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Publisher's version / Version de l'éditeur:
https://doi.org/10.3390/batteries10010024
Batteries, 10, 1, 2024-01-09

batteries

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Review

An Industrial Perspective and Intellectual Property Landscape on Solid-State Battery Technology with a Focus on Solid-State Electrolyte Chemistries

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Abstract: This review focuses on the promising technology of solid-state batteries (SSBs) that utilize lithium metal and solid electrolytes. SSBs offer significant advantages in terms of high energy density and enhanced safety. This review categorizes solid electrolytes into four classes: polymer, oxide, hybrid, and sulfide solid electrolytes. Each class has its own unique characteristics and benefits. By exploring these different classes, this review aims to shed light on the diversity of materials and their contributions to the advancement of SSB technology. In order to gain insights into the latest technological developments and identify potential avenues for accelerating the progress of SSBs, this review examines the intellectual property landscape related to solid electrolytes. Thus, this review focuses on the recent SSB technology patent filed by the main companies in this area, chosen based on their contribution and influence in the field of batteries. The analysis of the patent application was performed through the Espacenet database. The number of patents related to SSBs from Toyota, Samsung, and LG is very important; they represent more than 3400 patents, the equivalent of 2/3 of the world's patent production in the field of SSBs. In addition to focusing on these three famous companies, we also focused on 15 other companies by analyzing a hundred patents. The objective of this review is to provide a comprehensive overview of the strategies employed by various companies in the field of solid-state battery technologies, bridging the gap between applied and academic research. Some of the technologies presented in this review have already been commercialized and, certainly, an acceleration in SSB industrialization will be seen in the years to come.

Keywords: solid-state electrolyte; catholyte; anolyte; Li metal; interface; battery manufacturer; patent application

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Citation: Karkar, Z.; Houache, M.S.E.; Yim, C.-H.; Abu-Lebdeh, Y. An Industrial Perspective and Intellectual Property Landscape on Solid-State Battery Technology with a Focus on Solid-State Electrolyte Chemistries. *Batteries* **2024**, *10*, 24. https://doi.org/10.3390/batteries10010024

Academic Editors: Claudio Gerbaldi and Diana Golodnitsky

Received: 18 October 2023
Revised: 21 December 2023
Accepted: 22 December 2023
Published: 9 January 2024

1. Introduction

As the demand for high-energy-density batteries continues to grow, the use of traditional graphite anode materials has reached its limits, which is far from meeting people's exigencies. One such alternative is the use of lithium metal due to its low redox potential (−3.04 V vs. SHE) and low density (0.53 g cm^{-3}), which can provide a high specific capacity of 3860 mAh g^{-1} and an energy density of 440 Wh kg^{-1}; this represents, respectively, ten times and two times more than the value of graphite anode [1,2]. However, the lithium metal negative electrode is incompatible with the traditional liquid electrolyte, necessitating the use of a solid electrolyte to prevent side reactions and short circuits [3]. There are two main types of SSBs: all-solid-state batteries and quasi-solid-state batteries with some liquid electrolytes. Since some solid electrolytes do not meet the requirements for good ionic conductivity and a good interface with the electrodes, the introduction of some liquid electrolytes into the electrode allows us to overcome this instability. However, the use of some liquid electrolytes should not compromise battery safety. The choice of solid electrolyte greatly influences the performance of the SSB, impacting factors such as power

and energy densities, cost, safety, cyclability, and temperature stability. In order to achieve high energy density, the challenge lies in fabricating dense (non-porous) and thin (<20 µm) solid electrolyte films, as this reduces the weight of inactive materials and the ohmic resistance. Indicators of a good solid electrolyte include high ionic conductivity at room temperature, low interfacial resistance, good chemical compatibility with the electrodes, good mechanical stability, simple and low-cost processability, and a wide electrochemical window greater than 4.3 V to prevent electrolyte decomposition [4]. Additionally, solid electrolytes offer the advantage of a long cycle life since they do not dry up during cycling and remain stable over a wide temperature range, unlike liquid electrolytes that tend to decompose [5]. When used in electric vehicles (EVs), users want fast recharging, similar to the time required for refueling an internal combustion vehicle. Therefore, achieving a high C-rate (high power density) can be more challenging due to the limitation of lithium diffusion in solid electrolytes.

The numerous advantages of solid electrolytes have led the scientific community to show a growing interest in them, as evidenced by the increasing number of scientific publications and patent applications over the past five years. While there are reviews on academic research highlighting the latest innovations and technological developments, with a deeper understanding of the fundamentals of material structure–property relationships and cell operations [6–8], there are none on the patent applications. Therefore, we have organized and summarized the recent knowledge and findings from patents related to solid electrolyte technology. The patent focuses on the challenges in SSB development from a different perspective and reveals research and development (R&D) efforts, with a focus on applied research compared to academic publications, which cover fundamental research mostly.

SSB R&D patent applications are dominated mostly by Asia (Japan, Republic of Korea, and China) thanks to the concentration of the battery industry in this region (Figure 1), which facilitates and encourages R&D and collaboration due to infrastructure and know-how in the field.

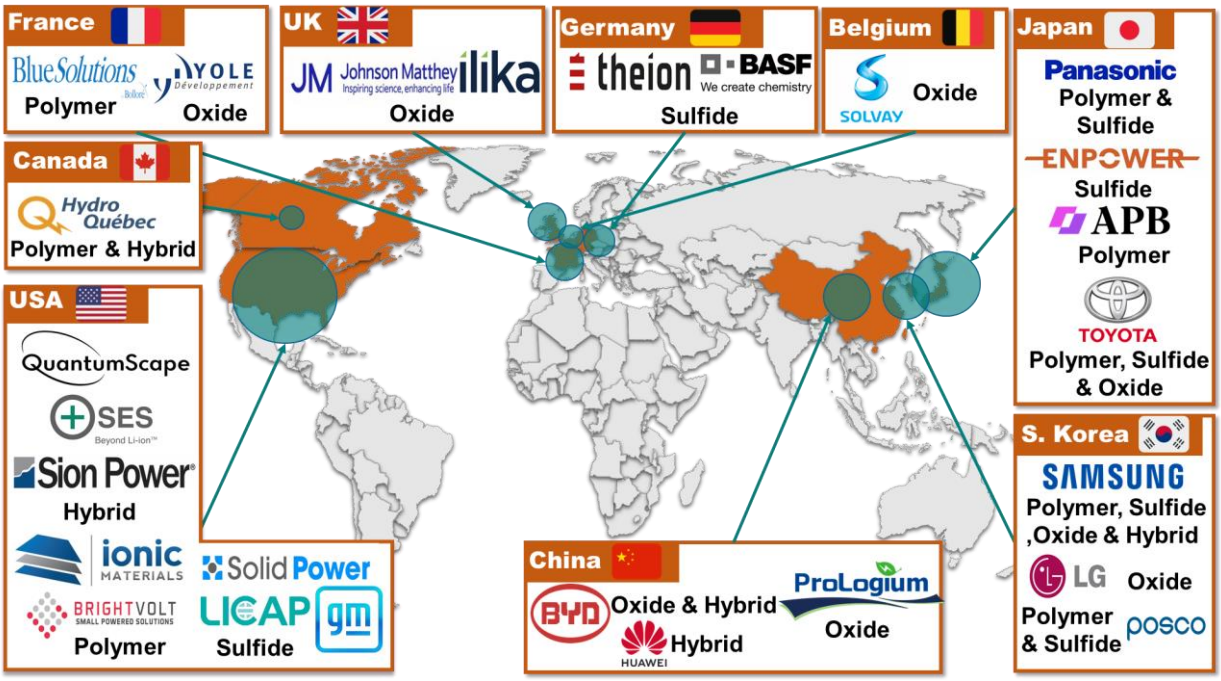

Figure 1. Location overview of companies developing solid-state technology.

The electrification of transport, which is a major challenge in the coming years, is prompting manufacturers to invest. Volkswagen invested USD 300 million into the QuantumScape start-up for the development of oxide-based solid-state electrolyte technology [9]. Ford, BMW, Hyundai, Samsung, and others have invested in solid polymer electrolyte

start-ups like Solid Power and Ionic Materials [10–12]. Numerous manufacturers, such as Nissan, Volkswagen, Toyota, Panasonic, and more, plan to invest in the commercial-scale production of solid-state lithium-ion batteries for electric vehicles [13]. Moreover, the recent announcements from automakers and suppliers wishing to establish themselves in Canada (Volkswagen, Ford, GM/Posco, LG/Stellantis, BYD, BASF, Umicore, etc.) show that the country is well-positioned to become a major player in this emerging market. The North American zero-emission vehicle (ZEV) market alone is projected to reach CAD 174 billion by 2030 [14]. Certainly, the country is on the cusp of seeing a reinvention of the North American automotive industry, which will position Canada and the USA as leaders in the manufacture of electric vehicles with local production, which will save greatly on transportation costs.

In this context, we introduce the latest research progress in solid-state electrolytes, followed by a critical analysis of patent applications. The new and most relevant patents to us are described here. Some patents present several embodiments; in this case, we have chosen the example giving the best results according to our knowledge in the field. The lack of details and limited available data make it difficult to compare electrolytes to each other. In this context, the goal of this review is to provide a comprehensive overview of the various strategies employed by the companies working on SSB technologies and to bridge the gap between applied and academic research. It is important to note that the companies' patents discussed in this paper are not limited to those described herein.

2. Facts and Discussion

The key material of SSBs is the solid electrolyte (SE). Currently, there is a large number of SE materials available, namely oxide electrolytes (oxide glass ceramics, anti-perovskites, peroskites, NASICON, and garnet), sulfide electrolytes (sulfide glass ceramics and argyrodite), halides, hybrids, and polymer electrolytes. Figure 2 provides an overview of the companies using these electrolytes. Toyota is the leading owner of SSB patents, with over 1700 patents, followed by Samsung with approximately 1060 patents, and LG with 697 patents (Figure 2). Research on the number of patents held by each company was conducted using Espacenet database [15], using the keywords "solid electrolyte", "polymer electrolyte", "oxide electrolyte," "hybrid electrolyte", "composite electrolyte", and "sulfide-based solid electrolyte" to perform the analysis. This review will present a summary of the usage of these SEs, along with useful case studies from patents.

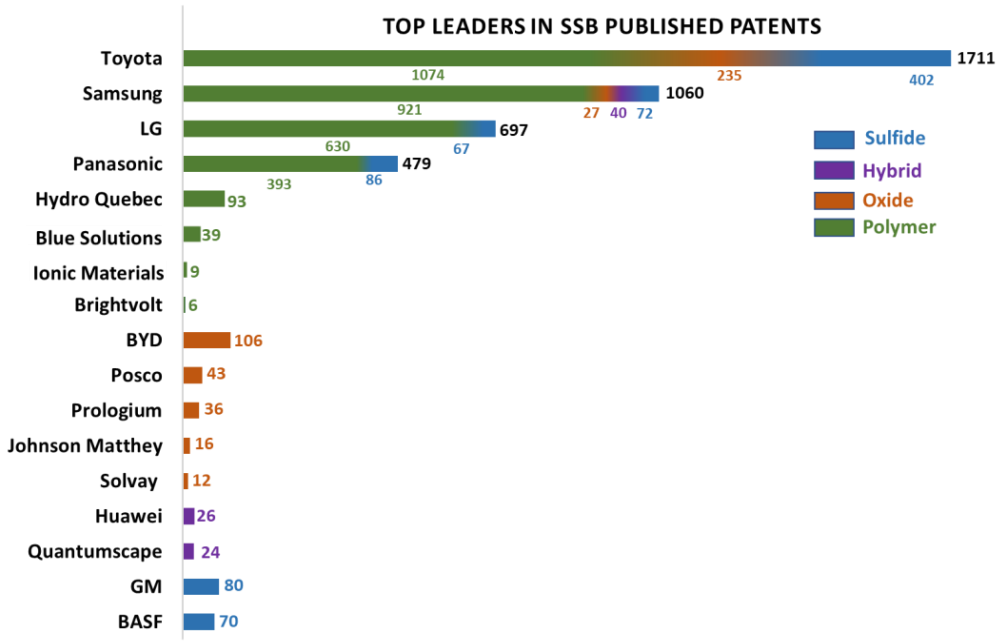

Figure 2. Number of patents related to solid-state technology according to Espacenet [15].

