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Ionic Liquid/Poly(ionic liquid)-based Semi-solid State Electrolytes for Lithium-ion Batteries

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Abstract Ionic liquids (ILs) have appeared as the most promising electrolytes for lithium-ion batteries, owing to their unique high ionic conductivity, chemical stability and thermal stability properties. Poly(ionic liquid)s (PILs) with both IL-like characteristic and polymer structure are emerging as an alternative of traditional electrolyte. In this review, recent progresses on the applications of IL/PIL-based semi-solid state electrolytes, including gel electrolytes, ionic plastic crystal electrolytes, hybrid electrolytes and single-ion conducting electrolytes for lithium-ion batteries are discussed.

Keywords Ionic liquids; Poly(ionic liquid)s; Semi-solid state electrolytes; Lithium-ion batteries

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INTRODUCTION

With the continuous advancement of science and technology, the accompanying wearable and portable devices provide convenience for people's daily lives. Therefore, high energy density and environmentally friendly energy storage devices are highly desirable.^[1,2] Lithium-ion batteries have been regarded as promising candidates for energy storage and conversion due to their lightweight, high energy density, and good cycling stability. However, traditional lithium-ion batteries based on organic liquid electrolytes usually suffer from potential fire and explosion hazards,^[3–6] mainly due to the leakage of organic liquid electrolyte. Solid state electrolytes have been regarded as the alternatives for batteries.^[7–9] Compared with liquid electrolytes, solid state electrolytes could overcome the leakage of liquid electrolyte, but they often exhibit relatively lower ionic conductivity and poor electrolyte/electrode interfacial contact.^[10–13] Therefore, preparation of ionic liquid (IL) and poly(ionic liquid) (PIL)-based semi-solid state electrolytes for lithium-ion batteries has been extensively studied.^[14–18]

Ionic liquids (ILs) are molten organic salts with negligible vapor pressures, high ionic conductivity, thermal stabilities, and wide electrochemical window.^[19] These properties enable their applications in the energy field, especially lithium-

ion batteries.^[20–22] On the other hand, poly(ionic liquid)s (PILs), which combine both the properties of ILs and mechanical durability of polymers, have also been widely used as semi-solid state electrolytes for energy devices.^[23–26]

This review focuses on IL/PIL-based semi-solid state electrolytes, including gel electrolytes, ionic plastic crystal electrolytes, hybrid electrolytes and single-ion conducting electrolytes for lithium-ion batteries.

IL-based Gel Electrolytes

The IL-based gels have been widely investigated as semi-solid electrolytes because of their relatively high ionic conductivity and low interfacial resistance.^[27–29] For example, IL-based click-ionogels have been recently synthesized.^[30] The prepared IL-based click-ionogels exhibit high mechanical properties and resilience, high ionic conductivity, transparency, and non-flammability performance over a wide temperature range (–75 °C to 340 °C). In addition, the IL-based gel exhibits extraordinarily high elasticity and flexibility. The promising features of click-ionogels promote innovative practical applications in flexible, ultra-thinning and safe devices.^[30,31]

Guo and co-workers reported the preparation of IL-based polymer gel electrolyte using core-shell structured SiO₂ nanoparticles as functional fillers.^[32] The shell layers of SiO₂-PAA@Li increased both lithium transference number and ionic conductivity of the electrolyte. The silica core structure improved thermal stability and increased compatibility between electrolyte and lithium electrode. The lithium dendrites growth during cycling could be inhibited by such a stable solid state electrolyte. The gel polymer electrolytes exhibited

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high ionic conductivity of $0.74 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at ambient temperature. The fabricated cell showed an initial specific capacity of $138 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at 0.05 C and only 13% capacity loss after 100 cycles.

Poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) with excellent electrochemical stability, easy thin film forming ability, and high thermal stability has been studied as potential matrices for gel electrolytes. Zhu *et al.* reported the preparation of a flexible thin-film IL-based gel electrolyte, composed of PVDF-HFP and a room temperature IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) (Fig. 1).^[33] The prepared gel electrolyte exhibited good thermal stability without weight loss up to 370 °C and relatively high ionic conductivity. The fabricated battery showed perfect flexibility and stable energy delivery capability. Singh *et al.* also prepared an IL-based gel electrolyte containing PVDF-HFP and imidazolium-type ILs.^[34] The prepared electrolyte showed good electrolyte/lithium electrode interfacial contact and high coulomb efficiency. Zhang *et al.* prepared IL-doped gel polymer electrolytes for flexible lithium-ion polymer battery.^[35] The fabricated cells exhibited perfect flexibility by bending easily without breaking and good discharge capacity.

Ionic Plastic Crystals Electrolytes

Ionic plastic crystals are compounds composed of organic molecules exhibiting disorder while reserving high diffusivity and plasticity.^[36] The intrinsic solid-solid phase transitions below their melting point endow organic plastic crystals with good mechanical flexibility and plastic properties.^[37] Therefore, they can be easily deformed without fracture under an applied force.

The pioneering application of ionic plastic crystals as solid state electrolytes was reported by Angell in 1986.^[38] The prepared electrolyte exhibited a small entropy of fusion at -90°C and high conductivity at 75°C . In 2011, MacFarlane *et al.* prepared pyrrolidinium salt-based ionic plastic crystal electrolyte for rechargeable lithium-ion batteries.^[39] The prepared cell exhibited good electrolyte/lithium electrode interfacial contact, and high performance even after 50 cycles (about

$110 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$ at 0.2 C). An pyrazolium type ionic plastic crystal, *N,N*-diethyl-3-methylpyrazolium bis-(trifluoromethanesulfonyl)imide (DEMPyr₁₂₃), was prepared by Armand *et al.*^[40] When 10 mol% lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) salt was added to DEMPy₁₂₃, the electrolyte showed an ionic conductivity of $1.7 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 20°C and a wide electrochemical stability window of 5.5 V. Ionic plastic crystals based on *N,N*-dimethylpyrrolidinium cation have also been reported.^[41,42] However, relatively narrow electrochemical window (-3.0 V to $+2.3 \text{ V}$) hindered their future applications in lithium-ion batteries. Howlett and co-workers reported a novel ionic plastic crystal electrolyte consisting of polyethylene separator and 4 mol% lithium bis(fluorosulfonyl)imide (LiFSI) doped triisobutylmethyl phosphonium bis(fluorosulfonyl)imide (P₁₄₄₄FSI), which exhibited a high electrochemical window ($\sim 6 \text{ V}$).^[43] Two phase transition temperatures (from 8°C to 24°C and from 24°C to 36°C) indicate they are typical plastic crystals (Fig. 2). The fabricated electrolyte showed a high conductivity ($0.26 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and good discharge capacity ($160 \text{ mA}\cdot\text{h}\cdot\text{g}^{-1}$) at 22°C . Recently, Pringle *et al.* reported an organic ionic plastic crystal electrolyte containing 90 mol% lithium bis(fluorosulfonyl)imide and 10 mol% pyrrolidinium bis(fluorosulfonyl)imide.^[44] The resultant quasi-solid state electrolyte exhibited a conductivity of $0.24 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at 30°C , and a lithium ion transference number of 0.68. This result showed a new approach for designing safer quasi-solid state electrolytes with good electrochemical and transport properties.

PIL-based Gel Electrolytes

PIL-based gel electrolytes have been extensively studied because of their manufactural feasibility, high conductivity, and thermal stability.^[45,46] Generally, PILs exhibit good physicochemical compatibility with ILs and ensure the long-term stability of the ternary lithium salt, exhibiting improved electrochemical performances and would be of great interest for developing high performance lithium-ion batteries.

