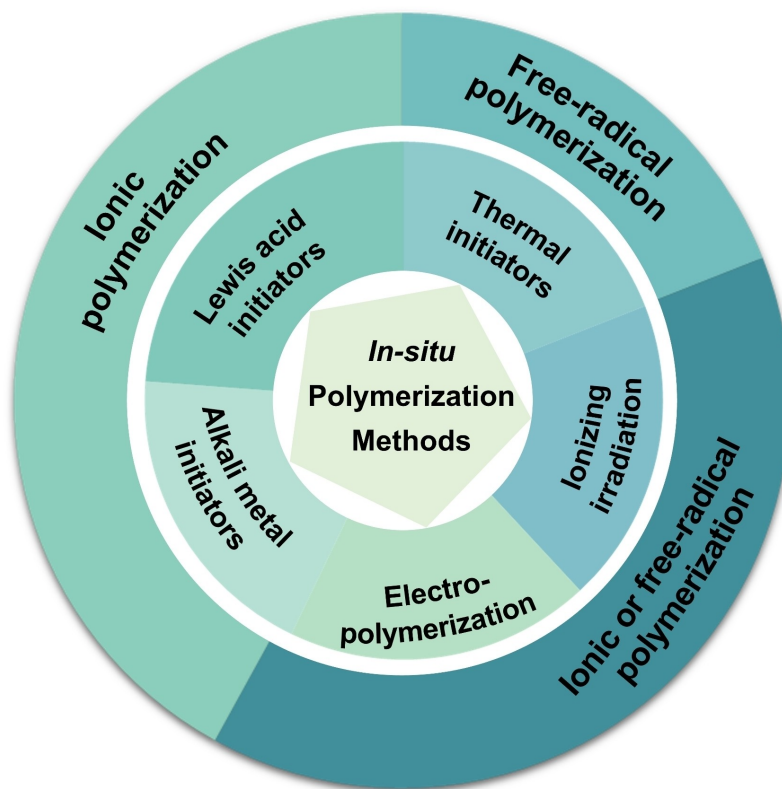


In-situ Polymerization Methods for Polymer-based Solid-State Lithium Batteries

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The *in-situ* polymerization methods (*in-situ* methods) have led to huge advancement in the development of solid-state batteries (SSBs) with intimate interfacial contacts and continuous pathways for the conduction of lithium ion. Though promising, they still face obstacles that hinder their practical application, such as poor interfacial stability between initiators and electrodes and scalability challenges. To date, most studies have been largely focused on the discovery of novel monomers/oligomers that can be *in-situ* polymerized. Additionally,

recent reviews have examined the progress of monomers/oligomers and advantages of *in-situ* methods. Recognizing this, in this review, we seek to summarize *in-situ* methods from the viewpoint of initiators. We provide realistic assessments of interfacial stability of initiators with electrodes, and analyze their challenges and perspectives for actual application. We hope to inspire deeper considerations on selection of initiators and offer guidance for *in-situ* preparation of SSBs with high performances.

1. Introduction

Lithium-ion batteries (LIBs) have been widely used in consumer electronics, electric vehicles and storing electricity generated from intermittent renewable sources (such as wind or solar energy).^[1] However, current LIBs employed liquid electrolytes (LEs) suffer from leakage, flammability and even explosion. In this context, the replacement of volatile and flammable LEs with nonflammable solid electrolytes (SEs) is generally expected to improve safety.^[1b] Typically, SEs are divided into sulfide, oxide and polymer electrolytes.^[2] Sulfide electrolytes show higher ionic conductivity at room temperature than others, while suffer from high preparation cost, air sensitivity and the instability with lithium metal.^[3] Oxide electrolytes with high mechanical strength, wide electrochemical window and physical stability are potential to resist dendrite growth, which fulfills the promise of high-energy-density batteries.^[4] Nevertheless, the application of oxide electrolytes is hindered by the brittleness, large grain boundary and high electrode/electrolyte interface resistance.^[5] In contrast, polymer electrolytes (PEs) possess excellent flexibility and processability, which is beneficial to forming the intimate electrolyte/electrode interfacial contact and large-scale production of solid-state batteries.^[6]

The early research and important milestone of PEs are summarized in Figure 1. The first report about PEs could be traced back to 1973, in which Wright and Fenton reported that crystalline complexes of alkali metal salts with poly(ethylene oxide) (PEO) could be used as ion-conductive materials.^[7] Since then, a large body of work has been centered on enhancing the ionic conductivity of PEO-based electrolytes. Armand et al. demonstrated that the ionic conductivity of the complexes

incorporated with PEO and lithium salt was about $10^{-4} \text{ S cm}^{-1}$ at 60°C .^[8] In 1975, the organic plasticizer was introduced into the above system by Feuillade et al.^[9] Skaarup et al. blended the ionic conductor of Li_3N with the PEO- LiCF_3SO_3 system by 1988. When the volume ratio of Li_3N was 5–10%, the ionic conductivity ($10^{-4} \text{ S cm}^{-1}$ at room temperature) was 3 orders higher than that of pure PEO-based electrolytes.^[10] In 1989, Wiczcerek et al. proposed that adding Al_2O_3 powders could increase the ionic conductivity of PEO-NaI electrolytes to $10^{-4} \text{ S cm}^{-1}$ (at room temperature) due to the decrease of the crystalline of PEO.^[11] In 1993, the concept of “polymer-in-salt” electrolytes (PISEs) was proposed.^[12] PISEs that were obtained by mixing small content ($< 50 \text{ wt}\%$) of polymer with lithium salts possessed high ionic conductivity and electrochemical stability, resulting from the decrease of uncoordinated ethoxy group and the high proportion of amorphous regions in this kind of electrolyte respectively. Specially, electric vehicles powered by PEO-based $\text{Li}/\text{LiFePO}_4$ batteries were launched by Bollcoré in 2011.^[13] However, electrochemical instability of PEO-based electrolytes at potentials higher than 3.8 V (versus Li/Li^+) constitutes the major barrier to combine with high-voltage cathodes.^[14] It is therefore imperative to explore electrolytes with wide electrochemical stability windows. On one hand, the strategies of preparing multilayer electrolytes^[15] (such as double-layer PEs and sandwich-type compatible solid-state electrolytes) and designing stable electrolyte/cathode interface^[16] have been proposed, which not only avoids the stability of PEO-based electrolytes with high-voltage cathode but ameliorates the ionic conductivity. On the other hand, a series of PEs that possess excellent ability to resist the oxidation and dissolve lithium salts are also developed, such as polyacrylonitrile (PAN), poly(vinylidene fluoride) (PVDF), poly(ethylene carbonate) (PEC), poly(trimethylene carbonate) (PTMC), poly(vinylene carbonate) (PVCA) and poly(propylene carbonate) (PPC)-based electrolytes.^[17] However, this class of PEs cannot fully satisfy the requirements in practical applications due to many issues, such as low conductivity ($< 10^{-4} \text{ S cm}^{-1}$) at room temperature, complex preparing processes and poor electrochemical/chemical stability with electrodes.^[18]

Various strategies have been proposed to improve the ionic conductivity, such as preparing branching PEs,^[19] random or comb copolymer electrolytes,^[20] designing organic/inorganic composite electrolytes with vertically aligned and continuous pathways of the conduction of lithium ion (Li^+)^[21] and developing gel polymer electrolytes by entrapping LEs in the

