Recent Progress in Flame-Retardant Polymer Electrolytes for Solid-State Lithium Metal Batteries

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Abstract: Lithium-ion batteries (LIBs) have been widely applied in our daily life due to their high energy density, long cycle life, and lack of memory effect. However, the current commercialized LIBs still face the threat of flammable electrolytes and lithium dendrites. Solid-state electrolytes emerge as an answer to suppress the growth of lithium dendrites and avoid the problem of electrolyte leakage. Among them, polymer electrolytes with excellent flexibility, light weight, easy processing, and good interfacial compatibility with electrodes are the most promising for practical applications. Nevertheless, most of the polymer electrolytes are flammable. It is urgent to develop flame-retardant solid polymer electrolytes. This review introduces the latest advances in emerging flame-retardant solid polymer electrolytes, including Polyethylene oxide (PEO), polyacrylonitrile (PAN), Poly (ethylene glycol) diacrylate (PEGDA), polyvinylidene fluoride (PVDF), and so on. The electrochemical properties, flame retardancy, and flame-retardant mechanisms of these polymer electrolytes with different flame retardants are systematically discussed. Finally, the future development of flame-retardant solid polymer electrolytes is pointed out. It is anticipated that this review will guide the development of flame-retardant polymer electrolytes for solid-state LIBs.

Keywords: flame retardant; solid polymer electrolyte; lithium metal batteries; security; lithium dendrites

1. Introduction

Excessive consumption of fossil fuels causes huge greenhouse gas emissions resulting in environmental pollution and the energy crisis. Numerous energy storage devices will inevitably be needed with the development of society [1]. Secondary batteries and fuel cells can convert intermittent energy into clean chemical energy including wind energy, solar energy, and hydropower [2,3]. The integration of rechargeable battery modules can convert and store renewable resources to form an energy storage system (ESS) to achieve large-scale energy storage [4,5]. Lithium-ion batteries (LIBs), due to their high energy density, superior rate capability, and long cycle life, have been widely used in mobile phones, laptops, electric cars, and other fields. However, current commercialized LIBs use liquid electrolytes, for which unavoidable risks of liquid leakage exist, as well as growth of lithium dendrites, which may be released suddenly in the form of a fire or explosion, resulting in devastating accidents [6]. The development of traditional liquid LIBs is also limited by the inherent problems of the difficulty of increasing energy density in a short period. The liquid electrolyte has high ionic conductivity and good interfacial contact [7]. However, the exothermic reactions that occur at the electrode surface rapidly increase the overall temperature of the energy store, causing more electrolyte decomposition and the production of flammable gases that are harmful to the environment. This is known as the infamous thermal runaway [8]. During this stage, the electrolyte is exposed to
air, and the device breaks down, resulting in fire, and even explosion [9]. Compared with liquid electrolytes, solid polymer electrolytes are new functional materials with good mechanical properties, no leakage, and easy processing. Constructing solid-state batteries is an important direction for development to improve LIBs’ energy density, operating temperature range, and cycle life [10].

Solid electrolytes can be divided into three main categories: polymer solid electrolytes, inorganic solid electrolytes, and organic–inorganic composite solid electrolytes [11]. The advantages of polymer solid electrolytes are that they can effectively inhibit the growth of lithium dendrites in the battery, have good contact with the electrode interface, have excellent flexibility, etc. [12]. Compared with inorganic solid electrolytes, polymer solid electrolytes have a more stable interface with electrodes. However, the ionic conductivity of polymer solid electrolytes is generally lower than that of inorganic solid electrolytes. Unfortunately, most solid polymer electrolytes are flammable, and the safety of batteries is challenged under extreme conditions (short circuit or high temperature) [13–18]. To pursue high energy density, the safety of LIBs becomes graver. Flammable polymer solid electrolytes are a safety hazard. Therefore, exploring flame-retardant polymer solid electrolytes plays an important role in the development of security and high-energy-density LIBs.

Herein, the main polymer solid electrolyte systems are summarized simply, including PEO (Polyethylene oxide), PAN (polyacrylonitrile), PEGDA (Poly (ethylene glycol) diacrylate), PVDF (polyvinylidene fluoride), and so on (Figure 1) [19]. PEO-based solid electrolytes have good mechanical properties and solubility, which can chelate with many lithium salts. The EO group in PEO can promote the transfer of Li⁺ ions. However, the PEO solid electrolytes still face low dielectric constant, poor stability, and a narrow electrochemical window, which has hampered their large-scale application. PVDF-based solid electrolytes possess good flexibility, a wide electrochemical window, excellent thermal stability, and a high dielectric constant, and they are conducive to the dissociation of lithium salts. The crystallinity of PVDF is relatively high, which is not a benefit to ion conductivity. PAN is a polymer with good stability, heat resistance, and flame retardancy. Nevertheless, the CN group in PAN is prone to attracting Li⁺ ions resulting in poor ion conductivity, and it is unstable for metallic Li. PEGDA-based solid electrolytes can achieve good interface contact with the electrode through in situ polymerization, and the interface impedance is low. But the cycling stability of PEGDA electrolytes is poor. This review also discusses the recent advances in flame retardants added to these polymer electrolytes to enhance flame retardancy. The common flame-retardant additives are discussed, including halides, metal hydroxides, phosphorus (P) and nitrogen (N) compounds, bio-based flame retardants, and ionic liquid flame retardants [20–26]. The flame retardancy effects of different flame retardants for various polymer electrolytes are analyzed, and future development prospects are put forward.

![Figure 1. Classification of polymer solid electrolytes and flame retardants.](image-url)
2. PEO-Based Flame-Retardant Polymer Electrolyte

PEO is the most common and ideal substrate material for solid polymer electrolytes [27]. PEO materials were the earliest to be discovered that can be complexed with many lithium salts, with good solubility. PEO polymer electrolytes have good flexibility, which can effectively ameliorate the stress originating from the volume expansion of the electrode during charging/discharging. However, the low dielectric constant of PEO limits the dissociation ability of lithium salt. Moreover, PEO polymers have high crystallinity resulting in very low ionic conductivity at room temperature [28]. However, PEO has high lithium-ion conductivity and low interfacial impedance with the electrode material at temperatures (>65 °C) for liquid-free solid electrolytes. Nevertheless, PEO is flammable, and it is necessary to add lithium salts and flame retardants to PEO to improve thermal stability. In the current research, phosphorus-based flame retardants, nano-metal oxides, nitrogen-based flame retardants, bio-based flame retardants, and halogen flame retardants are usually applied to PEO-based electrolytes. Adding flame retardant not only improves the flame retardancy of the PEO electrolytes, but they also benefit from the special structure of the flame retardant building Li⁺ diffusion channels, thus enhancing the electrochemical performance.

2.1. Phosphonium Flame Retardant

Organophosphorus flame retardants are widely welcomed for their good thermal stability, high environmental safety, and high flame-retardancy efficiency. Han et al. applied aluminum diethylhypophosphate (ADP) as a flame retardant and obtained an ADP/PEO solid polymer electrolyte (SPE) [29]. The addition of ADP nanoparticles can effectively inhibit the crystallization of PEO polymers and improve the ionic conductivity of SPEs. During the charge–discharge cycle, ADP nanoparticles are decomposed to form an Al- and P-rich SEI layer, which successfully suppresses the growth of Li dendrites. Furthermore, the high Coulombic efficiency of all-solid-state batteries proves that there are fewer side reactions, better cycle life, and superior cycle stability. When the PEO is ignited, it produces a blue flame (Figure 2c), and the PEO begins to melt as the temperature increases. In contrast, PEO/15%ADP does not melt when ignited (Figure 2d), and the flame self-extinguishes after 80 s, demonstrating its excellent flame retardancy. As shown in Figure 2e, electrolytes containing 15%ADP in the cell have good long cycle stability and achieve a maximum discharge capacity of about 146.5 mAh g⁻¹ at 1.0 C with a Coulomb efficiency of ~99.96%. Even after 1000 cycles, the cell can still obtain a discharge capacity of 123.2 mAhg⁻¹, with a capacity retention of 84.09%.

