

Toward Sustainable Solid Polymer Electrolytes for Lithium-ion Batteries

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ABSTRACT: Lithium-ion batteries (LIBs) are the most widely used energy storage system due to their high energy density and power, robustness and reversibility, but they typically include an electrolyte solution constituted of flammable organic solvents, leading to safety risks and reliability concerns for high energy density batteries. A step forward in Li-ion technology is the development of solid-state batteries suitable in terms of energy density and safety, for a next generation of smart, safe and high-performance batteries. Solid-state batteries can be developed based on a solid polymeric electrolyte (SPE) that may rely on natural polymers in order to replace synthetic ones to take into account environmental concerns.

This work provides a perspective on the current state-of-the-art of sustainable SPEs for lithium-ion batteries. The recent developments are presented with a focus on natural polymers and their relevant properties in the context of battery applications. In addition, the ionic conductivity values and battery performance of natural polymer based SPEs are reported and it is shown that sustainable SPEs can become essential components of a next generation of high-performance solid-state batteries synergistically focusing on performance, sustainability and circular economy considerations.

1. INTRODUCTION

The current spreading of the implementation of the concepts of digitalization of the society and the Internet of Things requires the development of small portable electronic devices powered by efficient electrical energy storage systems ¹. One of the most widely used energy storage systems that have been integrated into these devices is lithium-ion batteries (LIBs) due to their high specific capacity and long-life cycles when compared to other battery systems ². Other properties of LIBs are their low cost and size, low self-discharge and prolonged service-life when compared to other battery types ³. Further, besides portable electronic devices, they are being used to power electric vehicles (EV) and hybrid electric vehicles (HEVs) ⁴⁻⁵.

Their basic constituents are the anode (negative electrode), cathode (positive electrode) and a separator/electrolyte. The separator is composed of a porous membrane soaked in electrolyte solution (lithium salts dispersed in organic solvent) and its function is to allow the flow of Li ions between the electrodes and consequently to avoid short circuits ⁶. The relevance of the electrolyte solution is to confer the necessary high ionic conductivity between the electrodes, but it is highly reactive and easily flammable, toxic and can leak out of the battery ⁷. In addition, another disadvantage of the electrolyte solution is the formation of a passivating layer, denominated solid-electrolyte interphase (SEI) during the first charge, resulting from the reactions with the anode electrode ⁸. Thus, in order to solve these issues, challenging efforts are being carried out to replace conventional separator/electrolytes by solid electrolytes, main types being organic (polymer) and inorganic electrolytes, in order to obtain solid-state batteries, as represented in Figure 1a).