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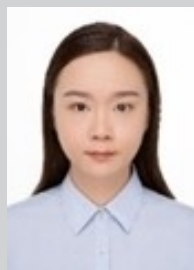
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polymer matrix,^[22] which also helps improve the ability of preventing lithium dendrites. Nevertheless, PEs are usually prepared by the solution-casting methods (*ex-situ* methods), which leads to the poor electrode/electrolyte interface contact especially in the batteries with high mass loading of electrode.^[18] The detailed process of *ex-situ* methods is shown in the Figure 2(a). Firstly, the polymer and alkali metal salts are dissolved in organic solvent (such as acetonitrile and *N,N*-dimethylformamide). Then the obtained precursor solution is poured into a mold or casted on a flat surface. After the solvent is removed through thermal evaporation, polymer electrolyte films are obtained and used to assemble solid-state batteries. The properties of PEs can be adjusted by polymer matrix or salts in *ex-situ* methods, while they usually involve complex processes and require organic solvents.^[23] In addition, side reactions between residual solvents and electrodes may lead to poor electrochemical properties.^[24] What's more, the point-to-point contact will result in the low utilization of active materials, which will be worsen in electrodes with high mass loading.^[25] In contrast, the direct preparation of PEs inside

batteries are usually referred as *in-situ* polymerization methods (*in-situ* methods).^[26] Typically, the precursor solution, including monomers, lithium salts and initiators, is directly injected into batteries (Figure 2b). The liquid precursor solution, similar to liquid electrolytes, infiltrates well into porous electrodes and PEs *in-situ* form at/inside the electrode surface under external energy (such as heat or irradiation), leading to the good electrode/electrolyte interfacial contact and continuous pathways for the conduction of Li^+ .^[27] Compared with *ex-situ* methods, *in-situ* methods avoid the uses of organic solvents and simplify the process of preparing solid-state batteries.^[24] Furthermore, the procedures of the *in-situ* methods could be compatible with commercial manufacturing of LIBs.^[28] Therefore, increasing attention has been attracted to the *in-situ* methods, and significant progress has been made in *in-situ* preparing PEs and solid-state batteries, such as zinc-air batteries,^[25b] solid-state zinc batteries,^[27c] Na-air batteries,^[26c] SiO_2 -based Li/LiFeO_4 batteries,^[29] poly(1,3-dioxolane)-based lithium-sulfur-polyacrylonitrile batteries^[26b] and poly(tetrahydrofuran)-based magnesium batteries.^[27b]



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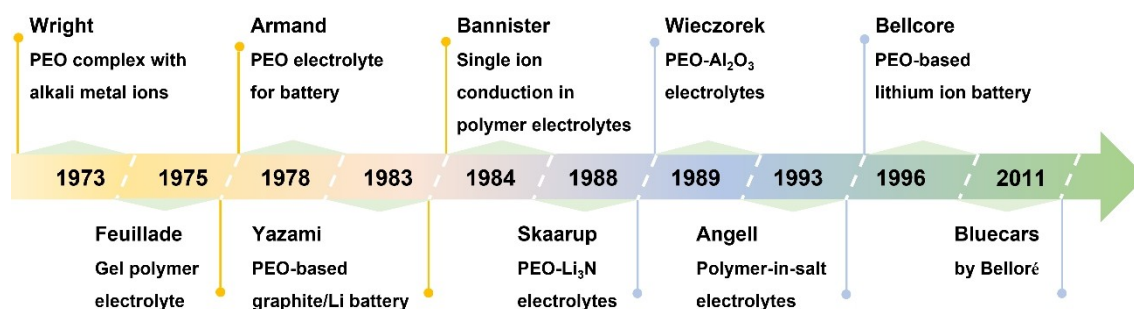
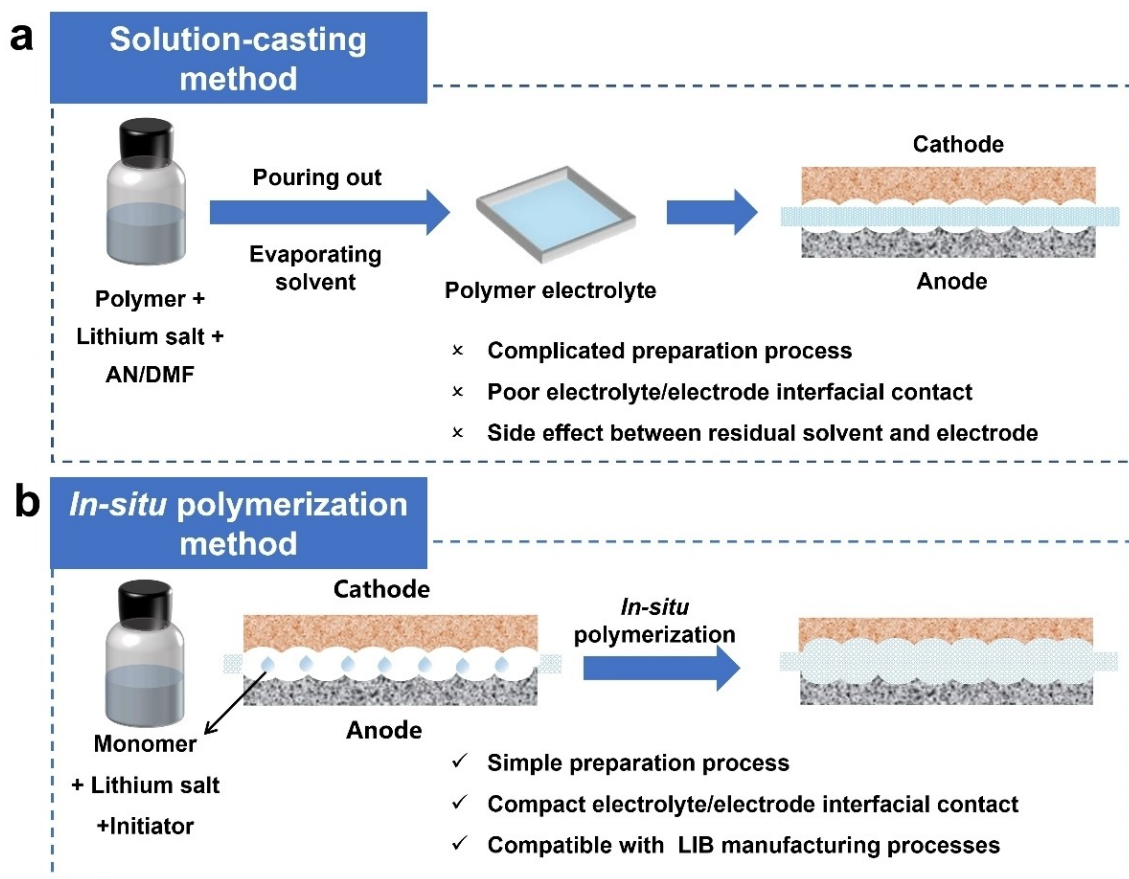


Figure 1. Key milestones of PEs.

Figure 2. Preparing solid-state batteries by a) the solution-casting methods and b) the *in-situ* polymerization methods and their advantages or disadvantages.

As mentioned above, the liquid precursors of the *in-situ* methods consist of monomers, alkali metal salts and initiators. In general, LiTFSI is widely used as the lithium salts due to the high dissociation constant, high thermal stability and great capability to restrain oxidative decomposition.^[30] To prepare PEs with capabilities of being compatible with different battery systems, countless efforts have been invested in researching and developing functional monomers/oligomers containing the unsaturated functional groups. Besides, review articles about *in-situ* methods are also inclined to focus on the progress of monomers/oligomers that can be *in-situ* polymerized, such as the types or polymerization mechanisms of monomers/

oligomers.^[31] However, the initiators, playing an important role in the *in-situ* polymerization process, also should be attached enough importance to obtain solid-state batteries (SSBs) with high energy density due to the following aspects. First of all, the polymerization conditions with regard to temperature and rate are determined by initiators, which is closely related with the cost of battery production as well. Moreover, physical properties of polymers, including melting temperature, recrystallization temperature, glass transition temperature and the molecular weight, storage/loss moduli and chain length, are affected by the concentration, types or activities of initiators. Specially, all the above-mentioned characters of polymer are

correlative with electrochemical properties of PEs (ionic conductivity, lithium-ion transference number and electrochemical window). What's more, understanding the chemical or electrochemical stability between initiators and electrodes is of utmost importance to the development of SSBs with superior cycling stability. Although numerous initiators have been proposed for *in-situ* preparation of PEs and SSBs, there are still no demonstrations that one can satisfy the highly interfacial stability during the long cycling and at practical conditions.