Liu et al. designed a new PBMP flame-retardant additive, and the synthesis route is shown in Figure 3a. Subsequently, they added to the solid PEO-based polymer to form a PEO/PBMP electrolyte film [30]. The flame-retardant test of PEO film and PEO/PBMP film is presented in Figure 3b. The results showed that the PEO film began to burn within 1 s, and the flame spread rapidly from the bottom to the top with a dripping phenomenon, while for the PEO/PBMP film, the flame extinguished within 1 s, and no fire spread and no dripping occurred, showing an excellent flame-retardant effect. In addition, PBMP can also be used as an effective plasticizer for PEO electrolytes to promote the dissociation of lithium salts and accelerate the ion transport rate, thus improving the cycle performance and multiplier performance of all-solid-state batteries (Figure 3d).

In addition, the flame retardancy of PEO electrolytes can be further improved by combining two phosphorus-containing flame retardants. Li et al. synthesized two phosphorus-containing monomers, which consist of 2-(bis(2-(2-(2-methoxy ethoxy) ethoxy) ethoxy) phosphoryl oxy) ethyl acrylate (BEPA) and ((oxo-phosphanetriyl)tris(oxo)) tris(Ethane-2,1-diyil) tri-acrylate (OPTTA) [31]. The preparation route of the three-dimensional IFR–SPE framework is exhibited in Figure 4a. The IFR–SPE was prepared by in situ cross-linking the two synthetic P-containing monomers using porous PI membranes as the carrier. As illustrated in Figure 4b, coin-type cells were assembled via in situ polymerization. The obtained IFR–SPE has excellent flame retardancy (Figure 4c) and sufficient flexibility for abuse such as twisting, folding, and unfolding. The acceptable electrochemical window
of IFR–SPE at 25 °C is up to 4.12 V. It is compatible with Li metal electrodes and could be used in Li/LiFePO₄ batteries. The flame-retardant mechanism of IFR–SPE is illustrated in Figure 4d. The phosphoric acid group in the polymer skeleton generates PO· free radicals in the polymer, which can react with H· and OH· free radicals to interrupt the combustion reaction, thus achieving the flame-retardant effect. Furthermore, the electrochemical properties of IFR–SPEs were investigated. As shown in Figure 4e, the Li/IFR-SPE/LiFePO₄ cell achieved 151.3 mAh g⁻¹ after 200 cycles in the voltage range of 2.0~4.0 V at 0.2C, and room temperature with capacity retention reached 94.8% and an average Coulomb efficiency of 99.4%.

Figure 2. (a,b) Schematic diagram of electrolyte cycling. (c) PEO electrolyte flame-retardant test. (d) PEO/15%ADP electrolyte flame-retardant test. (e) Comparison of long-term cycling performances of PEO/LiTFSI and PEO/LiTFSI/15% ADP in LiFePO₄//Li cells at 1.0 C and 60 °C. Reproduced with permission [29] Copyright 2021 American Chemical Society.
Figure 3. (a) Synthetic procedure of diphenyl methylphosphonate (DPMP) and poly(bis(4-phenoxyl)propane methylphosphonate) (PBMP). (b) Combustion behavior comparisons of PEO and PEO/PBMP electrolyte films. (c) Charge/discharge profiles of LiFePO$_4$/SPE/Li cell at 0.02 C and 55 °C. (d) Cycling performance of LiFePO$_4$/SPE/Li cell at 0.02 C and 55 °C. The red and gray circles are represent the Coulomb efficiency and specific capacity, respectively. Reproduced with permission [30] Copyright 2020, Elsevier.

In general, phosphorus-based flame retardants can greatly improve the thermal stability and flame retardancy of PEO-based solid electrolytes. Some phosphorus-based flame retardants can also improve the electrochemical performance of the electrolyte. For example, adding ADP can reduce the crystallinity of PEO polymers and improve the ionic conductivity of the electrolytes. The addition of PBMP can promote the dissociation of lithium salts, thereby accelerating the ion transport rate. Adding BEPAH and OPTTA, different types of phosphorus-based flame retardants, at the same time has a synergistic effect and greatly improves the flame retardancy of the electrolyte.
Nano-metal hydroxides also have the functions of flame retardants, which can neutralize the acid and corrosive gases produced in the combustion process [32,33]. The highly dispersed nano-metal hydroxide can greatly improve the machining properties of polymer flame-retardant materials, and it can fundamentally solve the serious damage to the mechanical properties of polymers caused by high filling volume. The flame-retardant performance nano-metal hydroxides are superior to their micron composites when they are in a composite with polymer electrolytes. The advantages of these nano-metal hydroxide composite polymer electrolytes can be summarized as follows: First, it has better mechanical properties and thermal properties; the bending modulus (rigidity) of these composites could increase 1.5~2 times; it has improved friction, wear, heat resistance, and thermal deformation temperature; and the thermal expansion coefficient is decreased to half of that of the original. Second, it endows the composite material with the barrier and has a flame-retardant function. Third, the nano flame retardants possess the advantages of good flexibility, low density, easy processing, inorganic filler strength and hardness, and good heat resistance, and they are not easy to deform at high combination.

As discussed above, introducing nanomaterials into polymer electrolytes can improve ionic conductivity and mechanical properties. Especially for nanowires, fillers can provide fast ion transport channels without cross-connections. Tao et al. prepared Mg$_2$B$_2$O$_5$ nanowires, and the synthetic route is exhibited in Figure 5a. Mg$_2$B$_2$O$_5$ nanowires were used as fillers for polyvinyl oxide (PEO) to form organic–inorganic composite solid electrolytes (Figure 5b). This rational design effectively improved the ionic conductivity, increased the mechanical properties, and enhanced the flame-retardant property of the solid electrolytes [34]. The flame-retardant test of electrolytes was conducted, and the results are displayed in Figure 5c. The control group was the PEO-LiTFSI electrolyte, which started to burn in a small fire 30 s after it approached the torch heater. When the flame was removed,
the fire immediately went out. After the combustion test, the PEO-LiTFSI electrolyte film failed to retain its original shape and became a viscous liquid. In contrast, the PEO-LiTFSI-Mg$_2$B$_2$O$_5$ electrolyte is almost incombustible. In addition, with the increase in the content of Mg$_2$B$_2$O$_5$ nanowires, the flame retardancy of Mg$_2$B$_2$O$_5$ nanowires also improved. This is because a heat- and fire-resistant carbon layer is formed during combustion. The existence of Mg$_2$B$_2$O$_5$ is not only beneficial to the carbon formation process, but it also improves the stability of the carbon layer. As a result, it prevents heat transfer to the solid electrolyte. The PEO-LiTFSI-10 wt% Mg$_2$B$_2$O$_5$ electrolyte was assembled into lithium metal batteries using LiFePO$_4$ and lithium metal as cathode and anode, respectively. As depicted in Figure 5d, the battery can still operate stably at 50 °C and 1C and possesses a high Coulombic efficiency and capacity retention rate (Figure 5d).

Figure 5. (a) Schematic illustration of the synthetic route of Mg$_2$B$_2$O$_5$ nanowires. (b) Schematics of Li$^+$ migration in PEO-LiTFSI-20 wt% Mg$_2$B$_2$O$_5$ composite SSEs. (c) Flammability tests of PEO-LiTFSI, PEO-LiTFSI-10 wt% Mg$_2$B$_2$O$_5$, and PEO-LiTFSI-20 wt% Mg$_2$B$_2$O$_5$ composite SSEs. (d) Cycling performance of solid-state LiFePO$_4$//Li with PEO-LiTFSI-10 wt% Mg$_2$B$_2$O$_5$ electrolyte at 1.0 C and 50 °C. The inset is a digital photograph of LEDs lit by LiFePO$_4$//Li batteries. The red and green are the Coulomb efficiency and specific capacity, respectively. Reproduced with permission [34] Copyright 2018 American Chemical Society.