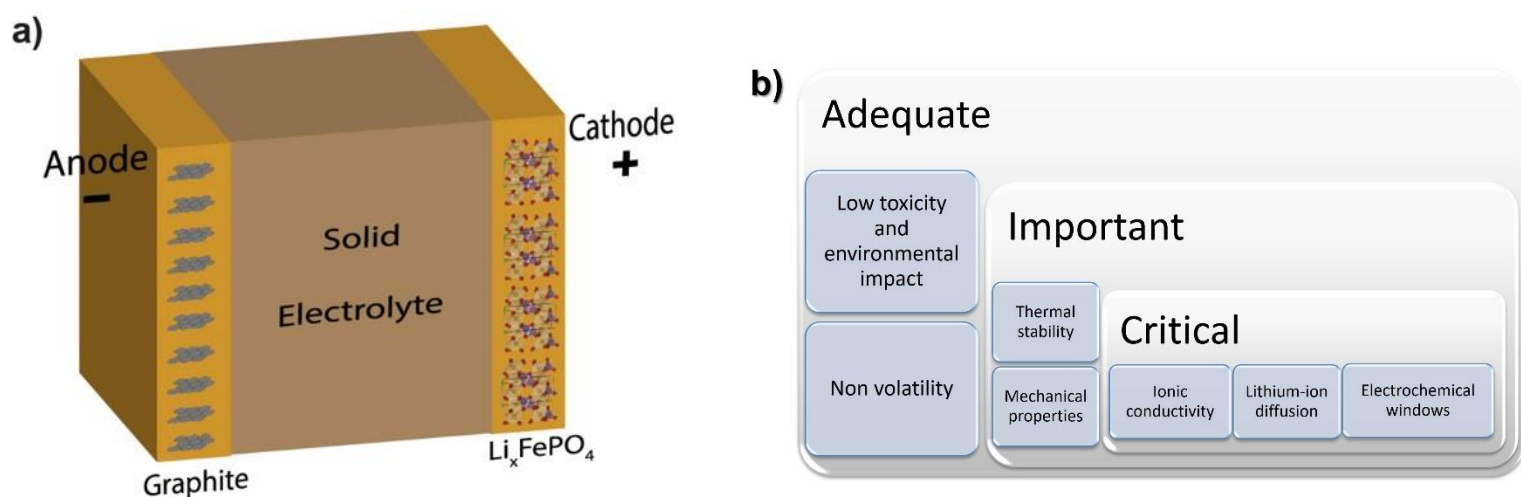


Figure 1. a) Schematic representation of a solid-state battery and b) main characteristics and requirement of solid electrolytes.

The main characteristics of solid electrolytes for battery devices (Figure 1b) are: wide electrochemical stability window, high ionic conductivity and lithium-ion transference number, excellent electrode compatibility and high cyclability. The two main types of solid electrolytes are organic and inorganic. Organic solid electrolytes are those based on polymer composites, whereas inorganic ones are the those based on different ceramic materials such as lithium superionic conductors (LISICON), sodium superionic conductors (NASICON), perovskite-type and garnet. Table 1 shows the many properties of both solid electrolyte types, together with the conventional one based on liquid electrolyte.

Table 1 – Many characteristics of the different electrolyte types

Electrolyte solution	Solid organic electrolyte	Solid inorganic electrolyte
<ul style="list-style-type: none">- high ionic conductivity,- wide electrochemical stability window,- formation of SEI layer in contact with electrodes,- highly reactive,- flammable.	<ul style="list-style-type: none">- low ionic conductivity,- excellent mechanical properties,- high interface resistance,- non volatility- low toxicity	<ul style="list-style-type: none">- high stability in contact with lithium metal,- wide electrochemical window,- high ionic conductivity at > 100 °C,- poor contact with electrodes,- low mechanical properties.

The polymer (organic) electrolytes are still characterized by low ionic conductivity, whereas inorganic ones show poor mechanical stability and difficult integration into large-scale battery production ⁷.

Solid polymer electrolytes (SPE) are thus among the most studied ones based on their large potential and versatility, being mainly composed by a polymeric matrix with one or more fillers that can be ceramic, lithium salts, or ionic liquids ⁹. Fillers are typically added to improve specific SPE properties, the main issue being to increase the ionic conductivity. Further, thermal and mechanical properties are being improved by the inclusion of fillers within the polymer matrix to maintain the necessary flexibility and thermal stability during battery operation ¹⁰. It is to notice that the inclusion of these fillers

typically also reduces the degree of crystallinity of the polymer, allowing also to improve further the ion transport and ionic conductivity ¹⁰. The overall goal is to replace the currently used electrolyte solution in most battery types, taking into account its drawbacks.

The most commonly used polymer matrixes as SPE are poly(ethylene oxide) (PEO) ¹¹, poly(vinylidene fluoride) (PVDF) ¹² and its co-polymers ¹³, poly(ethylene glycol) (PEG) ¹⁴, poly(acrylonitrile) (PAN) ¹⁵ and poly(ethylene carbonate) (PEC) ¹⁶.

