SSEs

For rechargeable Li° batteries, an ideal electrolyte should allow rapid migration of lithium-ion during charge/discharge processes and remain chemically inert

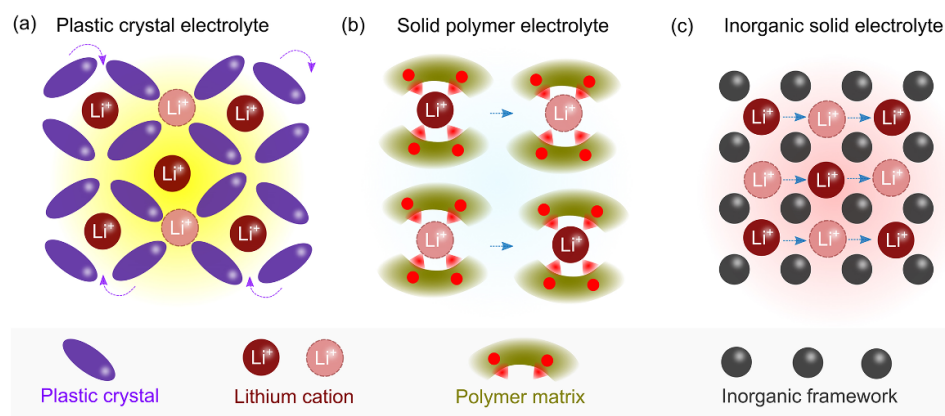


Figure 2. Features of solid electrolytes developed for rechargeable Li metal batteries. (a) Organic plastic crystal electrolyte, in which the ion transport is commonly realized via the ‘paddle-wheel’ mechanism. (b) Polymer electrolyte, in which the Li^+ usually migrates via the segmental motion of polymer chains. (c) Inorganic electrolytes, in which the transportation of Li^+ is generally achieved via the ‘ion-hopping’ mechanism.

against electrode materials [11–13]. In the case of non-aqueous liquid electrolytes, the dissolution of Li salts in aprotic solvents affords an ionic solution with the capability of transporting solvated Li^+ [13]. Such scenarios change dramatically when shifting to the field of solid lithium-ion conductors. For organic plastic crystal electrolytes, the migration of Li^+ generally occurs through the rotation of crystal sites without positional changes (figure 2(a)). This is commonly known as ‘paddle-wheel’ processes, as described in previous work [14, 15].

For SPEs, the dissolution of Li salts is possible due to the strong solvating ability of electron-donating groups in polyethers [e.g. poly(ethylene oxide), (PEO)] or polyesters [e.g. polycaprolactone, (PCL)]; however, the motion of solvated Li^+ along with the solvation sheath is unlikely to take place as those in liquid electrolyte, due to the significantly higher molecular weights of polymeric solvents vs. small organic solvents [e.g. ca. $1 \times 10^6 \text{ g mol}^{-1}$ (PEO) vs. 90 g mol^{-1} (1,2-dimethoxyethane)]. The migration of Li^+ becomes possible with the segmental relaxation processes of polymer chains (figure 2(b)), following the ‘dynamic percolation’ model described by Ratner and Shriver [16]. For inorganic electrolytes, the migration of Li^+ tends to occur in the presence of certain defects allowing ready accommodations of adjacent Li^+ , which is described as ‘ion-hopping’ mechanism [17, 18].

3. Organic-based SSEs

3.1. Organic plastic crystal electrolytes

Organic plastic crystals represent an exceptional and increasingly promising family of SSEs for Li^+ batteries [19, 20]. These materials have a long-range crystalline lattice but short range rotational and/or translational motion of the molecules/ions, soft mechanical properties, and display one or more solid-solid phase transitions before melting [21]. They can be classified in two different groups: (1) molecular plastic crystals, known since the 1960s [22] and, (2) the more recently known organic ionic plastic crystals (OIPCs) [23–26].

3.1.1. Plastic crystal electrolytes. The plastic crystal electrolytes composed of Li salt and plastic crystals with solvation capability are particularly appealing because of their distinctive thermal stability and ionic transport behavior [27].

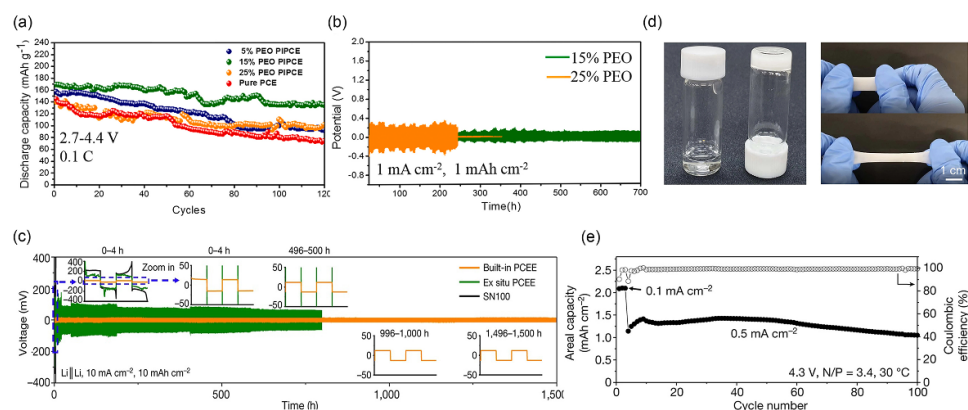


Figure 3. (a) Long-term cycling performance of Li^o||NMC532 cells using SN-based electrolytes with different PEO concentration. (b) SN-based electrolyte using 15% PEO and 25% PEO under a current density of 1 mA cm⁻² and areal capacity of 1 mAh cm⁻². Reprinted from [30], Copyright (2021), with permission from Elsevier. (c) Cycling performance of the Li metal symmetric cells of *in-situ* and *ex-situ* prepared SN-based electrolytes. (d) Digital photo images of a homogeneous solution before (left) and after polymerization (right). © Long-term cycling performance of the full cell using NMC-83 as active material in the voltage range of 2.7–4.3 V at 30 °C. Reproduced from [31], with permission from Springer Nature.

Succinonitrile (SN) is the most used plastic crystal that can dissolve various Li salts and facilitates rapid ion transport due to the high polarity of nitrile groups [28, 29]. Moreover, the SN-based plastic crystal electrolytes present high voltage stability and, additionally, benefit from the properties of nonflammability and nonvolatility, which makes them an attractive matrix in SSEs. However, they are unstable against Li^o due to the side reactions, namely, the polymerization of nitriles catalyzed by Li^o. To overcome this drawback, the utilization of polymer in plastic crystal electrolyte was suggested [30], in which a PEO-based polymer in SN electrolyte was designed to achieve relatively stable cathode/electrolyte and anode/electrolyte interface simultaneously through strong intermolecular interactions as revealed by microstructural analysis. By FTIR and Raman, it was demonstrated that Li⁺ interacted with SN, PEO and TFSI anion, simultaneously. Therefore, the reduction of free SN on Li^o is restricted due to these strong intermolecular interactions. The as-obtained electrolyte allowed stable operation of Li^o symmetric cells for 700 h at 1 mA cm⁻² and also endowed lithium nickel manganese cobalt oxide [Li(NiMnCo)O₂, NMC]-based cell with a high discharge capacity of 169 mAh g⁻¹ and long-term cycling stability, as seen in figures 3(a) and (b). Another strategy is the *in-situ* crosslinked plastic crystal electrolyte that leads to high-energy-density battery systems with superior safety and temperature tolerance behavior [27]. This can be achieved by: (1) mixing Li salts with SN that can serve as an efficient ion transport medium, (2) mixing a robust polymer monomer with high polar groups on the chain segments [i.e. ethoxylated trimethylolpropane triacrylate (ETPTA) or poly(ethylene glycol) diacrylate] (PEGDA) and, (3) introducing a certain amount of fluorinated additive segments [i.e. fluoroethylene carbonate] (FEC) to further reinforce the electrode/electrolyte interphase [28, 31]. Lee *et al* suggested the *in-situ* crosslinking of a SN-based polymer electrolyte that presented high ionic conductivity (1.10×10^{-3} S cm⁻¹ at 20 °C) and excellent performance of Li^o symmetric cells, being able to cycle at a current density of 10 mA cm⁻² for more than 1500 h. Moreover, the NMC-based full cells delivered a high capacity of 1.1 mAh cm⁻² with a coulombic efficiency of 99.4% at 0.5 mA cm⁻² after 100 cycles at 30 °C (figures 3(c)–(e)) [31].