This review intends to present an overview on initiators of *in-situ* methods and put forward the challenges faced by the *in-situ* methods for preparation of practical SSBs. To better understand the *in-situ* methods, we firstly give a brief overview on the monomers/oligomers associated with *in-situ* polymerization, and the corresponding advantages/disadvantages are analyzed. Then, types, limitations, strengths and application in different battery systems of initiators are summarized. Particularly, the stability of initiators with electrodes and potential issues of polymerization reaction carried out inside batteries are analyzed, which may help researcher reasonably select the initiators. In addition, possible solutions to the existing problems of various *in-situ* methods are proposed. Finally, the challenges and prospects for the development are proposed from the perspective of constructing high-energy-density solid-state LMBs, aiming to promote further development of *in-situ* methods.

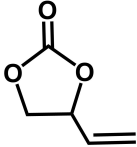
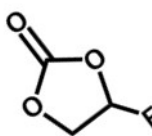
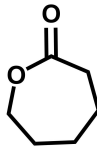

2. *In-situ* Polymerization Methods

For *in-situ* polymerization, monomers/oligomers and initiators are essential since their functions determine the properties of PEs and reaction conditions of polymerization respectively. Therefore, understanding the characteristics of monomers and initiators is necessary for *in-situ* preparation of the PEs possessed excellent electrochemical properties and solid-state batteries with high energy density.

2.1. Monomers for *in-situ* polymerization

In this section, features of different types of monomers are summarized and compared. In general, monomers are mainly classified as organic compounds containing unsaturated C=C bonds, cyclic carbonates, cyclic esters and cyclic ethers (Table 1). In terms of the first category, it mainly includes acrylate, allyl, and vinyl ether monomers/oligomers, while the main differences between different kinds of monomers lie in the chemical and electrochemical properties. A general standpoint demonstrates that ether-based monomers/oligomers are well compatible with lithium (Li) metal but are vulnerable to oxidation when facing high-voltage cathodes.^[32] Compared with ether-based monomers, carbonate and ester-based monomers present the high ionic conductivity and wide electrochemical window due to their high dielectric constant and low

Table 1. The advantages and disadvantages of monomers, the *in-situ* polymerization process and corresponding polymer electrolytes.

Characteristics of monomers or oligomers	Example	Advantages /Disadvantages of polymerization process	PEs	Advantages /Disadvantages of PEs
–C=C–		Side reaction between thermal initiator and electrode		
Cyclic carbonates		Gaseous products such as CO ₂ and HF	Polycarbonate	Wide electrochemical window High ionic conductivity High t_{Li^+} (> 0.4) Poor (electro)chemistry stability against lithium metal anode
Cyclic ester		Mild polymerization conditions	Polyester	
Cyclic ether		Mild polymerization conditions	Polyether	Good (electro)chemical stability against lithium anode Excellent ability to complex with Li ⁺ Narrow electrochemical window (< 3.8 V) Low ionic conductivity 10 ^{−7} to 10 ^{−6} S cm ^{−1} at room temperature Low t_{Li^+} (0.2–0.3)

energy level of highest occupied molecular orbital.^[17a,18a] In addition, the polymerization mechanisms of these monomers are also diverse. Polymerization of monomers/oligomers containing conjugated C=C bonds is usually triggered by azo compounds or peroxides such as azobis(isobutyronitrile) (AIBN) and methyl dibenzoyl peroxide (BPO),^[33] which belongs to the free radical polymerization. But the inevitable parasitic reactions (thermal decomposition of the salt or side reactions between alkali metal and initiator) have negative impacts on the electrochemical performance of the obtained solid-state batteries.^[24,34] As for the ring-opening polymerization cyclic carbonates, gases may be generated in the process, which further increases the resistance of electrode/electrolyte interface and lower the utilization of active material.^[24] However, the reaction conditions of cyclic esters and ethers are relatively mild, thus receiving extensive attentions especially for ether-based monomers/oligomers. In short, the chemical and electrochemical properties of monomers/oligomers should be primarily considered for *in-situ* methods.

2.2. Initiators of *in-situ* polymerization methods

The physical properties of polymers, such as glass-transition softening temperature and melting points, and molecular weight, are affected by the reaction rate, which also leads to different electrochemical properties of PEs. Therefore, selecting the suitable initiators is crucial. Thermal initiators, non-ionizing irradiation (such as UV light) and ionizing irradiation (for example, high energy electron-beam, β -ray and γ -ray) can initiate free radical polymerization of monomers/oligomers containing conjugated C=C bonds, but the alkali metal initiators can trigger the anion polymerization.^[22] Lewis-acid initiators are usually used to initiate the ring-opening polymerization of heterocyclic compounds.^[35] Particularly, non-ionizing irradiation with limited energy (several electron volts) is too weak to break chemical bonds or lead to the formation of ions. Thus, non-ionizing irradiation can only initiate the polymerization of monomers/oligomers containing conjugated C=C bonds on the electrode surface due to the limited penetration depth,^[36] not consistent with the concept defined by this review and not discussed accordingly. In addition to free radical polymerization and ionic polymerization, monomers can be polymerized during the process of charging or discharging, which is defined as the electro-polymerization.

2.2.1. Thermal initiators

Thermal initiators used in the *in-situ* polymerization process are mainly azo compounds and peroxides, such as azobis(isobutyronitrile) (AIBN) and benzoyl peroxide (BPO) (Table 2). The *in-situ* polymerization initiated by thermal initiators has been proposed in 1997, where the authors fabricated carbon/LiCoO₂ (LCO) cells based on terpolymer and liquid electrolytes.^[37] Thanks to the high ionic conductivity of $1.3 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, the capacity retention

Table 2. The thermal initiators usually used in the *in-situ* process.

Initiator type	Initiator	Reaction temperature
azo compounds	AIBN	45–80 °C
	ABVN	45–80 °C
peroxides	BPO	60–80 °C

reached 80% over 500 cycles. In 2002, Kim et al. *in-situ* assembled graphite/LCO cells using BPO as initiators and tri(ethylene glycol) dimethacrylate as monomers.^[38] When the volume ratio of monomer to liquid electrolytes equaled 5:95, the cell was able to work at 20 °C and even –10 °C. Since then, employing thermal initiators to initiate the *in-situ* polymerization of acrylate, allyl, and vinyl ether monomers/oligomers has been developed in various battery systems, such as Li-sulfur (S), magnesium-metal, sodium metal and zinc-ion batteries. In 2016, Kang et al. reported pentaerythritol tetraacrylate (PETEA)-based polymer electrolytes induced by AIBN (0.1 wt% of PETEA), which showed an extremely high ionic conductivity ($1.1 \times 10^{-2} \text{ S cm}^{-1}$) due to the high content of liquid electrolytes (98.5 wt%).^[39] Benefiting from the flexible and stable passivation layer and compact electrolyte/electrode interface contact, the polysulfide diffusion was effectively inhibited and the *in-situ* assembled Li–S batteries (heating at 70 °C for 2 h) showed stable cycling at a current rate of 3C and capacity retention of 91.9% after 500 cycles. It is worth noting that the high content of liquid electrolytes (>90 wt%) is introduced in the above systems, which is in favor of enhancing the ionic conductivity and electrochemical properties of batteries.^[21] However, the safety, mechanical toughness and energy density of the obtained batteries could be compromised. On the other hand, the process of heating and the additional ionic liquid will inevitably lead to the decomposition of LiPF₆ and the increase of viscosity of liquid precursor, respectively.^[40] Therefore, *in-situ* preparing PEs that show high ionic conductivity, good interface stability but contain no or a tiny amount of liquid electrolytes is crucial to high-energy-density solid-state LMBs.