The filler incorporated into the polymer matrix can have either active or passive roles with respect to battery electrochemical performance. The most used passive fillers are ceramic, (Barium titanate (BaTiO_3) ¹⁷, Aluminum oxide (Al_2O_3) ¹⁸, Silicon dioxide (SiO_2) ¹⁹, Titanium dioxide (TiO_2)) ²⁰), or carbonaceous (graphite ²¹), with the function of improving properties such as mechanical or thermal stability. The most common active fillers are ionic liquids (1-Ethyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imide, [EMIM][TFSI] ²², 1-Butyl-3-methylimidazolium Chloride, [BMIM][Cl] ²³ and various lithium salts (Lithium tetrafluoroborate (LiBF_4) ²⁴, Lithium hexafluorophosphate (LiPF_6) ²⁵, Lithium hexafluoroarsenate (LiAsF_6) ²⁶, Lithium perchlorate (LiClO_4) ²⁷, and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) ²⁸), among others, with the function of increasing SPEs ionic conductivity, both in terms of its intrinsic value and its thermal characteristics. With respect the materials selection for SEP development, it is also important to notice that the ionic conductivity of SPE is strongly affected by ion-dipole interactions between ion and polymer matrix, as they supports lithium salt dissociation, increasing lithium ion transfer number and mobility ³⁰. The main requirements and characteristics of SPE are indicated in Figure 1b).

Considering circular economy considerations and the growing concern on environmental issues, there is an increasing focus on the replacement of the most used materials by environmentally friendlier ones, even when in some cases they are not so functionally effective. In the following, the recent advances in SPE based on sustainable materials (natural and biopolymers, degradable and chemically recyclable polymers with also sustainable fillers) are presented, representing one of the most interesting and needed challenges in the battery field.

2. LITHIUM-ION BATTERIES: PERFORMANCE AND SUSTAINABILITY

As stated before, a transition to more sustainable materials in LIBs is required in order to reduce the environmental impact caused by a digital society. Despite several advances in this field, the use of these materials leads to less performative and efficient devices, with limited battery capacity and less durability than conventional ones ³¹. Thus, at the present technological stage it is important to find a suitable balance between performance and sustainability, as some applications do not need high performance to work properly. This is the case of implantable biomedical devices, smart cards, Radio-Frequency Identification (RFID) tags, disposable devices or small sensors in remote locations, where batteries do not require high capacity to power those devices but they may need other characteristics such as, for example, being easily degraded or recycled after their end of life ³². So, by applying LIBs with just the needed performance for specific application opens space for a new generation of more sustainable batteries ¹⁰ (Figure 2a).