3.1.2. Organic ionic plastic crystal electrolytes. OIPCs, a class of solid-state analogues of ionic liquids at room temperature, have been pursued as

next-generation solid electrolyte materials due to their good thermal stability, nonflammability, non-volatility, and excellent electrochemical stability [32, 33]. OIPCs are composed of small organic cations and anions with short-range molecular rotational/orientational motions and long-range crystalline structures. These structural features as well as performance-controllability through the design of anion and cation could give OIPCs several unique properties. For instance, the ionic conductivity of OIPCs is highly associated with the motional modes of cations, anions, and their correlation to defect formation [e.g. vacancies] during structural rearrangement [34, 35]. For this reason, the understanding of the relationship between phase behaviors and ion transport is critical for the design of high-performance OIPC-based electrolytes [36, 37].

In the last years, Forsyth *et al* have dedicated a great effort to investigating the impact of the anion structure on the properties of OIPCs. They discovered that some OIPCs with rigid anions [e.g. PF_6^- , BF_4^-] show high thermal stability and can keep their solid-state nature at high temperatures; however, the low-temperature conductivity is not suitable for battery application. On the other hand, systems with more flexible anions [e.g. $\text{CF}_3\text{SO}_2\text{N}^{(-)}\text{SO}_2\text{CF}_3$ (TFSI $^-$), $\text{FSO}_2\text{N}^{(-)}\text{SO}_2\text{F}$ (FSI $^-$)] present high ionic conductivity at room temperature, while they are too soft to be used as free-standing electrolytes [20, 38]. For these reasons, and to apply the OIPCs in practical devices, composite OIPC-based electrolytes have been proposed by several groups in the last decade [39–41].

The doping of salt increases the concentration of defects in OIPCs, resulting on a substantially increased conductivity [42–46]. Jin *et al* proved that the addition of 4 mol% of lithium bis(fluorosulfonyl)imide (LiFSI) in triisobutyl(methyl) phosphonium bis(fluorosulfonyl)imide ($\text{P}_{1444}\text{FSI}$) results in a conductivity increase of more than 3.5 orders of magnitude in the solid phase (0.26 mS cm^{-1} at 22°C), as compared to the pristine material [47]. At the C-rate of 0.1 mA cm^{-2} , a discharge capacity of ca. 160 mAh g^{-1} was achieved at 20°C for $\text{Li}^\circ\|\text{LiFePO}_4$ (lithium iron phosphate) cells. The discharge capacity exceeded a respectable value of ca. 130 mAh g^{-1} at higher C-rates, figures 4(a) and (b). This remarkable performance was the first example of an OIPC electrolyte system performing at practical rates at room temperature. However, the use of a porous polyethylene separator was needed for battery assembly due to the weak mechanical properties of the electrolyte.

Another strategy to improve the mechanical properties and/or the ionic conductivity of OIPCs, is the addition of polymers [e.g. polyvinylidene fluoride (PVDF), PEO] [48]. Howlett *et al* demonstrated that the use of PVDF fibers presents promising electrochemical and mechanical properties of OIPC electrolytes [49, 50], obtaining self-standing membranes with an order of magnitude higher conductivity than that of the bulk material. However, the understanding of the mechanism of polymer surface effects remains unresolved due to the complicated geometry of the fibers [51]. To overcome this issue, PVDF nanoparticles with controlled particle size have been added into OIPCs to analyze the effect of the interfacial region on the composite properties [52, 53]. The addition of PVDF nanoparticles showed an increase in the ionic conductivity compared to the composites using PVDF nanofibers. Moreover, it was observed that with increasing loading of PVDF nanoparticles, higher Li^+ transference number (T_{Li^+}) could be obtained due to the higher specific contact area between PVDF and OIPCs depressing the mobility of the anions in a fluorophilic effect [19]. The cycling performance for the $\text{Li}^\circ\|\text{NMC111}$ cells using composite OIPCs with PVDF nanoparticle and fibers were compared. It was observed that the cell containing PVDF nanoparticles showed a much better discharge capacity retention than that with PVDF fiber at 50°C , figures 4(c) and (d) [48]. Guan *et al* proposed the use of PEO-based membranes reinforced with an OIPC

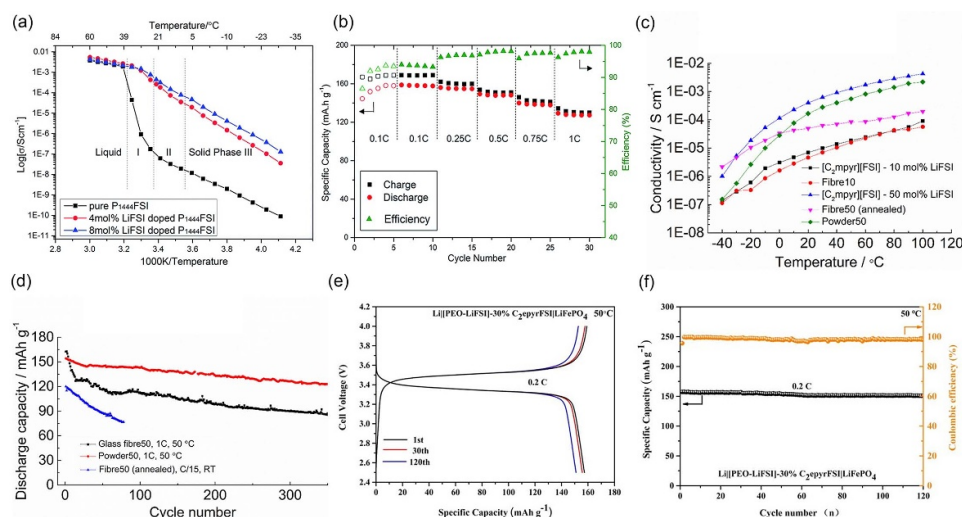


Figure 4. (a) Temperature dependent conductivity data for pure, LiFSI doped P₁₄₄₄FSI and (b) cell capacity retentions at different charging-discharging rate. Reproduced from [47] with permission from the Royal Society of Chemistry. (c) Reported ionic conductivity of [C₂mpyr][FSI] with different LiFSI concentration, and PVDF fibers or PVDF particles and (d) Comparison of discharge capacities of Li⁺||LiNMC111 full cells cycling at 1 °C at 50 °C with glass fibre50, PVDF-based composites at a rate of 1 °C at 50 °C, and PVDF fiber-based electrolyte at a rate of C/15 at RT. Reprinted from [48], Copyright (2021), with permission from Elsevier. © Charge and discharge profiles of the first, 30, and 120 cycles of Li⁺||PEO-LiFSI-30% C₂mpyrFSI||LiFePO₄ cell at 0.2 C at 50 °C, and (f) specific discharge capacity and coulombic efficiency evolution with the number of cycles. Reprinted from [40], Copyright (2021), with permission from Elsevier.