2.1. Solid Polymer Electrolytes

Solid polymer electrolytes (SPEs) are promising materials because of their good mechanical processing and film-forming properties [16,17]. However, the use of SPEs is still limited due to their narrow electrochemical potential window, low transport number, low ionic conductivity requiring elevated temperatures to operate, and incompatibility with lithium metal. In fact, during cycling, the volume change of the lithium metal anode deforms the solid electrolyte and lithium dendrites can be generated, which can cause internal short circuits and a fade in electrochemical performance. Despite the anodic instability and oxidation/decomposition above 4.2 V vs. Li/Li^+ for polyethylene oxide (PEO)-based solid electrolytes, PEO remains one of the most widely studied polymers used in SPEs [18–22]. The technology based on PEO electrolytes, developed by Armand in 1978, was commercialized by Hydro-Québec and is now used by Blue Solutions (Bolloré group) [23,24]. However, PEO-based electrolytes still suffer from a lack of thermal stability, which renders them inadequate when used alone for constructing high-safety and high-temperature-resistant batteries. Many researchers use cross-linked photo/thermal polymerization as a strategy to enhance the safety and elastic properties of PEO-based SPEs [25,26]. This approach improves both the amorphicity and the ionic conductivity of the polymer, which provides one of many possible strategies [27,28]. An alternative approach to enhance battery safety is through the use of a single ion-conducting polymer electrolyte (SICPE) [29,30]. Despite the high lithium-ion transfer number (tLi^+) of the SICP, its ionic conductivity remains relatively low [31]. In order to obtain an SICP with a high ionic conductivity and high tLi^+, the research work on the synergy in the properties of polymers is in a stage of vigorous development [32]. In general, a polymer with a lower Tg value will have a high mobility in the chain segments, which tends to facilitate the migration of cations and, consequently, improve the ionic conductivity of SICPEs. Mecerreyes's research group [25] synthesized a copolymer through the combination of ethylene oxide and ester groups, contributing to the remarkable flexibility of SICPEs. Recently, the same group reported the development of SICPEs exhibiting high ambient ionic conductivity (0.71×10^{-3} S cm^{-1} at 25 °C) and transference numbers of up to 0.85. These advancements were achieved through boron-based polymer formulations [33,34]. Research efforts are also delving into the exploration of complex chain structures, such as tri- and multiblock-copolymers that showcase a range of diverse properties [35,36]. Gerbaldi et al. [37] reported the synthesis of carbonate-based block copolymers with SIC properties. Due to the abundance of carbonate groups, the SICPE demonstrated an impressive tLi^+ of 0.91 and a high stability window of up to 4.8 V. As a well-recognized technique, the Passerini three-component polymerization is a method to form a single new product via a one-step reaction of three monomers under gentle conditions. In this process, anions are incorporated into the polymer matrix, enabling high tLi^+ and preventing the formation of concentration gradients [38,39]. More recently, Passerini's team demonstrated the advantages of a single-ion conducting artificial solid electrolyte interphases based on polystyrene and polymethacrylate [40]. This innovative concept enhances the distribution of current density, reduces the concentration gradients near the lithium metal, and mitigates the direct contact between the lithium metal anode and the separator. SPEs are not only unstable at the anode, but also at the cathode at voltages above 4.2 V vs. Li/Li^+. Many strategies are employed to overcome this problem, such as the addition of inorganic fillers in the positive electrode ($LiAlO_2$) [41], surface protection (or coating) of high-voltage cathode materials by inorganic substances ($LiNbO_3$, Li_3PO_4, metal oxides, and phosphates etc.) [42], and the use of a buffer layer between the SPE and the cathode [43,44]. The different strategies used by companies are reviewed in this section.

Blue Solutions

Blue Solutions is a pioneering French company in the field of SSBs that developed the first commercial lithium metal polymer (LMP) technology. The batteries are produced at the main facilities located in France and Canada. This technology is composed of a PEO-LiTFSI-based solid electrolyte and $LiFePO_4$ (LFP) as the cathode [11]. To counter

the low conductivity of the polymer, the battery is heated between 60 °C and 80 °C, but it can operate within a wide external temperature range of −30 °C to 60 °C. This LMP technology is the only one on the market and is used in Mercedes eCitaro buses, delivering a high energy density of 380 Wh L^{-1} for over 4000 cycles [45]. Previously, this technology was launched in a pilot car sharing program, but without commercial success in the mass-market adoption for passenger cars. Firstly, PEO is unstable at high potential, limiting the choice of the cathode to LFP and resulting in a low energy density of 250 Wh kg^{-1}. Secondly, PEO needs to be heated to perform, which adds extra time to start the vehicle, which makes this technology inconvenient for consumers' needs. This technology fits very well in buses with constant use in full-day operations during the week. The fabrication process of LMP batteries consists of solvent-free extrusion and the coating process of ultra-thin films of anodes, electrolytes, and cathodes. Despite the technology being deployed worldwide, there are still challenges that need to be addressed, such as the need for a large excess of Li metal to ensure good electrochemical performance, the poor ionic conductivity of the electrolyte at room temperature, and the limited electrochemical stability window of the polymer electrolyte, which restricts the choice of positive electrode materials to LFP [46]. Many efforts have been made in recent years in terms of R&D, as evidenced by the growing number of patents. In the electrolyte area, Blue Solutions filed patents on the following subject: a fabrication method and uses of a tri-layer of non-porous and dense fibrous ceramic membrane complexed by lamination between two gel electrolytes [47]. This tri-layer assembly was sandwiched between a positive electrode film and a lithium metal negative electrode. This patent discloses scanning electron microscope (SEM) images, the evolution of the capacity, the coulombic efficiency, and the evolution of the internal resistance according to the number of cycles. Extensive research has also been carried out on solid electrolytes based on cross-linked copolymers [48,49]. These latest patents are well-detailed, with data about the mechanical strength of the copolymer as a function of the mass content of lithium salt, ionic conductivity, glass transition temperature, and the melting temperature as a function of the mass content of lithium salt, cycling curve, and coulombic efficiency according to the number of cycles. Battery life is closely related to the quality of the passivation layer. In order to enhance the quality of the passivation layer, lithium nitrate was added to the electrolyte, as explained in these two patents [50,51]. These patents disclose cycling curves, coulombic efficiency, and lifespan. The mechanical strength of PEO films is low, particularly within the temperature range in which LMP batteries operate. In order to improve the mechanical strength of the electrolyte, a strategy was developed, involving the combination of the PEO polymer with a halogenated polymer (Poly (vinylidene fluoride-co-hexafluoropropylene): PVDF-HFP) [52]. The introduction of the HFP group into PVDF reduces its crystallinity and thus makes it more flexible. In an effort to reduce the internal impedance of the battery, a heat treatment process has been developed. This process involves heating the battery and applying pressure at a specific temperature [53]. The patent discloses the evolution of the internal resistance, capacity, tension over time, the dt/dV function of voltage, and the Ragone diagram (power function of the energy).

Hydro-Québec

The Québec Center of Excellence in Transportation Electrification and Energy Storage (CETEES) commercializes Hydro-Québec's battery technologies, which are protected by over 100 patent families [54]. Hydro-Québec partnered with Mercedes-Benz (formerly Daimler) to develop the SSB for electric vehicles. Hydro-Québec is the first company in the world to use LFP cathodes for grid-scale energy storage.

Actually, the company specializes in non-PEO polymer solid electrolytes and polymer-hybrid ceramic electrolytes, utilizing a sulfonamide-based polymer, as detailed in one of its patents [55]. The polymer is synthesized through an oxidative catalytic reaction involving sulfonamide, one or more diols, copper salt, and, optionally, a lithium base. This patent provides detailed information, including Fourier-transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR), thermogravimetric analysis (TGA), and ionic

conductivity results. In another patent, the company synthesized a polymer obtained by polymerizing diethylene glycol with lithium bis (chlorosulfonyl) imide. This polymer was used in a solid electrolyte and demonstrates good stability between 2.5 and 5 V, and an ionic conductivity of 3.25×10^{-4} S cm^{-1} at 50 °C and 2×10^{-5} S cm^{-1} at 20 °C [56]. The originality of this electrolyte results in the use of an ionically conductive polymer and an aqueous solvent without the use of lithium salt. To compare, other polymers were used as high-voltage stable polymers (HSVP), as described by Zaghib et al. [57]; it consists of a star-type polyether of at least four branches with a hybrid termination (acrylate or methacrylate and alkoxy, allyloxy, or vinyloxy). This polymer is transparent and has a voltage stability higher than 4 V vs. Li/Li^+. The other polymer is described by Harvey et al. [58] and consists of a copolymer of ethylene oxide and at least one substituted oxirane carrying a cross-linkable function. In another patent, the company focused on lithium metal and coated the lithium metal anode with a metal fluoride (i.e., aluminum trifluoride, AlF_3) and fluoro alkylene carbonate (i.e., fluoroethylene carbonate, FEC) in order to avoid unwanted chemical reactions in the lithium metal batteries [59].

In another patent, the company focused on the manufacturing processes and the use of ionic plastic crystals as a solid-state electrolyte in electrochemical cells [60]. Ionic plastic crystals are considered promising candidates for solid electrolytes due to their high flexibility, plasticity, non-flammability, exceptional ionic conductivity, and good thermal and electrochemical properties. However, the conduction mechanisms and the relationship between cations or anions and the physical properties of these materials are not well understood. Hydro-Québec synthesized a multitude of plastic crystals in this patent, accompanied by characterizations such as ionic conductivity, NMR, high-performance liquid chromatography (HPLC), and SEM. The company emphasizes the importance of the combination of high pressure and heat to ensure optimal contact between the electrode and the solid electrolyte, thus avoiding the formation of dendrites, which can cause the battery to short circuit. Another patent describes a process consisting of the preparation of multilayer components (a layer of solid electrodes and an electron-conducting layer) [61]. The solid electrolyte is obtained by compressing ceramic particles, and the electrode is obtained by mixing the electrochemically active material, ceramic particles, and an electron-conducting material, the mixture being solvent-free. The electrode mixture is then applied to the solid electrolyte in order to obtain a bilayer material. From the examples claimed, the materials possibly used in the electrolyte are LAGP ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$), an amorphous polymer ($C_3H_4O_3$) n (QPAC 25 (poly(ethylene carbonate)), vapor-grown carbon fibers (VGCF), and LFP. This solid electrolyte cathode is assembled with a metallic lithium film and a protective layer of PEO-LiTFSI between the metallic lithium anode and the ceramic electrolyte. Hydro-Québec reported a hot-pressing method of at least 50 kg cm^{-2} and a temperature in the range of about 400 °C to 900 °C, in order to densify the bilayer.

BrightVolt

BrightVolt Inc., previously known as Solicore Inc., manufactures thin-film primary SSBs with high-energy $LiMn_2O_4$ cathodes and lithium metal anodes [62]. This company was founded in 2013 in Redmond, WA, USA. Brightvolt filed a patent for a polymer matrix electrolyte (PME) with a high ionic conductivity of 5.5×10^{-3} S cm^{-1} at 50 °C and 3.3×10^{-3} S cm^{-1} at 20 °C [63]. Moreover, this electrolyte exhibits excellent interlayer adhesion and is environmentally safe. The polymer electrolyte is composed of a salt, a polymer, and a solvent to dissolve the salt. We could speculate several possibilities about the components used, such as PEO, PMMA, PVDF, PVDF-HFP, PAN, or polyimide for the binder; while for lithium salt: LiTFSI, LiFSI, $LiPF_6$, or LiBOB. Solicore Inc. was involved in the development of polyimide-based solid electrolytes [64–68] but Brightvolt has not disclosed whether it continues to work with this binder.