Pumchusak et al., by using halolite nanotubes (HNTs) as nano-packing and uniformly dispersing it in the electrolyte under ultra-sounding, prepared a PEO–LiCF$_3$SO$_3$–HNT-15US electrolyte [35]. HNTs have a large surface area, high porosity, and adjustable surface chemistry, and their chemical structure consists of a silica tetrahedron on the outer surface and an alumina octahedron on the inner surface, with a central cavity. These properties promote the ion transfer, and the ion conductivity reaches $1.1 \times 10^{-4}$ S cm$^{-1}$. The FE-SEM-EDS mapping shows that Si and Al elements are evenly distributed on the surface of the PEO–20%LiCF$_3$SO$_3$–5%HNT electrolyte. The increased ionic conductivity can be attributed to the interaction between the oxygen atoms of PEO and Li$^+$ ions on the outer surface of the HNT (–Si-O-Si– groups) [36] and the formation of hydrogen bonds between the anion (CF$_3$SO$_3$–) and the -OH groups on the inner surface of the
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The addition of halolite nanotubes (HNTs) increased the flame retardancy of the electrolyte. The flame-retardant test results of PEO−20%LiCF₃SO₃−5%HNT−15US in the air shows that the PEO−20%LiCF₃SO₃−5%HNT−15US melts at 10 s and ignites after 30 s and then self-extinguishes at 40 s. These results indicate that homogeneous dispersion of HNTs in composites improved flame retardancy. The Nyquist diagram of PEO−20%LiCF₃SO₃−5%HNT−15 US shows only sharp peaks, indicating good ionic conductivity. The addition of HNTs can improve ionic conductivity. The ionic conductivity of PEO−20%LiCF₃SO₃−5%HNT reaches $1.1 \pm 0.19 \times 10^{-4}$ S cm⁻¹.

Overall, inorganic metal oxide flame retardants significantly improved the flame retardancy of PEO-based solid electrolytes. Adding metal oxide flame retardants also enhanced the ionic conductivity and mechanical properties of the electrolyte. The flame-retardant efficiency of metal oxide flame retardants is lower than that of phosphorus-based flame retardants.

### 2.3. Nitrogenous Flame Retardants

Nitrogenous flame retardants have excellent flame retardancy and environmental protection advantages. The retardancy function of nitrogen-based flame retardants is mainly based on decomposing heat and generating noncombustible gases to dilute combustible materials. The nitrogen element in nitrogen-based flame retardants can stably exist in a polymer. Adding nitrogen-based flame retardants to PEO-based polymer electrolytes can also increase thermal stability and improve mechanical properties.

Zhang et al. developed a low-cost polybenzimidazole (PBI) and PEO composite electrolyte by using a simple and scalable hybrid method [38]. PBI is an aromatic heterocyclic polymer with excellent heat resistance, mechanical strength, chemical stability, and flame-retardant properties, making it one of the best flame retardants for polymer electrolytes. PBI has good compatibility between its imidazole group and polar electrolyte, which can effectively inhibit the crystallization of PEO and promote the transmission of Li⁺. The LIB diaphragm with PBI has good thermal stability and electrochemical performance, which greatly improves the safety and performance of LIBs.

### 2.4. Bio-Based Flame Retardant

Bio-based flame retardants have environmental advantages compared to other types of flame retardants [39]. The reason why bio-based materials can become raw materials of flame retardants is that many bio-based materials have high carbon content and a multi-hydroxyl structure, so they have excellent charring performance. Charring performance is the most important action mechanism of intumescent flame retardants. The flame retardancy of intumescent flame retardants mainly depends on the formation of a porous foam coke layer on the material surface [40]. It is a multiphase system, containing solid, liquid, and gaseous products [36]. The flame-retardant properties of the carbon layer are mainly reflected in making it difficult for heat to penetrate the condensed phase, preventing oxygen from entering the combustion area and preventing the gas or liquid products generated via degradation from overflowing onto the material’s surface. The formation process of the coke layer is as follows: at around 150 °C, the acid source produces esterifying polyols and acids that can serve as dehydrating agents; at slightly higher temperatures, the acid undergoes esterification with the carbon source, while the amine group in the system catalyzes the esterification reaction, accelerating the reaction. The system is melted before and during esterification, and incombustible gas is generated in the molten state. At the same time, the polyol and ester are dehydrated and carbonized to form inorganic compound substances and carbon residues, and the system is further foamed. When the reaction is nearly completed, the system gelatinizes and solidifies, and it finally forms a porous foam carbon layer.

Chen et al. introduced sodium alginate (SA) into PEO with nanofiber membrane structured SPEs, improving the mechanical properties and the security of LIBs [41]. SA is a natural and water-soluble polysaccharide that can be extracted from brown algae [42].
to the synergistic effect of its abundant carboxyl groups and coordinating cations, SA is inherently flame-retardant [43]. The PEO/SA electrolyte has excellent flame retardancy, with a limiting oxygen index (LOI = 28.6) of 28.6; excellent thermal stability (>120 °C); and a wide electrochemical window (>4.6 V).

Wang et al. synthesized an alginate fiber (AF)-grafted polyether amine (AF-PEA) diaphragm with high Li⁺ transport efficiency and excellent flame readability (Figure 6a) [44]. The final PEO-based solid electrolyte was synthesized using AF-PEA as a skeleton (PEO@AF-PEA). The grafted PEA acts as a Li⁺ transport segment and provides more anchor points for rapid Li⁺ transporting. PEO@AF-PEA electrolytes achieved excellent ionic conductivity (σ = 6.7 × 10⁻⁴ S cm⁻¹) and high ionic mobility (t_{Li⁺} = 0.58). According to the thermal stability test (Figure 6b), PEO@AF-PEA SPE can still maintain its original shape at a high temperature of 200 °C, showing excellent thermal stability and flame-retardant qualities. Figure 6c shows the Nyquist diagram of LiFePO₄//Li batteries at 80 °C using PEO@AF-PEA and PEO SPEs, respectively. The interface resistance of the PEO@AF-PEA electrolyte was reduced to less than 165 Ω; this can be ascribed to the special 3D structure of the diaphragm compatible with PEO, which thus improves the overall ion transport capacity of the electrolyte and enhances the transmission of Li at the electrode/electrolyte interface. After 1500 cycles (Figure 6d), the capacity of LiFePO₄//Li batteries remained at 103.5 mAh g⁻¹ with a Coulomb efficiency above 98.5%, and no short circuit occurred.

Figure 6. (a) Schematic illustration of the synthesis of the AF-PEA separator and PEO@AF-PEA electrolyte. (b) Thermal stability photos of PEO@AF-PEA from 20 to 200 °C. (c) Nyquist plots for LiFePO₄//Li batteries using PEO@AF-PEA electrolytes at 80 °C. (d) Cycling performance of LiFePO₄//Li batteries at 2 C and 80 °C. Reproduced with permission [44] Copyright 2022 American Chemical Society.
In general, adding bio-based flame retardants to PEO-based electrolytes is more environmentally friendly than using other types of flame retardants. The rich carboxyl groups in some bio-based flame retardants are coordinated with cations, thus improving the ionic conductivity of electrolytes.

2.5. Halogen Flame Retardants

Halogenated flame retardants are the earliest type of flame retardants, due to their low price, good stability, and ability to maintain the original physical and chemical properties of flame-retardant products. Bromine-based flame retardants have a high flame retardancy efficiency, which is twice that of chlorine-based flame retardants. Therefore, their relative dosage is relatively low, and due to their good compatibility with the matrix resin, their impact on the mechanical properties of the material is small [45,46]. Halogen flame retardants release halogen radicals or halide when heated to scavenge flame-maintaining free chain radicals, achieving the goal of flame retardancy.