[*N,N*-diethylpyrrolidinium bis(fluorosulfonyl)imide (C₂mpyrFSI)] as electrolyte for Li batteries [40, 41]. The as-prepared electrolyte exhibited high ionic conductivity of $3.02 \times 10^{-4} \text{ S cm}^{-1}$ at 50 °C, an extremely wide electro-chemical window (5.1 V), and decent mechanical properties. The Li⁺ symmetric cells could cycle for 2000 h at a current density of 0.1 mA cm^{-2} without short circuiting at 50 °C. Furthermore, the LiFePO₄-based cells delivered a high initial discharge specific capacity of 157.3 mAh g^{-1} at 0.2C and a capacity retention rate of 96% after 120 cycles, figures 4(e) and (f) [40].

In short, OIPCs are an emerging family of solid-state ion conductors that are potential candidates to replace traditional ceramic and polymer-based electrolytes [25]. They have been demonstrated to be safe and stable electrolytes in several electrochemical devices. Moreover, their enhanced interfacial stability and ability to form stable, low resistance interfaces at electrodes after charge–discharge processes has increased the research interest on OIPCs [20]. Their favorable plasticity, which can highly improve the solid/solid contact, favors the formation of a highly conductive and stable solid electrolyte interphase (SEI) layer able to suppress the growth of lithium dendrites [40]. However, further improvement in the solid-state conductivity and transport of the target ions while suppressing the transport of the counter anions are needed. One alternative that is currently pursued is the use of single Li⁺ conducting fibers or particles combined with OIPCs to obtain conducting composites with improved mechanical properties, making use of the interface to dope the OIPC and provide a conductive pathway for Li⁺ [20]. On the other hand, the cathode design is a key factor to achieve practical all-solid-state and high energy density devices. OIPCs are good candidates to replace traditional PVDF binders in cathodes due to their high flexibility which could lead to the improvement of electrode/electrolyte contact. Nevertheless, the cost of the OIPCs needs to be reduced in order to commercialize cost-effective technology.

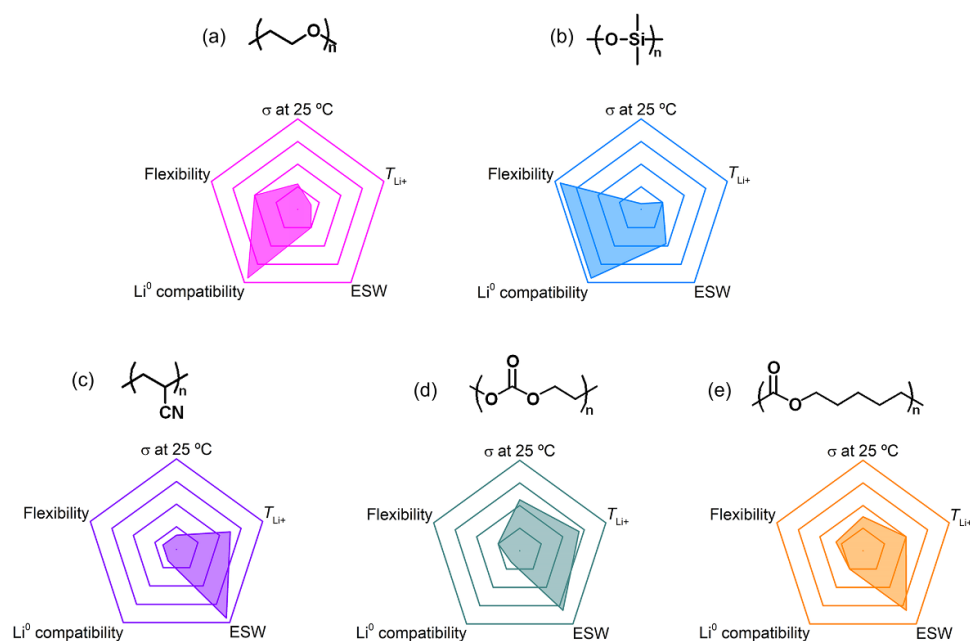


Figure 5. Key properties of the different polymers used as polymer matrices for SPEs as Radar Plots: (a) PEO, (b) poly(dimethylsiloxane) (PDMS), (c) poly(acrylonitrile) (PAN), (d) poly(ethylene carbonate) (PEC), and (e) poly(ϵ -caprolactone) (PCL). Explanations of the indicators are given below: ionic conductivity (σ), Li^+ transference number (T_{Li^+}), electrochemical stability window (ESW), compatibility towards Li metal (Li° compatibility).

3.2. Solid polymer electrolytes

Due to their high molar mass and consequently high thermal stability, polymers are considered a safe alternative to replace conventional carbonate-based liquid electrolytes. Since the first proposal of PEO as a solvating matrix for different ions, several chemical groups have been suggested (figure 5): polymers based on siloxane ($-Si-O-Si-$), nitrile ($-CN$), and carbonyl ($-C=O$) functionalities. However, high performance requirements remain a challenge for this class of electrolytes. An amorphous polymer with low glass transition is required to promote segmental motion, which is one of the main parameters that govern transport mechanisms within the polymer matrix. Another key parameter is the contribution of Li^+ to the total ionic conductivity, defined as T_{Li^+} , since it is the only ionic species that will contribute to the electrochemical reactions within the cell. However, most of the polymer electrolytes exhibit T_{Li^+} values below 0.5, denoting that the ionic conductivity is mainly accomplished by the anion. These phenomena are ascribed to the intra- or inter-coordinating sites for Li^+ along the polymer chains that reduce its diffusivity. In addition, high voltage stability of the polymer electrolyte is desired to achieve high energy density. This requirement is compromised by the chemical functionalities on the polymer chain and the anion chemistry/concentration. In addition, the implementation of Li° as negative electrode requires the control of Li dendrite growth. The role of the polymer in this regard is to provide mechanical strength. At the same time, compatibility, good interfacial contact, and adhesion need to be guaranteed.

As can be observed from figure 5, each polymer chemistry has its own virtues and defects. The high crystallinity of ethylene oxide-based polymers [e.g. PEO] and its narrow chemical stability, limits the application to standard $LiFePO_4$ -based cathode at high temperature ($>60^\circ C$) [54, 55]. At this temperature, the polymer is molten and good contact between the electrolyte and the electrodes is ensured. Siloxane-based polymers [e.g. poly(dimethylsiloxane)]

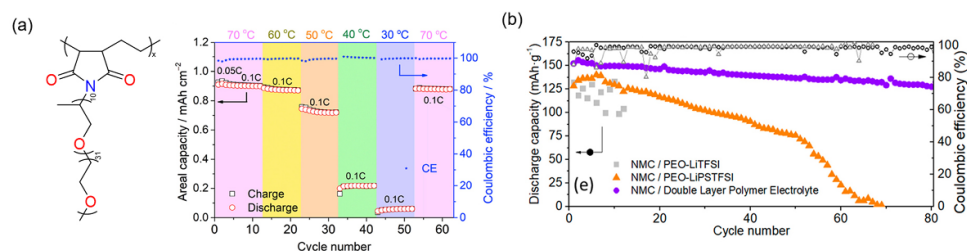


Figure 6. (a) Temperature dependence study of mechanically reinforced PEaMA-g-Jeffamine® in Li|SPE|LiFePO₄ cell at C/10. Reprinted from [66], Copyright (2019), with permission from Elsevier. and (b) Li|SPE|NMC622 cell cycling at 70 °C and at C/20 with dual-layer polymer electrolyte (DLPE) approach. Reprinted with permission from [67]. Copyright (2022) American Chemical Society.