To achieve high-performance and stable solid-state LMBs, Kim and Lee et al. used AIBN as an initiator (The content is 0.5 mol% compared with the monomers.) to develop elastomeric PEs, which showed superior mechanical properties (extensibility of about 300%), high ionic conductivity (1.1 mS cm^{-1} at 20 °C) and lithium-ion transference number (0.75). Even at harsh conditions (the mass loading of LiNi_{0.83}Mn_{0.06}Co_{0.11}O₂ cathodes is higher than 10 mg cm⁻² and negative-to-positive capacity ratio is 3.4), the *in-situ* fabricated solid-state LMBs at a high voltage of 4.5 V (vs. Li/Li⁺) presented the stable cycling and the high specific energy exceeded 410 Wh Kg⁻¹ (Figure 3a).^[41] Particularly, the *in-situ* assembled Li/Cu batteries possessed a Coulombic efficiency of 100% at current densities of 2 mA cm⁻² and 5 mA cm⁻² with capacities of 4 mAh cm⁻² and 10 mAh cm⁻². Such a pleasing result will draw more researchers to focus on this field. In addition, Fan et al. used 2,2'-azobis-(2,4-dimethylvaleronitrile) (ABVN) as thermal initiators (1 wt% of the monomer and heating at 60 °C for 3 h) to *in-situ* fabricate composite electrolytes based on

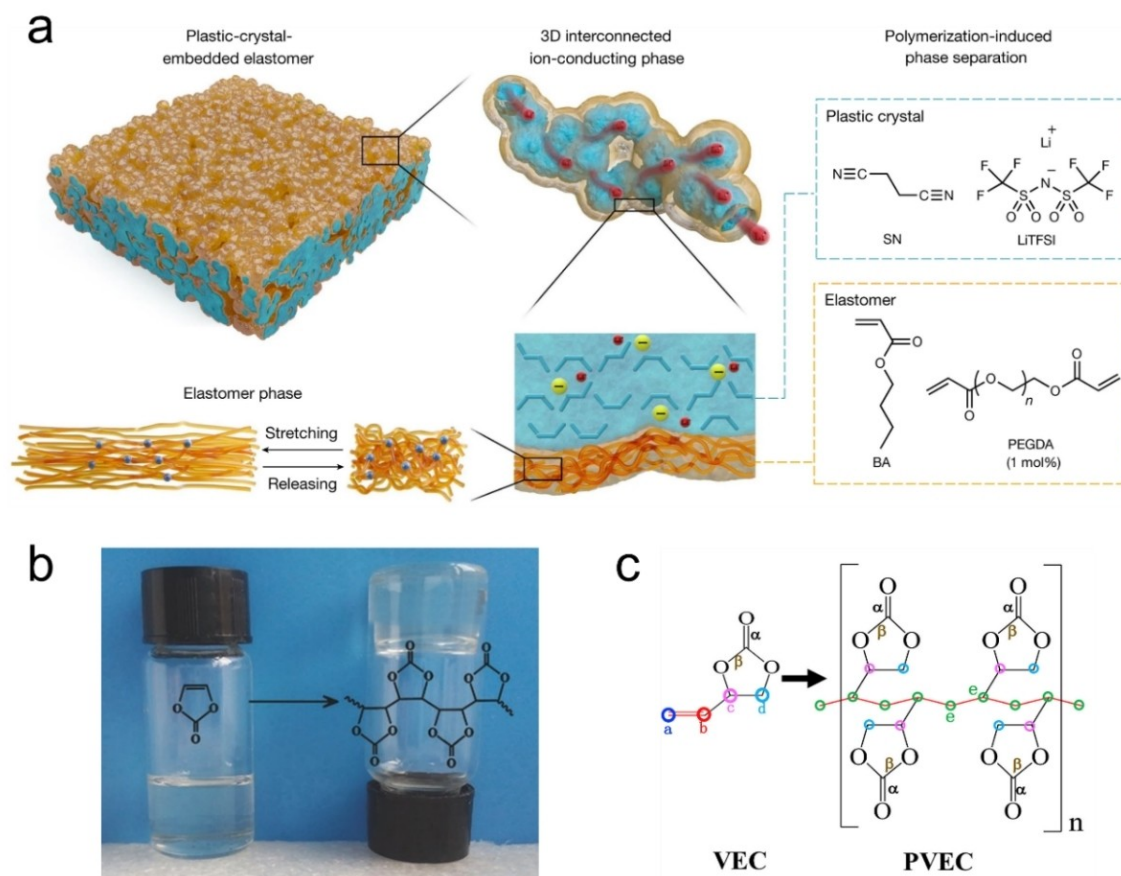


Figure 3. Schematics of a) plastic-crystal-embedded elastomer electrolytes through thermal initiator. Reproduced with permission from Ref. [41]. Copyright (2022) Springer Nature. b) Poly(vinylene carbonate)-based polymer electrolytes. Reproduced with permission from Ref. [43]. Copyright (2016) The Authors. Published by Wiley-VCH. c) Poly(vinyl ethylene carbonate)-based polymer electrolytes. Reproduced with permission from Ref. [48]. Copyright (2020) Elsevier.

monomers of tripropylene glycol diacrylate and inorganic electrolytes of $\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZAO).^[42] The electrolytes with 10 wt% LLZAO showed the ionic conductivity of $8.43 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C and lead to excellent cycling performance of $\text{Li}/\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ batteries (4.3 V, vs. Li/Li^+).

Thermal initiators are also employed to initiate the polymerization of organic compounds with the small molecular weights and simple structures, which dramatically decreases the proportion of liquid electrolytes but holds the slight effect on the ionic conductivity. Vinylene carbonate (VC) containing $\text{C}=\text{C}$ conjugated bonds is usually used as an additive for batteries due to the good interfacial compatibility. Cui et al. *in-situ* prepared a novel poly(vinylene carbonate) (PVCA)-based polymer electrolytes ($8.9 \times 10^{-5} \text{ S cm}^{-1}$ at 50°C) triggered by AIBN (0.1 wt% of VC) (Figure 3b).^[43] The *in-situ* fabricated solid-state $\text{Li}/\text{PVCA}/\text{LCO}$ pouch batteries were obtained by keeping at 60°C for 24 h and 80°C for 10 h, which not only showed the high capacity retention of 84.2% at 50°C but also achieved high safety after nail penetration tests. To improve the ionic conductivity of PVCA-based electrolytes, Cui et al. proposed the strategy of *in-situ* preparing PVCA- $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$ (sulfide solid-state electrolyte) composite electrolytes by employing AIBN as an initiator (0.3 wt% of VC), which showed an ion conductivity of

$2.0 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature and the ability to mitigate the dissolution of Mn of $\text{LiFe}_{0.2}\text{Mn}_{0.8}\text{PO}_4$ (LFMP).^[44] After retaining at 60°C for 120 h, the solid-state Li/LFMP batteries could be obtained and delivered stable cycling at room temperature. However, there is no discussion about the effects of polar solvent of VC on the crystal structure of $\text{Li}_{10}\text{SnP}_2\text{S}_{12}$. Guo et al. introduced the flame-retardant triethyl phosphate (TEP) into VC-based precursor (5:5, volume ratio) and designed the non-flammable PEs.^[45] The solid-liquid hybrid electrolyte (SLHE) initiated by AIBN (0.1 wt% of VC) simultaneously featured excellent electrochemical performances and a high Young's modulus of 12.4 GPa. Specially, the Ah level $\text{Li}/\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ pouch cells *in-situ* formed by standing for 24 h at 45°C also exhibited enhanced safety. This research provides the practical guidance of *in-situ* construction of safe and high-energy-density solid-state LMBs. Nevertheless, the poor compatibility between phosphate and Li metal will lead to a high-impedance solid electrolyte interphase.^[46]

Vinyl ethylene carbonate (VEC) containing $\text{C}=\text{C}$ bonds at the branch position is also an organic compound of a five-membered ring. In the presence of thermal initiators, the $\text{C}=\text{C}$ can be opened but keep the original ring structure.^[47] Yu et al. employed AIBN as thermal initiators to fabricate poly(vinyl

ethylene carbonate) (PVEC)-based Li/LiFePO₄ (LFP) batteries (80 °C for 12 h) which demonstrated a high discharge capacity at 25 °C and even at –15 °C due to the high ionic conductivity ($2.1 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature) (Figure 3c).^[48] This work not only proposes a new polymer electrolyte but also leads researchers to notice the electrochemical properties at low temperature. In addition, the poly(ionic liquid)-based electrolytes also have been developed. Thermal initiators also have been used to *in-situ* prepare poly(ionic liquid)-based electrolytes. Kang et al. used AIBN (0.1 wt% of the monomer) to *in-situ* initiate the polymerization of 1,4-bis[3-(2-acryloyloxyethyl)imidazolium-1-yl]butane bis[bis(trifluoromethanesulfonyl)imide] (C1-4TFSI), leading to electrolytes with the high ionic conductivity ($> 10^{-3} \text{ S cm}^{-1}$ at 25 °C), satisfying electrochemical stability, inherent incombustibility and excellent thermal stability.^[49] And solid-state Li/LFP batteries (heating the liquid-state batteries at 60 °C for 12 h) exhibited outstanding cycling performances (capacity retention of 97.7 % after 100 cycles) at 25 °C. However, the high viscosity and cost of ionic liquid inhibit the extensive application in the batteries.