In 2009, PIL-based gel electrolytes containing poly(diallyldimethylammonium) backbone were reported by

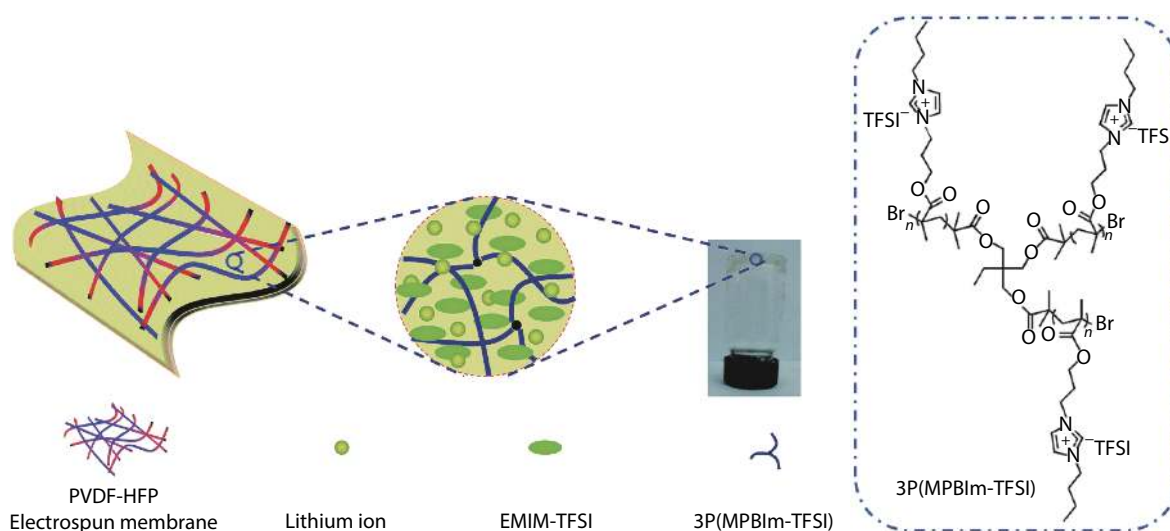


Fig. 1 The schematic illustration of gel polymer electrolyte and chemical structure of 3P(MPBIm-TFSI). (Reprinted with permission from Ref. [33]; Copyright (2016) The Royal Society of Chemistry).

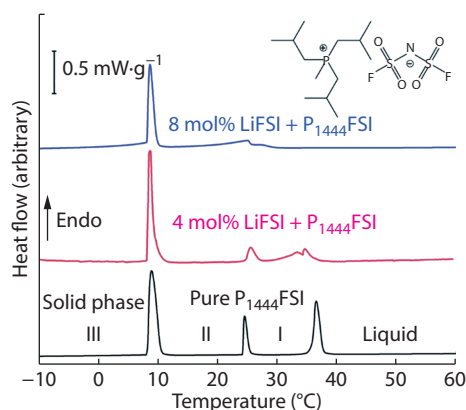


Fig. 2 DSC profiles of organic ionic plastic crystal containing different molar fractions of LiFSI. Inset shows the chemical structure of P_{1444} FSI. (Reprinted with permission from Ref. [43]; Copyright (2014) The Royal Society of Chemistry).

Mecerreyes *et al.*^[47] and Appetecchi *et al.*^[48] The prepared PIL showed high chemical stability after contact with lithium anode, as well as acceptable room temperature conductivity and wide electrochemical stability window (about 7.0 V). Preliminary battery tests showed that Li/LiFePO₄ solid-state cells could deliver about 140 mA·h·g⁻¹ at 40 °C. Yang *et al.* prepared a class of solid state polymer electrolytes *via* dipping the PIL matrix with organic ionic plastic crystal,^[49] *N*-ethyl-*N*-methylpyrrolidinium bis(fluorosulfonyl)imide (P_{12} FSI) (Fig. 3). The prepared PIL- P_{12} FSI-LiTFSI electrolyte revealed flexible mechanical characters, broad operating temperature range

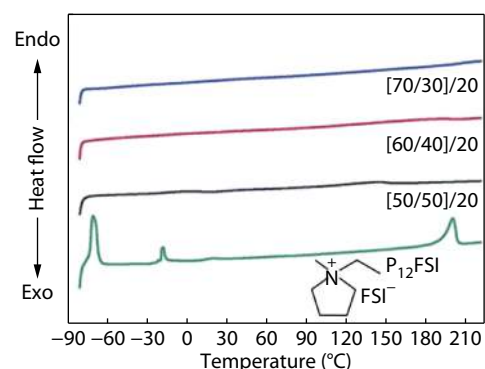


Fig. 3 DSC profiles of PIL- P_{12} FSI electrolyte containing different weight fractions of P_{12} FSI. Inset shows the chemical structure of P_{12} FSI. (Reprinted with permission from Ref. [49]; Copyright (2017) The Royal Society of Chemistry).

