

# Incombustible Polymer Electrolyte Boosting Safety of Solid-State Lithium Batteries: A Review

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Lithium-ion batteries with their portability, high energy density, and reusability are frequently used in today's world. Under extreme conditions, lithium-ion batteries leak, burn, and even explode. Therefore, improving the safety of lithium-ion batteries has become a focus of attention. Researchers believe using a solid electrolyte instead of a liquid one can solve the lithium battery safety issue. Due to the low price, good processability and high safety of the solid polymer electrolytes, increasing attention have been paid to them. However, polymer electrolytes can also decompose and burn under extreme conditions. Moreover, lithium dendrites are formed continuously due to the uneven charge distribution on the surface of the lithium metal anode. A short circuit caused by a lithium dendrite can cause the battery to thermal runaway. As a result, the safety of polymer solid-state batteries remains a challenge. In this review, the thermal runaway mechanism of the batteries is summarized, and the batteries abuse test standard is introduced. In addition, the recent works on the high-safety polymer electrolytes and the solution strategies of lithium anode problems in polymer batteries are reviewed. Finally, the development direction of safe polymer solid lithium batteries is prospected.

## 1. Introduction

Lithium-ion batteries (LIBs) are broadly used in power fields such as cell phones, computers, cars, and storage stations owing to their high energy density, reusability, and portability. The need for higher-energy-density LIBs has prompted further improvements in the energy density of LIBs.<sup>[1]</sup> But safety issues of higher-energy-density LIBs have always existed and

even become more severe. Improving the safety of LIBs to allay concerns about energy equipment is key to the further development of LIBs. For LIBs, the safety of different components varies. Commonly used LIBs mainly comprise cathode materials, anode materials, electrolytes, and separators.<sup>[2]</sup> For cathode materials, including LiCoO<sub>2</sub>, LiNiO<sub>2</sub>, olivine-structured LiFePO<sub>4</sub>, and LiNi<sub>x</sub>Mn<sub>y</sub>Co<sub>z</sub>O<sub>2</sub>, research is focused on the development of high specific energy and voltage cathode material.<sup>[3]</sup> For anode materials, how to resolve the expansion of the electrode volume, lithium dendrite's growth, and solid electrolyte interphase (SEI) layer's stability during charge and discharge are hot topics of research.<sup>[4]</sup> In addition to the cathode and anode parts of batteries, the electrolyte and separator are extremely flammable parts of batteries. Current commercial LIBs comprise low-boiling carbonate solvents and lithium hexafluorophosphate (LiPF<sub>6</sub>).

The composition of the electrolyte is very complex, and a good electrolyte needs to comprehensively consider physicochemical properties and stability of electrolyte and electrode.<sup>[3a,5]</sup> LIBs using traditional commercial electrolytes are prone to thermal runaway under extreme conditions such as overcharge, short-circuiting, squeezing, and high temperatures. When thermal runaway occurs, the SEI film decomposes first, followed by electrolyte oxidation, anode and cathode breakdown, and their interactions. The rupture of the cell leads to an outflow of electrolyte, in which organic molecules can easily burn or even explode.<sup>[4a,6]</sup> Therefore, how to improve the safety of electrolytes has become crucial.

Technological innovations in electrolytes are necessary for next-generation LIBs.<sup>[7]</sup> Replacing organic liquids electrolytes with solid polymer electrolytes (SPEs) can significantly enhance battery safety. Polymer electrolyte do not suffer from leakage problems. The higher thermal decomposition temperature of polymers leads to better thermal stability of the cells. Meanwhile, all-solid-state batteries containing SPEs can further improve the cycle life and energy density of the batteries (Figure 1a). The solid/solid interface reaction of polymer solid-state batteries is slower, while polymer materials have excellent mechanical strength and stability, which can suppress the volume change of the electrode material, reduce the peeling of the electrode active material, and inhibit the generation and

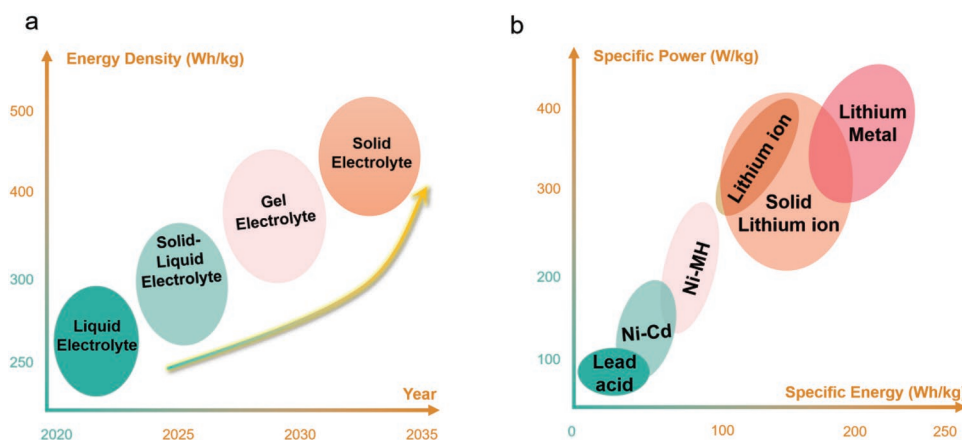
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**Figure 1.** a) Roadmap for the development of different batteries. b) Comparison of specific power and specific energy of different batteries. Replacing liquid electrolytes with polymer solid electrolytes can effectively increase the energy density of batteries, which is the direction of electrolyte development.

growth of lithium dendrites inside the electrode. This gives it a significant advantage in cycling performance. Compared with traditional liquid electrolytes, SPEs can form a thinner electrolyte layer, the distance between the electrodes is smaller, which increases the energy density of batteries. In addition, the lower density of SPEs means that more electrode can be accommodated in the same volume, further increasing the energy density of batteries. In this regard, there is a growing interest in SPEs.<sup>[8]</sup>

There are many types of SPEs, among which the poly (ethylene oxide) (PEO) polymer solid electrolyte has been most popular because of its high conductivity, low price, and controllable size.  $(-\text{CH}_2\text{CH}_2\text{O}-)_n$  in PEO can facilitate the transfer of lithium ions. Lithium salts matching PEO SPEs include LiTFSI,  $\text{LiClO}_4$ , and  $\text{LiPF}_6$ . Among them, PEO SPEs containing LiTFSI have received numerous attentions owing to their excellent electrochemical properties. Gel polymer electrolytes (GPEs) can solve the problem of battery leakage and maintain high ionic conductivity.<sup>[9]</sup> In addition, the flexibility and elasticity of GPEs can easily withstand volume changes in the electrode material and dendrites of lithium metal. GPEs are in tighter contact with the electrodes and thus have a lower interfacial impedance than SPEs. Focus has shifted to how solid electrolytes can be used in batteries.<sup>[10]</sup> In these ways, better GPEs can be obtained. The electrochemical and mechanical properties of GPEs can be effectively improved by reducing the size of inorganic particles to the nanometer level. Different from dual-ion conductors such as PEO-based SPEs, single-ion conductor SPEs have gradually attracted attention, with anions anchored to the backbone via covalent bonds or fixed by neutral molecules via classical Lewis acids. Inside such polymer electrolytes, cations are mobile and associate with anions through weak electrostatic forces because of anionic charge delocalization and can be transported between electrodes by hopping.

In addition to the above-mentioned SPEs other polymer electrolytes such as polyphosphazene, polysiloxane, polycarbonate and others. Polysiloxane shows high thermal stability, non-flammability, small bond rotation potential of  $\text{Si}-\text{O}-\text{Si}$  bond ( $0.8 \text{ KJ mol}^{-1}$ ), strong chain movement ability. Polycarbonate SPEs have higher dielectric constants. By modifying the polymer, the electrochemical and mechanical properties of

the polymer can be effectively improved by associating different groups on the polymer side. For example, polyphosphazene is obtained by ring-opening polymerization of hexachlorocyclotriphosphazene. Because the main chain of phosphorus and nitrogen atoms alternates between single and double structures, phosphorus and nitrogen elements have good flame-retardant properties. Simultaneously, the chlorine atoms of the side chains are highly active and can react with multiple groups, enabling the design of high ionic conductivity SPEs.

The use of SPEs greatly improves the safety of polymer solid-state lithium batteries compared to liquid electrolytes, but certain dangers exist. For example, it will burn under extreme conditions, such as high temperatures and flame baking. The safety of polymer electrolytes can be effectively improved through the design of SPEs. Further, flame retardants are added to SPEs to obtain non-flammable SPEs or flame-retardant SPEs are obtained by introducing flame retardant group into polymer molecular chain. On the other hand, the formation of lithium dendrites can also cause a short circuit in batteries.<sup>[8a,11]</sup> By surface modification of lithium metal anodes, the SPEs are designed to effectively suppress lithium dendrites. For cathode, besides the lithium dendrite problem, its stability cannot be neglected.

For LIBs, using a lithium metal anode instead of a graphite anode is an excellent solution to improve energy density (Figure 1b). But the stability of lithium metal anode with high specific capacity is not good enough. Lithium metal is relatively stable under closed conditions, and thus is relatively stable when lithium metal batteries are working properly. But lithium metal is extremely unstable in air, water, and environmental elements. When batteries with lithium metal anodes are misused, it can cause the cell casing to deform and break. Damaged cell housing can bring lithium metal into contact with air, which reacts with it to release hydrogen and a lot of heat that will lead to thermal runaway of batteries, leading to greater harm.