Cui et al. reported a fire-resistant ultra-light SSE with excellent electrochemical performance for LIBs [47]. As shown in Figure 7a, the solid-state electrolyte (SSE) uses a polyimide (PI) membrane and the light flame-retardant material decabromodiphenylethane (DBDPE) to form dual-function main skeletons. This material not only has mechanical strength that can prevent the penetration of Li dendrites but also has fireproofing ability. The mechanism of the fire resistance of DBDPE is the free radical scavenging reaction (Figure 7b). DBDPE degrades at high temperatures to produce bromine free radicals (Br•). The highly active free radicals H• and OH• released during electrolyte combustion can be captured by Br• and then interrupt the combustion chain branching reaction [48]. In addition, the release of HBr, H2O, and Br2 in the free radical scavenging reaction limits heat and mass transfer and dilutes the oxygen concentration between the heat source and electrolyte, thereby delaying self-sustaining combustion [49]. The flame retardancy of DBDPE was tested, and the results are shown in Figure 7c. The solid polymer electrolyte with DBDPE added shows good flame retardancy. The SET value of PEO/LiTFSI gradually decreases with the addition of DBDPE. When the concentration of DBDPE in PEO/LiTFSI increases to 15 wt%, the SET value decreases to zero. PI/DBDPE film has excellent thermal stability, nonflammability, and mechanical strength, which can prevent short circuits in Li//Li symmetric batteries over cycling for 300 h. LiFePO4//Li half cells with PI/DBDPE/PEO/LiTFSI exhibited superior rate performance (131 mAh g−1 at 1C, Figure 7d) and stable cycling performance at 60 °C (300 cycles at C/2, Figure 7e).

In general, adding halogen flame retardants to PEO electrolytes can greatly improve flame retardancy, but most halogen flame retardants will produce harmful gases, which will pollute the environment and corrode the instrument.

Figure 7. Cont.
When using a flame retardant containing P and N elements, the P and N elements were the earliest type of flame retardants used. Halogenated flame retardants have the best flame-retardant effect, they will produce harmful gases when burned, which will corrode instruments and endanger the environment. Although halogen flame retardants have the best flame-retardant effect, they will produce harmful gases when burned, which will corrode instruments and endanger the environment.

3. PVDF-Based Flame-Retardant Solid Polymer Electrolyte

PVDF-based solid electrolytes can be traced back to the 1980s [50]. The advantages of PVDF-based electrolytes can be summarized as follows [51]: (1) good mechanical strength and toughness; (2) a wide electrochemical window; (3) high thermal stability with long-term working temperature up to 150 °C; (4) high electrochemical stability and no adverse reaction with other materials; (5) high dielectric constant; and (6) good machinability. Combining the characteristics of PVDF materials, excellent and stable polymer electrolytes can be produced when using some modification strategies. To improve the ionic conductivity of PVDF-based electrolytes, the crystallinity of the polymer chain can be reduced, and the kinematic ability of the polymer chain can be enhanced by blending, cross-linking, or doping inorganic fillers [52–54]. Adding flame retardants to PVDF-based solid electrolytes can further enhance their flame retardancy.

3.1. Halide Flame Retardant

Halogenated flame retardants, as an important variety of organic flame retardants, were the earliest type of flame retardants used. Halogenated flame retardants have the advantages of low price, good stability, low addition, and good compatibility with synthetic resin materials. Halide flame retardants have been widely used because they can maintain the original physical and chemical properties of flame-retardant products. Deng et al.
reported a nonflammable quasi-solid polyethylene electrolyte (ED@PVDF) plasticized with organic fluorides [55]. ED@PVDF is a sulfur-based electrospun PVDF fiber framework created via an alcohol-ene click reaction of ethoxylated trimethylolpropane triacrylate (ETT) and 3,6-dioxo-1,8-octanedithiol (DODT). ED@PVDF has excellent flame retardancy and cannot be ignited by flames. ED@PVDF has high ionic conductivity (4.41 mS cm\(^{-1}\) at 30 °C). ED@PVDF promoted the formation of LiF-rich SEI and effectively suppressed the dendrite growth on the Li metal anode. The LiFePO\(_4\)/ED@PVDF/Li battery exhibited good cycle performance (capacity retention of 81.4% after 1000 cycles at 1 C) and excellent rate performance (123.8 mAh g\(^{-1}\) at 5C rate).

3.2. Phosphonium Flame Retardant

Phosphorus-based flame retardants have many advantages and are widely used. Except when directly adding flame retardants to the polymer electrolyte system, phosphorus derivative molecules can also be connected to the polymer long chain to form a topological structure. Compared to linear polymers, different polymer topologies can significantly alter the properties of polymers (such as crystallinity and thermal stability). Therefore, introducing phosphorus derivatives into PVDF-based SPEs may be an important strategy to simultaneously address its side reactions and flammability issues for high-voltage cathode materials.

Guo et al. incorporated 1-ethyl-3-methylimidazolium trifluoromethane sulfonate (EMITFSI) and Li\(_{1.5}\)Al\(_{0.5}\)Ge\(_{1.5}\)(PO\(_4\))\(_3\) (LAGP) ceramic fillers into PVDF-HFP-prepared PVDF/LAGP/EMITFSICPE (ILGPE) (Figure 8a) [56]. A flame-retardant test was conducted using a spray gun (Figure 8b), confirming that ILGPE does not burn and demonstrates good flame retardancy. The performance of the LiFePO\(_4\)/ILGPE-10%/Li was tested, and the results are depicted in Figure 8c. At a current rate of 0.05C, it displayed a relatively stable discharge capacity and high Coulombic efficiency. Figure 8d shows the discharge capacity of LiFePO\(_4\)/ILGPE-10%/Li at different current rates. It was found that the discharge capacity decreased from 0.05 to 2C, and when returned to 0.05C, the discharge capacity returned to the original level, indicating good stability.

Mi et al. uniformly grafted phenyl lithium phosphate (LPPO) on polyvinylidene fluoride (PVDF) through hydrogen defluorination and a Friedel–Crafts alkylation reaction and constructed a multifunctional PVDF-LPPOSPE electrolyte [57]. LPPO, as a single ionic conductor, flame retardant, and interface-forming agent of a cathode electrolyte, not only greatly improves the ionic conductivity, fire resistance, and electrochemical stability of SPEs, but also significantly inhibits the side reaction with the cathode and Li metal anode. LPPO constructed an additional Li\(^+\) transport pathway to significantly reduce the activation energy of PVDF-LPPOSPE and increase its Li\(^+\) transfer number.

Han et al. prepared PVDF-HFP/TPU/PVDF-HFP sandwich films using an electrospinning apparatus [58]. Adding LiPF\(_6\) to thermoplastic polyurethane (TPU) can improve the flame retardancy of the electrolyte. The flame-retardant mechanism is that LiPF\(_6\) is heated to form LiF and PF\(_5\). Then, PF\(_5\) reacts with H\(_2\)O to generate H\(_4\)P\(_2\)O\(_7\) and H\(_3\)PO\(_4\). Decomposition products H\(_4\)P\(_2\)O\(_7\) and H\(_3\)PO\(_4\) will form protective coatings on the surface of TPU fibers to isolate oxygen and heat. The TPU GPE adsorbed with 60 wt% of 1 M LiPF\(_6\) in (v/v) EC/DMC electrolytes also contracted when exposed to a fire source, but it did not burn. If the TPU GPE is kept in contact with the ignition source, it will not catch on fire. The combustion test results indicate that TPU GPE possesses a flame-retardant effect.

Lin et al. successfully prepared a flexible composite polymer–polymer electrolyte (PPE) by adding flame-retardant trimethyl phosphate (TMP) into the solution of polyimide (PI) and polyvinylidene fluoride (PVDF) (Figure 9a) [59]. Trimethyl phosphate (TMP) is the most widely used phosphate flame retardant due to its excellent flame-retardant efficiency [60–64]. The optimized noncombustible PPE exhibits excellent mechanical properties (Figure 9b) (high tensile strength of 29.6 MPa and elongation at break of 87.2%), as well as high Li salt solubility. Good mechanical properties ensure inhibition of Li dendrites, while high Li salt solubility further improves ionic conductivity
The obtained symmetrical battery (Li/PPE-50/Li) provides excellent Li stripping/plating stability for 1000 h at 0.5 mA cm\(^{-2}\)/0.25 mAh cm\(^{-2}\) and 600 h at 2.0 mA cm\(^{-2}\)/1.0 mAh cm\(^{-2}\), respectively. In addition, the LiFePO\(_4\)/PPE-50/Li cell achieved high cycling performance (a reversible capacity of 135.9 mAh g\(^{-1}\) after 300 cycles at 1 C) and superior rate capability (117.2 mAh g\(^{-1}\) at 4C) (Figure 9c). As shown in Figure 9d, the original PP separator is highly flammable and continues to burn after ignition. While the PPE-0 exhibits fire-fighting properties due to the presence of the flame-retardant TMP, only the PPE-0 has a slight shrinkage. When TMP and PI are added at the same time, the fire resistance of the PPE-50 is greatly improved. After the combustion test, the PPE-50 maintains its original shape, exhibiting good fire resistance.