(25–80 °C), as well as potential to suppress the lithium dendrite growth.

Other than cationic PILs, polyelectrolyte and polyanion have also been employed as polymer matrices for gel polymer electrolytes. An imidazolium type dicationic PIL, poly(*N,N,N*-trimethyl-*N*-(1-vinylimidazolium-3-ethyl)-ammonium bis(trifluoromethanesulfonyl)imide) was synthesized by Yin and co-workers.^[25] The electrolyte showed low glass transition temperatures at around 54 °C, high thermal stability to about 330 °C, as well as high ion conductivity at around 10⁻⁴ S·cm⁻¹ at low medium temperatures. The excellent battery performance promotes the application of dicationic PIL-

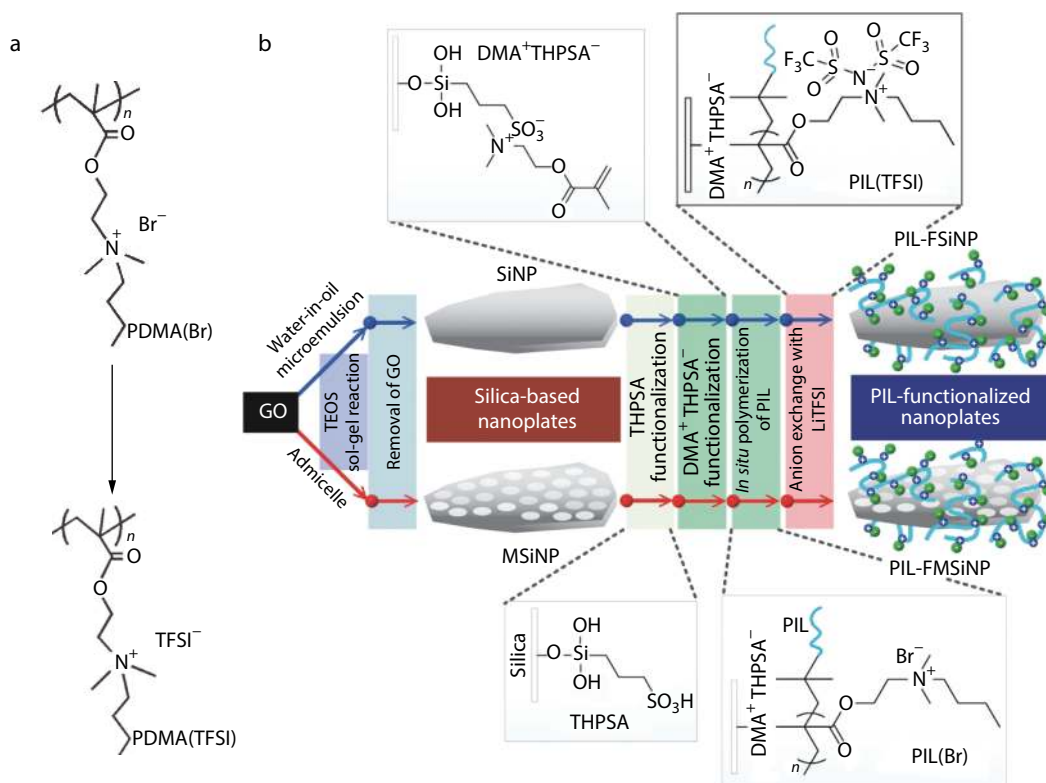


Fig. 4 (a) Anion exchange for PDMA(TFSI). (b) The preparation processes of PIL-functionalized nanoplates. (Reprinted with permission from Ref. [55]; Copyright (2017) Elsevier).