Ionic Materials

Ionic Materials focuses on the development of SPEs, anolytes, and catholytes. The catholytes and anolytes refer to an organic gel electrolyte made of an organic polymer or organic liquid enclosed in the electrode space. The company has mastered the key tech-

nologies, such as coating, roll-to-roll processing, and bonding technology of electrolytes and electrodes. Ionic Materials is able to tailor each polymer-based layer to suit the needs of a particular anode or cathode chemistry. The company has developed an excellent global network, with joint development agreements with many partners, including A123 Systems, Hitachi Chemical, Hyundai, Renault-Nissan, and Saft. Its partnership with A123 is particularly worth noting, as the company is now testing Ionic Materials's first-generation polymer in a standard production environment for 10 Ah cells with graphite anodes and NMC 811 cathodes [69]. Recently, Ionic Materials filed a patent on solid electrolytes based on charge-transfer complexes polymer (CTCP) [70]. The CTCP improves the ionic conductivity of the polymer electrolyte by promoting lithium salt dissociation. The formation of CTCP induces an electron density from donor to the acceptor, causing a charge separation at the surface of the polymer, resulting in a lithium-dominant surface. Ionic Materials employed a polymer electron donor (polyphenylene sulfide or polymethylphenylsilane) and a small molecule electron acceptor additive (chloranil). With the CTCP, the electron density is shifted from the polymer backbone to the chloranil. Consequently, the polymer backbones are positively charged, while the chloranil near the backbone are negatively charged. Upon the addition of chloranil, the Zeta potential reversed, and the polyphenylene sulfide particles become negatively charged, causing a negatively charged polymer. The vicinity of the surface of the polymer (diffuse layer) became dominated by Li^+ ions in order to counterbalance the negative surface charge. Some of the Li^+ are physiosorbed to the surface, forming a Stern layer, while other Li^+ ions form a layer with rapid thermal motion, therefore forming a diffuse electric double layer (EDL). Finally, the higher concentration of lithium (due to the use of CTCP) combined with higher lithium mobility (due to the use of additives) is believed to confer high lithium-ion conductivity. Generally, electrolytes containing CTC are stable at high voltages (up to 5.4 V vs. Li/Li^+) due to the formation of a protective CTC layer on the polyphenylene sulfide particles, which prevents the oxidation of the polyphenylene sulfide material [71].

Most studies focus on the cathode/catholyte and the electrolyte development, but it is also important to develop compatible anodes with electrolytes [72]. The anolyte refers to an Li-ion conductor electrolyte mixed with the negative electrode, providing an ionic pathway for lithium through the electrode. In that way, Ionic Materials has demonstrated that the cycling results of a graphite electrode containing an SPE in its composition, known as anolyte, are greatly influenced by the type of binder used at the anode [73]. The SPE used is described in the previous patent (Zimmerman et al. [74]) and is composed of an ionic semi-crystalline poly (phenylene sulphide), an additive such as ZnO, Li_2O, or LiOH, and a doping agent such as an electron acceptor, e.g., 2,3-dicyano-5,6-dichlorodicyanoquinone (DDQ). When the film is extruded into a thin film via a roll-to-roll process at 295 °C, the crystallinity of the polyphenylene sulphide (PPS) increases. The change in film color indicates that ionic CTC are being formed, and the material is activated to become ionically conductive. As the material is in a glassy state, there cannot be any associated segmental motion; therefore, ionic diffusion must be enabled via a different ion conduction mechanism in which segmental motion is not required. The lithium diffusion is two orders of magnitude higher in this solid polymer ionically conductive material than in the PEO-LiTFSI polymer electrolyte. Moreover, at low temperatures, the performance of this solid ionically conductive polymer material surpasses that of typical liquid battery electrolytes. This polymer electrolyte is non-flammable and performs in the range of −40 °C to 150 °C, with low-cost manufacturing and minimal degradation. This solid ionically conductive polymer electrolyte prevents water from degrading the electrolyte, as evidenced by the absence of any capacity fade with the use of CMC: SBR binder in the anode formulation, whereas the use of a PVDF binder with organic solvent (N-méthyl-2-pyrrolidone, NMP) leads to a rapid capacity fade. Thus, the combination of the aqueous binder and the solid polymer electrolyte provides superior electrode performance. This electrolyte is also compatible with $LiFePO_4$, $LiMn_2O_4$, $LiCoO_2$, and $Li_{10}GeP_2S_{12}$ cathodes, and lithium metal anodes [75].

LG Chemical Ltd.

LG Chem was the world's first battery manufacturer to make lithium-ion batteries for electric vehicles since 2009. LG Chem has supply agreements with several automakers, such as GM, Volvo, Ford, Hyundai, Kia, Audi, and Daimler. For automotive systems, LG Chem uses a multilayer SPE that avoids the insufficient mechanical contact between the electrode and the solid electrolyte membrane that would be the source of an air gap increasing the resistance and adversely affecting the lifespan performance of the battery [76]. The best capacity retention was achieved with succinonitrile (SN) plasticizer and LiTFSI as lithium salt, which acts as a phase conversion layer between the electrode and the SPE layer. Subsequently, a porous polyethylene polymer (20 µm) was laminated onto the phase conversion layer. Afterwards, an SPE layer (PEO, LiTFSI, 100 µm) was prepared and laminated onto the porous polyethylene polymer. The SPE layer softened due to the liquefaction of the phase conversion layer with heat, which improved the adhesion between the porous polyethylene polymer layer and the SPE layer.

LG Energy Solution Ltd. patented a coating layer of silver-PEO (Ag-PEO)/LiTFSI that helps the transfer of Li ions toward the current collector [77]. This coating layer inhibits the growth of lithium dendrites and reduces overpotential when forming a seed, thereby improving the lifespan while helping to prevent short circuits. During cycling, lithium is uniformly plated under the coating layer and above the current collector. The optimal quantity of Ag is 20 wt.%; if this content is too high, it tends to form a network with an electrical conduction channel, making it impossible to measure ionic conductivity. Moreover, with a high quantity of Ag, the electrons tend to concentrate on the Ag particles exposed on the top of the coating layer, which accelerates the short circuit of the cell.

In another patent, LG Chemical Ltd. [78] synthesized various solid electrolytes, and the one that offered the best compromise between ionic conductivity (0.11 mS·cm^{-1} at 5 °C) and mechanical stability was prepared by cross-linking multifunctional acrylate-based polymers (trimethylolpropane ethoxylate triacrylate, ETPTA) with PEO to form semi-interpenetrating polymer networks (semi-IPN). This was followed by the addition of a flame-retardant polymer (polyphosphonate-based polymer, Nofia HM1100 (FRX polymer company)), a lithium salt (LiTFSI), and a non-aqueous solvent (methylsulfonylmethane, $DMSO_2$). The synthesized electrolyte has a high solid content (50–70 wt.%) and shows a flame-retardant effect. After mixing and coating the slurry, the electrolyte is melted, followed by a UV photo-polymerization of the molten electrolyte, with 2-hydroxy-2-methylpropipphenone (HOMPP) as a photo-initiator. It was confirmed that excellent ion conductivity, voltage stability, and flame-retardant properties are shown while maintaining the mechanical strength of the solid electrolyte. Meticulous control of the powder quantity is required in order to ensure the quality of the electrolyte. For example, the lower the IPN content, the worse the mechanical resistance, and the higher the IPN content, the lower the ionic conductivity. In the same strategy, LG Chemical Ltd. crosslinked a thiol-based polymer and a fluorinated polyether diacrylate polymer [79]. Therefore, it can be seen that the fluorinated polyether diacrylate crosslinking agent is more effective in mitigating the heat generation of the lithium secondary battery compared to the non-fluorinated agent. Their research demonstrated improvements in lithium-ion conductivity, oxidation stability, and the prevention of leakage by minimizing the quantity of organic solvents used. Moreover, the addition of VC in the composition improved the performance, with a capacity retention of 93.6% after 100 cycles and an ionic conductivity of 2.2×10^{-3} S cm^{-1} at room temperature.

2.2. Oxide-Based Solid Electrolyte

Oxide solid electrolytes are promising because of their favorable ionic conductivity (compared to polymer electrolytes) and a wide electrochemical potential window. The wide variety of oxide-based components (garnet, perovskite, and NASICON) and the possibility of atomic substitution facilitate the improvement of ionic conductivity [80–82]. In addition, oxides exhibit air stability and are more manageable compared to sulfide electrolytes. Most oxide materials are not malleable, which means they cannot be adequately compressed by

pressing alone. Consequently, an additional high-temperature sintering process becomes necessary, as it allows the creation of highly dense layers with fewer grain boundaries and high ionic conductivities. Moreover, the mechanical property of oxides reduces the risk of dendrite penetration because of their high Young modulus [83]. Unfortunately, these compounds are stiff and brittle, which complicates their processability in the usual roll-to-roll process and makes rolling up in the usual cylindrical cell impossible [4]. However, prismatic or pouch cells do not require sheet bending and allow for easy handling of oxide electrolytes. Another challenge is the interfacial stability between the electrodes and the electrolyte, which is complex due to the insufficient wettability and rigidity of the ceramic, causing a void space and an increase in interfacial resistance. A common way to remedy the poor contact is (1) to sinter the powder at a high temperature for a specific duration during which bulk densities and internal pores are greatly reduced, and (2) to apply external pressure to the battery [84]. New advances in these oxide-based electrolytes are presented in this section.

2.2.1. Garnet

Garnet-type oxides have an ideal structure of chemical formula A_3B_2 $(XO_4)_3$ and generally crystallize into a body-centered cubic lattice belonging to the laM space group [85]. Synthetic garnets are mainly known for their magnetic and dielectric properties. It has been observed that certain garnets may have a high lithium ionic conductivity, making them usable as solid electrolytes. Other studies also showed that the ionic conductivity is highest when the garnet has a cubic structure rather than a tetragonal structure [86]. Also, the ionic conductivity is improved when the $Li_7La_3Zr_2O_{12}$ (LLZO) garnet comprises another chemical element, such as aluminum or niobium [87].

Samsung Electronics Co., Ltd.

Samsung Electronics Co., Ltd. is a lithium-ion battery manufacturer for automotive, stationary, and consumer electronic goods. Supply agreements with automakers are not as robust as those of their competitors. Samsung filed more than 10,000 patents related to batteries, and around lithium–sulfur and solid-state electrolytes, surpassing many of its competitors.

Recently, Samsung researchers were active in filing patent applications on garnet-type solid electrolytes. The garnet-type oxide was prepared by combining precursor compounds in stoichiometric amounts to form a mixture, followed by a heat treatment [88]. The garnet-type electrolyte was used as a pellet and was substituted by a small amount of metal with electrochemical activity, such as Ru and Ir. Interestingly, $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ has the highest ionic conductivity (8.36×10^{-4} S cm^{-1} at 25 °C) and interfacial resistance (89 Ω cm^2) compared to $Li_{6.5}La_3Zr_{1.4}Ta_{0.5}Ru_{0.1}O_{12}$ (6.14×10^{-4} S cm^{-1} at 25 °C and 27 Ω cm^2). Moreover, if Ir is used instead of Ru, the interfacial resistance is even lower (14 Ω cm^2). Interestingly, there is no change in the crystal structure regardless of Ru substitution.