(PDMS)] also provide low and stable interfacial resistances due to the extremely high segmental motion [56]. However, the mechanical properties are not sufficient to stop the Li dendrite growth and the Si–O bond is cleaved by Li⁰. Nitrile-based [e.g. poly(acrylonitrile) (PAN)] and carbonyl-based [e.g. poly(ethylene carbonate) (PEC) and PCL] polymers, due to the high anodic stability (4.5 V vs. Li/Li⁺) are suitable for high voltage battery application [57–60]. In addition, the high dielectric constant provided by these chemical groups improves the T_{Li}^{+} number compared to ethylene oxide-based SPEs ($T_{Li}^{+} \approx 0.5$ vs. 0.2) [57, 59]; however, they are also not stable towards Li⁰ [61].

Considering all chemistries and their characteristics, a tailor-made polymer should be designed according to its final use in the battery: as an electrolyte (separator) or as a catholyte (binder). The polymer electrolyte should have sufficient ionic conductivity at the target temperature and should effectively prevent the growth of Li dendrites, while the catholyte should provide enough cathodic stability within the working potentials of the positive electrode material.

One of the main challenges of polymer electrolytes is to decrease the operating temperature of the battery. In the case of PEO-based SPEs, different strategies have been proposed to decrease crystallinity. Aldalur and co-workers developed brush polymers, in which polyether side chains (so-called Jeffamine®) were grafted to poly(ethylene-*alt*-maleic anhydride) (PEaMA), with the aim of surpassing the limited ionic conductivity of PEO-based SPEs at temperatures below 70 °C [62, 63]. By balancing the ratio between propylene oxide and ethylene oxide units present in Jeffamine® crystallinity was curtailed and sufficient ionic conductivity was ensured at room temperature using both LiFSI and lithium bis(trifluoromethane)sulfonimide (LiTFSI) as Li⁺ source. Generally, an increase in ionic conductivity leads to a deterioration in mechanical properties, which impairs the ability to stop Li dendrites. Although, these systems can be used as a buffer layer to improve the interfacial resistance [64], different approaches have been described to improve the mechanical properties: (1) polymer blending; (2) copolymer synthesis; or (3) cross-linking. Some of these strategies have been applied to PEaMA-g-Jeffamine® polymers enabling self-standing SPE membranes. On the one hand, polystyrene (PS) blocks were introduced into the aforementioned polymer matrix structure where the soft Jeffamine® chains guarantee the ionic conductivity, and the hard PS blocks reinforce the mechanical properties without intervening into the Li⁺ transport mechanism [65]. On the other hand, PVDF nanofibers were fabricated to mechanically reinforced Jeffamine® based polymer by blending, figure 6(a) [66]. Even if the ionic conductivity decreased slightly, the practical application of the self-standing SPE was confirmed in Li|SPE|LiFePO₄ based cell, which delivered a decent discharge capacity of 145 mAh g⁻¹ at 50 °C.

Despite the high ionic conductivity and excellent stability against Li° , polymers containing ethylene oxide units (EO) suffer from low anodic stability restricting their use to low voltage cathode active materials, and thus leading to SSLMPBs with limited energy density. Hence, it is required to explore polymers delivering higher voltage stability such as, for example, the ones based on carbonyl or nitrile functionalities. Mindenmark *et al* thoroughly investigated the possible application of copolymers based on poly(ϵ -caprolactone)-*co*-poly(trimethylcarbonate) increasing the voltage range operation [58], and Zhang *et al* demonstrated the potential application of PPC as SPE with $\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ high cut-off voltage cathode active material, with no sign of oxidation after 100 cycles [68]. However, some works have demonstrated the degradation of the carbonyl group in the presence of the highly basic/reducing nature of Li° , attributing the high ionic conductivity to the plasticizing effect of the decomposition product [69]. This concern recommends the use of carbonyl-based polymers in contact with cathode materials (as catholyte) and a Li° stable polymer as an electrolyte matrix: i.e. the design of a double-layer polymer electrolyte (DLPE).

When developing the DLPE, the solvating ability of the used chemical groups needs to be considered. Several studies revealed that Li salt coordinates preferentially with ethylene oxide units rather than with carbonyl-based systems [70, 71]. This feature provokes a salt migration from the less solvating chemical group to the more preferential matrix. To avoid this issue, Arrese-Igor *et al* introduced a single-ion conducting polymer electrolyte into the poly(propylene carbonate) (PPC)-based catholyte and in the PEO-based electrolyte. As shown in figure 6(b), the NMC622 cell could be cycled with a DLPE approach at 70 °C for 80 cycles with a high-capacity retention (>80%) [67, 72].

Overall, as can be seen in table 1, further research is needed in the field of high energy density polymer-based batteries. Yet, the areal loading, charge/discharge time and the operational temperature are limited by electrolyte chemistry. The DLPE strategy or the addition of a buffer layer will open new battery configurations that overcome the limits of energy densities. Moreover, when considering the use of Li° as negative electrode as well as high voltage active materials in the positive electrode it is necessary to control the SEI and cathode electrolyte interphase that it is formed. Having stable and conductive interphases with a decrease interfacial resistance will help to improve the cell performance. This cannot be only attained with polymer chemistry, but the selection of the employed Li salt will also play a pivotal role. On this regard, several examples can be found in literature where LiFSI is commonly used salt for SEI formation. However, a rational design of new Li salts and additives is still required.

4. Inorganic-based SSEs

Inorganic SSEs are inorganic materials that can allow for the diffusion of Li^+ through their lattice. In these inorganic materials, as opposed to the conduction in polymer and liquid electrolytes, there is only Li^+ diffusion taking place, the T_{Li^+} is theoretically equal to 1. Sufficient Li^+ conductivity is achieved through a highly interconnected network of wide ion-channels and/or defects that can accommodate the Li^+ . In this section three promising and well-known families of ISEs are introduced and the issues and strategies on how to mitigate them are discussed.

4.1. Oxide-type inorganic SSEs

Two well studied types of oxide materials are NASICON and garnets. NASICON (Sodium Super Ionic Conductor) materials for SSLMBs can be described as

Table 1. Summary state-of-art of Li-based full cells using solid and plasticized polymer electrolytes.