The *in-situ* free radical polymerization initiated by thermal initiators has been widely used in LIBs, LMBs and other systems. Compared with BPO and ABVN, AIBN shows good storage and transportation stability so that it has been the most commonly used thermal initiators. What's more, only a small amount of thermal initiators is able to initiate the *in-situ* polymerization. However, the reports about influences of polymerization reaction time on physical properties of polymer (for example, crosslinking degree and mechanical strength) and the electrochemical properties of PEs are severely lacking. Furthermore, the shortcomings may need to be addressed in the future research, such as N₂ arising from the decomposition of azo compounds, CO₂ causing by the degradation of peroxides and the side reactions between initiators of azo compounds and electrodes. To thoroughly eliminate the effects of additional initiators on the electrode/electrolyte interface, an initiator-free polymerization method may be a possible solution, for instance, using ionizing irradiation to initiate the polymerization, or finding temperature-sensitive monomers.

2.2.2. Ionizing irradiation

The ionizing irradiation with high energy (a few millions electron volts) suffices to break chemical bonds and furtherly form new bonds. Free radicals, anions and cations will form when monomers are exposed to ionizing irradiation.^[50] And the reactive species are able to induce the polymerization. Usually, the polymerization of olefin monomers/oligomers involves free radical polymerization, while the polymerization of other monomers (such as heterocyclic compounds) refers to ionic polymerization.^[50] Thus, ionizing irradiation can trigger the polymerization of various monomers and does not require any additional initiators. In addition, the ionizing irradiation is enough to penetrate battery materials (such as the low density of aluminum-plastic film) and able to trigger *in-situ* polymer-

ization of liquid electrolyte components within cell. What's more, the polymerization induced by ionizing irradiation can be carried under room temperature or lower temperature. And the process of ionizing irradiation requires less than one minute, which is convenient and highly efficient compared with non-ionizing irradiation requiring inert atmospheric conditions and taking a long time. γ -ray is designated the electromagnetic spectrum but the wavelength is lower than 0.1 nm, resulting in the high energy (a few millions electron volts) and penetration depth. In 2004, Chen et al. *in-situ* prepared poly(methyl methacrylate) (PMMA)-based graphite/LiNi_{0.8}Co_{0.2}O₂ batteries by γ -ray irradiation.^[34a] Due to the high penetration depth, the liquid-state coin cells (CR2032) were directly *in-situ* transformed into solid-state batteries, while the capacity retention was only 85 % after 20 cycles. The decline of discharge capacity may result from the high interface resistance and degradation of PMMA-based electrolytes during charging. However, the influence of ionizing irradiation dosage wasn't examined. In 2017, Zhai et al. also employed γ -ray irradiation to *in-situ* prepare gel polymer electrolytes and discussed how ionizing irradiation dosage and dose rate influenced the ionic conductivity of electrolytes.^[34b] The optimal dosage was 35 kGy and the ionic conductivity of electrolytes was $3.05 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. The capacity retention of graphite/LFP pouch cells was 86 % after 50 cycles. Whereas, there are still high content of liquid electrolytes (93 wt%) in the above systems, which is unfavorable for improving safety and energy density. Xie et al. used electronic beam (e-beam) irradiation to *in-situ* prepare solid-state Li/LFP cells based on VEC and poly(ethyleneglycol) dimethacrylate (PEGDMA), which delivered a high discharge capacity retention of 85.0 % over 270 cycles (Figure 4).^[51] And the content of remained VEC monomer was only 12.8 wt% (compared to the original mass of VEC) and much less than the above systems. The solid-state Li/LFP pouch cells also exhibited excellent cycling performance and superior safety.

Ionizing irradiation with high energy and penetration depth is a clean, effective and promising technology, which has been widely used to *in-situ* production of PEs and solid-state batteries based on monomers/oligomers containing C=C bonds. However, inhibitors are usually added to these monomers/oligomers to prevent the inadvertent initiation of the free radical reactions during storage and transport, which makes the battery systems more complex. Therefore, evaluating the effects of inhibitors on battery performances is necessary. Additionally, there are some problems should be paid attention, such as how ionizing irradiation influences on structure of electrode materials and binder, the uniformity of polymerization and so on.

2.2.3. Alkali metal initiators

Alkali metal initiators (such as Li, Na, K) can initiate the anionic polymerization of vinyl monomers containing electron-withdrawing groups (such as –C≡N or –NO₂) and the ring-opening polymerization of cyclic monomers with high electrophilicity.^[52]

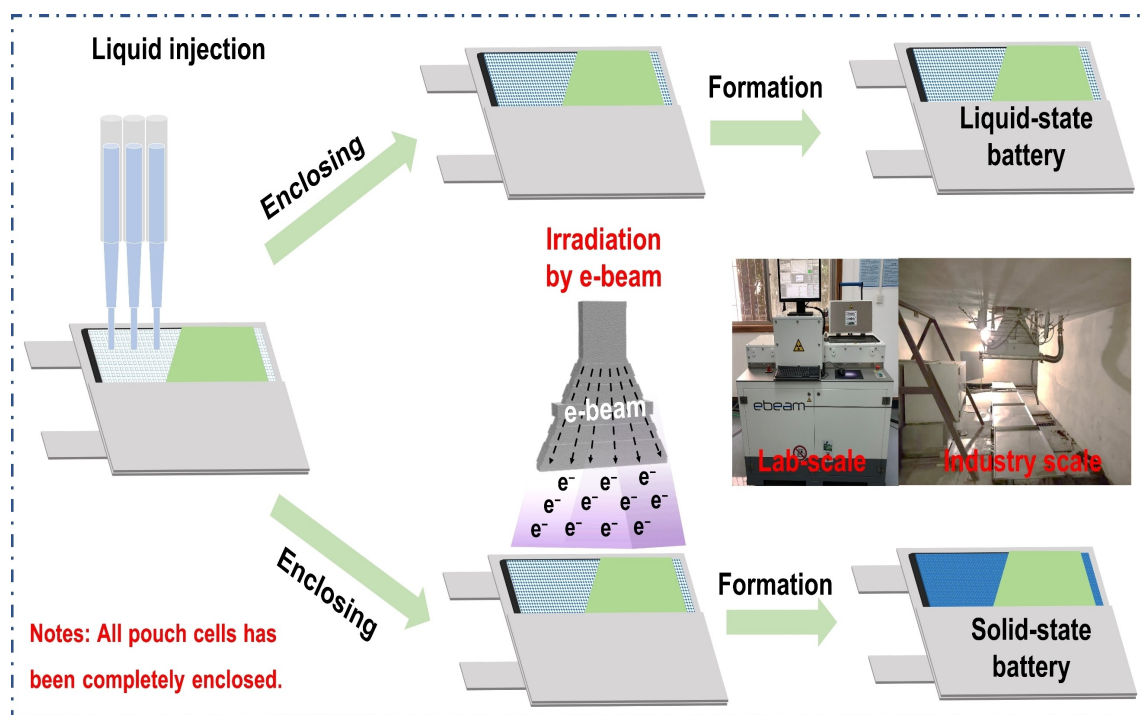


Figure 4. The process of current lithium-ion batteries and *in-situ* preparing solid-state batteries by e-beam irradiation. Reproduced with permission from Ref. [51]. Copyright (2022) Elsevier.