Herein, first, we briefly analyzed the mechanism of thermal runaway of cells. Only with a full understanding of the thermal runaway mechanism of lithium batteries can the core problems affecting thermal runaway be found. Second, the current battery safety test standards and common safety test methods (electrical abuse tests, thermal abuse tests,

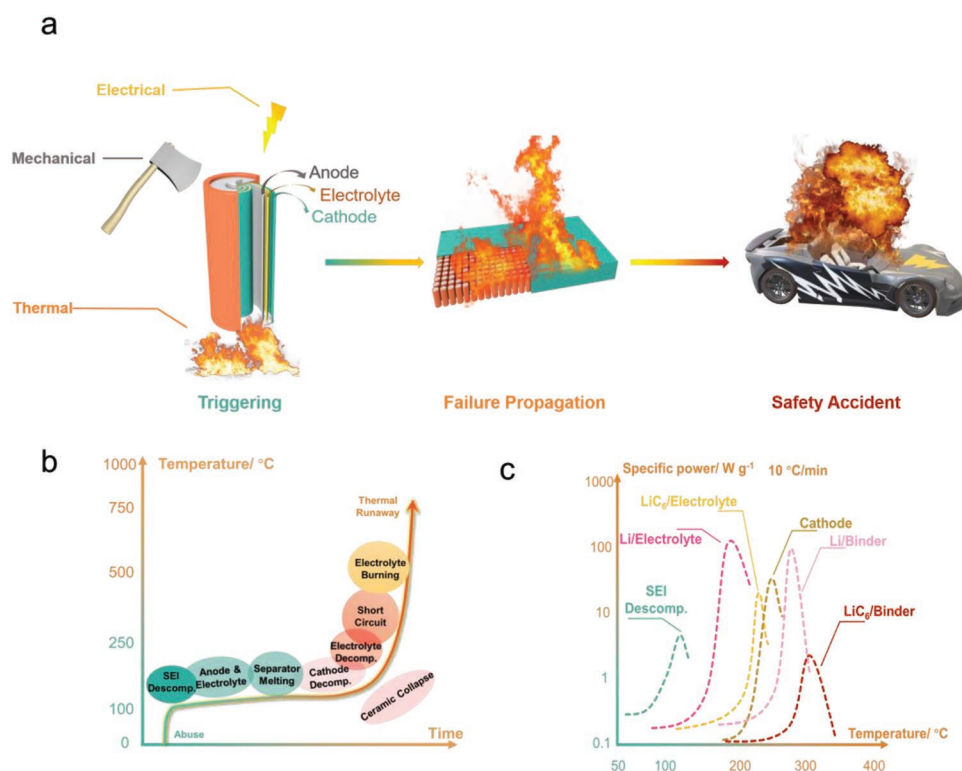
mechanical abuse tests) are introduced. Through the understanding and comparison of different test standards, the test method which is more suitable for different thermal runaway experiments can be found. Third, the recent researches on safe polymer solid-state lithium batteries are reviewed. Classify and introduce different works about high-safety polymer electrolytes. From different angles and different methods to solve safety issues of solid-state lithium batteries. Finally, a prospect on the research direction of safe lithium anodes is made. With the continuous expansion of the application range of lithium batteries, the safety and energy density of lithium batteries have become an important index for the selection of lithium batteries. High-safety solid-state lithium batteries can effectively solve these problems and become the focus of research. Hopefully, this review will serve as a reference for safe polymer solid-state lithium batteries.

### 1.1. Thermal Runaway Mechanisms of Lithium Batteries

In general, the thermal runaway caused by the battery under extreme conditions can lead to a chain reaction. As shown in **Figure 2a**, when the internal cells are subjected to thermal, mechanical, or electrical abuse, it can cause the individual cells to heat out of control. When a single battery gets out of control, it will cause a rapid rise in the temperature around the cell. A thermal runaway cell is likely to further burn or explode,

which will cause thermal runaway of the surrounding cells. The spread of thermal runaway batteries can lead to the thermal runaway of battery packs, leading to more extraordinary safety incidents.

To design safer lithium batteries, we need to understand not only the process of thermal runaway from a macroscopic point of view, but also the internal changes of the battery when it goes out of control. The commonly used thermal runaway process in lithium-ion batteries is also a chain reaction. The pyrolysis temperatures of different battery components are different. **Figure 2b** shows the pyrolysis of the battery components as the temperature increases during the thermal runaway process. Pyrolysis occurs in the unstable SEI layer when the battery is out of control. The interface between the electrode and the electrolyte will also be pyrolyzed. At the same time, the melting of the separator absorbs some of the heat and slows the rise of the battery temperature. As the temperature continues to rise to the point of decomposition of the positive electrode, the oxygen released by the pyrolysis of the cathode will aggravate the electrode, and the pyrolysis of the electrolyte causes a sharp rise in the temperature of the cell. The rising temperature gasifies and burns the electrolyte. The increase in the internal temperature and pressure of the cell leads to thermal runaway. In addition to the different pyrolysis temperatures, the specific power during pyrolysis is also different for various cell components. The pyrolysis of the SEI membrane releases less heat, while the pyrolysis of the electrode releases oxygen and more heat. The



**Figure 2.** a) The schematic diagram of battery system thermal runaway process. b) Variation curves of pyrolysis process of different battery components with time. c) Variation curves of pyrolysis process of different battery components with temperature. Thermal, mechanical and electrical abuse can cause the battery to heat up out of control. The thermal stability of the different components of the cell is different, and the different components continuously decompose as the temperature increases. At the same time, the content and specific power of different components are different, so a systematic understanding of the thermal runaway process is fundamental for battery safety studies.

oxygen generated by the pyrolysis of the cathode will react with the anode to generate about 80% of the total heat. The accumulated heat will cause the battery temperature to rise continuously. The specific power of different components is shown in Figure 2c.<sup>[7,12]</sup>

Compared with the lithium-ion batteries, the thermal runaway of the polymer solid-state batteries is different. The pyrolysis of the cathode and SEI layers is like that of lithium-ion batteries. The thermal runaway of the polymer solid-state batteries can be divided into three stages. In the first stage, with the gradual increase of temperature, the batteries begin to produce heat, and in the second stage, the batteries heat production intensified, and the temperature continued to rise at a uniform rate. As the temperature continues to increase, the cathode and anode electrodes of the batteries are pyrolyzed, and the temperature of the batteries increases rapidly. In the third stage, the batteries temperature rises sharply to the maximum temperature.<sup>[13]</sup> For common PEO polymer electrolytes, the pyrolysis temperature of PEO is about 400 °C. The oxygen released from cathode pyrolysis will promote pyrolysis and combustion of the PEO. The effects of different cathodes on the safety of polymer solid-state batteries are different. The commonly used LFP cathode has higher stability, lower and better stability than the NCM cathode, which is more conducive to improve the safety of polymer solid-state batteries. NCM high voltage cathode has higher energy density and poor stability, which also makes polymer solid-state battery more dangerous. Lithium metal anode will melt when the temperature rises to 189 °C. Lithium metal is extremely quickly oxidized and burns when molten lithium metal comes into contact with air.<sup>[14]</sup>

## 1.2. Safety Tests for Lithium Batteries

LIBs are widely used, and different countries have different safety standards for LIBs. With the development of the times and technology, the test standards of battery safety are constantly

improved. Different countries have different requirements for battery safety. Therefore, different test standards can be comprehensively considered to select the test standards that meet the requirements.<sup>[15]</sup> Table 1 shows the main safety tests used to evaluate LIBs. There are corresponding safety tests for different test standards. In the safety test, the test steps that do not affect the results can be simplified to facilitate the test, so the thermal runaway characteristics of lithium-ion batteries could be measured in the laboratory. In order to provide a good reference for the thermal runaway in the actual use of the battery, the test needs to meet the following requirements: i) Test feasibility: For safety tests, the operation of real batteries can be simulated by simplifying the test; ii) Consistency of test results: For the same safety test, the results of battery safety tests under the same conditions should be consistent; iii) Test reproducibility: At different times, places, and personnel, the safety test results of batteries under the same conditions should be the same.

## 1.3. Electrical Abuse Tests

Under normal conditions, the battery may experience overcharge or overdischarge operation. Therefore, it is necessary to test the safety of the battery against overcharge and overdischarge for the batteries to be widely used.

### 1.3.1. Overcharge Tests

The IEC standard test evaluates the overcharge safety of the battery. The overcharge test is conducted at  $20 \pm 5$  °C. First, the cell is discharged at a constant current of  $0.2 I_t$  A to a voltage specified by manufacturer and then charged at a constant current  $2.0 I_t$  A. The supply voltage of single cell/cell block batteries is 1.4 times the upper limit charging voltage but should not exceed 6.0 V. The upper limit charging voltage of different anode and cathode are different. Please refer to the standard

**Table 1.** Comparison of the same test items under different test standards. The contents of the same test items in different test standards are shown in this table.