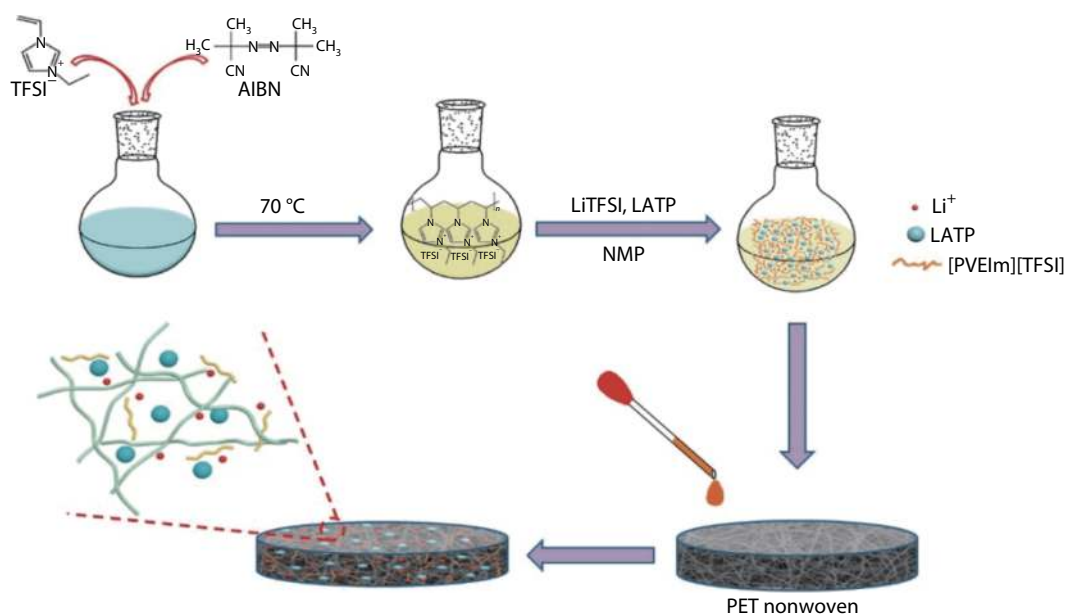


Fig. 5 Preparation processes of PIL-based hybrid electrolyte. (Reprinted with permission from Ref. [15]; Copyright (2019) American Chemical Society).