Entry	Polymer matrix	Cell configuration	Cathode mass loading (mg cm ⁻²)	C-rate	Temperature (°C)	Capacity (mAh g ⁻¹)	References
1	Poly(PEGM)- <i>b</i> -poly(LiMTFSI)	Li ^o LiFePO ₄		C/15, C/10, C/5, C/10	70	50 (100)	[73]
2	P(LiMTFSI- <i>b</i> -PEO- <i>b</i> -P(LiMTFSI)	Li ^o LiFePO ₄	0.5–0.9	C/2	70	77 (300)	[74]
3	LiFSI/PEaMA- <i>g</i> -Jeffamine	Li ^o LiFePO ₄	0.8	C/10	T effect (70)	120 (60)	[63]
4	LiFSI/PEaMA- <i>g</i> -Jeffamine as buffer layer LiFSI/PEO	Li ^o LiFePO ₄		C/20, C/10, C/5, C/2 C/5	70	100 (200)	[64]
5	PVDF nanofiber reinforcement LiFSI/PEaMA- <i>g</i> -Jeffamine	Li ^o LiFePO ₄	0.7	C/10	T effect (70)	159 (60)	[66]
6	LiTFSI/PEaMA- <i>g</i> -(Jeffamine- <i>co</i> -PS)	Li ^o LiFePO ₄		C/20, C/10	70	115 (30)	[65]
7	LiTFSI/P(CL- <i>co</i> -TMC)	Li ^o LiFePO ₄	0.3–0.4	C/50, C/20, C/10, C/20, C/50, C/20	RT	80 (40)	[58]
8	LiTFSI/P(CL- <i>co</i> -TMC)	Li ^o LiFePO ₄		C/20, C/10, C/5	60	140 (30)	[75]
9	LiTFSI/Cross-linked P(CL- <i>co</i> -TMC)	Li ^o LiFePO ₄		C/2	80	150 (300)	[76]
10	DLPE- LiFePO ₄ (LiPSTFSI/PPC—LiPSTFSI/PEO)	Li ^o LiFePO ₄	0.7	C/20, C/10	70	150 (120)	[71]
11	DLPE-NMC622 (LiPSTFSI/PPC—LiPSTFSI/PEO)	Li ^o LiFePO ₄	1.0	C/20	70	130 (80)	[67]

Abbreviations are listed as follows: poly(ethylene glycol) methyl ether methacrylate block poly(lithium) 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide) (poly(PEGM)-*b*-poly(LiMTFSI); poly(lithium) 1-[3-(methacryloyloxy) propylsulfonyl]-1-(trifluoromethylsulfonyl)imide) (poly(LiMTFSI); Jeffamine® copolymerized with polystyrene grafted to poly(ethylene-alt-maleic anhydride) (PEaMA-*g*-(Jeffamine-*co*-PS)); poly(trimethylene carbonate) (PTMC).

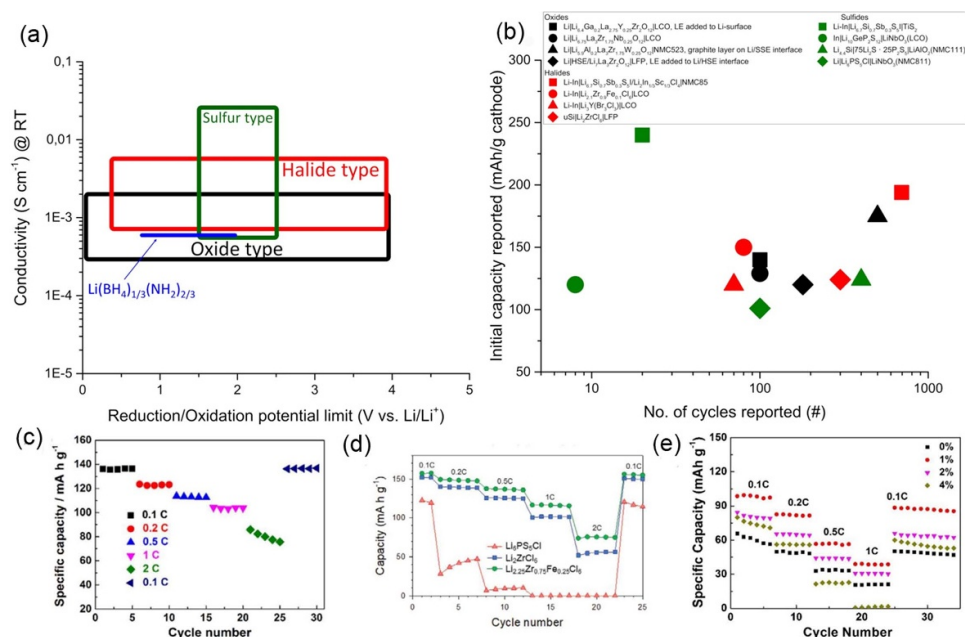


Figure 7. (a) The approximate range of conductivity and reduction/oxidation limits reported for sulfur, halide, oxide and borohydrate type SSE, (b) a selection of the reported capacity and number of cycles reported for different full cell configurations using sulfur, halide and oxide SSEs [77–88]. Full cell capacity retention of (c) $\text{Li}^+|\text{HSE}/\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}|\text{LiFePO}_4$. Reprinted from [80], Copyright (2018), with permission from Elsevier. (d) $\text{Li-InLi}_{2.25}\text{Fe}_{0.25}\text{Zr}_{0.75}\text{Cl}_6|\text{LCO}$. Reprinted from [82], Copyright (2018), with permission from Elsevier. And (e) $\text{Li}^+|\text{Li}_6\text{PS}_5\text{Cl}|\text{LiNbO}_3(\text{NMC811})$, Reprinted from [87], Copyright (2018), with permission from Elsevier.

$\text{Li}_{1+x}\text{Ti}_2\text{M}_x(\text{PO}_4)_3$ ($\text{M} = \text{Al}, \text{Cr}, \text{Ga}, \text{Fe}, \text{Sc}, \text{In}, \text{Lu}, \text{Y}, \text{La}$), were the highest conductivities have been reached when using Al or Sc [89]. The conductivity can reach up to $1.12 \times 10^{-3} \text{ S cm}^{-1}$ and was achieved for $\text{Li}_{1.4}\text{Ti}_{1.6}\text{Al}_{0.4}(\text{PO}_4)_3$ (LATP) using plasma sintering to reach a nano-sized ceramic material [90]. However, due to the reduction instability of Ti^{4+} , the electrochemical stability window (2.65–4.60 V) [91] is too narrow to be used with Li° [92]. By substituting the Ti^{4+} with Ge^{4+} , forming $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) the ESW can be improved to 1.85–4.9 V [91] vs. Li/Li^+ , which means that a protective layer is still necessary if LAGP is used with Li° [89]. Garnets, such as the Li^+ containing $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), have several interesting properties; doping the Zr^{4+} -sites with Nb^{5+} enables a wider electrochemical window, reaching 0 V vs. Li/Li^+ , and enabling Li° anode to be used without protective layers [93, 94]. Doping with Ga, La or Sc has also been shown to increase the conductivity at room temperature to up to $1.3 \times 10^{-3} \text{ S cm}^{-1}$ [92, 95, 96]. LLZO also has good mechanical properties such as a shear modulus of 61 GPa [97] or 15 times higher than that of Li° , which in theory should prevent Li dendrites [98]. However, Li dendrite growth is still a common problem for LLZO electrolytes due to electron tunneling/metal nucleation within the ceramic at the grain boundaries [99]. But as seen in figure 7(b), cycling has been achieved to up to 400 cycles at RT using a NMC523 cathode by adding a thin graphite layer between the Li° and garnet, reducing the interfacial resistance and Li dendrite growth.