Test content	GB/T 31485 <sup>[19]</sup>	IEC 62133 <sup>[20]</sup>	UL2580 <sup>[15g]</sup>	SAE J2464 <sup>[15a]</sup>	JIS C8715-2 <sup>[15d]</sup>	USABC-GM <sup>[15h]</sup>
Overcharge	100% SOC Overcharge to $1.5 V_{\max}$ or charge for 1 h at 1 C	Overcharge to 250% SOC at 1 C	Overcharge to 200% SOC at 1 C	Overcharge to 200% SOC at 1 C	Allow the maximum charging current to charge to the maximum voltage	Overcharge the 100% SOC cell at 1 C for 1 h or $1.5 V_{\max}$ or venting
Over-discharge	Over-discharge the 100% SOC cell at 1 C for 1.5 h	Over-discharge the 0% SOC cell at 1 C for 90 mins	Over-discharge the 0% SOC cell at 1 C for 90 mins	Over-discharge the cell to – 100% SOC	/	Over-discharge the 100% SOC cell at 1 C until venting
Heating	Heating at 5 °C/min from 25 to 130 °C, hold for 30 mins	130 °C, 10 mins	$150 \pm 2$ °C, 60 mins	Max. stable temperature	Heating at $5 \pm 2$ °C/min to $85 \pm 5$ °C, hold for 3 h	0.5 °C/min, 50 – 150 °C, hold for 30 mins
Short-circuit	Short circuit for 10 mins, $R \leq 5 M\Omega$	$80 \pm 20 m\Omega$	Short with $R \leq 5 m\Omega$ until explosion, fire or no temp change	$R \leq 5mX$ for hard short; $R \leq 5mX$ for soft short	$30 \pm 10 m\Omega$ after connecting, 6 h (External short-circuit); $80 \pm 20 m\Omega$ (Internal short-circuit)	Short circuit for 10 mins, $R \leq 5 m\Omega$
Nail penetration	Penetration rate 25 mm/s, steel needle diameter is 5 – 8 mm, 100% depth	/	80 mm/s, steel needle diameter is 3 mm, 100% depth	80 mm/s, steel needle diameter is 3 mm, 100% depth	80 mm/s, steel needle diameter is 3 mm, 100% depth	80 mm/s, steel needle diameter is 3 mm, 100% depth



for detailed data. During the whole test, the battery is considered to have passed the safety test if it does not burn or explode. The overcharge safety of the battery can be evaluated by testing different components separately by changing the electrolyte, separator, etc. For other batteries or test requirements, the test conditions can also be changed, such as by studying different charging rates to evaluate the overcharge safety of the battery.

### 1.3.2. Overdischarge Tests

In addition to overcharging, overdischarging can also lead to battery failure. Too low voltage due to excessive discharge will cause the decomposition of SEI film to produce gas. The gas inside the cell can cause the cell to bulge, causing poor contact with the electrode and electrolyte. At the same time, excessive discharge may lead to the instability of electrode structure and the attenuation of battery capacity. For different test standards, the battery overdischarge test conditions are different. According to the IEC standard, the 0% soc battery is required to continue to discharge for 1 hour at the rate of 1 C.

## 1.4. Thermal Abuse Tests

Batteries are generally assembled from anode, cathode, separator and electrolyte by specific processing methods. In general, batteries can be used commonly under normal environmental conditions. But in extreme cases, batteries can become unstable, short-circuit, bulge, or even explode. Therefore, it is also crucial to test the safety of batteries in different environments.

### 1.4.1. Thermal Abuse Tests

Batteries are used in some appliances in our daily life. Conditions of normal use are milder. But once a battery is placed in an extreme environment, such as a high temperature, it is likely to swell and cause a fire or explosion. Because of the large amount of electrical energy stored inside the battery, high temperatures can cause the separator to melt and cause the battery to short circuit. The released heat in turn leads to electrolyte decomposition and interfacial electrode-electrolyte reactions. Therefore, a heating test should be performed to check its electrochemical and mechanical performance in high temperature. Heating can study the thermal stability of the LIB, and then the battery pack can be designed to better manage the battery. The test standard of heat abuse is introduced in detail in GB/T31485. Put the battery sample to be tested in the oven and the oven heats up to  $130 \pm 2^\circ\text{C}$  at a rate of  $5^\circ\text{C min}^{-1}$ . A battery passes the test if it does not leak, burn or explode after standing for half an hour.

### 1.4.2. Simulated Fire Tests

Batteries can burn or even explode in extreme conditions. Therefore, it is essential to test the fire resistance of the battery. According to GB 38031, the battery is exposed to the gasoline

flame for 70 seconds, and the condition of the battery is observed for 2 hours after leaving the flame. The battery passes the test without burning or exploding.

## 1.5. Mechanical Abuse Tests

In some unexpected situations, lithium batteries can be squeezed, dropped or punctured by hard objects. Mechanical abuse can lead to a battery deformation and liquid leakage, which leads to thermal runaway. For example, the accident of new energy vehicles causes the battery to be crushed and deformed, and the mobile phone falls to cause the battery to be violently collided, etc., which may pose a threat to the safety of people's lives. To sum up, it is important to evaluate the safety of batteries, especially whether the battery can pass the mechanical abuse test.

### 1.5.1. Short Circuit Tests

Improper operation of a battery may lead to the external anode and cathode contact, which may cause the battery to generate a lot of heat. Rising battery temperatures can cause separators to melt, electrolytes to vaporize, and electrodes to break down, which can cause the battery to burn up or explode. Therefore, it is crucial to test the safety of batteries under external short-circuit conditions. According to the GB31485-2015, the battery can stand for half an hour after being fully charged at  $25 \pm 2^\circ\text{C}$ . Then connect the external positive and negative terminals with a  $5\text{ m}\Omega$  resistance. Check for changes in the battery voltage and temperature throughout the test. If the battery does not explode or burn, it passes the test.

### 1.5.2. Drop Tests

A drop in a battery due to an emergency may cause the battery valve to short-circuit and cause thermal runaway. According to the national standard test instructions, the battery is free to fall to the concrete board or metal floor 3 times at a height of 1 m at an ambient temperature of  $20 \pm 5^\circ\text{C}$ . A battery is considered safe if it does not burn or explode during testing.

### 1.5.3. Nail Penetration Tests

Some tiny impurities in a battery preparation process will cause the battery to occur. At the same time, during actual use, hard objects can pierce the battery, causing it to short-circuit, and leaks of liquid can cause the battery to become thermally runaway. The acupuncture test steps according to GB/T31485 are as follows, high temperature resistant steel nails with a diameter of  $5 \sim 8\text{ mm}$  at  $25 \pm 5\text{ mm s}^{-1}$  insert the battery at a speed perpendicular to the direction of the plates. The conical nail tip angle is  $45 \sim 60^\circ$  and the surface of it is clean and flat. The steel needle is inserted at a certain rate from the center of the battery and retained for a period. If the battery does not explode or burn, the test is considered successful.

#### 1.5.4. Crush Tests

When a battery is impacted by external force, the battery will be squeezed and damaged. According to GB/T31485, the battery is first charged to 4.2 V under 1 C. Place the battery between two planes of a semi-cylinder with a radius of 75 mm and squeeze the battery at a rate of 5 mm s<sup>-1</sup> to observe the temperature and morphological changes of the battery. The experiment is terminated when the voltage drops to 0 V, the deformation exceeds 30% or the load reaches 200 kN. If the battery does not get out of control, the battery is considered to pass the test.

### 1.6. Polymer Solid-State Lithium Batteries Safety Tests

The safety tests of polymer solid-state lithium batteries can learn from the safety tests of LIBs. At the same time, the preparation of large-capacity polymer solid-state lithium batteries is also difficult, so there are some other methods to test the safety of polymer solid-state lithium batteries.

#### 1.6.1. Flame Combustion Tests

The safety of polymer solid-state lithium batteries is related to the safety of polymer electrolyte. Place the electrolyte on top of the flame to see if the polymer electrolyte can be ignited. The fire safety of polymer can be observed intuitively.<sup>[16]</sup> UL-94 and LOI test can also test the fire hazard of polymer electrolyte.

#### 1.6.2. Thermogravimetric Analysis (TG) Tests

TG test can be used to test the thermal stability of polymer electrolytes. The weight change of polymer electrolyte was monitored during the programmed heating process to illustrate its stability. The TG instrument can be used with different testing instruments such as TG-IR, TG-GCMS to detect the gas components produced during the pyrolysis of polymer electrolytes to further analyze its stability mechanism.<sup>[17]</sup>

#### 1.6.3. Cone Calorimeter (CC) Tests

CC is a new generation instrument for measuring the flammability of polymer materials based on the principle of oxygen consumption. The combustion parameters of materials in fire, such as total release rate (TRR), heat release rate (HRR), smoke production rate (SPR) can be obtained by cone calorimeter. The data obtained can quantitatively describe the fire risk of combustible materials. In the future, the assembled solid-state lithium battery can be further tested by this instrument.<sup>[10,18]</sup>

### 1.7. Improve the Safety of Polymer Solid-State Lithium Batteries

LIBs are increasingly used in various energy storage devices, for instance, computers, mobile phones, automobiles, and energy storage stations. The safety of batteries has become

a major concern as their energy density and capacity have increased. LIBs composed of organic electrolytes are prone to leakage, combustion and explosion in extreme conditions. Therefore, battery safety has received unprecedented attention. SPEs have been welcomed for their ability to effectively address safety issues such as battery leakage and bulges, while further improving the energy density of batteries. But SPEs are not safe either. First, the polymer will undergo pyrolysis at high temperature to generate flammable molecular segments. Second, organic polymers composed of hydrocarbons and oxygen are flammable, releasing large amounts of heat during combustion, and the accumulated heat may cause further pyrolysis of the polymer. Third, in addition to the flammability of the polymer, the lithium dendrites generated during the charging and discharging process of LIBs will pierce the polymer electrolyte. Therefore, it is essential to understand how to improve the safety of SPEs.