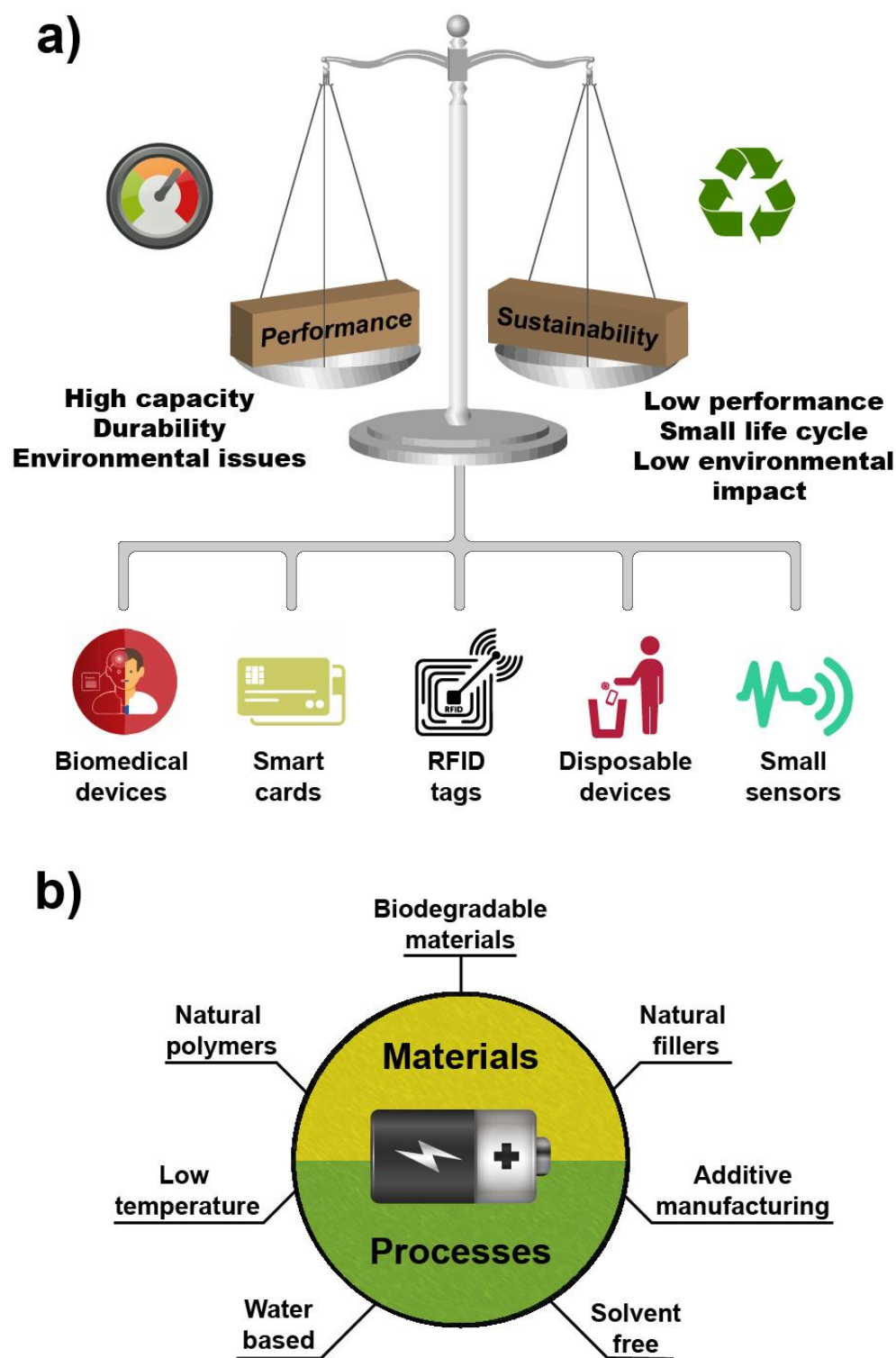


Figure 2. a) Attributes of performance vs sustainability at the technological development stage and b) relevant issues to take into consideration with respect to materials and processes for sustainable SPEs.

This means that research is headed towards properly addressing both targets of performance and sustainability. In particular, SPEs are one of the most studied battery components with this purpose, and the improvement in sustainability can be achieved both with respect to materials selection and processing methods (Figure 2b). At the materials level, the most common approaches are the use of natural polymers, as polymers have a significant presence in battery architecture ³³. Natural polymers are usually easy to produce and process, and are also degradable, which makes them an excellent choice for small lifecycle batteries ³⁴. The selection of materials for other battery components, such as anode and cathode, can also be carried out based on bio-based materials, which eliminates the need of synthetic processing (Figure 2b). Regarding processes, there are also some interesting options. Low temperature processes reduce the overall energetic cost of the battery production, reducing their environmental footprint. Water based, or even solvent free processes also decrease the toxicity of the battery production ³⁵⁻³⁶. These topics are strongly related with the use of natural polymers, as frequently these polymers can be processed with water and at low temperatures. Finally, an approach that is gaining interest in recent years is additive manufacturing, which allows the production of custom and complex structures with defined shapes, in a layer by layer approach, reducing the amount of wasted materials ³⁷.