The second patent focuses on developing a garnet-type solid electrolyte with interlayers between the anode and the cathode [89]. As it is well known, lithium tends to deposit at the interface between the solid electrolyte layer and the anode during cycling, which can cause a short circuit in the battery. To solve the problem of lithium depositing at the interface between the solid electrolyte layer and the anode during cycling, a first layer of lithium-containing silver and a second layer of graphite are placed between the solid electrolyte and the anode. The porosity of the solid electrolyte is 40% or less and silver is found inside the pores, forming a uniform interface. In order to reduce the interfacial resistance between the solid electrolyte layer and the anode, the strategy is to protonate the surface of the solid electrolyte with an acid treatment. This treatment generates porosity and roughness of the solid electrolyte, which improves the covalent bonding force with the first anode layer. Hence, the covalent and/or ionic bonds are the result of the thermal bonding between the solid electrolyte and the first anode material. The interfacial resistance was 53 Ω cm^2 at 25 °C when the heat treatment of the solid electrolyte layer (LLZO) and Li-containing silver (Ag) was performed at 300 °C.

In order to avoid any sintering and densification of the garnet, Samsung Electronics Co., Ltd., in collaboration with the Massachusetts Institute of Technology (MIT) [90], worked on the wet chemical direct deposition techniques. This work consists of a bilayer solid electrolyte processed by the spray pyrolysis of the dense nitride-LLZO film (non-porous) on a porous yttria-stabilized zirconia (YSZ) substrate, followed by an annealing step at 550 °C. To mitigate volume changes, an ionic liquid is added between the solid-state electrolyte and the positive electrode to create a hybrid lithium battery.

Johnson Matthey

Johnson Matthey, an international specialty chemicals company, was established nearly two centuries ago in London, United Kingdom [91]. The company owns more than 200 battery-related patents, and its Canadian entity, Johnson Matthey Battery Materials Ltd. based in Candiac, Canada, was acquired by Nano One in 2022.

In a recent patent, Johnson Matthey Plc. produced SSBs by using $Li_7La_3Zr_2O_{12}$ cubic garnet material as a lithium-ion conductive solid electrolyte [92]. The preparation follows these steps: (a) grinding a mixture containing one or more precursor compounds in an aqueous solution, with the precursor compounds including lithium, lanthanum, zirconium, and, optionally, dopant elements, to provide a milled slurry; (b) spray drying the milled slurry to produce a spray-dried powder; and (c) conducting an annealing process on the spray-dried powder. This patent disclosed particle size distributions, X-ray powder diffraction (XRD) analysis, and SEM images.

BYD

BYD Co., Ltd. is the predominant producer and only firm possessing its own EV battery manufacturing technology. BYD is also the world's largest manufacturer of electric buses and the fourth largest automotive company behind Tesla, Toyota, and Volkswagen. BYD uses LFP technology in their batteries to reduce overall vehicle costs [93].

In their patent filing, BYD Co., Ltd. shows the formation of lithium dendrite can be suppressed by coating lithium fluoride salt on oxide electrolytes (LLZO) [94]. LiF-coated LLZO is obtained by spray-drying and subsequent sintering at 500 °C. The coated LLZO inhibits the growth of lithium dendrites, resulting in a longer battery cycle life. The electrochemical performance of the coated LLZO shows significant improvement, with good stability observed up to 500 cycles, compared to only 56 cycles for the uncoated LLZO.

Solvay

Solvay is a Belgium-based chemical corporation that is engaged in various sectors, including the development of electrode binders, separator coatings, and electrolyte additives. All these elements enhance battery safety, efficiency, and longevity. The company claims that its polymers can replace metal parts within battery modules for hybrid and electric vehicles. Such a substitution could lead to reduced weight, improved electrical insulation, and mechanical properties [95]. Solvay, in a joint venture with Orbia, will build a new plant to make PVDF, creating the largest capacity in North America.

Solvay, in collaboration with CNRS and Clermont Auvergne University, has filed a patent for protecting LLZO garnet using a fluorination method [96]. LLZO garnet's surface can be altered upon exposure to moisture and carbon dioxide present in the atmosphere, ultimately affecting the conductivity at the solid's interface. The fluorination process involves exposing difluorine gas to an inorganic compound with a garnet-type structure. Importantly, the fluorination does not affect the crystallinity of the inorganic compound, which retains its original crystalline structure.

QuantumScape

QuantumScape develops solid-state ceramic next-generation batteries using an oxide-based solid electrolyte paired with an anode-free battery design and a catholyte. This anode-free concept allows the company to reduce costs associated with lithium metal anode production, and the battery can achieve a higher energy density. QuantumScape has filed more than 200 patents on the fabrication process and cell material components. The company has declared a partnership with Volkswagen, thereby securing the capital to scale up.

QuantumScape patented the sintering of lithium-stuffed garnet thin films over 900 °C [97]. The dense composite films were produced using lithium-stuffed garnet LLZO·x Al_2O_3 (LLZO: e.g., $Li_7La_3Zr_2O_{12}$, x = 0.05 − 1), a polyvinyl butyral (PVB) binder, and di-butyl phthalate plasticizer. Binder removal treatment was carried out under argon at 600 °C, followed by sintering at 975–1125 °C for 1–8 h in an oxygen atmosphere. The resulting sintered film exhibits low surface defects and good flatness, ensuring its application in SSBs. The use of Al_2O_3 improves conductivity (>10^{-4} S cm^{-1} at room temperature) and reduces grain size. Higher conductivity is observed when some of the Zr is partially substituted by higher valence species, such as Nb, Ta, Sb, or combinations thereof. In some examples, the conductivity reaches as high as 10^{-3} S cm^{-1} at room temperature. Finally, these lithium-stuffed garnets can serve as electrolytes, catholytes, and/or anolytes [98]. Recently, QuantumScape disclosed a patent showcasing the achievement of a high-density LLZO ($Li_7La_3Zr_2O_{12}$·0.5Al_2O_3) composite film reaching 4.7 g/mL density through the utilization of various dispersants [99].

2.2.2. Perovskite

Perovskite-based electrolytes have the general formula ABO_3 (A = Ca, Sr or La; B = Al, Ti) [79]. The most studied perovskite electrolyte is $Li_3xLa_2/_3-xTiO_3$ (LLTO), with its bulk lithium-ion conductivity reaching 1 mS·cm^{-1} at 25 °C [100]. The thermal stability of perovskite is lower than that of garnet but higher than NASICON-type oxides. Unfortunately, LLTO is unstable at a low voltage below 1.8 V vs. Li/Li^+, which makes it incompatible with lithium metal and can be decomposed by the reduction of Ti^{4+} [101,102].

Toyota

Toyota has been working on a different SSB chemistry to use either in hybrid models or purely electric cars. Toyota has a joint venture with Panasonic and will begin producing electric vehicles equipped with SSBs by 2025. Recently, Reuters mentioned that Toyota developed a way to make batteries more durable, with a range of 1200 km and that could charge in 10 min [103].

Recently, Toyota Central R&D and Toyota Motor Corp. filed patents regarding the strategy to reduce the reduction potential (begins at 1.8 V) of perovskite-type oxide [104]. This reduction potential is high, and its characteristics are not sufficient to outperform. Therefore, a novel oxide perovskite, containing La, Mg, and W that is chemically stable at a low reduction potential has been synthesized. This perovskite-type ionic conductive oxide, $Li_{1/6}La_{11/18}Mg_{0.5}W_{0.5}O_3$, has an ionic conductivity of 2.0 × 10^{-5} S cm^{-1} at room temperature, with a potential window of 5 V.

2.2.3. NASICON-Type Oxides

The name NASICON comes from sodium (Na) conducting oxides, and Na was replaced by Li to be usable in lithium batteries. The two main types of NASICON electrolytes are LATP ($Li_{1+x}Al_xTi_{2-x}$ $(PO_4)_3$) and LAGP ($Li_{1+x}Al_xGe_{2-x}(PO_4)_3$) [105,106]. These electrolytes have higher ionic conductivity compared to perovskite and garnet-based electrolytes. However, this compound remains unstable toward the lithium metal and suffers from low thermal resistance [107]. Strategies to limit these issues are detailed below.

Prologium

Prologium is a Chinese company that has developed an innovative SSB electrolyte with 90 wt.% ceramic oxide and 10 wt.% gel-based electrolyte. This flexible electrolyte is designed to resist puncture and folding [108]. Prologium is currently working on the development of an SSB with a silicon oxide anode and has established partnerships with Mercedes-Benz and Automotive Cells Company (ACC). The company plans to start SSB production in 2023, with mass production scheduled for 2024 [67].

Prologium Tech Co., Ltd. and Prologium Holding Inc. [109] have patented a contact surface adjusting material for solid electrolytes and composite electrolyte systems to address the issue of high interface resistance in inorganic solid electrolytes. This contact surface adjusting material includes a polymer substrate and additives. The polymer substrate

facilitates the movement of metal ions, while the additives can dissociate metal salts and serve as plasticizers. The composite electrolyte system comprises a first inorganic solid electrolyte, a second inorganic solid electrolyte, an inert ceramic material or an active material, and a first shell that covers the outer surface of the first particle. The first and second inorganic solid electrolytes could be made with LATP. Additionally, the company recently filed a patent regarding the deposition of a protective layer on LATP to prevent the reduction reaction of titanium and enhance electrochemical resistance at low voltages [110].

Posco

Posco is a South Korean company that recently inaugurated a solid electrolyte factory. In a joint venture with the American multinational automotive company, General Motors Co., the company has plans to establish a plant in Bécancour, QC, Canada, for the production of materials for electric vehicles. Furthermore, Posco is investing in Prologium for collaborative component development. As evident from these patents, Posco is actively exploring various chemistries, including sulfide [111], NASICON [112], Na battery [113], etc.

In a patent application from Posco JK Solid Solution Co., Ltd., in collaboration with Jeongkwan Display Co., Ltd. (Seoul, Republic of Korea) [114], they outline an approach that involves using an oxide composed of LAGP and BiSr-MgO. This material does not decompose at high voltages, exhibits high ionic conductivity, excellent thermal stability, and can be prepared in an air environment. The ionic conductivity of LAGP-BiSr reaches 7.3×10^{-4} S cm^{-1} with a glass transition (Tg) of 503.4 °C. When incorporating just 3 wt.% MgO, the ionic conductivity increases to 8.2×10^{-4} S cm^{-1}, with a Tg of 501.2 °C. The addition of MgO enhances high-temperature fluidity and promotes particle binding without reducing the ionic conductivity of the solid electrolyte. Furthermore, sintering can be performed without side reactions by positioning the solid electrolyte between the positive and negative electrodes, even at 750 °C.

2.3. Interphase Layer and Hybrid Electrolyte

Some research focuses on composites of polymers and ceramics, in the hope that they could benefit from the best of both worlds: the ease of processability of polymers, and the hardness and ionic conductivity of ceramics [115,116]. However, this combination may have limitations, such as a lack of mechanical stability, which can prevent the growth of dendrites and may lead to instability when used with lithium metal or at high voltages. As shown below, one of the strategies employed by many companies is to use multilayer electrolytes that do not react with lithium metal and exhibit high stability at high voltages. The multilayer approach reduces the electric double layer (EDL) by adjusting carriers at the solid/solid electrolyte interface [12]. The EDL effect involves the presence of an electron layer on the electrode and an oxygen vacancy layer within the electrolyte [117]. This occurs when negatively charged ions from the electrolyte adsorb to the electrode surface, making the surface negatively charged. To counterbalance this negative surface charge, Li^+ is physisorbed to the surface, hindering lithium mobility. The addition of an interlayer between the electrode and the solid electrolyte reduces the EDL effect and improves flexibility, wettability, and contact. Consequently, this minimizes interfacial resistance and enables a more uniform Li+ mobility at the interface, suppressing dendrite formation [118].

Samsung Electronics Co., Ltd.