### 1.8. Additive Flame Retardants to SPEs

Combustion of SPEs can be effectively suppressed by adding flame retardants to the polymer electrolyte. Generally, there are many types of flame retardants commonly used commercially, which are generally divided into additive and reactive flame retardants. Additive flame retardants are classified into organic flame retardants and inorganic flame retardants according to their composition. Organic flame retardants are classified as halogen-based, phosphorus-based, nitrogen-based, and others. Because the composition of the flame retardant is different, the mechanical and electrochemical properties of the polymer electrolyte will be affected. How to select flame retardants that can not only improve the safety of SPEs, but also improve the mechanical and electrochemical properties of batteries still needs to be studied continuously. For the flame retardants which are not suitable to be added directly to the SPEs, the flame retardants surface coated with high stability materials can be added to the SPEs. Cui's group reported the fabrication of high-safety separators by wrapping flame retardant in PVDF-HFP fiber membranes using electrospinning techniques. Flame retardants have a large impact on the electrochemical properties of lithium batteries. The electrolyte added with flame retardant makes the battery unable to cycle, so this technology can be applied to flame retardants that are not suitable for direct use.<sup>[21]</sup> The flame retardant can also be wrapped around the inside of the polymer ball through chemical coating techniques. Ki Jae Kim et al. prepared a flame-retardant microsphere coated with a polymethyl methacrylate polymer. The microspheres were glued to the surface of the separator to prepare a high-safety separator.<sup>[22]</sup> Flame retardants coated in this way can also be applied to SPEs.

#### 1.8.1. Halogen Flame Retardant

Halogen-containing flame retardants are used because of their obvious flame-retardant effect. In general, brominated flame retardants are more commonly used. Cui groups reported a fireproof, ultra-light polymer solid-state electrolyte (Figure 3a).

Polyimide (PI) fiber membrane is used as supporting layer, decabromodiphenyl ethane (DBDPE) plays a role of flame retardant, and PEO is used as lithium matrix to prepare polymer solid electrolyte. This ultra-light polymer solid electrolyte is difficult to ignite. DBDPE is decomposed to form bromine free radical ( $\text{Br}\cdot$ ).  $\text{Br}\cdot$  can capture the highly active free radicals  $\text{H}\cdot$  and  $\text{OH}\cdot$  produced by the pyrolysis of electrolytes and slow down the pyrolysis of PEO electrolytes. At the same time, products such as  $\text{HBr}$ ,  $\text{H}_2\text{O}$  and  $\text{Br}_2$  dilute the concentrations of combustible gases and oxygen, thus delaying the combustion of polymer electrolytes. Ultra-thin and ultra-light polymer solid electrolytes can effectively improve the energy density of batteries. PI/DBDPE thin films have thermal stability, non-flammability and mechanical strength. The flexible package battery made of polymer solid-state electrolyte (SSE) works well even in the flame abuse test.<sup>[23]</sup>

### 1.8.2. Organophosphorus Flame Retardants

Halogen flame retardants are banned in many countries because they release toxic gases during the combustion of polymers. Phosphorus-based flame retardants have attracted attention as halogen-free flame retardants with high flame retardancy. Liu et al. designed a novel poly(bis(4-phenoxy) propane methylphosphonate) (PBMP) alkyl polyphosphonate flame retardant (Figure 3b). PBMP flame retardants can effectively improve the fire safety of PEO. The addition of 3 wt.% phosphorus to PEO results in a UL94 V-0 rating with a LOI of 25.6%. Phosphate flame retardants work in both the gas and condensed phases. Phosphorous flame retardant added to polymer matrix can effectively inhibit polymer combustion.<sup>[17]</sup> Hu et al. found that diethyl aluminum hypophosphite (ADP) can effectively improve the cycle stability of batteries and inhibit the growth of lithium dendrites. Figure 3c shows that ADP plays a role in PEO SSE. ADP flame retardants break down and produce phosphate and phosphate oxygen radicals, which diffuses into the gas phase to combine with the combustible radical to inhibit the polymer combustion. At the same time, phosphoric acid and its derivatives dehydrate the polymer to form a carbon layer that slows heat transfer and traps oxygen, preventing decomposition and combustion of the polymer. Therefore, the combustion of SPE is effectively suppressed in ADP and the LOI value of this SSE is 22% (The LOI value of PEO is about 16%).<sup>[14a]</sup> The Meng team developed a polymer electrolyte with a single ion conductor with high ionic conductivity. The gel electrolyte added with 5% ethoxy (penta electrolyteuoro) cyclotriphosphazene is hard to ignite. Flame retardants containing phosphorus, nitrogen and fluorine are effective in inhibiting the combustion of polymer electrolytes.<sup>[24]</sup>

### 1.8.3. Inorganic Phosphorus-Based Flame Retardants

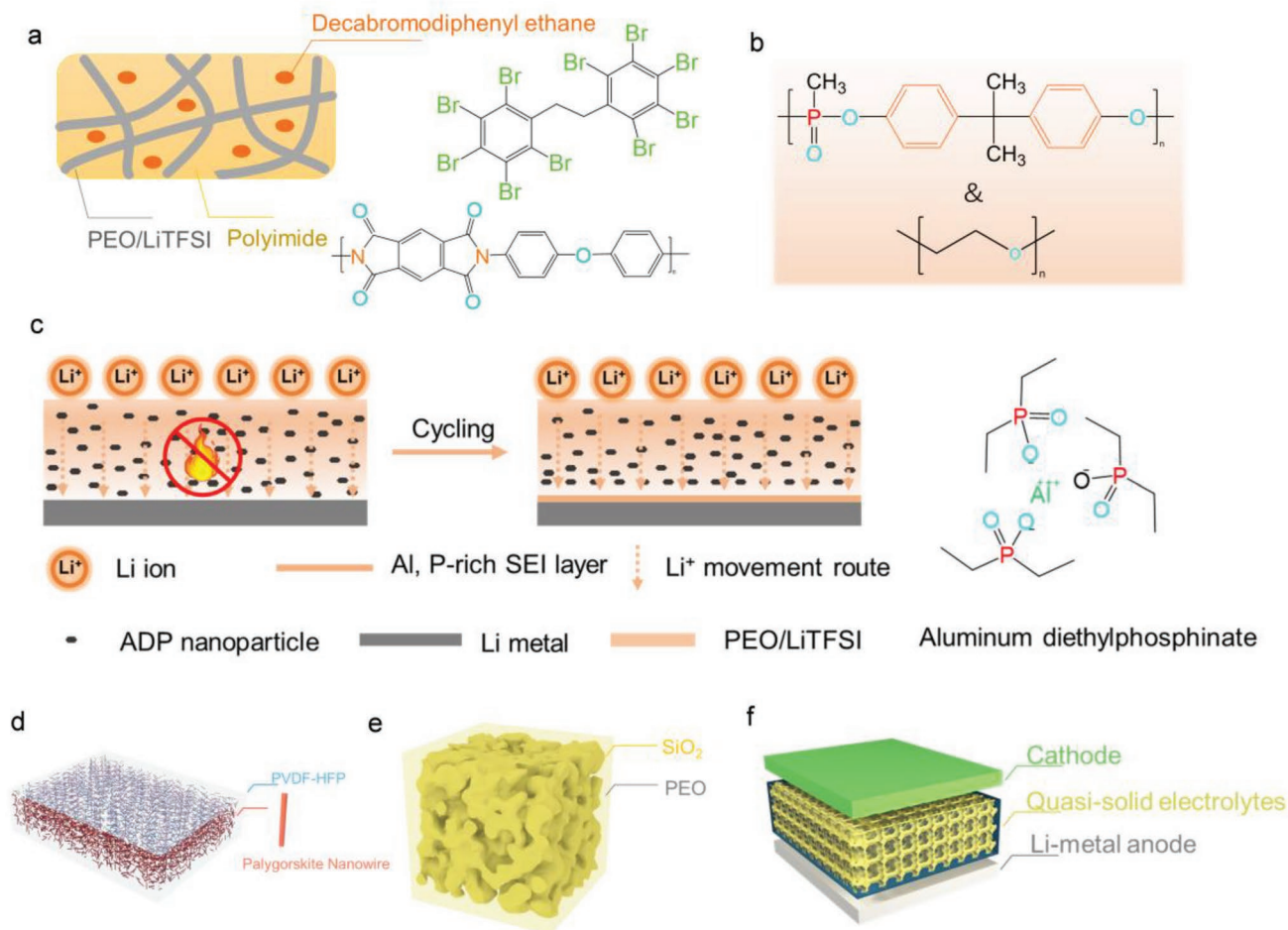
Because of lower toxicity and lower price, inorganic flame retardants have attracted extensive attention. For instance, red phosphorus and black phosphorus have attracted extensive attention because they can improve the safety of polymers and the electrochemical performance of SPEs.<sup>[25]</sup> Fu et al.

prepared cellulose acetate/poly (lactic acid)/bismuth black phosphate sulfide ( $\text{PCA/Bi}_2\text{S}_3\text{-BP}$ ) electrospinning membrane and absorbed electrolyte to prepare high safety gel polymer electrolyte membrane. The electrospinning film containing BP cannot be ignited by flame, and the gel electrolyte prepared can homogenize the charge on the surface of lithium metal, which makes it difficult to form lithium dendrites.<sup>[26]</sup>