Lv et al. introduced two-dimensional hydroxyapatite (HAP) nanomaterials in collaboration with N-methyl pyrrolidone (NMP) in a PVDF–HFP polymer matrix constructed with a solid-state electrolyte (PLNH, Figure 10a) [65]. HAP fillers form a hydrogen bond network with the PVDF–HFP matrix. The synergistic effect with NMP and PVDF–HFP promoted the dissociation of LiTFSI and improved the mechanical strength. The PLNH electrolyte achieved a high ionic conductivity of 7.4 \(\times\) \(10^{-4}\) S cm\(^{-1}\) and possesses strong resistance to Li dendrites and excellent thermal stability. As shown in Figure 10b, the PLN SPE does not retain its original shape after the ignition source is removed, while the PLNH SPE retains its
original shape and size. This phenomenon is ascribed to its self-extinguishing ability, which avoids violent combustion. Therefore, the excellent thermal stability and fire resistance indicate that HAP fillers can effectively improve the thermal stability of SPEs [66]. The LFP/PLNH/Li batteries exhibit excellent rate performances of 156.1, 151.7, 148.5, 142.3, and 130.2 mAh g\(^{-1}\) at 0.1, 0.2, 0.3, 0.5, and 1 C, respectively. As shown in Figure 10c, LFP/PLNH/Li batteries attain a capacity exceeding 116.5 mAh\(\cdot\)g\(^{-1}\) after 600 cycles with 0.5C with an average Coulombic efficiency of \(\sim99.3\%\), reflecting the excellent performance of the PLNH electrolyte.

In PVDF-based solid electrolytes, the commonly used flame retardants include phosphorus-based flame retardants and halogen flame retardants. Grafting phosphorus derivatives onto the long chains of PVDF polymers to form a topological structure can further improve the flame retardancy of the electrolyte. The topological structure provides an additional Li\(^{+}\) transport path, which significantly reduces the number of Li\(^{+}\) transports and improves the electrochemical performance of the electrolyte.

Figure 9. (a) Schematic diagram of PPE electrolyte. (b) Photographs of the ignition evaluation of PPE-50, PPE-0, and PP separator, respectively. (c) Cycling performance of the LFP/PPE-50/Li and LFP/PPE-0/Li batteries at 1 C and 2.0–4.2 V and (d) rate performance of LFP/PPE-50/Li at different rates. The red and blue arrows in sub-figure d point to the corresponding ordinates of the curves, respectively. Reproduced with permission [59] Copyright 2022 Elsevier.
4. PAN-/PUA-Based Flame-Retardant Solid Polymer Electrolyte

Polyacrylonitrile (PAN) is one of the popular solid polymer matrices. The research on PAN-based polymer electrolytes can be traced back to 1975. It cannot conduct Li\(^+\). So, its conductivity and mechanical properties are often improved by adding inorganic compounds, plasticizers, lithium salt, and other components. Each repeating unit contains a nitrile group, which has a low HOMO energy level, providing excellent electrochemical stability for PAN. In addition, the nitrile group (C≡N) is a strong polar group that can coordinate with metal cations and dissociates metal salts, playing a key role in the transport of Li\(^+\) along the polymer molecular chain [67]. The advantages of PAN electrolytes are the extremely high dipole moment of the cyano group, strong electron absorption ability, high oxidation resistance, nonflammability, stable chemical properties, and excellent mechanical properties. To further enhance the safety of all-solid-state batteries, flame retardants are also investigated as to whether PAN-based polymer electrolytes enhance flame retardancy.
4.1. Nitrogenous Flame Retardants

Nitrogen-containing flame retardants have high flame-retardancy efficiency, low toxicity, and low corrosiveness to electrical appliances caused by combustion gases. Nitrile materials exhibit high thermodynamic stability and excellent electrochemical oxidation resistance [68]. Nitrile materials used in LIB electrolytes can improve the flame retardancy of SPEs. The interaction between nitrile groups (-C≡N) and Li\(^+\) ions can improve the ionic conductivity of electrolytes [69].

Zhou et al. prepared a graded SPE based on nitrile materials through an in situ synthesis route (Figure 11a) [70]. The dispersed cationic polymerized cyanoethyl polyvinyl alcohol (PVA-CN) and lithium salt in succinonitrile (SN) to obtain an elastic PVA-CN/SN electrolyte. The molten PVA-CN/SN electrolyte is filled in a PAN-based electrospun fiber membrane network to form a nitrile-based material (SEN) SSE. The ignition test is displayed in Figure 11b-d. Compared with the highly flammable liquid electrolyte (Figure 11b) and the PVA-CN-type flammable gel polymer electrolyte (Figure 11c), PVN-CN/SNSPE shows obvious low flammability (Figure 11d). Although the SN-based solid electrolyte absorbed in the electrospun fiber membrane can melt at higher temperatures, the cross-linked PVA-CN can maintain SEN in a quasi-solid state without melt leakage. The interfacial resistance (Rf and Rct) of the LiFePO\(_4\)/SEN/Li battery is almost unchanged after 100 cycles (Figure 11e). The stability of the interfacial resistance indicates that SEN keeps the electrode/electrolyte interface stable during charging/discharging [71]. The rate performance of LiFePO\(_4\)/SEN/Li at 25 °C at different rates of 0.1 to 1C is depicted in Figure 11f. At 1C rate, the LiFePO\(_4\)/SEN/Li cell delivers an acceptable capacity of 100 mAh g\(^{-1}\).

4.2. Phosphonium Flame Retardant

LvP et al. manufactured a polymer electrolyte (FR-SPE) film composed of flame-retardant polyurethane acrylate (PUA) oligomers, nitrile, alumina (Al\(_2\)O\(_3\)), and lithium salts (Figure 12a) [72]. Reactive flame retardant 9,10-dihydro-9-oxa10-photosphaphenanthrene-10-oxide (DOPO) is grafted onto polyurethane acrylate (PUA) as the main structure of the electrolyte (Figure 12b). To balance mechanical and electrochemical properties, solid plasticizer SN and a small amount of Al\(_2\)O\(_3\) were added to the electrolyte. Cross-linked PUA ensures excellent mechanical properties and high flame retardancy of FR-SPE. When the grafting rate of DOPO on PUA reaches 39%, the flame retardancy of FR-SPE reaches the highest fire-resistance level tested by UL-94. The ionic conductivity of the obtained FR-SPE is as high as 2.66 \(\times\) 10\(^{-4}\) S cm\(^{-1}\) at room temperature, with a wide electrochemical stability window of 5 V and a high Li\(^+\) transport number of 0.55. As shown in Figure 12c, FR-SPE-0 can be ignited for 84 s until it burns out. When the DOPO grafting rate on PUA reaches 39%, FR-SPE exhibits obvious self-extinguishing characteristics (Figure 12d). The continuous combustion time for FR-SPE-0 can be ignited for 84 s until it burns out, while the first time is only 1 s, and the second time is 3 s, reflecting excellent flame retardancy. As exhibited in Figure 12, the fully charged LiFePO\(_4\)/Li\(_4\)Ti\(_5\)O\(_{12}\) cell with liquid electrolyte (LE) is seriously inflated, and the gassing behavior of the cell with FR-SPE-4 is suppressed compared with that of the LE. The assembled LiFePO\(_4\)/Li\(_4\)Ti\(_5\)O\(_{12}\) solid batteries displayed good rate performance (Figure 12f), indicating good ion conductivity and interface stability of FR-SPE. It can be seen that the battery shows a discharge capacity of 144.6 mAhg\(^{-1}\) and capacity retention of 96.3% after 100 cycles (Figure 12g), reflecting a good interface compatibility between FR-SPE and electrodes.