The anion polymerization can be carried out at room temperature or even at low temperature, so alkali metal initiators are one of promising candidates for *in-situ* preparing PEs with high performances. In 2017, Cui et al. employed Li metal as initiators to *in-situ* prepare a poly(ethyl cyanoacrylate) (PECA)-based gel polymer electrolytes at room temperature for 2 h (Figure 5a).^[53] Electrons transfer from Li metal to the unsaturated C=C, which leads to the generation of anion active species to initiate the polymerization. The high voltage LMBs of Li/LiNi_{0.5}Mn_{1.5}O₄ (5.0 V, vs. Li/Li⁺) showed a capacity retention of 93% after 100 cycles due to the high ionic conductivity of $2.7 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature. But the content of liquid electrolytes was up to 75% (volume ratio). Chen et al. also used Li as an initiator to *in-situ* construct a multifunctional solid electrolyte interface on Li surface (Figure 5b).^[54] The interface effectively suppressed the density growth. The similar strategies also were proposed by Ding et al.^[55]

The reports about *in-situ* polymerization initiated by alkali metal initiators are limited and thus there are still more opportunities for exploring the application in this field. Specially, using Li metal as initiators is possible to *in-situ* fabricate gradient electrolytes that consist of PEs on the surface of anode but liquid or hybrid solid/liquid electrolytes inside the cathode. Nevertheless, the *in-situ* polymerization initiated by alkali-metal initiators is confronted with the dilemma of difficult chain termination, which may lead to the low ionic conductivity and high interface resistance. Thus, controlling the chain growth of polymer inside the batteries is crucial to adjust the electrochemical performances.

2.2.4. Lewis-acid initiators

Recently, the ionic polymerization induced by Lewis-acid initiators has also been widely studied. Reported Lewis-acid initiators include AgSbF₆,^[56] Al(OTf)₃,^[57] BF₃,^[58] LiPF₆,^[59] Sn(OTf)₂,^[60] SnF₂,^[61] and so on. In 1991, Abraham et al. firstly employed AgSbF₆ as initiators to *in-situ* prepare poly(1,3-dioxolane) (PDOL) and poly(tetrahydrofuran) (PTHF)-based electrolytes.^[56] The ionic conductivity was $4.3 \times 10^{-6} \text{ S cm}^{-1}$ and $1.2 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature, respectively, while the related battery performances were scarce. In 2018, Guo et al. reported that PDOL-based gel polymer electrolytes were *in-situ* prepared under room temperature, where PF₅ stemmed from the decomposition of LiPF₆ played a key role of initiators (Figure 6a).^[62] It was worth mentioning that the author found the molecular weight of PDOL increased but the ionic conductivity of PDOL-based electrolytes decreased with the increase of the polymerization time. When the polymerization was over 10 h, both gradually stabilized due to the existence of inhibitor of trace H₂O. Under the optimal conditions, the *in-situ* fabricated Li/S batteries showed excellent capacity retention of 73.7% after 1000 cycles and Li/LFP batteries also demonstrated stable cycling. However, there was still high content of liquid 1,2-dimethoxyethane (DME), which may be one of the reasons that the ionic conductivity holds constant after certain hours. In 2019, Archer et al. also *in-situ* prepared PDOL-based electrolytes using Al(OTf)₃ as initiators (Figure 6b).^[57a] Specially, the author discussed the influences of concentration of Al(OTf)₃ on physical properties of PDOL and electrochemical properties of PDOL-based electrolytes. When the concentration of Al(OTf)₃

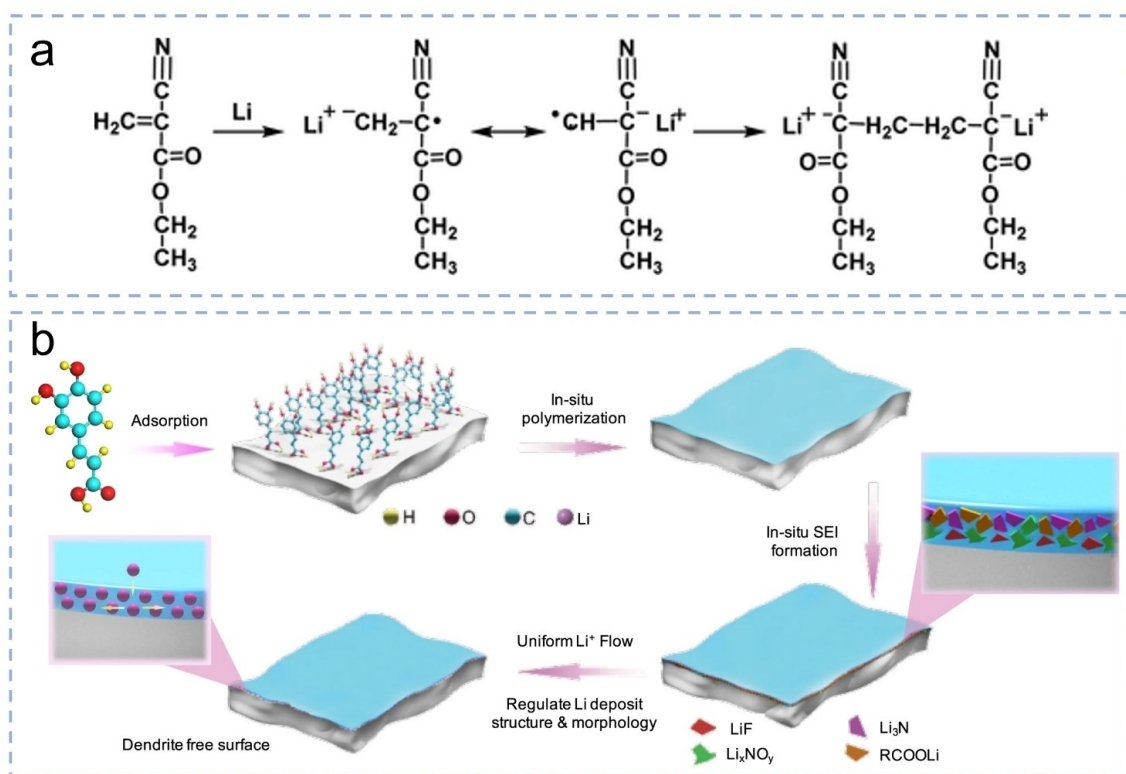


Figure 5. a) Li metal *in-situ* induced poly(ethyl cyanoacrylate)-based electrolytes. Reproduced with permission from Ref. [53]. Copyright (2017) American Chemical Society. b) Li metal *in-situ* induced poly(cafeic acid)-base electrolyte interface. Reproduced with permission from Ref. [54]. Copyright (2021) The Authors. Published by Springer Nature.

was 0.5 mM, the ionic conductivity at room temperature was about 1 mS cm^{-1} and the PDOL-based electrolytes could enable the Li/S, Li/LFP and Li/LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ batteries to show long cyclability. After that, more studies focused on initiators for *in-situ* polymerization of DOL and constructing PDOL-based LMBs

have sprung up, which is summarized and shown in Table 3. Note that the strategy of selecting the lithium salts (LiPF₆, LiDFOB and LiFSI) as initiators can enable advanced SSBs with long cycling stability and a fairly reinforced interfacial stability. However, the energy density of batteries is severely limited by

Table 3. The thermal initiators usually used in the *in-situ* process.