### 1.8.4. Inorganic Nano-Filler Flame Retardant

The morphology of the nanoparticles has an impact on the electrochemical and safety performance of the electrolyte. Compared with 0 dimensional nanoparticles, the 1D passive nanowire network provides a better permeable lithium ion conduction pathway. The electrochemical and mechanical properties of the electrolyte can be significantly improved by controlling the orientation of the 1D nanowires. Unlike inert ceramic fillers, Lithium conduction filler can promote the migration of lithium ions and further improve the ionic conductivity.  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO), perovskite-structured  $\text{Li}_{3x}\text{La}_{2/3x, 1/32}\text{TiO}_3$  (LLTO), and sulfide solid-state electrolytes are some commonly used lithium conductive ceramic particles. The increase in electrolyte conductivity is more obvious by adding them to polymer electrolytes, so it is expected that the total ionic conductivity will be higher than that of polymer electrolytes with inert additives. Meanwhile, inorganic nanofillers with high Young's modulus can successfully hinder the production and growth of lithium dendrites. Therefore, polymer dielectrics containing inorganic nanofillers can not only improve the safety of SPEs, but also improve the electrochemical performance. As shown in Figure 3d, Yang et al. demonstrated that the elastic modulus of PVDF SPE can be increased to 96 MPa and the yield stress can be increased by 200% by adding only 5 wt.% of palygorskite nanowires. Moreover, a pouch cell with PVDF CPE, NMC cathode and lithium anode passed the nailing test and PVDF CPE is also not ignitable under fire.<sup>[27]</sup> In addition to 1D nanowires, 2D nanosheets also have good flame retardancy due to their ability to block thermal diffusion. Using clay sheet additives, PEO improves thermal stability while reducing electrolyte flammability.<sup>[28]</sup> Figure 3e shows that the 3D-structured inorganic nanonetwork also greatly improves the electrochemical performance and safety of polymer electrolytes. Cui et al. reported a 3D silica aerogel framework for polymer solid-state electrolytes. The interconnected  $\text{SiO}_2$  aerogel not only enhances the strength of PEO electrolyte, but also the highly ionic surface enhances the ionic conductivity of the electrolyte. Meanwhile, the addition of silica aerogel can effectively inhibit the pyrolysis of polymer solid electrolyte and improve the thermal stability of polymer electrolyte. The flame burns the electrolyte and does not ignite it.<sup>[29]</sup> Unlike the typical bulk liquid electrolyte, the electrolyte confined in the 3D structure of MOF shows exceptional performance: higher boiling point, high ionic conductivity, high oxidation resistance and non-flammability at high temperature (Figure 3f).<sup>[30]</sup>

The earliest developed halogen flame retardants were favored because of their high efficiency. However, the poisonous gas produced by its decomposition is harmful to the human body. Therefore, halogen-free flame retardants such as phosphorus



**Figure 3.** a) The fireproof and lightweight solid-state polymer electrolyte with PI and DBDPE. b) PEO/PBMP flame retardant solid polymer electrolyte. c) Schematic diagram of high safe ADP/PEO SPEs. d) Flexible and flame retardant PVDF/palygorskite composite SPEs. e) 3D SiO<sub>2</sub>-aerogel@PEO solid polymer electrolytes. f) Safe and stable MOF based quasi-solid electrolyte in lithium batteries.

flame retardants and inorganic flame retardants are gradually used in the field of polymers. Generally, inorganic flame retardants have little effect on the electrochemical properties of batteries, and some of them can improve the conductivity of electrolytes and inhibit the growth of lithium dendrites. However, the flame-retardant efficiency of inorganic flame retardants is lower than that of phosphorus flame retardants. Phosphorus flame retardants generally form phosphoric acid and its derivatives on the polymer surface, which form a protective layer on the polymer surface to inhibit the combustion of the polymer. The combination of phosphorus flame retardant and inorganic flame retardant will improve the safety and electrochemical performance of the battery.

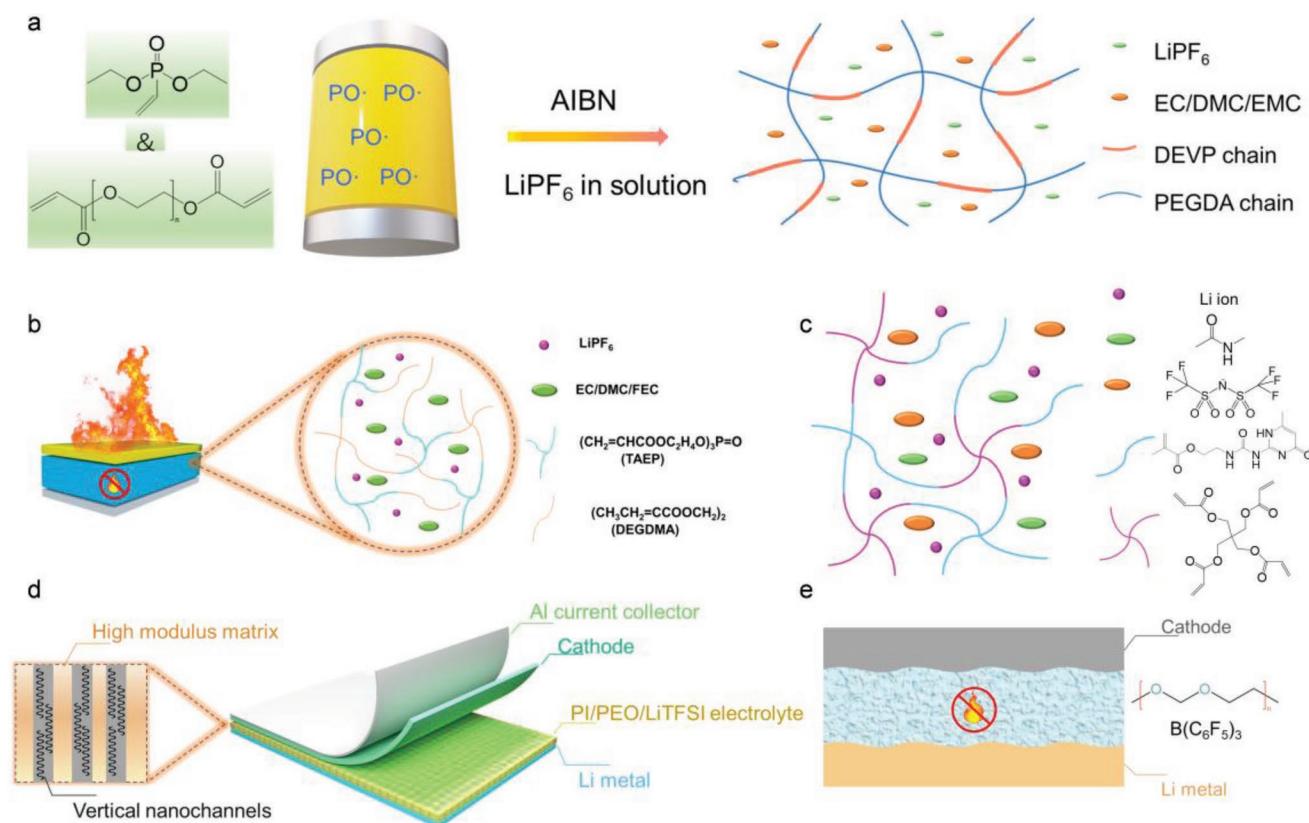
### 1.9. Reactive Flame Retardants

Additive flame retardants are of low cost and easy to operate. Although additive flame retardants are easy to manipulate, they have a large impact on the electrochemical properties of SPEs. At the same time, the added flame retardant has a large effect on the physical and chemical properties of the polymer, and the

retardant is prone to precipitate. Reactive flame retardants react with polymer to obtain polymer electrolytes that are not combustible by themselves. On the one hand, the mechanical and electrochemical properties of the intrinsically non-combustible polymer electrolyte are relatively stable, and the flame-retardant effect is more durable. Structurally, compared with liquid electrolyte, the gelation of electrolyte can solve the leakage problem. At the same time, the gel electrolyte is also less flammable.

As shown in Figure 4a, Yang et al. produced a 3D network gel polymer electrolyte that is ring-opening polymerized by a simple initiator-free. This 3D-GPE has high fire safety and high electrochemical properties.<sup>[13]</sup> The phosphorus-containing crosslinked gel polymer electrolytes prepared by Zhang et al. have good flame retardancy. Using the assembled 1.8-Ah G//NCM811 pouch cell for ARC test, it is found that the thermal runaway time of the pouch cell is delayed. These GPEs can well inhibit the heat accumulation of the battery and delay the occurrence of thermal runaway.<sup>[13b]</sup> Hu groups found that by adding as little as 7.5 wt.% of the phosphate-containing flame retardant to the gel electrolyte they could produce an interfacial stable, flame retardant gel electrolyte. High-performance GPE were prepared by in situ polymerization of tri(acryloyloxyethyl)





**Figure 4.** a) Schematic diagram of preparation of gel polymer electrolyte with high ionic conductivity, high flame retardant. b) Schematic diagram of safety-reinforced SSE. c) Schematic illustration of high-safety nitrogen-containing gel polymer electrolyte. d) Schematic showing the design principles of non-flammable PI/PEO/LiTFSI solid polymer electrolyte in lithium battery. e) Schematic diagram of polymer solid-state battery containing boron flame retardant. Polymerized 1,3-dioxolane electrolyte solid polymer electrolyte shows high ionic conductivity, good interfacial stability, and is flame-retardant.