2.1.Recent advances and current needs in solid polymer electrolytes

The tendency in are of SPE development is to increase structure's complexity. The first SPEs consisted in just one polymer and one filler, however, nowadays it is increasing the development of complex blends of several polymers and various fillers (more one fillers) with distinct functions in the SPEs. As an example, one filler can be selected to improve the ionic conductivity value whereas the other may creates ions pathways, improve

contact with the electrodes and stabilize thermal and mechanical properties³⁸. The most successful approach seems to rely on the use of two complementary fillers, one active filler with the function of increasing the overall ionic conductivity and a passive filler which improves other properties of the SPE, such as mechanical or thermal stability¹⁰. The most used active fillers in recent literature are different kinds of lithium salts, such as LiTFSI³⁹⁻⁴² and LiClO₄⁴³. These salts are responsible for a direct increase in the number of charge carriers and, consequently, of the ionic conductivity. Ionic liquids have also been intensively and increasingly studied due to their capacity to reduce the crystallinity of the polymer matrix, which indirectly increases the conduction⁴⁴.

Recently, an interesting SPE was developed based on poly(ethylene oxide) (PEO) as polymer matrix, LiTFSI and 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, Pyr14TFSI. It was reported that controlling the surface characteristics of the SPE allows to improve the interface with lithium metal and consequently the Li electrodeposition/electrodissolution⁴⁵. In addition, LiTFSI salt was used for the production of different SPEs composed by poly(ethyleneglycol)diacrylate (PEGDA) and a succinonitrile plasticizer, reaching a high ionic conductivity of ~0.43 mS/cm at room temperature⁴⁰, UV photocurable polyurethane acrylate (PUA) with 30 wt% LiTFSI content allowed to reach a maximum ionic conductivity of 0.0032 mS/cm at room temperature⁴¹. Further, ether-based electrolytes in situ polymerized by a ring-opening reaction in the presence of aluminum fluoride (AlF₃) show promising characteristics to overcome the limited oxidative stability and poor interfacial charge transport of current SPE⁴².

There are many options when it comes to passive fillers, including ceramics⁴⁶, carbon based materials⁴⁷ or metal-organic frameworks⁴⁸, each one with distinct effects in the

SPE properties. Zeolites are appearing as a promising option, due to their ability to stabilize the SPE structure, improving the cyclability of the battery ¹⁰.

The improvement of the SPE ionic conductivity is not the only concern in current research. Significant work is devoted to the improvement of the interfacial compatibility with the electrodes to enhance the SPE functional performance ⁴⁹. Other important features as flame retardance ability ⁵⁰, lithium dendrite inhibition ⁵¹, shutdown function ⁵² and self-healing ²² are being tested and implemented for the next generation of advanced SPEs, as represented in Figure 3. Flame retardancy increases the safety of the battery by reducing the risk of fires, usually by limiting the amount of oxygen available for combustion ⁵⁰. Lithium dendrites are a common problem in conventional batteries, in which lithium structures grow at the anode interface with the separator, puncturing it and causing short circuits. Some components can be added to the SPE to prevent their occurrence by improving the solid electrolyte interface (SEI) formation ⁵³. Shutdown function is a feature that creates an insulator layer in the SPE when a given temperature is achieved, preventing battery operation when overheating ⁵⁴. Self-healing batteries allow the repairing of small damages in the battery structure, after a stimulus is applied (temperature, pressure or pH variation) without the need of external intervention ⁵⁵. Thus, these features are critical to improve battery safety and durability.