4.2. Sulfide-type inorganic SSEs

Sulfides are of interest due to the higher Li^+ conductivity compared to both halides and oxides, explained by the lower electronegativity of the sulfur and larger galleries allowing for a faster Li^+ diffusion [100]. Sulfides also form long-range disordered structures which also greatly facilitates Li^+ diffusion

[101], reaching Li^+ conductivities up to $2.5 \times 10^{-2} \text{ S cm}^{-1}$ at room temperature for $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ [85]. Sulfide synthesis generally requires milder conditions than oxides and can be prepared at room temperature by high-power ball milling [102]. On the other hand, sulfides are more reactive, and have a narrower ESW (approx. 1.5–2.5 V vs Li/Li^+) than oxides and halides [103, 104], as illustrated in figure 7(a). This makes protective coatings necessary for both Li° and high-voltage cathodes, which impacts the performance. Sulfides are also very sensitive to water, releasing toxic H_2S when in contact with humidity, making large dry rooms necessary [103].

4.3. Halide-type inorganic SSEs

Halides have received increased attention due to high Li^+ conductivity, relatively mild synthesis and processing conditions required [105]. The general formula is Li_3MX_6 (M = Trivalent rare-earth element, in with $\text{X} = \text{F}, \text{Cl}, \text{Br}$ and I) and can form a wide range of structures [106]. In general, the highest conductivity is found for halides with the monoclinic structure, reaching up to $7.3 \times 10^{-3} \text{ S cm}^{-1}$ [83]. The electrochemical stability depends mainly on the choice of halide ion and affects the oxidation stability roughly according to $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ [105]. Fluorine containing halide electrolytes show a good oxidation stability up to 6.5–7 V vs. Li/Li^+ , but their conductivity is too low [105]. Chlorine and bromine containing halides offer a good middle of the road stability up to 4 V and good ionic conductivity [107]. Stability against Li° is also a problem for halides and protective layers or the use of alloys are necessary for stable cycling [108].

4.4. Other promising inorganic SSEs

LiPON is an interesting material free of expensive and rare elements [109]. Bulk-type LiPON ($\text{Li}_{3.6}\text{PO}_{3.4}\text{N}_{0.6}$) have shown a conductivity of $10^{-6} \text{ S cm}^{-1}$ at 70 °C and a wide potential window of 0–5 V vs. Li/Li^+ [110]. But the most interesting aspect of LiPON is that it can be sputtered as thin-films and serve as a protective layer to a more sensitive solid electrolyte such as sulfides or LATP [109, 111, 112]. Finally, Lithium borohydrides have shown promising properties [113] such as an ionic conductivity of $6.4 \times 10^{-3} \text{ S cm}^{-1}$ for $\text{Li}(\text{BH}_4)_{1/4}(\text{NH}_2)_{3/4}$ at 40 °C and good cycling stability in LTO half-cells. However, a narrow ESW of 1–2 V vs. Li/Li^+ limits practical applications [114]. LiBH_4 has also been found to work as an additive to $0.75\text{Li}_2\text{S} \cdot 0.25\text{P}_2\text{S}_5$, producing a composite that is stable against Li° and with a factor of ten improvement in ionic conductivity compared to neat $0.75\text{Li}_2\text{S} \cdot 0.25\text{P}_2\text{S}_5$ [115].

To conclude the state-of-art description of the inorganic SSEs, a side-by-side comparison with respect to some important parameters can be seen in figure 8, summarizing the discussion above.

Overall, there are distinctive issues that needs to be resolved for SSEs to be applied in commercial products, for oxides the issues are in many ways related the grain boundaries: they facilitated dendrite growth and the high temperature required to sinter the electrolyte, up to 1200 °C for 36 h for LLZO [116] and 1300 °C for LAGP [117], makes large-scale commercial production difficult. Sol-gel, microwave and plasma assisted techniques has been suggested as methods to lower the synthesis temperature of oxides [89]. The formation of Li dendrites has also been shown to rely on the properties of the grain boundaries which is also related to the processing conditions. It has been shown that applying a force perpendicular to the dendrite growth direction effectively prevents them from short-circuiting the cell [118], the same paper suggests that this could be

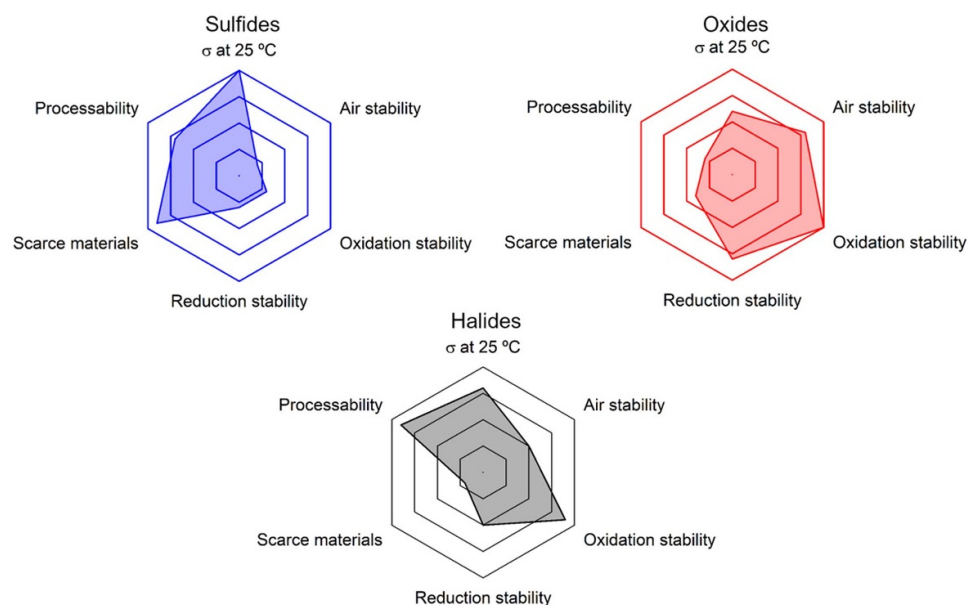


Figure 8. Radar plot of key properties of different classes of inorganic materials: sulfides, oxides and halides. Explanations of the indicators are given below: ionic conductivity (σ), the ability to withstand contact with air without affecting material properties (air stability), electrochemical stability at high/low potentials (oxidation/reduction stability), the need of scarce elements to produce the electrolyte (scarce materials), how easy the electrolyte is to synthesis and prepare (processability).

achieved by making the thermal expansion coefficient non-homogenous in the electrolyte by e.g. doping.

The electrode/electrolyte interfaces are often an issue with oxides, for example the interphase between the Li° and the electrolyte is critical to avoid dendrite formation so some of the results in figure 7 uses drops of liquid electrolyte at both electrolyte/electrode interfaces, to improve the contact which is not viable for an all-solid-state battery (ASSB). But there are also examples of solid-state approaches such as polymer and graphite layers, showing very good results, as shown in figure 7(b). For the cathode interface the problem is to achieve good contact and good Li^+ conductivity through the cathode composite, since most materials cannot tolerate the high sintering temperatures of oxides. To improve the cathode interface mixing the cathode composite with other solid Li^+ conducting materials, such as a polymer [80], instead of the oxide have been suggested.