Details about this company were presented in the previous section. This battery configuration is based on a hybrid solid electrolyte developed by Samsung SDI Co., Ltd., as represented in Figure 3. This patent describes a catholyte capable of delaying the formation of dendrites on the surface of the negative electrode and improving the ionic conductivity of the positive electrode [119]. This catholyte comprises a cross-linked polymer, a lithium salt, and a liquid electrolyte containing a nitrile-based compound. The patent discloses cycling curves and lifespan figures. In another patent, the solid electrolyte layer was prepared by sintering the LLZO pellet and has a thickness of about 495 µm [120]. The capacity retention at the 50th cycle is excellent, with a value of 99.87%. The limiting current density was

measured by determining the current at which the battery experienced a short circuit. The increase in limiting current density was attributed to the improved uniformity of lithium deposition in the anode or dissolution from the anode during cycling. The best limiting current density in this patent is 2 mA cm^{-2}, while the critical current density of liquid electrolytes can reach up to 10 mA cm^{-2} at room temperature [121,122]. Unfortunately, lithium dendrites are formed at low current densities (below 2 mA cm^{-2}) in SSBs, which can compromise battery safety.

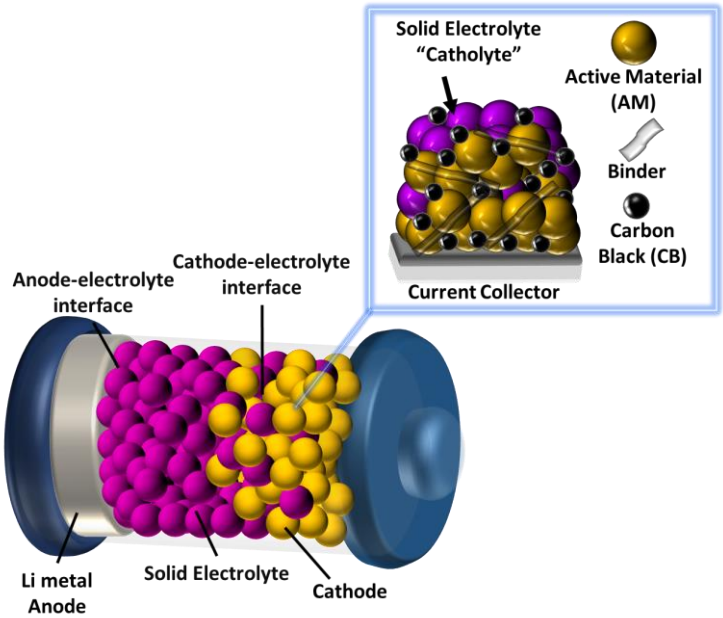

Figure 3. Cross-sectional view of an all-solid secondary battery.

Huawei

Huawei is a Chinese multinational company that develops, produces, and sells telecommunications equipment, consumer electronics, and various smart devices. Recently, Huawei has produced SUV models in partnership with an American company, Seres. The company continues to demonstrate a commitment to innovation in the field of batteries and solid electrolytes, evident by their numerous patents.

To inhibit the growth of lithium dendrites, Huawei Co., Ltd. employs a strategy which consists of coating ceramic materials with an insulating polymer to create a composite solid electrolyte material [123]. The composite solid electrolyte material, $Li_{10}GeP_2S_{12}$ (LGPS), coated with the electronically insulating polymer known as parylene, exhibits a much higher capacity retention rate of approximately 70% after 50 cycles. In contrast, coating with polyethylene results in about 60% capacity retention, and no coating leads to a short circuit occurring after 30 weeks. The coated ceramic is cold pressed at room temperature. The catholyte used contains $LiCoO_2$ positive electrode active material, a buffer coating layer of $LiNbO_3$, LLZO solid electrolyte powder, and conductive carbon black. The performance of parylene is attributed to its high degree of adhesion, the quality of the coating (uniform, continuous, dense, and free of pinholes), and its stability at high voltages (absence of unsaturated bonds). In general, the solid electrolyte coated with an electronically insulating polymer layer isolates the electrons from the negative electrode, preventing them from entering the solid electrolyte. This inhibition of lithium dendrite growth improves resistance to short circuits caused by lithium dendrites and enhances overall efficiency in managing lithium dendrites. They used an acrylamide-based interlayer between the polymer electrolyte and the electrodes to avoid thermal shrinkage when heated and melted [124]. Interestingly, the cell with an aramid interlayer has a capacity retention of 85%, compared to 70% for the cell without interlayer, after 800 cycles. The aramid fiber layer can increase the rupture temperature of the composite separator, reduce the

risk of separator rupture under high-temperature conditions, suppress further internal short-circuit heating, and reduce the probability of battery heating and burning.

BYD

BYD Co., Ltd. synthesized different solid electrolytes; according to the embodiments, the coulombic efficiency and capacity retentions exceed 99% after 200 cycles [125]. The electrolyte is composed of a stacked trilayer structure, consisting of a gel polymer electrolyte (GPE) layer at the positive electrode, an SPE layer (Al_2O_3, PEO, DMF, LiTFSI), and a porous ceramic coating (ceramic particle: ZnO, dispersant: sodium polyacrylate, DMF) at the negative electrode.

Hydro-Québec

Hydro-Québec has patented a hybrid electrolyte comprising inorganic particles (LLZO) and a cross-linked aprotic polymer (a copolymer of PEO) that is stable at voltages exceeding 4 V (vs. Li/Li^+) [126]. In order to enhance adhesion and reduce interface resistance, an intermediate lithium-ion conductive layer is placed between the electrolyte and the negative and/or positive electrodes. The pores between the inorganic particles of the electrolyte and the electrode are filled with the aprotic polymer precursor in its liquid phase before cross-linking. The polymer precursor is an aprotic poly (ethylene oxide) copolymer made of acrylate functional groups. After curing by UV irradiation, a polymer network is formed in the positive electrode and electrolyte layer.

In another patent, Hydro-Québec presents a composite material consisting of inorganic particles, a fluorinated amide, and, optionally, a polymer [127]. The patent utilizes a combination of LITFSI, TEGDME, methyltrifluoroacetamide (NMTFAm), and LATP or LLZO as an inorganic compound of SE. The synthesized composite electrolyte membrane is polymerized using UV irradiation in a nitrogen environment. This patent is well detailed, with figures showing results of infrared spectroscopy, solid-state NMR, Young's modulus, ionic conductivity as a function of temperature, potential as a function of time, electrochemical stability, capacity and coulombic efficiency according to the number of cycles, and galvanostatic charge and discharge curves according to the number of cycles. More precisely, ^{6}Li NMR and IR characterizations show the interaction between the fluorinated amide and the LATP ceramic. In a different patent, LAGP was employed as an electrolyte by mixing it with PVDF-HFP or poly (ethylene carbonate) and a solvent [128]. In this example, a PEO LiTFSI intermediate layer is applied between the lithium anode and the ceramic electrolyte. Subsequently, the cycling of the electrolyte is carried out at a temperature of 80 °C due to the use of the PEO-LiTFSI mixture.

QuantumScape

QuantumScape Corp., in collaboration with Kyoto University, has filed a patent for a chemically cross-linked gel made from polyacrylonitrile (PAN) that is swollen with adiponitrile, resulting in a solid-like behavior [129]. The resulting compound contains amide bonds, which remain stable at high voltages, in contrast to ester and ether bonds, which are unstable at high voltages. This patent provides data on molecular weight, size exclusion chromatography, ^{6}F NMR and the frequency dependence of storage modulus, loss modulus, and phase angle. Recently, QuantumScape Battery Inc. prepared a gel electrolyte by mixing PAN or PVF-HFP, 1M $LiPF_6$ EC-PC, and THF solvent, and depositing the mixture onto a garnet substrate ($Li_7La_3Zr_2O_{12}Al_2O_3$) [130]. QuantumScape cathodes are composed of a combination of conventional cathode active materials (NMC) with gel-based catholytes. The gel electrolyte did not react with garnet, even at high voltages. This is due to the viscosity of the gel, which can inhibit the diffusion of carbon dioxide and slow the diffusion of solvents and salts in the gel. The gel electrolyte was spin-cast on garnet at a low rpm (thick gel) with a PVDF-HFP (50%)-based gel electrolyte that has a lower interfacial area-specific-resistance (ASR) of 65 ohm cm^{-2}. However, at a high rpm, PAN (18.4%) showed a lower ASR of 200 ohm cm^{-2} compared to PVDF-HFP (50% and 30%), with 400 ohm cm^{-2} and 900 ohm cm^{-2}, respectively. This is probably associated with better mechanical stability and homogeneity for PAN-based thin films. It was found that the impedance of the garnet-liquid electrolyte interface was in the order of 5000 Ω cm^2

(Figure 4). These results demonstrate that a liquid reacts with the Li metal anode, forming a lithium carbonate layer and resulting in a high ASR. The garnet was also combined with a solid (a lithium–phosphorus–sulfide electrolyte) or a polymer bonding layer (PEO with $LiClO_4$). These results show that gels, as compared to liquids, solids, or polymers, pair with garnet electrolyte separators to protect the Li metal negative electrode and provide a low ASR interface. The lower interfacial ASR of a gel compared to a liquid is due to the wetting enforcement of the interface with the gel, whereas many liquids do not easily wet the separator interface. This patent provides comprehensive details, including figures illustrating the electrochemical performances, SEM images, impedance analysis, and contact angle measurements.

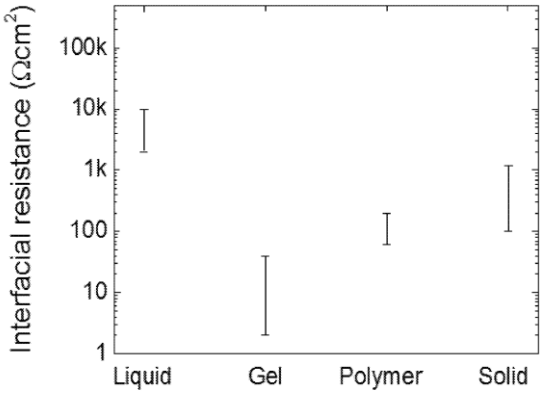

Figure 4. Interfacial impedance ($\Omega \cdot cm^2$) as a function of the type of electrolyte material (liquid, gel, polymer, and solid) at 45 °C from [130].

2.4. Sulfide-Based Solid Electrolyte

In comparison to oxide solid electrolytes and polymer electrolytes, sulfide solid electrolytes have the promising properties of exhibiting high ionic conductivity, being more malleable, mechanically softer, and not require sintering [131]. Sulfide electrolytes, specifically the Li_2S-SiS_2, were among the earliest materials studied as lithium-ion conductors; thereafter, sulfide glass (Li_2S-XS_2 with X = Si, Ge) and glass-ceramic ($Li_7P_3S_{11}$) emerged, displaying high ionic conductivity and a wide electrochemical window [132]. These compounds exhibit high ionic conductivity due to their lower electronegativity and the large-sized sulfur ions. This characteristic enables more mobility for lithium ions within the structure. Hence, sulfide electrolytes are highly promising candidates for high-power-density batteries that can charge and discharge at a high current rate. However, sulfide electrolytes are thermodynamically unstable and react both on the high-voltage cathode and the low-voltage lithium metal side [133]. Additionally, they react with atmospheric water, inducing the formation of H_2S gas [134–136]. Therefore, it is essential to develop strategies to improve air stability to prevent moisture forming on sulfide solid electrolytes. Some of the strategies include doping [137,138], surface functionalization of the solid electrolytes [139], and the use of polymer [140,141]. The doping strategy improves the electrolyte's performance by generating defects in the crystal structure and enlarging the Li^+ transport pathways [142]. Also, the addition of halides can improve the conductivity of glass electrolytes [143,144]. Due to the "mixed anion effect," mixing two distinct anions, such as sulfides and oxides, can be a useful technique to increase the conductivity and safety performance of glass electrolytes [145]. The substitution of an oxygen atom for a sulfur atom in a sulfide solid electrolyte glass can enhance the electrochemical stability of argyrodite Li_6PS_5X (X = Cl, Br, I) against Li metal and cathodes [146,147]. Moreover, this substitution limits the production of H_2S gas when exposed to air. Also, the introduction Li_2O into the sulfide solid electrolytes tends to limit the production of H_2S gas in air and increase the crystallization temperature of $75Li_2S$-$25P_2S_5$ glass-ceramic, thereby enhancing thermal stability [148]. Furthermore, Li_2O does not impact the electrical conductivity of the glass. The substitution of P_2S_5 with P_2O_5 in Li_2S-P_2S_5-P_2O_5 oxysulfide glass electrolytes