Initiator	Precursor composition	Ionic conductivity (RT) [S cm ⁻¹]	Battery systems	Cut-off voltage [V]	Reference
Al (OTf) ₃	2 M LiTFSI + DOL	1.0×10^{-3}	Li/S	3.0	[57a]
Al (OTf) ₃	2 M LiTFSI + DOL	2.39×10^{-3}	Li/LFP	4.0	[57b]
Al (OTf) ₃	2 M LiTFSI + DOL	1.2×10^{-4}	Li/LFP	4.0	[57c]
Sn (OTf) ₂	2 M LiTFSI + DOL	6.16×10^{-5}	Li/LCO	4.2	[60]
SnF ₂	1 M LiTFSI + DOL	1.7×10^{-5}	Li/LFP	4.0	[61]
AlI ₃	1 M LiTFSI + 1.5 wt% LiDFOB + DOL	/	Li/NCM811	4.2	[68]
AlF ₃	2 M LiTFSI + DOL	1.5×10^{-3}	Li/NCM622	4.2	[69]
LiDFOB (BF ₃)	2 M LiTFSI + DOL + 0.2 M LiDFOB + 25 wt% SN + 5 wt% FEC	1.06×10^{-4}	Li/LFP	4	[70]
BF ₃	1 M LiTFSI + 0.1 M LiBF ₄ + DOL	9.34×10^{-6}	Li/LFP	4	[71]
LiPF ₆ (PF ₅)	1 M LiTFSI + 1 wt% LiPF ₆	1.8×10^{-4}	Li/NCM622	4.3	[59a]
LiPF ₆ (PF ₅)	1 M LiTFSI + LiPF ₆ + DOL/FEC/MP (4:1:5, volume ratio)	2.8×10^{-3}	Li/NCM811 (-20 °C)	4.3	[59b]
LiPF ₆ (PF ₅)	EC + DOL + 1 M LiPF ₆	3.2×10^{-5}	/	/	[59c]
LiPF ₆ (PF ₅)	1 M LiTFSI + 2 M LiPF ₆ + DOL/DME	3.8×10^{-3}	Li/S	3.0	[62]
LiPF ₆ (PF ₅)	1 M LiTFSI + 2 M LiPF ₆ + DOL/DME	1.71×10^{-3}	Li/NCM811	4.3	[72]
LiPF ₆ (PF ₅)	1 M LiTFSI + 0.2 M LiNO ₃ + 2 M LiPF ₆ + DOL/DME	7.81×10^{-4}	Li/LFP	4.0	[73]
LiFSI	3.5 M LiFSI + DOL	7.9×10^{-3}	Li/LFP	4.0	[74]
3TB	2 M LiTFSI + DOL	1.12×10^{-3}	Li/NCM622	4.3	[75]
Nafion	1.0 M LiTFSI + DOL/DME	1.04×10^{-4}	Organic cathode	3.5	[76]

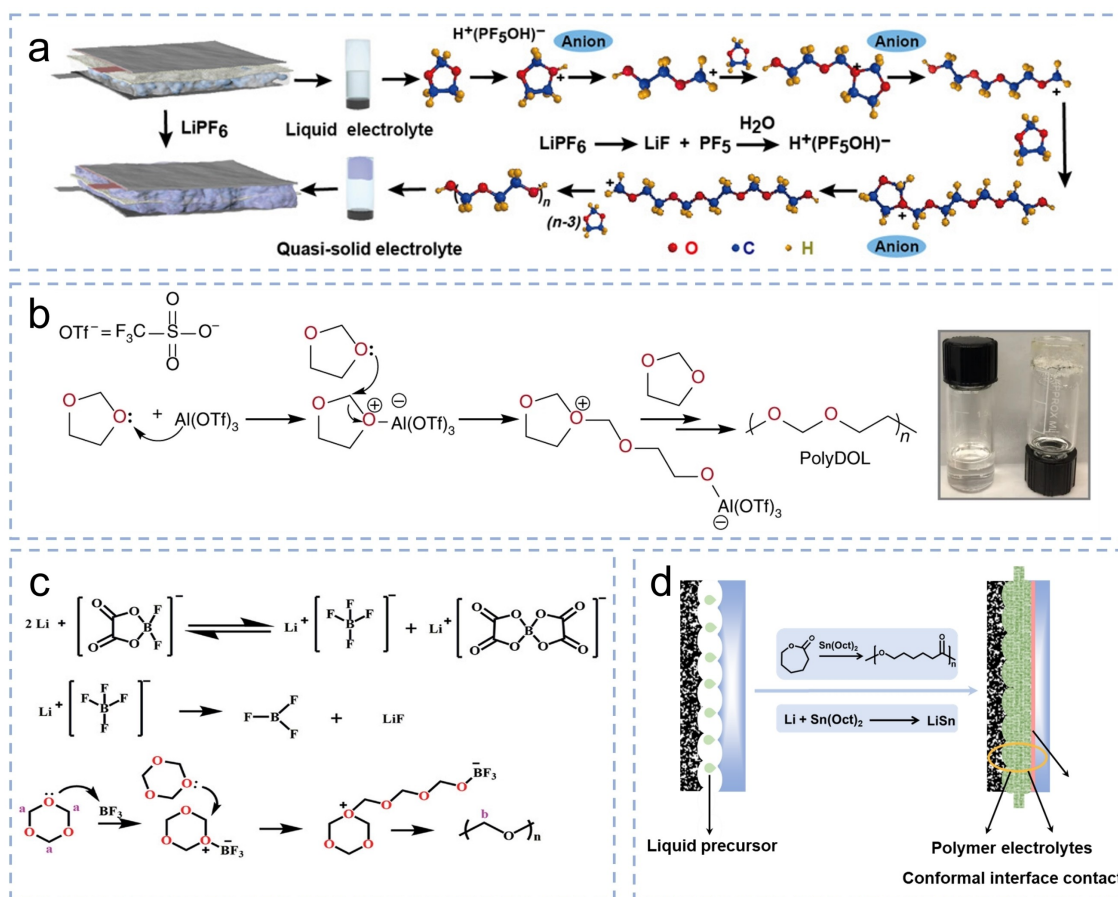


Figure 6. a) LiPF_6 *in-situ* induced poly(1,3-dioxolane)-based electrolyte. Reproduced with permission from Ref. [62]. Copyright (2018) The Authors. Published by Science Advances. b) $\text{Al}(\text{OTf})_3$ *in-situ* induced poly(1,3-dioxolane)-based electrolyte. Reproduced with permission from Ref. [57a]. Copyright (2019) Springer Nature. c) LiDFOB *in-situ* induced poly(trioxymethylene)-based electrolyte. Reproduced with permission from Ref. [63]. Copyright (2020) The Authors. Published by Wiley-VCH. d) $\text{Sn}(\text{Oct})_2$ *in-situ* induced poly(ϵ -caprolactone)-based electrolyte. Reproduced with permission from Ref. [64]. Copyright (2021) Elsevier.

the low mass loading of cathodes and a high negative-to-positive capacity ratio.

Besides initiators, the potential application of PDOL-based electrolytes on high or low temperature has also been explored. Zhou et al. not only proposed SnF_2 initiator for *in-situ* open-ring polymerization of DOL, but also discussed the decomposition of PDOL-based and liquid DOL-based electrolytes under 110°C , showing that the thermostability of PDOL-based electrolytes was higher than that of DOL.^[61] Ciucci et al. used LiPF_6 as initiators to *in-situ* prepare PDOL-based quasi-PEs with outstanding ionic conductivity ($1.2 \times 10^{-3} \text{ S cm}^{-1}$ at -30°C) and wide electrochemical window by ingenious formulation of electrolyte ingredients.^[59b] The *in-situ* fabricated quasi-solid Li/NCM811 batteries could work at -20°C , resulting from the addition of methyl propionate with a melting point of -88°C . Moreover, BF_3 with good interface stability was also proposed to be an initiator to *in-situ* prepare poly(tetrahydrofuran) (PTHF)- LiClO_4 electrolyte by Cui et al. (The concentration of boron trifluoride diethyl ether was 0.6 mol L^{-1} and the reaction required 7 days at room temperature), while the solid-state Li/LFP batteries only worked at 60°C due to the low ionic conductivity ($2.3 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C).^[58] Both trioxymethylene

(TOM) and THF were classified as the ether-based monomers, while *in-situ* poly(trioxymethylene) (PTOM)-based system employed LiDFOB as initiators and lithium salts could be applied in Li/LCO batteries (Figure 6c).^[63] Therefore, the rational design of electrolytes is an effective strategy to improve the electrochemical properties and the bifunctional initiator with good interface compatibility is also an ideal selection for *in-situ* polymerization.