phosphate and triethylene glycol dimethacrylate added to the cell. The flame retardancy and electrochemical properties of this GPE can be significantly improved (Figure 4b). The GPE cannot be ignited by the flame. LFP//GPE-3//graphite pouch cell with a capacity of 950 mAh will produce a lot of smoke but will not burn in the thermal runaway test.<sup>[32]</sup> Wu et al. also prepared GPE electrolyte which is high temperature resistant and non-combustible. GPE that can withstand 200 °C and high ionic conductivity have a good match with lithium metal.<sup>[33]</sup> In addition to phosphorus-containing groups, nitrogen-containing groups also have a certain flame-retardant effect. Figure 4c revealed that Wang et al.<sup>[34]</sup> reported an unsteady quasi-solid-state lithium-metal batteries. The electrolyte contains deep eutectic solvent (DES) and has self-healing properties. 2-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl) ureido) ethyl methacrylate (UPyMA) and pentaerythritol tetraacrylate (PETEA) monomers were polymerized to form an electrolyte. This polymer electrolyte doesn't burn even in flames and has a high ionic conductivity. Kyu et al. prepared a polymer electrolyte film with flame retardant and high temperature resistance, which is polymerized by cross-linkable polyurethane precursor polyethylene glycolbis-carbamate dimethacrylate. Solvent-free, transparent and flexible nitrogen-containing polymer electrolytes do not burn in flame. In addition, this SPE with high ionic conductivity ( $8 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C) and high oxidation

resistance are suitable for different shapes of batteries.<sup>[35]</sup> In addition to the polymerization of phosphorus-containing flame-retardant monomers and multi-functional monomers to obtain high-safety polymer solid electrolytes, safe polymer electrolytes can also be obtained by introducing ionic liquids into polymer molecular chains. The introduction of ionic liquids not only improves the safety of polymer electrolytes, but also improves their ionic conductivity and cycle stability.<sup>[36]</sup>

## 1.10. Others

In addition, there are several other flame retardants and methods that can effectively improve the safety of polymer batteries. Organic non-combustible 3D frameworks can also improve the safety of solid electrolytes. As shown in Figure 4d, Cui reported an ultra-thin polymer solid electrolyte. By pouring PEO solid electrolyte onto the ultra-thin polyimide (PI) films, 8.6  $\mu\text{m}$  polymer electrolyte film was obtained. This PI/PEO/LiTFSI polymer electrolyte has high cycle stability at 60 °C. The prepared pouch cell will not burn even when bent and sheared.<sup>[16a]</sup> In addition to the commonly used flame retardants introduced above, boron has a flame-retardant effect. Figure 4e shows that Huang et al. proposed a flame-retardant polymer electrolyte (PDE). Polymer electrolytes were prepared

by polymerization of 1,3-dioxane initiated by tris (pentafluorophenyl) borane (TB) as initiator. This polymer electrolyte film and lithium metal stability is good, and can stabilize the electrolyte and electrode interface. At the same time, the non-combustible polymer electrolyte film in the battery effectively improves the safety of the battery.<sup>[37]</sup> The safety of SPEs cannot be improved by only one flame retardant. Safer polymer solid-state lithium batteries can be prepared by combining different flame retardants and different materials.

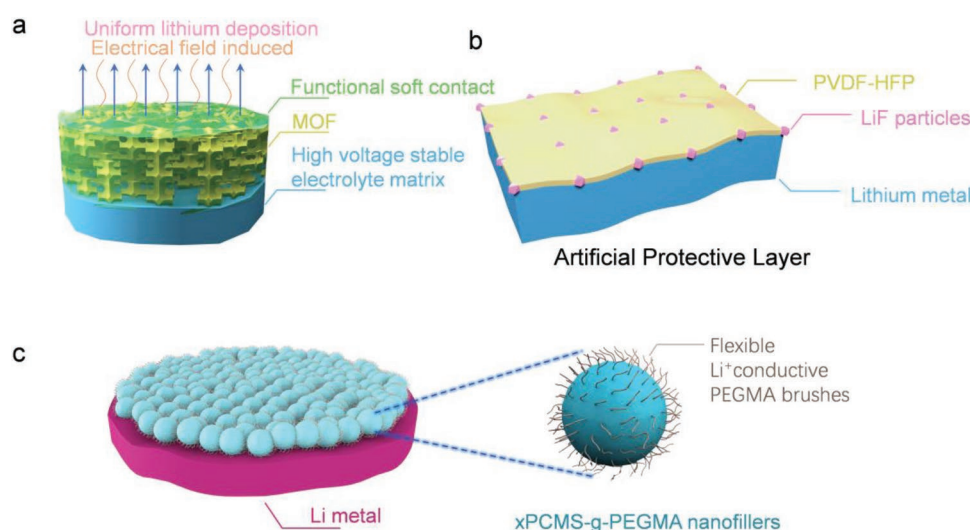
### 1.11. Addressing Lithium Anode Problems

Compared with other anodes, lithium metal has a higher theoretical specific capacity ( $3860 \text{ mAh g}^{-1}$ ). At the same time, it has the lowest reduction potential ( $-3.04 \text{ V}$  vs standard hydrogen electrode). Therefore, the energy density of lithium batteries can be significantly improved by using lithium metal instead of the traditional negative electrode. But the current battery with lithium anode is not efficient enough. SEI films can be formed by reaction of lithium metal batteries with currently used electrolytes.

Generally speaking, the mechanical properties and lithium conduction performance of the generated SEI film are poor, and it will be broken and regenerated in the cycle process, which will continuously increase the internal resistance of the batteries. In this way, new SEIs are continuously generated. During lithium stripping, the dendritic lithium readily breaks off from the root and becomes isolated lithium. Therefore, the preparation of SPEs with inhibited Li dendrite growth is crucial. Modification of the Lithium metal successfully inhibits the growth of Lithium dendrites. Wang groups reported  $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$ /polyvinylidene fluoride-co-hexafluoropropylene were used as the toughening matrix and MOF/poly (ethylene oxide)/PVDF-HFP as the layer composite gel polymer electrolyte. The Li/SPEs/Li battery can cycle 1700 h

(Figure 5a).<sup>[38]</sup> Zhang et al. reported the bilayer films protected Li metal anodes by immersing Li sheets in a fluoroethylene carbonate solvent. This protective layer has two components. The upper layer is a flexible protective layer ( $\text{ROCO}_2\text{Li}$  and  $\text{ROLi}$ ) to improve the interfacial property, and the lower layer is a rigid protective layer ( $\text{Li}_2\text{CO}_3$  and  $\text{LiF}$ ) to inhibit the production and growth of lithium dendrites.<sup>[39]</sup> In addition to suppressing Li dendrites by a double protective layer, the stability of Li metal anodes can also be improved by constructing artificial protective layers. By suppressing the random deposition of lithium, the dendrite-free negative electrode can be obtained with this efficient protective layer (Figure 5b).<sup>[40]</sup> 2D layered inorganic nanomaterials have high Young's modulus, and sheet-like 2D materials can effectively restrain lithium dendrites growing. A 2D layered lithium montmorillonite, polyethylene carbonate, LiFSI, high-pressure vinyl fluoride, and high-mobility intercalation composite SSE were synthesized by a combination of solution casting and hot pressing. Intercalated electrolytes with high mobility numbers can suppress the formation of lithium dendrites.<sup>[41]</sup> Wu reported a flexible interface protective layer, through the reasonable integration of molecular brushes based on porous polymers grafting, hypercrosslinking) to achieve efficient and non-dendritic lithium metal negative electrode. The multihole xPCMS core and high strength hypercrosslinked skeleton significantly improves the mechanical strength (Figure 5c).<sup>[42]</sup>

The commonly used anode for batteries is the lithium metal anode. Compared to the graphite anode, the lithium metal anode can meaningfully enhance the energy density. The lithium metal without oxidation has a silver metal luster, the texture is soft, and the melting point is  $189^\circ\text{C}$ . The lithium metal is very stable in inert gases, but the lithium anode is unstable in air. Lithium metals react with nitrogen, carbon dioxide and oxygen to form lithium nitride, lithium carbonate and lithium oxide. Lithium metal releases hydrogen and generates lots of heat when put into water. When the battery is abused, the thermal

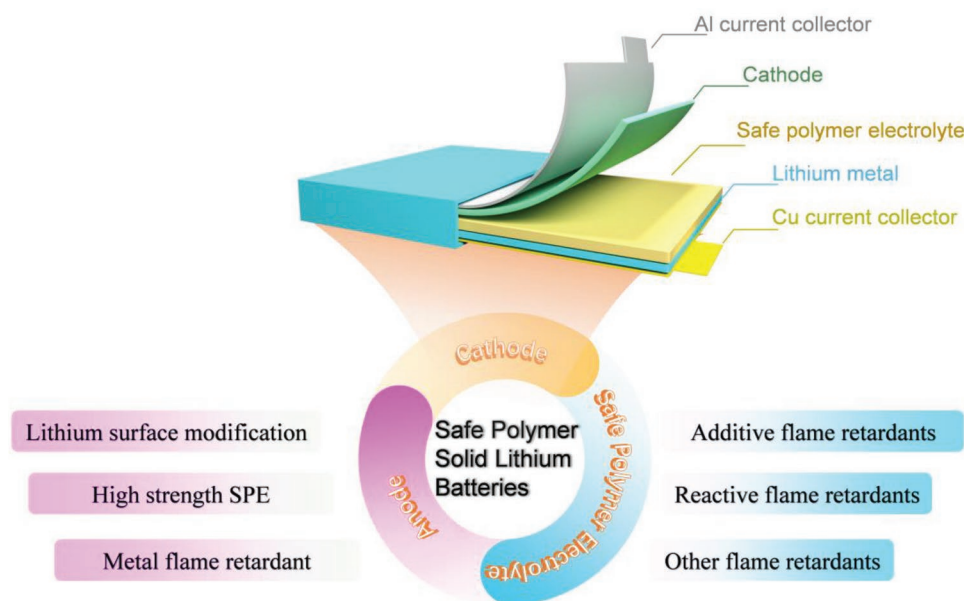


**Figure 5.** a) Schematic diagram of the mechanism of Li deposition process concerning PMLSE in solid polymer battery. b) Schematic diagram of artificial protective layer coated on lithium metal. c) The high-performance lithium anode was prepared by coating the surface of lithium metal with a flexible high strength protective layer of porous xPCMS-g-PEGMA nanofillers.