improves both chemical stability and ionic conductivity [149]. The study revealed that the ionic conductivity of oxygen sulfide glass electrolytes decreases with an increase in the amount of P_2O_5. In order to avoid direct exposure to moisture, research was undertaken on protecting the sulfide electrolyte by surface functionalization with a coating layer. The core-shell strategy is an effective approach to entrap and limit the decomposition of the sulfide solid electrolytes [150,151]. Interestingly, the functionalization of Li_6PS_5Cl with a superhydrophobic Li^+-conducting protective layer enables the sulfide solid electrolytes to resist extreme water exposure [134]. Additionally, the use of polymer in the formulation is a promising approach to mitigate air instability. In addition to the capability to protect the sulfide solid electrolytes, the polymer enhances the mechanical flexibility and processability of sulfide SEs. Due to the reactivity of sulfide with water, a non-polar organic solvent is required with the use of styrene butadiene rubber (SBR) instead of the usual PVDF and carboxymethyl cellulose (CMC) binder. In order to improve the interface compatibility and limit the mass transfer resistance, sulfide is added to the cathode composition (catholyte), and a coating layer of the sulfide solid electrolytes is deposited on top of the cathode and the anode [152,153]. The different strategies employed by companies are discussed in the section below.

Toyota Motor & Panasonic Corp.

When a sulfide-based electrolyte is used, it can undergo oxidative decomposition (for example, $2Li_3PS_4 \rightarrow Li_4P_2S_6 + 2S + 2Li^+ + 2e^-$), resulting in the formation of $Li_4P_2S_6$, which exhibits high ionic conductivity and facilitates the movement of lithium to the negative electrode. As a result, it is presumed that the precipitation of Li and a short circuit are likely to occur. The voltage at which a short circuit occurred (a drop in voltage) was defined as the "withstand voltage". In this patent, Toyota Motor Co., Ltd. [154], was the first to use a halide solid electrolyte (Li_3YCl_6) in the positive electrode layer. The product of the oxidative decomposition of this halide solid electrolyte ($Li_3YCl_6 \rightarrow YCl_3 + LiCl + Cl_2$ (g) $+ 2Li^+ + 2e^-$) has low ionic conductivity. Therefore, the amount of lithium generated in the positive electrode is reduced because the oxidative decomposition reaction is less likely to occur and to move to the positive electrode layer, resulting in an improved withstand voltage. In order to increase the voltage of the batteries, several unit batteries were laminated in series. With the use of Li_3YCl_6 as a solid electrolyte in the positive electrode and $75Li_3PS_4$-15LiBr-10LiI in the solid electrolyte, the withstand voltage was 55 V, whereas the voltage decreased to 30 V when $75Li_3PS_4$-15LiBr-10LiI is used instead of Li_3YCl_6 in the positive electrode. Using Li_3YCl_6 in both the positive electrode layer and as a component in the solid electrolyte with $75Li_3PS_4$-15LiBr-10LiI remarkably improves the voltage withstand capability(110V).

Interestingly, another patent was filed by Toyota Motor Corp. [155] where no lithium metal is present during cell assembly, which is referred to an anode-free concept. Lithium is extracted from the positive electrode and enables very thin layers without direct handling of fragile, thin lithium foil, and can lead to high energy densities since there is no excess lithium. In this anode-free concept, the dendrites tend to grow along the grain boundaries in the separator, and the voids between the particles and the occurrence of a short circuit may not be sufficiently suppressed. To address these issues, this patent emphasizes the importance of the solid electrolyte's formulation and its impact on the filling rate. For example, if the proportion of the sulfide solid electrolyte (Li_6PS_5Cl) is too low or too high, a sufficient filling factor may not be obtained due to a low solid content ratio and a large amount of solvent, which generates voids during the drying process. Conversely, at a high solid content ratio (>30 wt.%), the sulfide glass could not be completely dissolved in the liquid, and the particles were taken into the separator thin film so that the grain boundaries and voids of the particles themselves were generated. Interestingly, substituting I by Cl in the Li_6PS_5Cl solid electrolyte enhances separator densification, leading to improvements in the filling rate and maintenance rate. It is shown that the optimal filling rate of sulfide solid electrolyte is around 20 wt.%. Moreover, the drying temperature should be near the boiling point of the solvent, in order to have a high filling rate and good ionic conductivity. A low or high drying temperature causes a high filling rate with a large solvent residue and low

Li-ion conductivity. At high temperatures, bumping of the solvent becomes dominant, and the flow rate when the solvent vapor escapes from the separator increases, which generates voids and defects. The figures disclosed in this patent present the capacity retention rate and packing fraction as a function of the solid electrolyte concentration and the lithium-ion conductivity, as well as solvent residues as a function of temperature.

It is worth noting that another patent was filed by Panasonic Corp. and Toyota Motor Co., Ltd. [156] with the use of both halides (Li_3YCl_6) and sulfides ($Li_2S{\cdot}P_2S_5$) solid electrolytes in the positive electrode. Utilizing halide solid electrolytes enhances the thermal stability of the solid electrolyte compared to sulfide solid electrolytes. It also has low reactivity with oxygen, and the amount of heat generated by the oxidation reaction is small. Moreover, the sulfide solid electrolyte has a lower Young's modulus and higher deformability than the halide solid electrolyte. As a result, a lower volume ratio of halide solid electrolyte leads to reduced interfacial resistance at the positive electrode. Hence, it is crucial to identify the right composition that strikes a balance between good mechanical deformability, high thermal stability, and low interfacial resistance.

In a patent jointly filed by Toyota Motor Co., Ltd. and Panasonic Corp. [157], the correlation between the average thickness of the solid electrolyte and the calorific value of the positive electrode material is explored. The catholyte is composed of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ coated with an $LiNbO_3$ protective layer and mixed with the first solid electrolyte ($Li_3YCl_4Br_2$) and carbon black. Thereafter, this coated catholyte is mixed with a second electrolyte ($0.75Li_2S$-$0.25P_2S_5$) and VGCF. As sulfide electrolytes are electrochemically incompatible with lithium metal, a silicon anode was used as an alternative. Hence, the cell uses a silicon and VGCF-based negative electrode with an undisclosed solid electrolyte layer between the cathode and the catholyte, which may be made of $0.75Li_2S$-$0.25P_2S_5$. The catholyte can suppress the resistance thanks to the first solid electrolyte and can suppress the exothermic reaction between oxygen released from the positive electrode active material at a high temperature and the second solid electrolyte. Resistance measurements and the calorific analysis are disclosed in the patent. The calorific test measures the heat generation of the positive electrode using a differential scanning calorimeter. Interestingly, the increase in the thickness of the first solid electrolyte layer around the active materials reduces the calorific value of the positive electrode material.

Another patent from Toyota Motor Corp. [158] provides a method capable of evaluating deterioration caused by cracks in an all-solid-state battery through impedance measurement. While the conventional impedance method can estimate the battery's deterioration state, it faces challenges in evaluating deterioration caused by cracks. In this patent, the upper limit of the frequency range of impedance measurement is set larger than that of the conventional one (usually 1 MHz), and the grain boundary resistance (first resistance) of the solid electrolyte is set based on the arc in the high-frequency region. Further, by comparing the first resistance value with the second resistance value, which is a reference resistance value that is not affected by the crack, the resistance change due to the crack is specified. This enables the assessment of deterioration caused by cracks. The first resistance value corresponding to the grain boundary resistance of the solid electrolyte is calculated based on the arc in the high-frequency region larger than 1 MHz, and the first resistance value and the reference resistance value without the influence of cracks are used.

Following the same principle, Toyota Motor Co., Ltd. filed a patent related to an SSB made with two solid electrolytes to mitigate pinholes that may penetrate the electrodes and cause a short circuit [159]. However, this bilayer solid electrolyte does not completely prevent the generation of cracks, which can propagate from one solid electrolyte layer to another due to the expansion or contraction of the active material during cycling. In this context, the patent introduces a method to inhibit crack propagation by applying pressure to the solid electrolyte layer. In order to evaluate the quality of this electrolyte, the short-circuit resistance was determined by measuring the ratio of the maximum height resistance of the first and the second solid electrolyte layers (Rz1/Rz2). When the ratio Rz1/Rz2 is excessively small, the difference in surface roughness between the first solid

electrolyte layer and the second is excessively large with voids. When the ratio of Rz1 to Rz2 is close to one, it indicates a large contact area between the layers, enabling the electrolytes to readily conform to each other, resulting in high ionic conduction paths between the layers. However, at high ratios, cracks easily propagate, and thus the short-circuit resistance capacity of the all-solid-state battery was reduced. Conversely, when the ratio Rz1 to Rz2 is low, the propagation of cracks in a solid electrolyte layer is suppressed, and the short-circuit resistance capacity increases.

Toyota Motor Corp. has patented a method for suppressing the generation of hydrogen sulfide, which is typically produced by a reaction with moisture in the air [160]. In this patent, Li was substituted with Na to create $Li_{5.1}Na_{0.3}PS_{4.4}Cl_{1.6}$, a monovalent metal element with a lower ionization tendency than Li. This substitution prevents the reaction with water, making it difficult for protons to replace Na. The figures disclosed in this patent provide information on the rate of hydrogen sulfide generation from the solid electrolyte and XRD diffraction analysis.

LG

In order to enhance the water resistance of the sulfide-based solid electrolyte, LG Energy Solution Ltd. and the Tokyo Institute of Technology have patented a method focusing on dew point temperature [161]. Sulfide-based solid electrolytes typically exhibit low water resistance and can react with moisture in the atmosphere, leading to the generation of toxic hydrogen sulfide (H_2S). Ideally, an environment with a dew point of −80 °C is required. However, in the existing lithium-ion battery manufacturing environment (with a dew point of about −45 °C), H_2S generation is possible, posing safety concerns. In order to address this, lithium bromide (LiBr), known as an absorbent for H_2S and H_2O, has been incorporated into the solid electrolyte formulation. The addition of LiBr improves the retention of ionic conductivity after a 2 h exposure at a dew point of −45 °C. Electrochemical cycling results showed that, following exposure of the solid electrolyte at a dew point of −45 °C for 2 h, the all-solid-state battery maintained a high initial charge capacity, initial discharge capacity, and initial coulombic efficiency.

In another patent, the solid-state battery does not contain a negative electrode (anode-free), and an improvement in ionic resistance and lifespan characteristics is observed when heat and pressure are applied to the cell [162]. Effectively, anode-free cells also experience volume changes during cycling, and high stack pressure helps inhibit cell swelling. Cold isostatic pressing is used to create uniform pressure in all directions, resulting in excellent homogeneity and minimizing the risk of damaging the all-solid-state battery with the pressing force. In this patent, LG demonstrates the benefits of heating and pressing the SSB. The solid electrolyte used in this patent is produced by mixing argyrodite (Li_6PS_5Cl) with polytetrafluoroethylene (PTFE) and anisole. The size and quantity of Li_6PS_5Cl solid electrolytes play a significant role [163]. Ionic conductivity tends to decrease as the content of the solid electrolyte decreases, and the transfer rate of lithium ions within the solid electrolyte layer is slowest for smaller-diameter solid electrolytes.