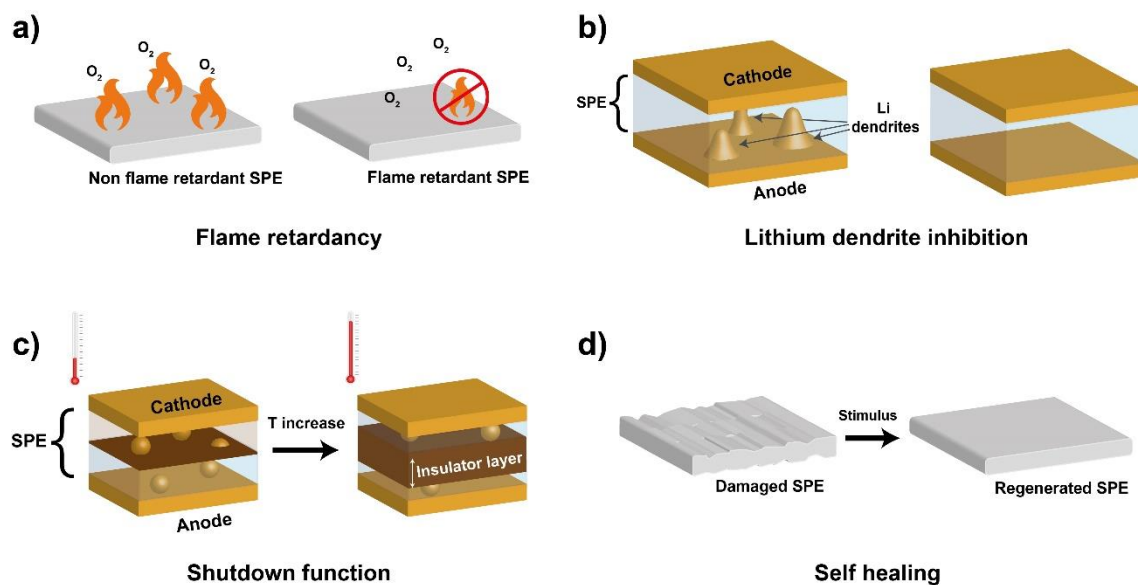


Figure 3. Key attributes under development for SPEs: a) flame retardancy; b) lithium dendrite inhibition; c) shutdown function; d) self-healing.

2.2.Sustainable materials for solid polymer electrolytes

As stated before, polymers have critical importance on the architecture and functional response of SPEs. Many efforts are being placed in the development of SPE based on natural, chemically recyclable and biodegradable polymers, as well as more sustainable fillers, which have the potential to reduce the environmental impacts associated with the widespread use of LIBs. As polymers are the main materials used in SPEs, most research is focused in this specific issue. Table 1 presents some representative sustainable SPEs produced in recent years.

Table 1. SPEs for LIBs developed in recent years based on natural polymers and corresponding fillers. PEO: Polyethylene Oxide, PEGMA: Poly(ethylene glycol) methacrylate

Polymer matrix	Fillers	Preparation Method	Ionic conductivity (S.cm ⁻¹)	Transference number	Battery performance (mAh.g ⁻¹)	Ref

Na alginate, PEO	LiTFSI	Solution casting	$\sim 10^{-4}$ (40°C)	-	152.5 (C/5, 60°C)	56
Cellulose triacetate, PEGMA	PYR14TFSI, LiTFSI	Solution casting	5.24×10^{-3} (25°C)	~ 0.43	125 (C/20, 25°C)	57
Gum tragacanth	LiN	Solution casting	8.28×10^{-3} (25°C)	0.989	-	31
Bacterial cellulose	LiPF ₆	Freeze-drying treatment	2.71×10^{-2} (25°C)	0.48	18 (C/5)	58
Tamarind seed	LiCF ₃ SO ₃	Solution casting	8.37×10^{-4} (30°C)	0.94–0.97	-	59
PMMA, natural rubber	LiBF ₄ , LiI	Solution casting	1.89×10^{-6} (25°C)	0.65–0.96	-	60
Pectin	LiCl	Solution casting	1.96×10^{-3} (30°C)	-	-	61
PEO	Chitosan- silica nanoparticles LiTFSI	Solution casting	1.91×10^{-4} (30°C)	-	147 (C/10, 60°C)	62