stability of lithium metal is very good under closed conditions. However, when the battery breaks, the lithium metal exposed to air becomes extremely unstable, significantly increasing the risk of the battery. At the same time, lithium metal anode will increase the firefighting cost of battery accidents. Currently, the use of water and carbon dioxide cannot deal with lithium metal fires. However, the safety of lithium metal anode is mainly focused on the inhibition of lithium dendrite. There is little research on how to address the safety of lithium metal negative electrodes in air and fire. It is increasingly important to address the safety of Li to make the negative electrode of lithium metal industrializable. Metal fire extinguishing agent is rarely used, and copper can be used as fire extinguishing agent for Li negative electrode. In a high temperature environment, lithium metal can form a lithium-copper negative electrode with copper to slow down metal burning. Therefore, batteries safety can be significantly improved by using lithium-copper composite negative electrode. On the other hand, the safety of solid-state batteries can be improved by reducing the amount of lithium metal. Ultra-thin lithium metal negative electrodes can be prepared under conditions that ensure the normal use of the battery and can be compounded with other materials to ensure their strength to further improve the safety of lithium metal negative electrodes.<sup>[14b]</sup> Compared with the traditional lithium metal battery, the anode-free lithium batteries can significantly improve the energy density and safety of the batteries, but the formation of SEI film and side reaction during the initial cycle will reduce the electrochemical performance of the battery, especially the cycle life. At the same time, there is still lithium metal in the negative electrode after the battery is charged, which is also a safety hidden danger. By modifying the negative current collector or electrolyte, a truly safe lithium batteries can be prepared.<sup>[43]</sup>

## 2. Considerations and Future Perspectives for Safe Solid-State Lithium Batteries

LIBs contributed considerably to the development of human society, but safety issues are becoming more prominent. Replacing liquid electrolyte with solid electrolyte still cannot meet people's demand for batteries safety. With further energy density improvement, capacity increment, and power battery packs usage, the safety hazards are becoming more severe. For polymer solid-state lithium batteries, their electrodes and electrolytes are dangerous in extreme environments. **Figure 6** summarizes the components and safety improvement strategies for lithium batteries. SPEs can significantly enhance the safety of lithium metal batteries, but they still have safety issues. Designing safer polymer-based solid-state batteries is challenging as they need to address the safety of electrolytes. The efficiency flame retardants can increase the safety of SPEs, but the flame-retardant additives have an effect on the electrochemical properties of the electrolytes. Also, the preparation of multifunctional additives that have both flame retardancy and other properties, such as improving electrical conductivity and inhibiting lithium dendrites, is also a key issue. In addition to the electrolyte, the safety of the electrodes is also paramount. For lithium metal batteries, the lithium metal anode will react violently to release a lot of heat when it encounters the air, producing flammable hydrogen when it meets water. It may lead to combustion and explosion. Therefore, high safety, no dendrite and good interface stability lithium metal anode can greatly improve the safety of batteries. The cathode material is stable, but it decomposes under high temperature and absorbs oxygen, thereby promoting battery combustion. Therefore, improving the battery cathode thermal stability is also very important.



**Figure 6.** Composition of polymer solid-state lithium batteries and safety research strategy of different components. For polymer solid-state lithium batteries, the electrochemical properties of batteries should be considered first. Without affecting the electrochemical properties, the safety design of different components is also different and needs to be designed according to the actual requirements.



The polymer solid-state lithium batteries have not been industrialized yet. Compared with the safety test standards of LIBs, the test standards of polymer solid-state lithium batteries remain to be proposed. The test standards of polymer solid-state lithium batteries can be used for reference to the safety test standard of LIBs. The fire safety and thermal safety testing of SPEs can learn from some safety testing methods of polymer materials. For example, a cone calorimeter test was determined to investigate the heat release and gas composition of SPEs. The limiting oxygen index test was used to test the fire safety of SPEs. Overall, designing safer electrolytes is an integral part of addressing the safety concerns of LIBs. Many scientific researchers are working to develop safer SPEs. Therefore, we believe the industrialization of safer, high-performance lithium metal solid-state batteries will be realized soon.

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## Conflict of Interest

The authors declare no conflict of interest.

## Author Contributions

L.F. wrote the original draft. L.W., Z.C., and Y.H. were involved in methodology, investigation, reviewing, and editing. Y.K. and H.Z. performed conceptualization, validation, reviewing, and editing. X.H. performed conceptualization, investigation, formal analysis, supervision, project administration, and acquired funding.

## Keywords

flame retardant, polymer electrolytes, safety, safety test standards, solid-state lithium batteries

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- [1] Q. Zhao, S. Stalin, C. Z. Zhao, L. A. Archer, *Nat. Rev. Mater.* **2020**, 5, 229.  
[2] a) A. M. Bates, Y. Preger, L. Torres-Castro, K. L. Harrison, S. J. Harris, J. Hewson, *Joule* **2022**, 6, 742; b) Y. Q. Chen, Y. Q. Kang,

- Y. Zhao, L. Wang, J. L. Liu, Y. X. Li, Z. Liang, X. M. He, X. Li, N. Tavajohi, B. H. Li, *J. Energy Chem.* **2021**, 59, 83.  
[3] a) Z. Li, S. T. Weng, J. L. Fua, X. X. Wang, X. Y. Zhou, Q. H. Zhang, X. F. Wang, L. Wei, X. Guo, *Energy Storage Mater.* **2022**, 47, 542; b) G. Liang, V. K. Peterson, Z. Wu, S. Zhang, J. Hao, C. Z. Lu, C. H. Chuang, J. F. Lee, J. Liu, G. Leniec, S. M. Kaczmarek, A. M. D'Angelo, B. Johannessen, L. Thomsen, W. K. Pang, Z. Guo, *Adv. Mater.* **2021**, 33, 2101413; c) H. Li, M. Li, X. Zhou, T. Li, *J. Power Sources* **2020**, 449, 227511; d) H. Li, M. Li, X. Zhou, T. Li, H. Zhao, *Sustainable Energy Fuels* **2020**, 4, 3871.  
[4] a) H. Cavers, P. Molaiyan, M. Abdollahifar, U. Lassi, A. Kwade, *Adv. Energy Mater.* **2022**, 12, 2200147; b) R. Chen, Q. Li, X. Yu, L. Chen, H. Li, *Chem. Rev.* **2020**, 120, 6820; c) S. C. Liu, J. F. He, D. S. Liu, M. H. Ye, Y. F. Zhang, Y. L. Qin, C. C. Li, *Energy Storage Mater.* **2022**, 49, 93; d) H. Li, M. Li, H. Zhao, T. Li, Z. Fang, *J. Power Sources* **2021**, 512, 230507.  
[5] a) J. Chen, Z. H. Liu, J. Y. Liu, X. Q. Liu, X. Yang, X. L. Jiang, *Mater. Chem. Phys.* **2022**, 279, 125763; b) K. Liu, Y. Y. Liu, D. C. Lin, A. Pei, Y. Cui, *Sci. Adv.* **2018**, 4, eaas9820.  
[6] Q. S. Wang, L. H. Jiang, Y. Yu, J. H. Sun, *Nano Energy* **2019**, 55, 93.  
[7] X. N. Feng, D. S. Ren, X. M. He, M. G. Ouyang, *Joule* **2020**, 4, 743.  
[8] a) L. Fan, S. Y. Wei, S. Y. Li, Q. Li, Y. Y. Lu, *Adv. Energy Mater.* **2018**, 8, 1702657; b) C. Wang, T. Deng, X. Fan, M. Zheng, R. Yu, Q. Lu, H. Duan, H. Huang, C. Wang, X. Sun, *Joule* **2022**, 6, 1770.  
[9] Z. Lin, Y. Wang, Y. Li, Y. Liu, S. Zhong, M. Xie, F. Yan, Z. Zhang, J. Peng, J. Li, A. Wang, X. Chen, M. Zhai, H. Zhang, J. Qiu, *Energy Storage Mater.* **2022**, 53, 917.  
[10] L. Han, C. Liao, Y. Liu, H. Yu, S. Zhang, Y. Zhu, Z. Li, X. Li, Y. Kan, Y. Hu, *Energy Storage Mater.* **2022**, 52, 562.  
[11] a) X. L. Cheng, J. Pan, Y. Zhao, M. Liao, H. S. Peng, *Adv. Energy Mater.* **2018**, 8, 1702184; b) C. W. Sun, J. Liu, Y. D. Gong, D. P. Wilkinson, J. J. Zhang, *Nano Energy* **2017**, 33, 363; c) S. A. Pervez, M. A. Cambaz, V. Thangadurai, M. Fichtner, *ACS Appl. Mater. Interfaces* **2019**, 11, 22029.  
[12] X. N. Feng, M. G. Ouyang, X. Liu, L. G. Lu, Y. Xia, X. M. He, *Energy Storage Mater.* **2018**, 10, 246.  
[13] a) S. J. Tan, J. Yue, X. C. Hu, Z. Z. Shen, W. P. Wang, J. Y. Li, T. T. Zuo, H. Duan, Y. Xiao, Y. X. Yin, R. Wen, Y. G. Guo, *Angew. Chem., Int. Ed. Engl.* **2019**, 58, 7802; b) Y. Zhang, L. Yu, X. D. Zhang, Y. H. Wang, C. Yang, X. Liu, W. P. Wang, Y. Zhang, X. T. Li, G. Li, S. Xin, Y. G. Guo, C. Bai, *Sci. Adv.* **2023**, 9, eade5802.  
[14] a) L. Han, C. Liao, X. Mu, N. Wu, Z. Xu, J. Wang, L. Song, Y. Kan, Y. Hu, *Nano Lett.* **2021**, 21, 4447; b) L. Fu, M. Wan, B. Zhang, Y. Yuan, Y. Jin, W. Wang, X. Wang, Y. Li, L. Wang, J. Jiang, J. Lu, Y. Sun, *Adv. Mater.* **2020**, 32, 2000952.  
[15] a) SAE, J2464 Electric Vehicle Battery Abuse, Testing **1999**; b) GB/T 31484 Cycle life requirements and test methods of power batteries for electric vehicles, **2015**; c) ISO, 16750–2 Road vehicles–Environmental conditions and testing for electrical and electronic equipment–Part 2, Electrical loads, **2010**; d) JIS C8715 Secondary lithium cells and batteries for use in industrial applications, **2019**; e) KC 62619 Technical Regulations for Electrical and Telecommunication Products and Components, **2017**; f) IEC, 62660-2 Secondary lithium-ion cells for the propulsion of electric road vehicles–Part 2: Reliability and abuse testing, **2010**; g) UL2580 Standard for Safety Batteries for Use in Electric Vehicles, **2016**; h) GM-Modified USABC General Motors Battery Test Standard for Electric Vehicles, **2016**; i) VW PV8450 Volkswagen battery test standards for electric vehicles, **2016**; j) SMTC 9 N20 011 Electrochemical performance test specification of electric vehicles for lithium-ion battery, **2018**; k) UN38.3 Transport of Dangerous Goods, **2015**.  
[16] a) J. Wan, J. Xie, X. Kong, Z. Liu, K. Liu, F. Shi, A. Pei, H. Chen, W. Chen, J. Chen, X. Zhang, L. Zong, J. Wang, L. Q. Chen, J. Qin, Y. Cui, *Nat. Nanotechnol.* **2019**, 14, 705; b) Y. S. Ye, L. Y. Chou, Y. Y. Liu, H. S. Wang, H. K. Lee, W. X. Huang, J. Y. Wan, K. Liu,