In order to minimize the risk of a short circuit, LG Energy Solution, Ltd. has developed an all-solid-state battery using two types of solid electrolyte layers to enhance the bonding surface between the solid electrolyte layer and the negative electrode [164]. During the charging process, lithium is plated on the anode current collector at the point where it makes contact with the solid electrolyte layer, while stripping occurs during discharge. Over repeated charge and discharge cycles, the size of the lithium attached to the negative electrode current collector gradually increases, allowing lithium dendrites to form. These dendrites can lead to a reduction in capacity and, potentially, a short circuit in the battery. The solid electrolyte in this design consists of a two-layered structure. The first solid electrolyte layer is created by mixing argyrodite (Li_6PS_5Cl) and polytetrafluoroethylene in a weight ratio of 95:5 in anisole. The second electrolyte is made by mixing argyrodite with anisole without the use of a binder and is positioned to face the negative electrode. This bilayer electrolyte design offers enhanced ionic conductivity and improved charging/discharging efficiencies compared to a single-layer design. Consequently, the bilayer

electrolyte promotes better interfacial contact between the electrode and electrolyte, potentially delaying the formation of lithium dendrites and maintaining a higher capacity retention rate.

BASF

BASF is a German multinational chemical company and one of the world's largest chemical producers. Its business segments are diverse, including chemicals, materials, industrial solutions, surface technologies, nutrition, care, and agricultural solutions. The company holds many patents on batteries and solid electrolytes. Recently, BASF announced its intention to construct a precursor material production facility in Bécancour, QC, Canada [165].

This patent filed by BASF [166] aims to enhance ionic conductivity and chemical stability by substituting lithium with other metals in the lithium argyrodite-type compound Li_6PS_5Cl. The introduction of Ca, Al, or Ga as a substitute for Li results in improved ionic conductivity, with values ranging from 3.12 to 3.5–3.7 mS·cm^{-1} without and with the use of metals, respectively. This increase can be attributed to the presence of divalent and trivalent metals, which create vacancies that boost the mobility and diffusivity of lithium ions. Among these substitutions, Ca yields superior ionic conductivity compared to Ga or Al for the same composition. The activation energy plays a critical role in governing ionic conductivity. Li_6PS_5Cl has an activation energy of 0.34 eV, with the lowest activation energy observed for materials that have undergone Ca substitution, specifically $Li_{5.35}Ca_{0.1}PS_{4.5}CI_{1.55}$ (0.30 eV). This reduction in activation energy is a result of the additional vacancies created at the lithium sites. The patent is well-documented with relevant information about XRD, Raman, neutron diffraction, MAS NMR, cyclic voltammetry, SEM, and ionic conductivity/activation energy analysis.

BASF SE, in collaboration with the University of Waterloo, has filed a patent [167] that combines the advantages of oxides, such as a stable structural framework leading to better chemical and electrochemical stability, and sulfides, such as higher ionic conductivity and easier processability. However, sulfide-based solid electrolytes can easily decompose and release H_2S gas due to moisture sensitivity. Surprisingly, it has been found that iodoboro-oxysulfides ($Li_{0.85}B_{0.38}Si_{0.2}O_{0.4}S_{0.82}I_{0.37}$) solid electrolyte exhibit favorable lithium-ion conductivity as well as electrochemical stability in direct contact with lithium metal and chemical stability against air and moisture. Apparently, the increase in the number of silicate groups in the sulfur-based electrolyte provides an improvement in chemical stability with a trade-off in ionic conductivity attributed to the improvement of the glass formation. $Li_{0.85}B_{0.38}Si_{0.2}O_{0.4}S_{0.82}I_{0.37}$ exhibits the highest ionic conductivity of 2.05 mS·cm^{-1} and an electronic conductivity of 5.93×10^{-9} S cm^{-1}. The incremental capacity (dQ/dV) provides information about the irreversible processes occurring during cycling. A peak at 2.15 V vs. Li/Li^+ appears for the first cycle, which completely disappears by the tenth cycle, suggesting the formation of a stable cathode–electrolyte interface with the use of an $Li_{0.85}B_{0.38}Si_{0.2}O_{0.4}S_{0.82}I_{0.37}$ solid electrolyte. The cell maintains a capacity of approximately ~239 mAh g^{-1} (theoretical capacity 240 mAh g^{-1}) for more than 130 cycles, with a high coulombic efficiency, averaging 99.9%, when cycling at C/10. Moreover, the iodoboro-oxysulfides appear promising because it may be reasonably expected that they evolve little to no H_2S within battery operation. This patent is well-documented, similar to the previous one, with XRD results, ionic conductivity data, cell resistance, charge-discharge curves, dQ/dV plots, and rate capabilities.

General Motors Global technology operations

General Motors Company (GM) is an American multinational automotive manufacturing company. GM operates manufacturing plants in nine countries and recently inaugurated the first large-scale electric vehicle manufacturing plant in Ingersoll, On, Canada. GM is very active in the intellectual property landscape associated with batteries and holds numerous patents on polymer-, sulfide-, and oxide-based solid electrolytes. GM has also invested in the SES AI start-up.

Recently, GM Global Technology Operations LLC. filed a patent on an interlayer between solid electrolyte and electrodes [168]. This patent aims to improve interfacial contacts between the negative electrode (comprising graphite or Si-containing high-energy active material, binder, and conductive additives), the positive electrode (based on $LiNbO_3$-coated $LiMn_2O_4$ and LGPS mixed with polymer), the solid electrolyte layer (sulfide-based SSE, such as LGPS), and the capacitor auxiliary interlayers used between electrodes and solid electrolytes. The first capacitor auxiliary interlayer placed between the negative electrode and the solid electrolyte layer includes a capacitor anode active material (for example, activated carbon, metal sulfides (Li_2S), or metal oxides (such as TiO_2)). The second capacitor auxiliary interlayer positioned between the positive electrode and the solid electrolyte layer is made of one or more polymer-based materials (for example, poly (ethylene glycol) methyl ether acrylate with Al_2O_3 and LiTFSI), inorganic materials (Li_2S-P_2S_5-P_2O_5), polymer-inorganic hybrids (PEO, LiTFSI with sulfide-based SSE like Li_2S-P_2S_5-P_2O_5), and metal and/or metal oxide materials (Nb, Al, Si, and/or Al_2O_3). The separator interlayers include a capacitor active material composed of at least one activated carbon (for example, graphene, carbon nanotube (CNT), or porous carbon materials) and conductive polymers like poly (3, 4-ethylenedioxythiophene), known as PEDOT. The capacitor auxiliary interlayer reduces the interfacial resistance between the positive electrode and the solid electrolyte, enables effective ion adsorption and desorption, and provides a fast power response for the solid battery cell due to its capacitor characteristics.

Samsung

Despite the excellent ionic conductivity of sulfide-based solid electrolytes, there is still a need for improvement in oxidation stability at high potentials during charging due to side reactions at the interface of the solid electrolyte in contact with the positive electrode layer. Samsung SDI Co., Ltd. patented the addition of nitrogen to the argyrodite crystal structure ($Li_{7-x-2y}PS_{6-xy}Cl_x$), allowing for the reduction of lithium voids and an improvement in ion conductivity associated with an interfacial stabilization effect by reducing the formation of a resistance layer [169]. The solid electrolyte was synthesized by mixing Li_2S, P_2S_5, LiCl, and Li_3N with a high-energy mill at 25 °C in an argon atmosphere for 20 h. The obtained powder was then heated at 500 °C for 12 h in a vacuum. The solid electrolyte $Li_{6.125}PS_{4.875}N_{0.125}Cl$ exhibited a high conductivity of 2.2 mS·cm^{-1}, with good stability at high voltages and at the interface with lithium metal electrodes, resulting in an improved cycle life and rate characteristics.

In another patent, Samsung Electronics Co., Ltd. worked on the use of a halide solid electrolyte material containing a halogen component instead of sulfide, in order to avoid the generation of hydrogen sulfide [170]. This glass halide solid electrolyte was obtained from LiBr, YCl_3, and NaBr through a mechanical and planetary ball milling process, followed by heat treatment at 550 °C for 12 h. $(Li_{2.975}Na_{0.025})YCl_3Br_3$ exhibits the highest ionic conductivity (3.4 mS·cm^{-1} at 25 °C) among the different electrolytes synthesized. In comparison, $Li_3YCl_3Br_3$, which does not contain an alkali metal element other than the lithium element, has a lower ionic conductivity of 1.5 mS·cm^{-1} at 25 °C. Surprisingly, it was found that the presence of halogen, lithium, yttrium, and alkali metal elements other than the lithium element improves ionic conductivity.

Samsung Electronics Co., Ltd. also filed another patent [171] regarding the inclusion of Br in halide-based solid electrolytes. The ionic conductivity of $Li_9N_2Cl_3$ and $Li_9N_2Cl_{1.5}Br_{1.5}$ at room temperature is 1.68 mS·cm^{-1} and 3.16 mS·cm^{-1}, respectively. These results demonstrate that the addition of a Br dopant significantly enhances conductivity. The halide electrolyte $Li_9N_2Cl_{1.5}Br_{1.5}$ has an anti-fluorite structure with the swapping of anions and cations. This electrolyte was synthesized through the mechanochemical milling of Li_3N, LiCl, and LiBr, followed by the deposition of the mixture on yttria-stabilized zirconia (YSZ). While other derivatives were also prepared, only XRD analysis was disclosed, and no information regarding ionic conductivity or electrochemical tests was presented.

Solid Power

Solid Power develops and manufactures SSBs that use a sulfide-based electrolyte compatible with high-nickel and conversion cathodes, as well as either lithium metal or silicon composite anodes. Solid Power, Inc. has established partnerships with BMW, Samsung, Ford, Hyundai, SK Innovation, and Volta Energy Technologies to advance SSBs. Furthermore, Solvay, a major electrolyte supplier, and Umicore have made investments in this company.

Solid Power Operating Inc. patented a study regarding the impact of adding a rheology-modifying component in the catholyte [172]. The addition of this rheology-modifying component prevents particle agglomeration and reduces viscosity while maintaining a high solid-to-solvent ratio. A high solid-to-solvent ratio is desirable for the rapid and uniform evaporation of a solvent during drying to prevent electrode cracking, consequently enhancing electrochemical performance, as evident in the images and electrochemical tests disclosed in the patent. The most effective rheology-modifying component comprises a poly (styrene-ethylene-butylene-styrene) block copolymer (SEBS) and a poly (styrene-butadiene-styrene) block copolymer (SBS). The solid-state electrolyte is a sulfide-based electrolyte comprising lithium, phosphorus, and halogen compounds. The cathode active material is NMC and the anode is selected from materials such as Si, Si alloys, graphite, Sn, Li, and lithium alloys.

In another patent, they synthesized an Li_6PS_5Cl argyrodite-type crystal structure, and observed an improvement in ionic conductivity when Li_2S is used as a starting precursor [173]. In yet another patent, they found that the sulfide-based electrolyte with antimony (Li_4SbS_4I, $Li_4Sb_{0.75}P_{0.25}S_4I$) exhibits a conductivity of 0.525 mS·cm^{-2} at room temperature. These values showed a slight decrease when the electrolyte was exposed to ambient conditions compared to the electrolyte formulation without antimony [174]. In a recent patent, oxygen was incorporated into the Argyrodite electrolyte formulation through water during the synthesis process [175]. The water is present during the milling of the solid electrolyte precursors and transforms into lithium–oxygen species and H_2S during electrolyte synthesis. Surprisingly, the presence of water unexpectedly improved both the ionic conductivity and the first coulombic efficiency. This enhanced performance might arise from a more effective connection between the cathode and electrolyte materials. Furthermore, the solid-state electrolyte material could establish a more stable interface with the cathode material, thereby reducing the degradation of the cathode material. When the electrolyte material itself contains some oxygen content, particularly near the surface where it interfaces with an oxygen-containing cathode material, the driving force for reactions diminishes, thereby resulting in fewer interfacial reactions.