Lewis-acid initiators are also able to initiate the polymerization of cyclic esters and fabricate solid-state batteries. Xie et al. *in-situ* fabricated poly(ϵ -caprolactone)-based LMBs by using a bifunctional initiator of $\text{Sn}(\text{Oct})_2$ (Figure 6d).^[64] In particular, $\text{Sn}(\text{Oct})_2$ (5 wt% of CL) not only induced the polymerization of ϵ -caprolactone (CL) inside the batteries (100°C for 3 hours), but also *in-situ* reacted with Li anode to form a LiSn alloy that could suppress the dendrite growth. Later, Xie et al. *in-situ* prepared "polymer-in-salt" electrolytes, which enabled the high-voltage LMBs with stable cycling.^[65] Yan et al. employed $\text{Sn}(\text{Oct})_2$ (1 wt% of FEC) to *in-situ* fabricate a high-voltage-tolerated poly(fluoroethylene carbonate) (FEC) (PFEC)-based batteries (80°C for 24 h and 100°C for another 24 h), which enabled 4.45 V-class LCO and 4.9 V-class

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ to exhibit stable cycling performance.^[66] However, the heat treatment during the *in-situ* process may lead to the defluorination of FEC to form HF, which can result in the significant dissolution of transition metal ions.^[67] In consequence, choosing suitable initiators and monomers in the *in-situ* process are vital for the battery performance.

Lewis-acid initiators are capable to initiate the cationic polymerization of monomers, while controlling the chain termination is difficult once the polymerization has started. Therefore, one of the key challenges is the control of polymer chain growth since the molecular weight of polymer is related with the ionic conductivity of PEs and the growing polymer chain may increase the interface resistance. Additionally, adjusting the concentration of initiators and polymerization time is crucial to regulate the electrochemical properties of PEs.

2.2.5. Electro-polymerization

Electrochemistry-induced polymerization is called as electro-polymerization, which is usually used to form a protective layer on the electrode surface. Monomers can be polymerized during the process of charging or discharging. In 2008, Zhan et al. found that DOL could be *in-situ* polymerized during charging but the cut-off voltage was a prerequisite for the polymerization of DOL, which was also affected by current density of charging.^[77] In 2017, Archer et al. reported that an ion-conductive membrane was formed on Na metal by *in-situ* electro-polymerization of ionic liquids containing unsaturated groups (Figure 7). The membrane could inhibit the parasitic reactions between liquid carbonate electrolytes and Na anode.^[78] Lucht et al. proposed that VC or FEC could be reduced to poly(VC) or poly(FEC) and the favorable solid electrolyte interphase (SEI) during cycling, leading to the enhanced electrochemical performances of batteries.^[79] In addition, VEC could be reduced at above 1 V (vs. Li/Li^+) and facilitate the formation of SEI on the surface of graphite, which prevented the co-intercalation of propylene carbonate and significantly improved the performances of batteries.^[80] Thus,

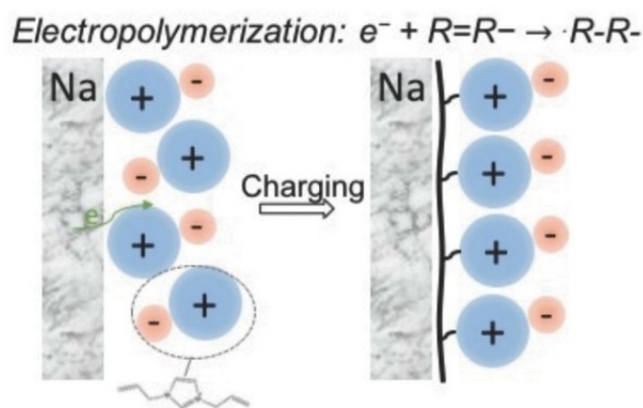


Figure 7. Schematic of the poly(ionic liquid) film on the Na metal electrode by electro-polymerization. Reproduced with permission from Ref. [78]. Copyright (2022) Wiley-VCH.

the electro-polymerization is an easy and effective strategy to fabricate a stable SEI, while the clear understanding of the polymerization mechanism is still lacking.

3. Conclusion and Perspectives

In-situ polymerization has been considered as a promising strategy to prepare solid-state batteries in a large scale, which not only simplifies the procedures but also forms compact electrode/electrolyte interface contact. What's more, it also shows many advantages, such as inhibiting dissolution of transition metal ions, suppressing growth of lithium dendrite and inhibiting polysulfides shuttling (Figure 8). In this review, we have summarized the *in-situ* polymerization methods and sectioned by the initiators, which mainly includes thermal initiators, ionizing irradiation, alkali metal initiators, Lewis-acid initiators and electro-polymerization. In the authors' opinion, ionizing irradiation with high energy (such as electron-beam, β -ray or γ -ray) may be a promising technique in the view of practical application due to some unique advantages: i) A mature technology has been widely used in many areas. ii) Ionizing irradiation is capable to trigger the polymerization of precursor inside the completely sealed cells. iii) Ionizing irradiation can induce the polymerization of various bonds of monomers/oligomers at room temperature or lower temperature and the method is free of initiator. However, there are still challenges for ionizing irradiation, for example, how ionizing irradiation influences on structure of electrode materials and binder (especially for β -ray or γ -ray), the uniformity of polymerization, and degradation of polymer electrolytes or other by-product resulted from the β -ray or γ -ray with high energy (a few millions electron volts). In addition, some common problems of these *in-situ* methods need to be paid attention.

- 1) Selecting suitable monomers and initiators. The chemical or electrochemical stability between monomers or initiators and electrodes is primary concern for developing solid-state batteries with high energy density and stable cycling life through the *in-situ* polymerization methods. The adverse reaction hidden in certain methods (for example, N_2 arising from the decomposition of azo compounds or CO_2 causing by the degradation of peroxides) should be investigated deeply.

Advantages of <i>in-situ</i> polymerization				
Inhibiting dissolution of transition metal ions	Forming intimate interface	Suppressing growth of lithium dendrite	Inhibiting polysulfides shuttling	Improving battery performance

Figure 8. The advantages of *in-situ* polymerization.

- 2) Analyzing the residual content of liquid monomers. Liquid-state precursors may not be completely *in-situ* transformed into solid-state electrolytes. Specially, the unreacted monomers promote ion transport but simultaneously attenuate the mechanical properties. Measuring the content of the residual monomers inside batteries is necessary to rationally design the electrolytes with excellent properties and achieve the actual solid-state batteries. Some strategies may be feasible, such as weighting the disassembled batteries before and after the process of vacuum evaporation treatment, gas chromatography or thermogravimetry.
- 3) Improving the compatibility of *in-situ* prepared PEs with electrodes especially for high-voltage cathodes. Most of *in-situ* prepared PEs suffer from low oxidative stability, which is not enough to enable stable cycling of LMBs versus a 4 V-class cathode. Designing blended-salt precursors including LiBF₄, LiBOB or LiDFOB may be a reasonable choice.
- 4) Enhancing the mechanical strength of *in-situ* prepared PEs. Only few studies pay attention to this point that is as vital as the other electrochemical properties. *In-situ* preparing PEs with crosslinking structure or composite electrolytes is an efficient way.
- 5) Developing new monomers with nonflammable properties. The monomers that have been reported focus on flammable carbonates and ethers. The thermal stability can be improved through introducing the flame-retardant additives and developing new monomers with nonflammable properties, and meanwhile employing the separator with high thermal stability (such as cellulose film, glass fiber separator or polyimide film) as support.
- 6) Exploring the application of *in-situ* polymerization methods on practical high-energy-density battery systems. The *in-situ* prepared solid-state batteries usually employ the cathode with low mass loading (< 1 mAh cm⁻²) and large amounts of precursors. Therefore, practical conditions of high cathode loading, low electrolyte-to-cathode ratio and low negative-to-positive capacity ratio should be considered in the future work.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: initiators · *in-situ* polymerization · monomers · polymer electrolytes · solid-state batteries

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