In general, nitrogen-based flame retardants and phosphorus-based flame retardants are mainly used in PAN-based and PUA-based solid polymer electrolytes. Nitrogen flame retardant has high flame-retardant efficiency and low toxicity, and the combustion gas is less corrosive to electrical appliances. The use of nitrile materials in polymer electrolytes can improve flame retardancy but will melt at high temperatures. Flame retardants can be grafted onto long chains of PUA polymers to form topological structures. While increasing
flame retardancy, it also increases the Li\textsuperscript{+} transmission channel to promote the transmission of lithium ions.

**Figure 11.** (a) Schematic illustration for the in situ synthesis route of SEN. (b) Combustion test of 1 M LiPF\textsubscript{6}-EC/EMC/DMC, (c) PVA-CN-based gel polymer electrolyte, and (d) PVA-CN/SN solid electrolyte. (e) EISs of the LiFePO\textsubscript{4}/SEN/Li cell and LiFePO\textsubscript{4}/1 M LiPF\textsubscript{6}-EC/EMC/DMC/Li cell after one cycle and 100 cycles at 0.1 C, measured at half discharge state. (f) Rate performance of the LiFePO\textsubscript{4}/SEN/Li cell. Reproduced with permission [70] Copyright 2015 WILEY-VCH.
Polyethylene glycol diacrylate (PEGDA) is a derivative of polyethylene glycol (PEG), which acts as a cross-linking agent to improve the mechanical stability of the electrolyte [73]. PEGDA can be polymerized via UV or heating under the action of photoinitiators or AIBN. Due to its high water content and good elasticity after polymerization, it has been widely used in tissue engineering [74]. PEGDA is mainly used as a cross-linking agent for copolymerization with other monomers for polymer electrolytes. PEGDA, a typical polymer with two reactive C=C end bonds is non-toxic and biodegradable [75]. The introduction of salt in PEGDA could increase the ionic conductivity, which could serve as a solid electrolyte for alkali metal batteries. Due to its ability to initiate in situ polymerization, it has good interface contact with the electrode. However, since PEGDA polymers are flammable, it is necessary to introduce flame retardants to improve the flame retardancy.

5.1. Phosphonium Flame Retardant

Most phosphonium flame retardants have advantages such as low smoke, non-toxicity, low halogens, and zero halogens, which are in line with the development direction of flame retardants and have good development prospects. Furthermore, organic phosphorus flame retardants have dual effects of flame retardancy and plasticization, which can achieve halogen-free flame retardants and improve flowability during processing and molding.
Zhang et al. prepared multi-scale radical annihilator hexachlorocyclotrichosphoronic-trilene (HCCP) cross-linked tannic acid (TA) microspheres (HTs) using a simple one-step precipitation polycondensation method (Figure 13a). High-pressure flame-retardant material PEGGPE@HT was prepared in situ by mixing HTs with a PEGDA polymer electrolyte (PEGGPE) [76]. HTs can not only annihilate the free radicals generated by the decomposition of PEGGPE at the high-pressure interface but also annihilate the free radical chain reaction at high temperatures. The Ph-OH in HTs is an antioxidant with efficient free radical scavenging ability, which is more competitive than other antioxidants [77–79]. However, Ph-OH will oxidize at high temperatures and lose its annihilation activity, which cannot hinder the combustion of the electrolyte. On the contrary, due to the high content of P/N, phosphazene will produce PO· at high temperatures, which is an efficient flame retardant for electrolytes. However, the active P-Cl bond in HCCP is incompatible with the Li metal anode due to nucleophilic substitution. Therefore, the cross-linking reaction between TA and HCCP not only endows HTs with the ability to eliminate free radicals at high temperatures but also stabilizes the active P-Cl bond. Therefore, PEGGPE@HT has enhanced oxidation stability to 4.5 V (Li/Li⁺) and negligible current leakage. In addition, the presence of HTs accelerates the migration of Li⁺ and inhibits the formation of Li dendrites. The flame-retardant effect of HTs for PEGGPE@HT electrolytes was verified through ignition tests (Figure 13b). Typical carbonate LEs are easy to ignite and burn vigorously for 49.7 s. Although PEGGPE has properties similar to solids, it is flammable, and the combustion time is up to 120.7 s, while PEGGPE@HT is difficult to ignite, reflecting excellent flame retardancy. The assembled NCM811//graphite batteries with PEGGPE@HT electrolytes demonstrated good rate performance and long cycle stability (Figure 13c).

Wang et al. introduced the flame retardant 9,10-dihydro-9-oxa-10-phosphatephenanthrene-10-oxide (DOPO) into the polymer chain by using the active P-H bond and prepared an organic gel electrolyte (Figure 14a) [80]. According to previous reports, DOPO is an excellent flame retardant in polymer materials [81]. The gel polymer electrolyte was prepared via copolymerization of hexafluorobutyl acrylate (HFBA) and hydroxyethyl methacrylate (HEMA) in the presence of LiTFSI, DOPO, and PEGDA (Figure 14a). The obtained gel
polymer electrolyte has good mechanical properties (maximum stress \( \approx 28 \) KPa, maximum strain \( \approx 305\% \)), good conductivity (4 mS cm\(^{-1} \) at 20 \(^\circ\)C), and good flame retardancy. In addition, the supercapacitor assembled with this gel electrolyte has good electrochemical performance (Figure 14b–d). After ignition, the polymer (HFBA\(_8\)-co-HEMA\(_1\)) without DOPO began to rapidly burn (Figure 14e). On the contrary, the poly(HFBA\(_8\)-co-HEMA\(_1\)) electrolyte with DOPO was ignited by the ignition source and did not burn after leaving the ignition source, indicating excellent flame retardancy. The flame retardancy of the poly(HFBA\(_8\)-co-HEMA\(_1\)) electrolyte is beneficial for improving the security of lithium metal batteries.

Figure 14. (a) Schematic diagram of fabrication of gel polymer electrolyte. (b) EIS spectra of the SCs assembled via liquid electrolytes and poly(HFBA\(_8\)-co-HEMA\(_1\)) electrolytes. (c) Specific capacitances of the electrode assembled via liquid electrolytes and poly(HFBA\(_8\)-co-HEMA\(_1\)) electrolytes under different current densities. (d) Cycle stability of poly(HFBA\(_8\)-co-HEMA\(_1\)) electrolyte-based SC at a current density of 1.25 Ag\(^{-1} \). (e) Burning testing of poly(HFBA\(_8\)-co-HEMA\(_1\)) without DOPO electrolytes and poly(HFBA\(_8\)-co-HEMA\(_1\)) electrolytes. Reproduced with permission [80] Copyright 2021 Wiley-VCH.
5.2. Ionic Liquid Flame Retardant

Ionic liquid (IL) is composed of cations and anions and has unique properties such as low vapor pressure, nonflammability, nonvolatility, and excellent chemical stability [82,83]. The ionic liquid is known as a low-temperature molten salt. Due to its conductivity, difficulty in volatilization, noncombustion, and large electrochemical stability potential window [84], the application of ionic liquids has been widely investigated. Adding ionic liquids can improve the conductivity of polymer solid electrolytes. Meanwhile, relying on excellent thermal stability, the flame retardancy of polymer solid electrolytes can be improved.

Liao et al. synthesized a novel bifunctional ionic liquid monomer [85]. It is not only used as a polymeric monomer (containing C=C) but also provides a cross-linking site (containing epoxy group) to construct a new double cross-linked PIL electrolyte (Figure 15a,b). Bis(trifluoromethyl sulfonyl group) imine (VEIM-TFSI) and poly (vinylimine) (PEI) and poly (ethylene glycol) diacylate (PEGDA), via a ring-opening reaction, obtained a PIL-PEI electrolyte (Figure 15a,b). This double cross-linking network PIL-PEI electrolyte exhibits satisfactory flexibility, excellent electrochemical performance (ionic conductivity, $1.03 \times 10^{-3}$ S cm$^{-1}$ at room temperature, and Li$^+$ transfer number 0.47), and thermal stability (Figure 15c). Compared with the LE-infiltrated commercial diaphragm (Celgard2400), PIL-PEI can still maintain the original morphology at the high temperature of 150 °C, and the ignition test shows that PIL-PEI is noncombustible (Figure 15d). Due to the high ionic conductivity of PIL-PEI, LiFePO$_4$/PIL-PEI/Li batteries displayed excellent rate performance (Figure 15e). The long charge–discharge results (Figure 15f) displayed high cycling stability with a capacity retention of 97.1% after 200 cycles.