3. Outlook

The extensive number of patents on solid electrolytes, published by numerous start-up companies and large corporations worldwide, highlights the potential of this emerging technology. This review consolidates the latest advancements in solid electrolytes and provides insights into materials considered promising by the industry. SSB technology is categorized into three main groups: polymers, oxides, and sulfides. Regardless of its chemistry, a solid electrolyte must satisfy two key metrics: high ionic conductivity at room temperature and high electrochemical stability. Figure 5 compares the ionic conductivity and electrochemical stability of various solid-state electrolytes, and also compares them with those of conventional liquid electrolytes. Polymer-based electrolytes have been on the market for over a decade, with Blue Solutions leading the way. This solid Li-metal polymer (LMP) battery boasts low manufacturing cost and strong compatibility with electrodes. However, the need to heat LMP batteries to overcome the low room temperature ionic conductivity of PEO-based electrolytes has driven companies to explore other polymer options. Ionic Materials, for instance, employs poly (phenylene sulphide) in their electrolyte and anolyte formulations in order to tackle the challenges associated with commercializing their technology. This innovative polymer electrolyte exhibits superior performance and voltage stability compared to PEO-LiTFSI-based electrolytes. Surprisingly, this polymer-

based electrolyte even outperforms typical liquid battery electrolytes at low temperatures. LG Chemical Ltd. utilizes polyacrylates with excellent ion conductivity, voltage stability, and flame retardancy. However, this battery technology, while enabling the use of Li metal and thus increasing the energy density of the battery, still incorporates organic components that do not address inherent safety concerns, particularly without the use of any flame retardants or other safety measures.

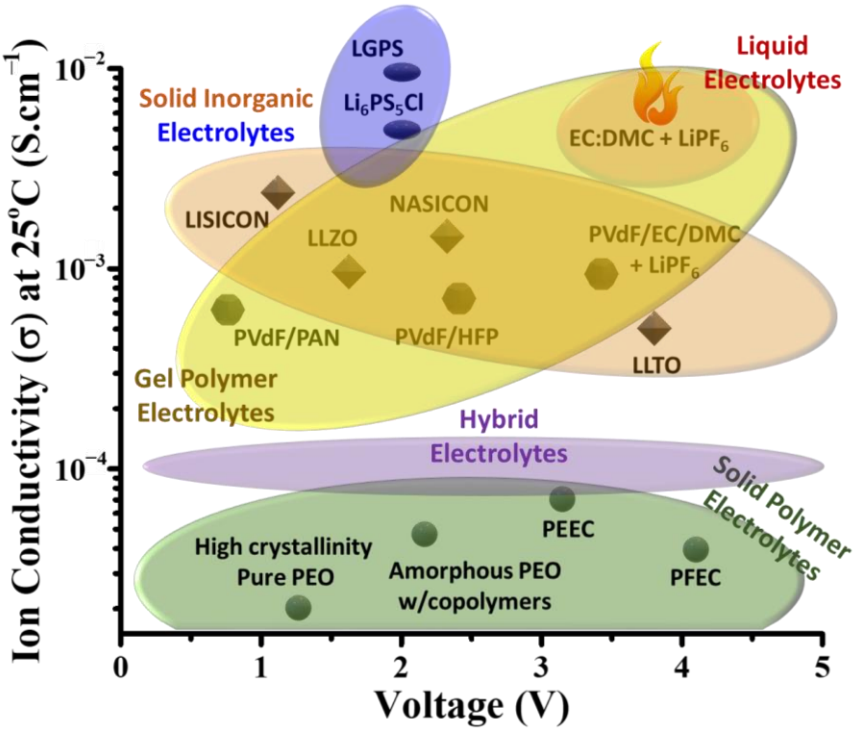

Figure 5. Li-ion conductivities and suitable voltage windows of different electrolytes. Adapted with permission from Ref [41].

Other research groups focus on inorganic electrolyte materials to address the inherent safety issues of organic components. The advantage of these electrolytes lies in their higher ionic conductivity compared to polymer electrolytes. Within the solid-state battery patent landscape, Toyota is the primary Japanese company. Toyota has co-filed numerous patents with research organizations and companies, establishing a robust collaborative network. Consequently, Toyota leads all other applicants in solid electrolytes and lithium-ion batteries as a whole. Here, we have summarized some of Toyota's recent patents on sulfur and oxide solid electrolytes, including the use of halide as catholytes (to prevent dendrite formation), the combination of emerging halides and sulfides in catholytes (to improve thermal stability and reduce interfacial resistance), the partial substitution of Li by Na in a sulfur-based electrolyte (to suppress the generation of hydrogen sulfide), and the synthesis of a new oxide perovskite ($Li_{1/6}La_{11/18}Mg_{0.5}W_{0.5}O_3$) with a wide potential window (5 V vs. Li/Li^+) and high ionic conductivity (approximately 2.0×10^{-5} S cm^{-1}) at room temperature.

One approach to enhance the ionic conductivity of oxides is substitution. Samsung replaced Zr with Ru in the garnet-based structure, resulting in improved interfacial resistance. Substituting with Ir further reduced interfacial resistance. Additionally, Samsung patented the use of a halide solid electrolyte material containing a halogen component to prevent the generation of hydrogen sulfide, and the addition of a Br dopant in a halide-based electrolyte improved ionic conductivity. QuantumScape has partially substituted Zr in LLZO with elements like Nb, Ta, and Sb, in order to enhance ionic conductivity. Solvay stabilized the LLZO surface through fluorination to prevent moisture contact and improve conductivity.

On the other hand, Posco employed an air-stable LAGP-based oxide, introducing BiSr and MgO in order to improve ionic conductivity without decomposition at high voltage.

While recent advancements in ionic conductivity and electrochemical windows are promising, the interface stability between the electrode and electrolyte remains a critical concern. Samsung is actively developing a garnet-type solid electrolyte with silver–carbon interlayers between the anode and the electrolyte, in order to prevent lithium metal dendrite formation. BYD, on the other hand, coated oxide electrolytes (LLZO) with lithium fluoride salt to suppress dendrite formation. Prologium addressed interfacial issues by introducing a polymer and an additive to adjust the contact surface of the LATP-based solid electrolyte.

Furthermore, these electrolytes need to be long-lasting, thin, and cost-effective in terms of materials and manufacturing processes. However, achieving low thickness with conventional sintering techniques for inorganic compounds is challenging. Thin inorganic electrolytes tend to be brittle and prone to cracking, making processing difficult. This issue can potentially be mitigated by applying constant pressure. Alternatively, a viable compromise is the use of hybrid electrolytes, which can facilitate the roll-to-roll process. Hybrid electrolytes offer advantages in terms of enhanced safety, improved ionic conductivity, better thermal stability, and resistance to compression. For optimal ionic transport, some polymer compositions may require the application of specific temperatures.

Samsung has developed a hybrid solid electrolyte, combining an LLZO pellet that is not in direct contact with lithium metal but is in contact with a second layer of anode made of Ag, polymer, and lithium salt. This configuration reduces interfacial resistance and increases limiting current density. Huawei employed an insulating parylene coating on LGPS electrolyte, providing strong adhesion, uniform coating quality without pinholes, and good stability at high voltages, with an absence of unsaturated bonds. Hydro-Québec also developed a multilayer electrolyte to improve adhesion and reduce interfacial resistance between the LLZO-based electrolyte and the negative and/or positive electrodes. While many polymer and hybrid electrolytes use PEO and PVDF, QuantumScape innovatively uses a PAN-type gel polymer on a garnet substrate ($Li_7La_3Zr_2O_{12}Al_2O_3$) to reduce interfacial resistance compared to PVDF-HFP-based gel.

Sulfide-based solid electrolytes have aroused significant interest from various companies due to their higher ionic conductivities and ease of processability. In an effort to increase the ionic conductivity of the argyrodite-type electrolyte Li_6PS_5Cl, BASF conducted substitutions, replacing Li with Ca, Al, or Ga. Notably, BASF discovered the iodoboro-oxysulfides $Li_{0.85}B_{0.38}Si_{0.2}O_{0.4}S_{0.82}I_{0.37}$, which show promise as electrolytes with high ionic conductivity, excellent compatibility with lithium metal, and chemical stability against air and moisture. Sulfide-based electrolytes often exhibit instability at high potentials. Samsung addressed this challenge by doping the argyrodite structure with nitrogen, leading to $Li_{6.125}PS_{4.875}N_{0.125}Cl$. This nitrogen doping improved ionic conductivity and provided interfacial stabilization. GM Global introduced capacitor auxiliary interlayers to enhance interfacial contacts between electrodes and solid electrolytes. To ensure the optimal performance of sulfur electrolytes, the key appears to be in developing a multilayer structure to stabilize the interface with electrodes and utilizing chemicals that remain stable in the presence of air. More efforts are still required to optimize the manufacturing process for these electrolytes while preventing the generation of toxic hydrogen sulfide gas.

The comprehensive performance of the electrolyte could be enhanced by adding active fillers, overcoming the single component defects. The composite characteristics were influenced by five main aspects that improve the mechanical strength, conductivity, and interfacial stability, including: morphology, content, arrangement, type, and surface groups of the fillers. Given their superior integrative performance, composites have been extensively studied in solid-state batteries assembled with high energy density anodes and cathodes [176].

Despite the aforementioned progress, it remains a need to develop batteries with high rates (>10 mA cm^{-2}), in order to compete with liquid electrolytes. Additionally, the manufacturing requirements of these electrolytes differ from those of traditional lithium-

ion technology, necessitating a re-evaluation of the entire process, which can potentially increase manufacturing costs. In the short term, we believe that hybrid technology offers the best chance for commercialization, alongside technologies based on modified polymer-based electrolytes. Looking ahead, we anticipate a multitude of solid-state electrolyte materials will enter the marketplace once the challenges related to the processability of oxides and the stability of sulfides are overcome. Ultimately, the sustainability and cost of the final product, including the use of sustainable, low-cost elements and the adoption of cost-effective manufacturing processes, will determine the commercial success of these technologies.

4. Conclusions

The world is increasingly realizing the significance of clean energy technologies in mitigating greenhouse gas emissions. In order to facilitate the widespread adoption of electrification in various sectors, including transportation, it is essential that high-quality energy storage materials that can meet the growing global demand for clean energy are developed. Among the various advancements, all-solid-state batteries (ASSBs) have emerged as a highly promising option to enhance both the safety and energy density of batteries.

Recent collaborations between battery manufacturers and the number of filed patents indicate that solid electrolyte technology holds significant potential as the next generation of battery technology. However, it is important to note that this technology is still in its early stages and will continue to evolve in the future. In order to explore new possibilities and drive innovation in the field of solid electrolytes, it is crucial that awareness is raised not only through academic publications, but also through patents. Asian companies like Toyota, Samsung, LG, and Panasonic have demonstrated their expertise in solid-state lithium batteries, as reflected in the multitude of patents they have secured. Ongoing research is being conducted on various types of solid electrolytes, including oxide, sulfide, and polymer-based materials. However, before these electrolytes can be successfully implemented in practical systems, technical challenges must be addressed through further efforts. Encouragingly, there have been promising results from small-scale prototype experiments.

However, the ability to bring this technology to the market will depend on the capacity of companies to scale up production to larger multi-stack cells. To remain competitive, companies must thoroughly reconsider the battery formation procedure and not solely focus on research aspects related to the improvement of power and energy density. Given that battery development is an interdisciplinary field, collaborations among different stakeholders will facilitate a better understanding of specific requirements. Overall, we are convinced that a breakthrough will happen in the future with the commercialization of a variety of solid electrolytes.

Author Contributions: Writing—original draft and editing, Z.K.; writing—review and editing, M.S.E.H., C.-H.Y. and Y.A.-L. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: We would like to thank the Office of Energy Research and Development (OERD) at the Natural Resources Canada for their financial support.

Conflicts of Interest: The authors declare no conflicts of interest.

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