- G. M. Zhou, Y. F. Yang, A. K. Yang, X. Xiao, X. Gao, D. T. Boyle, H. Chen, W. B. Zhang, S. C. Kim, Y. Cui, *Nat. Energy* **2020**, *5*, 786.
- [17] X. Q. Liu, C. Zhang, S. Y. Gao, S. J. Cai, Q. F. Wang, J. Y. Liu, Z. H. Liu, *Mater. Chem. Phys.* **2020**, *239*, 122014.
- [18] J. L. Wang, D. C. Zhang, Y. Zhang, W. Cai, C. X. Yao, Y. Hu, W. Z. Hu, *J. Hazard. Mater.* **2019**, *362*, 482.
- [19] Z. Y. Zhang, L. Z. Zhang, L. Hu, C. X. Huang, *Int. J. Energy Res.* **2020**, *44*, 2535.
- [20] IEC 62133 Secondary cells and batteries containing alkaline or other non-acid electrolytes-Safety requirements for portable sealed secondary cells, and for batteries made from them, for use in portable applications, **2017**.
- [21] K. Liu, W. Liu, Y. Qiu, B. Kong, Y. Sun, Z. Chen, D. Zhuo, D. Lin, Y. Cui, *Sci. Adv.* **2017**, *3*, e1601978.
- [22] T. Yim, M. S. Park, S. G. Woo, H. K. Kwon, J. K. Yoo, Y. S. Jung, K. J. Kim, J. S. Yu, Y. J. Kim, *Nano Lett.* **2015**, *15*, 5059.
- [23] Y. Cui, J. Wan, Y. Ye, K. Liu, L. Y. Chou, Y. Cui, *Nano Lett.* **2020**, *20*, 1686.
- [24] K. R. Deng, T. Y. Guan, F. H. Liang, X. Q. Zheng, Q. G. Zeng, Z. Liu, G. X. Wang, Z. P. Qiu, Y. F. Zhang, M. Xiao, Y. Z. Meng, L. Wei, *J. Mater. Chem. A* **2021**, *9*, 7692.
- [25] R. Rojaee, S. Cavallo, S. Mogurampelly, B. K. Wheatle, V. Yurkiv, R. Deivanayagam, T. Foroozan, M. G. Rasul, S. Sharifi-Asl, A. H. Phakatkar, M. Cheng, S. B. Son, Y. Y. Pan, F. Mashayek, V. Ganesan, R. Shahbazian-Yassar, *Adv. Funct. Mater.* **2020**, *30*, 1910749.
- [26] Y. Huang, Y. Wang, Y. Fu, *Composites, Part B* **2022**, *230*, 109501.
- [27] P. Yao, B. Zhu, H. Zhai, X. Liao, Y. Zhu, W. Xu, Q. Cheng, C. Jayyosi, Z. Li, J. Zhu, K. M. Myers, X. Chen, Y. Yang, *Nano Lett.* **2018**, *18*, 6113.
- [28] a) W. J. Tang, S. Tang, C. J. Zhang, Q. T. Ma, Q. Xiang, Y. W. Yang, J. Y. Luo, *Adv. Energy Mater.* **2018**, *8*, 1800866; b) Q. Liu, A. Zhao, X. He, Q. Li, J. Sun, Z. Lei, Z.-H. Liu, *J. Alloys Compd.* **2021**, *861*, 157950; c) Q. Liu, A. R. Zhao, X. X. He, Q. Li, J. Sun, Z. B. Lei, Z. H. Liu, *Adv. Funct. Mater.* **2021**, *31*, 2010944.
- [29] D. Lin, P. Y. Yuen, Y. Liu, W. Liu, N. Liu, R. H. Dauskardt, Y. Cui, *Adv. Mater.* **2018**, *30*, 1802661.
- [30] Z. Chang, H. Yang, X. Zhu, P. He, H. Zhou, *Nat. Commun.* **2022**, *13*, 1510.
- [31] Q. Lu, Y. B. He, Q. Yu, B. Li, Y. V. Kaneti, Y. Yao, F. Kang, Q. H. Yang, *Adv. Mater.* **2017**, *29*, 1604460.
- [32] X. W. Mu, X. J. Li, C. Liao, H. Yu, Y. Jin, B. Yu, L. F. Han, L. K. Chen, Y. C. Kan, L. Song, Y. Hu, *Adv. Funct. Mater.* **2022**, *32*, 2203006.
- [33] M.-C. Long, T. Wang, P.-H. Duan, Y. Gao, X.-L. Wang, G. Wu, Y.-Z. Wang, *J. Energy Chem.* **2022**, *65*, 9.
- [34] P. Jaumaux, Q. Liu, D. Zhou, X. Xu, T. Wang, Y. Wang, F. Kang, B. Li, G. Wang, *Angew. Chem., Int. Ed. Engl.* **2020**, *59*, 9134.
- [35] G. P. Fu, M. D. Soucek, T. Kyu, *Solid State Ionics* **2018**, *320*, 310.
- [36] Y. H. Li, Z. J. Sun, L. Shi, S. Y. Lu, Z. H. Sun, Y. C. Shi, H. Wu, Y. F. Zhang, S. J. Ding, *Chem. Eng. J.* **2019**, *375*, 121925.
- [37] J. W. Xiang, Y. Zhang, B. Zhang, L. X. Yuan, X. T. Liu, Z. X. Cheng, Y. Yang, X. X. Zhang, Z. Li, Y. Shen, J. J. Jiang, Y. H. Huang, *Energy Environ. Sci.* **2021**, *14*, 3510.
- [38] J. Q. Sun, X. M. Yao, Y. G. Li, Q. H. Zhang, C. Y. Hou, Q. W. Shi, H. Z. Wang, *Adv. Energy Mater.* **2020**, *10*, 2000709.
- [39] C. Yan, X. B. Cheng, Y. Tian, X. Chen, X. Q. Zhang, W. J. Li, J. Q. Huang, Q. Zhang, *Adv. Mater.* **2018**, *30*, 1707629.
- [40] R. Xu, X. Q. Zhang, X. B. Cheng, H. J. Peng, C. Z. Zhao, C. Yan, J. Q. Huang, *Adv. Funct. Mater.* **2018**, *28*, 1705838.
- [41] L. Chen, W. Li, L. Z. Fan, C. W. Nan, Q. Zhang, *Adv. Funct. Mater.* **2019**, *29*, 1901047.
- [42] S. Li, J. Huang, Y. Cui, S. Liu, Z. Chen, W. Huang, C. Li, R. Liu, R. Fu, D. Wu, *Nat. Nanotechnol.* **2022**, *17*, 613.
- [43] a) L. Kong, Y. Li, W. Feng, *Electrochem. Energy Rev.* **2021**, *4*, 633; b) Y. Pang, J. Pan, J. Yang, S. Zheng, C. Wang, *Electrochem. Energy Rev.* **2021**, *4*, 169.



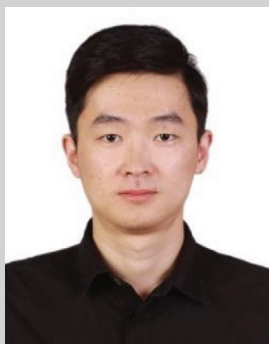
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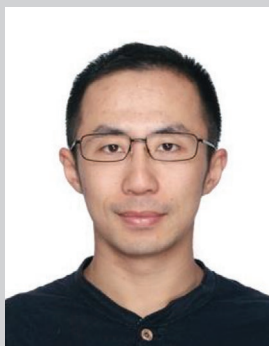
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