For sulfides the electrochemical stability needs to be improved [119] and the reactivity towards moisture should be reduced. The overall poor performance of the sulfides seen in figure 7(b) could be explained by the extra coating needed on the cathode material. The only example where a high capacity is reached is for the low potential cathode TiS_2 . In figures 7(c)–(e) it is also clear that the protective layer affects the performance at higher C-rates, despite the sulfide having the highest conductivity of these three materials. There have been some improvements regarding the oxidation and environmental stability by including oxygen in the material, at the cost of a lower conductivity [120]. It is also interesting to note that the highest capacity over extended cycling in figure 7(b) is a composite between a halide and a sulfide [81]. Another practical issue with sulfides is that the synthesis can be quite complicated for industrial applications. With sulfide electrolytes the interfacial challenges are different compared to oxide electrolytes, since no sintering is necessary the electrodes can be pressed together with the electrolyte, ensuring an intimate contact. However, the sensitivity to both reduction and oxidation makes interphacial modifications necessary to protect the electrolyte. Polymer coatings are mostly used to stabilize the interface between

the Li° and the electrolyte [121], besides good stability vs. reduction these layers should be thin, robust and have good Li^+ conductivity. For the cathode material mainly, inorganic materials are used to protect the electrolyte [87, 88], these materials should have a high Li^+ conductivity and be thin.

Finally, halides are promising in many aspects but, like sulfides, more work needs to be done on improving the reduction stability to be able to use Li° as anode material. However, the most important issue to resolve is the use of very rare and expensive elements [105], some work has been done on substituting these elements with cheaper elements such as iron [82]. Computational methods could be a useful tool to evaluate different substitution strategies and their effect on conductivity and electrochemical stability. The interfacial properties of halide electrolytes are more like sulfides than oxides since they do not need to be sintered. For the cathode interface the main issue is to ensure good contact. However, protective layers are still necessary if Li° is used as an anode due to the reduction sensitivity of the transition metal component.

5. Organic/inorganic hybrid SSEs

The combination of inorganic and organic SEs forms the so called organic/inorganic hybrid electrolyte. With different volume ratios of organic and inorganic phases, these electrolytes are classified as ceramic-in-polymer (organic material >50 vol%) and polymer-in-ceramic (>50 vol% inorganic phase) [122, 123]. Both approaches aim to improve the properties of polymer or inorganic electrolytes alone.

5.1. Ceramic-in-polymer hybrid SSEs

Ceramic-in-polymer hybrid SSEs decrease the crystallinity of the organic phase, consequently increasing the amorphous phase compared to that of the polymer alone, enhancing its ionic conductivity (figure 9(a)) [124]. This effect is highly dependent on the type, amount and size of inorganic particles [125, 126]. These particles may be inactive [i.e. Al_2O_3] or active [i.e. NASICON, garnet], depending if they participate in the Li^+ conduction or not. Inactive fillers do not contribute to the conduction of Li^+ cations, but their surface chemistry may impact the ionic conductivity of the electrolyte [127, 128]. Active inorganic particles present a higher Li^+ conductivity than the polymer phase, as described in previous sections; however, the combination in organic/inorganic hybrid SSEs leads to complex Li^+ diffusion mechanisms. This diffusion will likely occur in the organic phase [122, 129]; additionally, the interfacial resistance between both phases will limit their Li^+ exchange [108, 130–132]. The interface between the negative electrode and the ceramic-in-polymer electrolyte is not expected to differ from the properties of the polymer electrolyte alone.

5.2. Polymer-in-ceramic hybrid SSEs

Polymer-in-ceramic hybrid electrolytes allow to improve the mechanical properties and processing of the inorganic phase, reducing the brittleness discussed in section 4 [133]. The higher ratio of inorganic phase increases the

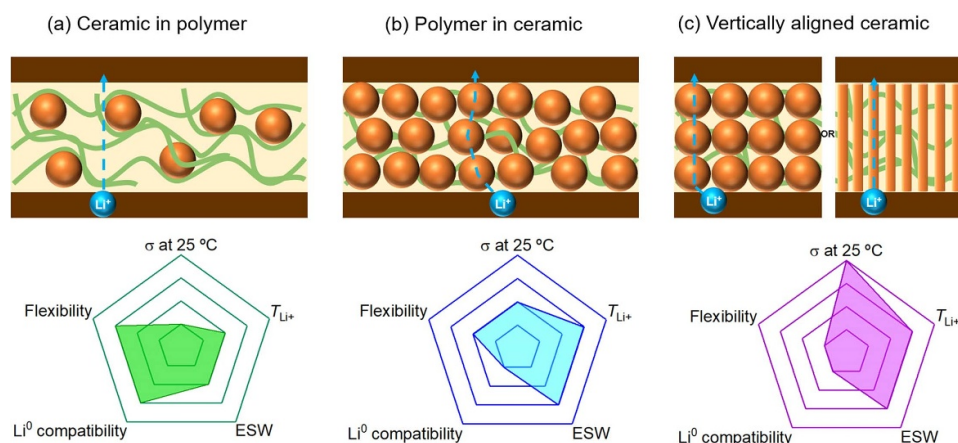


Figure 9. Radar plot of main properties of (a) ceramic-in-polymer, (b) polymer-in-ceramic and (c) vertically aligned ceramic hybrid electrolytes. Explanations of the indicators are given below: ionic conductivity (σ), Li^+ transference number (T_{Li^+}), ESW, compatibility towards Li metal.

ESW generally to values above 4.5 V vs. Li/Li^+ (figure 9(b)) [133, 134]. In addition, the formation of a 3D percolation network creates a pathway for Li^+ transport [122]. Consequently, the resulting hybrid SSE may lead to higher ionic conductivity compared to the sole polymer matrix owing to the higher contribution of the inorganic phase to the ionic conductivity [131, 135]. Nevertheless, the overall ionic conductivity is lower than for the inorganic phase alone, possibly due to the mentioned high organic/inorganic interfacial resistance, the tortuosity of the inorganic pathway and the grain boundaries [130, 131]. Additionally, the interface between the negative electrode and the polymer-in-ceramic electrolyte is complex and may be reactive, depending on the selected ceramic species.

5.3. Structurally ordered hybrid SSEs

In recent years, several studies aimed to circumvent the high organic/inorganic interfacial resistance and the tortuosity of the ceramic phase in hybrid SSEs. These works intended to create direct and vertical Li^+ pathways between the electrodes, usually in the inorganic phase, maintaining a certain polymer content as binder (figure 9(c)). The analysis of tortuosity suggests that vertically aligned structures are the optimal configuration to create pathways with high ionic conductivity, while the polymer phase provides mechanical support and flexibility [136]. These ordered structures generally show improved ionic conductivity ($10^{-4} \text{ S cm}^{-1}$ at room temperature) and ($T_{\text{Li}^+} \sim 0.7$) compared to randomly distributed inorganic fillers in any ratio [137–139]. This is attributed to the low tortuosity and fast Li^+ transportation in the inorganic phase, without any organic/inorganic interface.

The resistivity of the interface between the negative electrode and structurally ordered hybrid SSE will depend on the inorganic ratio; thus, it will show a similar behavior as its parent composition: ceramic-in-polymer or polymer-in-ceramic composites. Nevertheless, due to the structural complexity of ordered structures, their processing and integration into practical devices remains to be investigated.

There are three different approaches in the literature for vertically aligned hybrid SSEs (table 2): (1) orienting inorganic particles, usually via ice-template processing [136, 140], (2) growing aligned 3D structures [137, 141–143], and (3) orienting inorganic nanowires [138, 141, 143]. The latter shows promising

Table 2. Summary of works comprising vertically aligned hybrid SSEs.