The crosslinking of sodium (Na) alginate in a PEO matrix filled with LiTFSI allowed the production of a SPE with significant flame retardant capacity and improved mechanical stability, showing also an stable electrochemical window up to 4.6 V ⁵⁶. Similar results were obtained for a more complex composite of poly(ethylene oxide) monomethacrylate, PEGMA, and cellulose filled with LiTFSI and 1-Butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, PYR14TFSI, ionic liquid, that achieved good cycling stability at room temperature with an average transference number (t^+) of ~ 0.43 and being electrochemically stable up to 5 V ⁵⁷. By combining different lithium salts in a PMMA matrix grafted with natural rubber, it is possible to reduce the crystallinity of the SPE, increasing the lithium transference number and consequently the ionic conductivity

⁶⁰. The use of cellulose has been a target of several studies over the years ³⁸. More recently, bacterial cellulose has been used combined with conventional LiPF₆ electrolyte and freeze dried, to obtain SPEs with high ionic conductivity, leading to low specific capacity ⁵⁸. Tamarind seeds show a good potential to be applied in batteries due to its high conductivity at room temperature ⁵⁹. Pectin has been also studied, allowing suitable ionic conductivity values ⁶¹. The use of gum tragacanth allows the fabrication of water based SPEs with low environmental impact. When filled with lithium nitrate, a solid electrolyte with high ionic conductivity, thermal stability and stable electrochemical window up to 3.4 V is obtained ³¹.

Fillers can also provide a significant contribution to improving SPEs sustainability. In this context, chitosan-silica hybrid nanoparticles have been added to a PEO matrix to reduce the crystallinity and improve Li ion migration, showing a wide electrochemical window of 5.4 V ⁶².

One of the major drawbacks of the current studies in sustainable materials for SPE is the lack of consistent battery results. Despite several suitable results regarding ionic conductivity, the natural polymer based SPEs typically fail to deliver good performance when it comes to battery cycling stability and capacity. This issue must be addressed in order to make this technology effective for practical applications. Also, the operation of the assembled batteries must be adjusted to the utilization temperature of common devices, as most research shows results regarding high temperature batteries, namely above 60°C, which are not applicable in real life situations.

Additive manufacturing (AM) techniques, which can represent an important step in the scope of improving sustainability and performance of the batteries, the latter by enhancing three dimensional ionic routes of the SPEs, are not yet enough investigated.

Finally, sustainable SPEs are essential in the scope of the increasing demand of batteries related to the implementation of the electric vehicle, in order to reduce the carbon footprints and to increase materials recycling⁶³.

3. MAIN CONCLUSIONS AND FUTURE TRENDS

Solid polymer electrolytes, SPEs, are among the most critical components for the development of functional solid-state batteries. These batteries are key for future applications in the scope of the expected growth in the implementation of electric vehicles and the massification of portable electronic devices. The increase in the demand of materials for these applications leads to significant environmental issues that must be addressed. In particular, an important step towards increasing safety and sustainability of next generation batteries is the elimination of liquid electrolytes from the battery structure, another being the implementation of more sustainable materials and processes, allowing to implement adequate recycling strategies, and improving the battery lifecycle in a context of circular economy.

In the particular case of SPEs, significant efforts are being placed in increasing sustainability through the replacement of synthetic polymers by natural polymers, which also allows for the use of less hazardous solvents and processing techniques. However, the literature in the field is not yet enough developed and lacks suitable results regarding battery performance at room temperature, despite the good electrochemical results at the ionic conductivity level. A better understanding on the conduction and diffusion mechanisms, the development of functionalization strategies and compatibilization between both polymer and fillers is needed in order to overcome this issue and allow natural polymers to be widely applied in the SPE field. Other important approaches are the improvement of thermal and mechanical properties of natural polymers and the

enhancement of the interfacial compatibility between the SPE and the electrodes through the application of additive manufacturing technologies, for example.

The integration of these properties with advanced features that are being developed in the SPE field, such as shutdown function or flame retardancy, will allow natural polymers to become key materials for the next generation of sustainable/high performance solid-state batteries.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript

Notes

The authors declare no competing financial interest.

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