Chen et al. synthesized an imidazole-based ionic liquid with vinyl and amino bifunctionality [86]. The synthesis route is shown in Figure 16a,b, in which 1-butyl-3-methylimidazole bis (trifluoromethyl sulfone) imide (BMIm[TFSI]) is confned to a cross-linked skeleton consisting of a double-bond cross-linked system (n-butyl acrylate, BA, and polyethylene glycol diacrylate, PEGDA). It was subsequently mixed with PIL ion gel electrolyte (cage epoxy polyhedral oligosiloxane, EPPOSS) to prepare a cross-linking system (POSS-CPIL). Due to the nonflammable POSS structure and stable imidazole-based ionic liquid, the POSS-CPIL ionic gel electrolyte has a thermal stability of up to 360 °C and shows ideal fire resistance (Figure 16c). The ether-dominant chain of PEGDA provides favorable ion conduction channels to ensure rapid ion transport, resulting in a high ionic conductivity of 2.5 mS cm$^{-1}$ (Figure 16d) [87]. The hybrid cross-linking network inhibits crystallization, increases the amorphous area, and promotes ion transport [88]. Figure 16e shows the rate performance of the LiFePO$_4$/Li cell from 0.1 to 4.0C. When the current density was back to 0.1C, the capacity of the LiFePO$_4$/Li cell recovered to its initial value, which indicates that POSS-PIL-5 has electrochemical performance. As shown in Figure 16f, the LiFePO$_4$/Li cell displayed a highly stable cycle life and a high Coulomb efficiency close to 98% after 200 cycles.

Figure 15. (a) Reaction scheme for VEMI-TFSI. (b) Synthesis of the double cross-linked PIL-PEI. (c) Comparison photographs of the dimensional stability of the PIL-PEI and Celgard 2400 tested at 25, 120, and 150 °C for 30 min. (d) Combustion testing of PIL-PEI1 and LE infiltrated Celgard 2400. (e) Rate performances of the LiFePO$_4$/PIL-PEI electrolyte/Li and LiFePO$_4$/LE/Li cells. (f) Cycling performance of the LiFePO$_4$/PIL-PEI electrolyte/Li and LiFePO$_4$/LE/Li cell at 0.1C. Reproduced with permission [85] Copyright 2021 Elsevier.
Chen et al. synthesized an imidazole-based ionic liquid with vinyl and amino bi-functionality [86]. The synthesis route is shown in Figure 16a,b, in which 1-butyl-3-methylimidazole bis (trifluoromethyl sulfone) imide (BMIm [TFSI]) is confined to a cross-linked skeleton consisting of a double-bond cross-linked system (n-butyl acrylate, BA, and polyethylene glycol diacrylate, PEGDA). It was subsequently mixed with PIL ion gel electrolyte (cage epoxy polyhedral oligosilsloxane, EPPOSS) to prepare a cross-linking system (POSS-CPIL). Due to the nonflammable POSS structure and stable imidazole-based ionic liquid, the POSS-CPIL ionic gel electrolyte has a thermal stability of up to 360 °C and shows ideal fire resistance (Figure 16c). The ether-dominant chain of PEGDA provides favorable ion conduction channels to ensure rapid ion transport, resulting in a high ion conductivity of 2.5 mS cm$^{-1}$ (Figure 16d) [87]. The hybrid cross-linking network inhibits crystallization, increases the amorphous area, and promotes ion transport [88]. Figure 16e shows the rate performance of the LiFePO$_4$/Li cell from 0.1 to 4.0C. When the current density was back to 0.1C, the capacity of the LiFePO$_4$/Li cell recovered to its initial value, which indicates that POSS-PIL-5 has electrochemical performance. As shown in Figure 16f, the LiFePO$_4$/Li cell displayed a highly stable cycle life and a high Coulomb efficiency close to 98% after 200 cycles.

Figure 16. (a) Schematic illustrates the reaction for VIm-NH$_2$ [TFSI] monomer. (b) Synthesis of the POSS-CPIL-n electrolyte. (c) Flammability test of PVDF-HFP and POSS-CPIL-5. (d) Temperature dependence of the ionic conductivity of electrolytes. (e) The rate capability of LiFePO$_4$/Li cell using liquid electrolyte, gel-state PVDF-HFP, and POSS-CPIL-5, respectively. (f) Long-term cycling performance of LiFePO$_4$/POSS-CPIL-5/Li cell under a current of 0.2 C. Reproduced with permission [86] Copyright 2022 Elsevier.
Chen et al. introduced the functional imidazole-based ionic liquid 1-cyanopropyl-3-vinylimidazole bis (trifluorane) sulfon imide with cyano and vinyl groups into the PEGDA matrix via in situ thermal polymerization and modified the quasi-solid polymer electrolyte (Figure 17a) [89]. The LiCoO$_2$ cathode can interact with the -C≡N group in cyanide through π-π coupling, which can reduce the rate of parasitic reactions and thus reduce the formation of by-products on the LiCoO$_2$ surface [90]. The stability window is effectively extended to about 5 V, and this ionic liquid has good anodic oxidation resistance. These functional ionic liquids-modified PEGDA-based electrolytes exhibited a high ionic conductivity of 4.97 × 10$^{-3}$ S cm$^{-1}$ at ambient temperature with a Li$^+$ migration number up to 0.69, and they showed excellent high-pressure anodizing resistance. The 1-cyanopropyl-3-vinylimidazole bis (trifluoromethane) sulfon imide ionic liquid increases flame retardancy and enhances the safety of PEGDA-based solid electrolytes. A cotton swab soaked in 1% IL-CN/PEGDA solid electrolyte was automatically extinguished within 2 s after ignition (Figure 17b), indicating good flame retardancy. The 4.6 V high-voltage LiCoO$_2$/Li solid-state batteries exhibit excellent cycling performance and rate capability at room temperature (Figure 17c–e).

Figure 17. (a) Fabrication diagram of LiCoO$_2$/GPEs/Li cells. Burning test of the cotton swabs impregnated with (b) 1% IL-CN/PEGDA GPE. Performance of LiCoO$_2$/GPEs/Li cells at 25 °C: (c) cycle performance of PEGDA GPE with different contents of IL-CN at 0.5C, (d) rate capability from 0.1 to 5C, and (e) cycling performance. Reproduced with permission [89] Copyright 2022 American Chemical Society.
Ionic liquid flame retardants displayed a good flame-retardant effect. Adding ionic liquid flame retardants to PEGDA-based polymer electrolytes improved the ionic conductivity of the electrolytes, increased the electrochemical stability of the electrolytes, and widened the electrochemical window. However, the electrolytes will melt at a high temperature, and the ionic liquid is expensive.

The flame retardancy of PEGDA-based electrolytes is dramatically improved by adding phosphorus-based flame retardants and ionic liquid flame retardants. These flame retardants not only enhanced flame retardancy but also improved ionic conductivity. Connecting the phosphorus-based flame retardant to the polymer chain of PEGDA via grafting also improved flame retardancy and ionic conductivity.

6. Summary and Prospects

With frequent fires and explosions of LIBs, battery safety has become a top priority, and research on flame-retardant solid polymer electrolytes has become a current focus. The types of flame retardants and electrochemical properties of flame-retardant electrolytes in this paper are summarized in Table 1.

Table 1. Different flame retardants for different polymer solid electrolytes and their electrochemical properties.