Entry	Polymer matrix	Ceramic	Ceramic content (wt%)	Ionic conductivity at 25 °C ($S\text{ cm}^{-1}$)	T_{Li}^{+}	Oxidation stability (V vs. Li/Li^{+})	References
Vertically oriented inorganic particles							
1	PEO-PEG-LiTFSI	Vertically aligned LAGP particles	63%	1.7×10^{-4}	0.56	—	[136]
2	PEO-PEG-LiClO ₄	Vertically aligned LAGP particles	65%	5.2×10^{-5}	—	—	[140]
Vertically aligned 3D structures							
3	PEO-PEG LiClO ₄	Vertically oriented LATP structure	11%	2.1×10^{-4}	0.70	5.5	[141]
4	SN-ETPTA LiTFSI	Vertically oriented LAGP structure	40%	1.2×10^{-3}	0.77	5.0	[142]
5	PVDF-HFP/PEO/LiTFSI	Vertically oriented LLZO structure	—	7×10^{-6}	—	5.0	[137]
6	PEO-PEG-LiClO ₄	Vertically oriented LLTO structure	—	4.7×10^{-4}	0.79	6.0	[139]
Vertically oriented inorganic nanowires							
7	PEO-PEG-LiClO ₄ -LiTFSI	Vertically aligned Al ₂ O ₃ nanowires	—	5.8×10^{-4}	—	—	[138]
8	PAN LiClO ₄	Vertically aligned LLTO nanowires	3%	6.0×10^{-5}	0.42	—	[144]
9	PAN LiClO ₄	Vertically aligned LLTO nanowires	15%	2.4×10^{-4}	—	5.2	[143]

results, as all the current density is concentrated in the nanowires, which offer ionic conductivity values up to 10^{-2} S cm $^{-1}$ [144]. Nevertheless, no works have reported ionic conductivity values for hybrid SSEs higher than those of the inorganic phase alone so far (10^{-3} S cm $^{-1}$).

Overall, organic/inorganic hybrid SSEs present promising prospects; nevertheless, their high complexity Li $^{+}$ conduction mechanisms and preparation routes are important setbacks for their development and stability. Further electrochemical characterization is required to understand the transport mechanisms and advantages of these aligned structures, particularly focused in understanding the Li $^{+}$ transport mechanisms across the electrolyte.

6. Commercialization of SSLMB

A common issue that is relevant for SSLMBs is the cell assembly procedure, which differs significantly from the cell assembly with liquid electrolytes. Tailor-made cell assembly lines will be necessary depending on the type of material. The main difference is the applying of pressure to the cell to densify the electrolyte and ensure an adequate contact between the electrodes and the electrolyte.

The ease of designing cost-effective materials and their up-scaling and processability will set the direction for SSLMBs and the speed of commercialization. When designing a new material, there are several parameters to consider: (1) cost-effectiveness, (2) scalability, (3) processability, (4), air stability/sensitivity. When it comes to the cell assembly, other indicators are of relevance, which are also related to the selected material: (1) contact, (2) pressure, (3) the need for a tailor-made cell design and process, (4) air sensitivity. Not all the material chemistries mentioned in the review are at the same level of maturity and require different development routes before commercialization.

Organic electrolytes are the most cost-effective and easiest materials to process [20]. Polymers have been processed for multiple applications in the plastic industry. For example, extrusion, injection, or 3D printing, can be implemented for the processing of SPEs or composites. For inorganic electrolytes the pressure normally needs to be higher, so the calendaring used for electrodes with liquid electrolytes is normally not enough, and uniaxial or preferably isostatic pressing is recommended which is generally more expensive [145]. Besides, inorganic electrolytes are generally air sensitive materials. Large, high-quality dry rooms could also be necessary to minimize exposure to the atmosphere, making the factories more expensive and energy consuming.

7. Future perspectives

In the present topic review, we give a brief outline on the development of various kinds of lithium-ion conducting SSEs for safe rechargeable Li metal batteries (RLMBs). On the basis of the literature survey and our accumulation in this domain, it is anticipated that the following aspects could be further strengthened in future work.

- (1) In terms of organic SSEs, the chemical structures of organic molecules play a decisive role in determining the overall properties of the electrolytes and the corresponding cell performances. Presently, intensive attention has been paid to the cycling performances of Li metal cells, but the assessment on the inherent characteristics of salt anions and solvents/polymers is still insufficient. For example, the decomposition processes of the sulfonimide anions (e.g. FSI $^{-}$) on the surface of Li metal remain to be elucidated, especially as these anions seem to be very effective in improving the stability of electrode-electrolyte interphases.

- (2) With respect to inorganic SSEs, an intense focus has been put on improving the ionic conductivity which has led to some impressive results. However, significant work is required in the chemical and electrochemical interfacial stability with Li metal electrodes. Future development of inorganic SSEs will explore the fabrication of dense electrolyte pellets free of grain boundaries, further increasing Li conductivity and promoting interfacial stability against Li metal, preventing dendrite formation. Sulfides, halides, and other new chemistries will enable a transition from current processing and interfacial issues toward scalable and electrochemically stable electrolytes.
- (3) For organic/inorganic hybrid SSEs, the addition of ceramic particles (<50 wt%) may improve mechanical and electrochemical properties of the organic SSE. For increased inorganic content, the tortuosity of the inorganic percolating network is the major limitation in terms of ionic conductivity. The implementation of vertically ordered inorganic structures in hybrid SSEs provides an interesting alternative due to their increase in ionic conductivity. Nevertheless, significant research is required in the electrode-electrolyte interphases, particularly with Li metal.

It has to be highlighted that a common problem for the development of SSLMBs is the interphases/interfaces and physical contact between the SSEs and the electrodes, despite the significant progress that has been achieved in the improvement of optimization ionic conductivity and electrochemical stability of SSEs. The interphases/interfaces should be carefully designed and regulated:

(1) by implementing different additives (e.g. new anions or SEI forming additives) in the electrolyte design; (2) by including an additional layer to promote the compatibility of the SSEs and the electrodes (e.g. double layer electrolytes); and/or (3) by surface treatment of the electrodes (e.g. thin protective layers, or particle coatings). The design and implementation of these improved interfaces must follow the principles of avoiding scarce or toxic materials, and offer a competitive cost. The former would limit the use of rare-earth elements and additives which would make cells inappropriate for commercialization (e.g. LiAsF₆). The latter refers to the fabrication cost of these additives, which should not represent a significant increase in the unit cell price. This is directly related to the discussion offered in the previous section (6. Commercialization of SSLMB).

From 2020, lithium is considered a critical raw material, meaning that it is among the most economically important and presents a high supply risk. Therefore, the connection between lithium-based systems and other cation-based rechargeable batteries (e.g. sodium batteries, potassium batteries, magnesium batteries, etc) still needs to be reinforced in future work, particularly considering the importance of these complementary battery technologies to avoid excessive use of lithium. This effectively requires further experimental verifications in other kinds of rechargeable batteries, to testify to the effectiveness of the know-how accumulated in the lithium-based systems.

In summary, with intensive research activities dedicated to the fundamentals of solid-state conductors, the key properties of SSEs required by practical solid-state RLMBs will be significantly enhanced, thereby promoting the commercialization of cost-effective and safe battery technologies for emerging applications.

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