<table>
<thead>
<tr>
<th>Electrolyte Type</th>
<th>Flame Retardant Type</th>
<th>Flame Retardant</th>
<th>Ionic Conductivity</th>
<th>Coulombic Efficiency</th>
<th>Li⁺ Transfer Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEO</td>
<td>Phosphonium flame retardant</td>
<td>ADP [29]</td>
<td>$3.7 \times 10^{-5} \text{ S cm}^{-1}$ (30 °C)</td>
<td>99.95% after 1000 cycles at 1 C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PBMP [30]</td>
<td>$1.25 \times 10^{-5} \text{ S cm}^{-1}$</td>
<td>~100% after 100 cycles at 0.02 C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BEPA/OPTTA [31]</td>
<td>$0.28 \times 10^{-3} \text{ S cm}^{-1}$ (25 °C)</td>
<td>~ 100% after 100 cycles at 1.0 C and 50 °C</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Metal hydroxide flame retardant</td>
<td>Mg₂B₂O₅ [34]</td>
<td>$1.53 \times 10^{-4} \text{ S cm}^{-1}$ (40 °C)</td>
<td>~ 100% after 100 cycles at 0.2 C and 60 °C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HNT [35]</td>
<td>$1.1 \times 10^{-4} \text{ S cm}^{-1}$</td>
<td>~ 100% after 100 cycles at 1.0 C and 30 °C</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>Nitrogenous flame retardants</td>
<td>PBI [38]</td>
<td>$1.8 \times 10^{-4} \text{ S cm}^{-1}$ (30 °C)</td>
<td>&gt; 98.8% after 1500 cycles at 2 C and 80 °C</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>Bio-based flame retardant</td>
<td>AF-PEA [44]</td>
<td>$1.8 \times 10^{-3} \text{ S cm}^{-1}$ (25 °C)</td>
<td>~100% after 300 cycles at 0.5 C and 60 °C</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Halogen flame retardant</td>
<td>DBDPE [47]</td>
<td>$6.7 \times 10^{-6} \text{ S cm}^{-1}$ (30 °C)</td>
<td>~100% after 1000 cycles at 0.2 C</td>
<td>-</td>
</tr>
<tr>
<td>PVDF</td>
<td>Halide flame retardant</td>
<td>ED [55]</td>
<td>$4.41 \times 10^{-3} \text{ S cm}^{-1}$ (30 °C)</td>
<td>~100% after 1000 cycles at 1 C and 30 °C</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LAGP [56]</td>
<td>$0.76 \times 10^{-3} \text{ S cm}^{-1}$ (30 °C)</td>
<td>~100% after 50 cycles at 0.05 C</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>LLPO [57]</td>
<td>$4.84 \times 10^{-4} \text{ S cm}^{-1}$ (25 °C)</td>
<td>~100% after 1000 cycles at 1 C</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TMP [59]</td>
<td>$1.86 \times 10^{-4} \text{ S cm}^{-1}$ (30 °C)</td>
<td>&gt;98.8% after 300 cycles at 1 C</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HAP [65]</td>
<td>$7.4 \times 10^{-4} \text{ S cm}^{-1}$</td>
<td>~99.3% after 600 cycles at 0.5 C</td>
<td>0.41</td>
</tr>
<tr>
<td>PAN/PUA</td>
<td>Nitrogenous flame retardant</td>
<td>SN [70]</td>
<td>$2.32 \times 10^{-3} \text{ S cm}^{-1}$ (25 °C)</td>
<td>99.9% at 0.1 C</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DOPO [72]</td>
<td>$2.66 \times 10^{-4} \text{ S cm}^{-1}$ (RT)</td>
<td>~100% after 100 cycles at 0.2 C</td>
<td>0.55</td>
</tr>
<tr>
<td>PEGDA</td>
<td>Phosphonium flame retardant</td>
<td>HCCP [76]</td>
<td>$9.86 \times 10^{-4} \text{ S cm}^{-1}$ (30 °C)</td>
<td>~100% after 400 cycles at 1 C</td>
<td>0.54</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DOPO [80]</td>
<td>$4 \times 10^{-3} \text{ S cm}^{-1}$ (20 °C)</td>
<td>~100% after 200 cycles at 0.1 C</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>Ionic liquid flame retardant</td>
<td>VEIM-TFSI [85]</td>
<td>$1.03 \times 10^{-3} \text{ S cm}^{-1}$ (RT)</td>
<td>~98% after 200 cycles at 0.2 C</td>
<td>0.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BMIm [TFSI] [86]</td>
<td>$2.5 \times 10^{-3} \text{ S cm}^{-1}$ (RT)</td>
<td>~99% after 115 cycles at 0.5 C</td>
<td>0.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IL-CN [89]</td>
<td>$4.97 \times 10^{-3} \text{ S cm}^{-1}$ (RT)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Despite the fact that adding flame retardants to polymer electrolytes can improve their flame retardancy, there are still many challenges that need to be addressed. Therefore, the following aspects may be included in the development direction for flame-retardant polymer electrolytes (Figure 18):

1. At present, the main flame retardants are phosphorus flame retardants, metal hydroxide flame retardants, nitrogen flame retardants, halogen flame retardants, bio-based flame retardants, and ionic liquid flame retardants. However, halogen flame retardants will produce harmful halogen gas and corrosive harmful hydrogen halide gas when burned and when encountering water. Therefore, it is necessary to explore environmentally friendly phosphorus-based and nitrogen-based flame retardants. Designing flame retardants that combine P and N elements will construct more efficient and environmentally friendly polymer electrolytes.

2. Although adding flame retardants can greatly improve the flame retardancy of solid polymer electrolytes, excessive addition affects ionic conductivity, interface stability, and mechanical properties. For instance, phosphorus introduced into the polymer skeleton will achieve compatibility and enhance the flame retardancy of the polymer. In the future, discovering polymers with good compatibility with flame retardants is in need of attention. The relationship between the content of flame retardants and the ionic conductivity of polymer electrolytes also needs consideration.

3. Adding flame retardants to increase flame retardancy will inevitably increase battery costs. To meet the needs of commercial large-scale production, it is necessary to reduce the cost of flame-retardant electrolytes. It is possible to consider adding multiple flame retardants utilizing the synergistic effect between different flame retardants to achieve better flame retardancy. Developing simple and low-cost flame-retardant solid polymer electrolytes is also a development direction for Li-metal batteries.

4. Polymer electrolytes have the advantages of high flexibility, low interfacial impedance, good film-forming properties, and low cost, but their low ionic conductivity seriously hinders their application in solid-state batteries. Adding an appropriate amount of lithium salt can improve ionic conductivity. So, exploring new types of lithium salt and constructing cross-linked network copolymer structures can improve ionic conductivity. The film-making process of polymer electrolytes needs innovation to reduce the thickness and improve ion conductivity.

**Figure 18.** Future research directions and prospects of flame-retardant solid polymer electrolytes.

In summary, this work reviewed the current use of (mainly) polymer electrolyte materials, including PEO, PVDF, PAN, and PEGDA. It especially concluded that the recent advance of phosphorus flame retardants, metal hydroxide flame retardants, nitrogen flame retardants, halogen flame retardants, bio-based flame retardants, and ionic liquid flame retardants, has led to applications in these four polymer electrolytes. It pointed out the merits, demerits, and flame-retardant mechanisms of these flame retardants. With the rapid expansion of electric vehicles and grid energy storage markets, safe and reliable flame-retardant batteries have a broad market prospect. Therefore, we hope that this review
guides other researchers toward developing environmentally friendly, simple, low-cost, and electrochemically stable solid electrolytes to meet the security demands for LIBs.

Author Contributions: Writing—original draft preparation, Y.L. and X.X.; conceptualization, J.L., Y.H. and J.Z.; writing—review and editing, Y.L., X.X., X.L. and J.L.; visualization, Y.L. and S.J.; supervision, J.L., Y.H., J.Z. and X.X.; project administration, J.L.; funding acquisition, Y.H., J.Z. and J.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key Research and Development Program of China (no. 2022YFB25020000), the National Natural Science Foundation of China (no. U21A2033251771076), Guangdong Basic and Applied Basic Research Foundation (nos. 2020B1515120049, 2021A1515010332), and the R&D Program in Key Areas of Guangdong Province (no. 2020B0101030005).

Data Availability Statement: Not applicable.

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

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