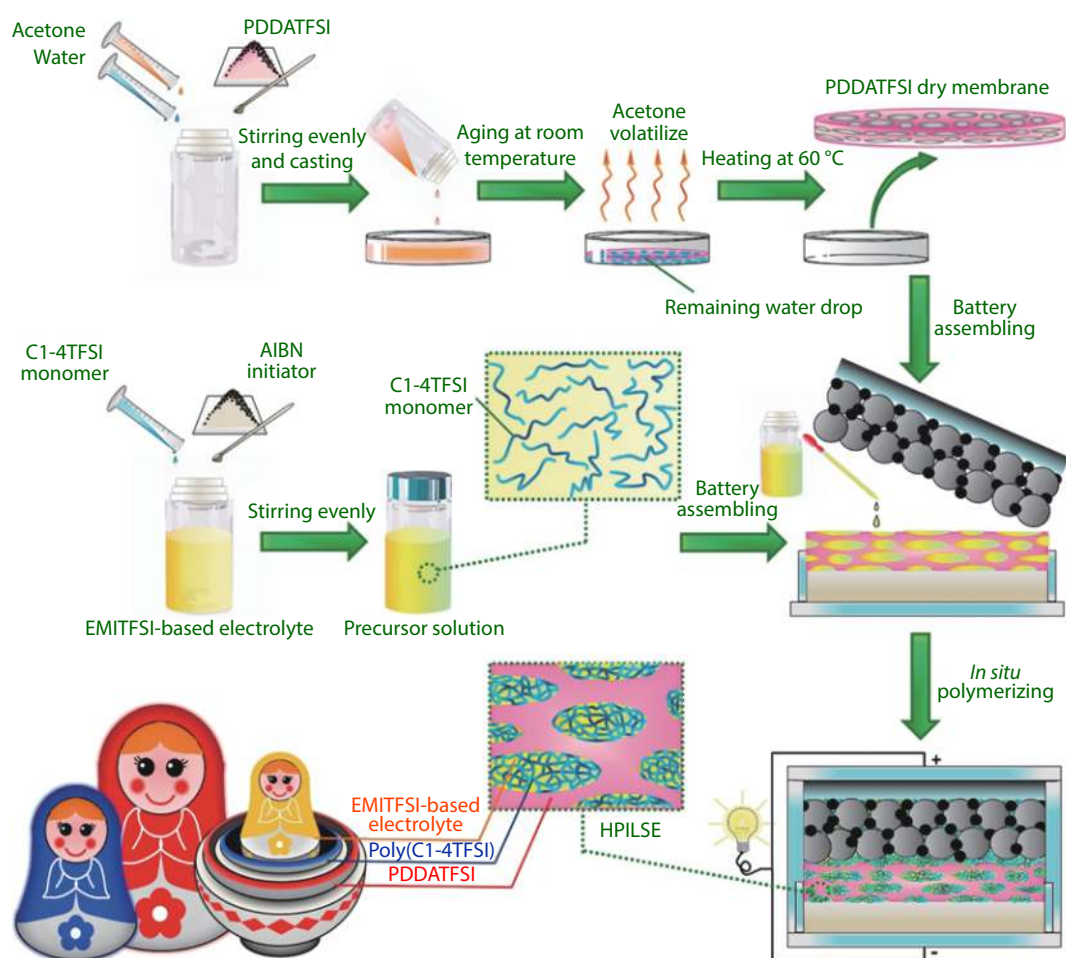


Fig. 6 Schematic illustration of synthesizing nesting doll-like hierarchical PIL-based solid-state electrolyte. (Reprinted with permission from Ref. [56]; Copyright (2017) Elsevier).

based electrolytes for lithium metal batteries.

Zwitterionic compounds (cationic and anionic charges are immobilized on the same molecule) are extremely effective Li-ion dissociation enhancers.^[50,51] Zheng *et al.* prepared a flexible polymer electrolyte film based on lithium-containing zwitterionic PIL.^[52] The lithium ion mobility of the polymer electrolytes can be improved owing to the Li⁺ dissociation generated by the zwitterionic effect. Peng *et al.* reported the preparation of a liquid-like polyanionic electrolytes.^[53] The Li/LiFePO₄ cell equipped with anionic PIL electrolyte performed high capacity, outstanding cycling stability and rate capability. The excellent performances of batteries may be due to the formation of stable solid-electrolyte interface film at the lithium-electrolyte interface during cycling.

PIL-based hybrid electrolytes where ionic moieties are chemically bound to the inorganic particles/substrates have been recently studied. Zhang *et al.* reported a high-performance PIL/silica hybrid ionogel electrolytes with LiTFSI/IL as the ion conducting phase.^[54] The electrolyte promoted a uniform Li electrodeposition and suppressed the growth and proliferation of lithium dendrites, which allowed the stable cycling of the Li symmetric cell for more than 500 h (0.1 mA·cm⁻²).

Similar work was recently reported by Ye and co-workers (Fig. 4).^[55] The ion transport properties of PIL-based polymer

electrolytes could be enhanced by the incorporation of 2D silica nanofillers, which provided continuous and interconnected ion transfer pathways. The hybrid electrolytes showed remarkably improved cycling performance and ionic conductivity (increased by 1130% at room temperature).

Recently, PIL-based hybrid electrolyte with Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) inorganic particles was reported by He and co-workers (Fig. 5).^[15] The poly(ethylene terephthalate) (PET) nonwoven was used as the backbone to improve the mechanical strength while the PIL-LiTFSI-LATP acted as ionic transport materials. The LiFePO₄/Li cells using PIL-LiTFSI-LATP (10 wt% LATP) as a solid-state electrolyte exhibited excellent rate performance and high capacity retention (close to 97% after 250 cycles at 60 °C).

Moreover, PIL-based electrolyte could be used as interlayer for lithium-sulfur battery. PPy@PIL-PAN nanofibers prepared *via* electrospinning were used as interlayers for lithium-sulfur batteries. The PIL-based electrolyte exhibited good capacity of 844 mA·h·g⁻¹ at 0.1 C and super absorbability of polysulfide.

Kang *et al.* reported a hybrid electrolyte which was prepared *via in situ* synthetic technique (Fig. 6).^[56] The hierarchical PIL-based solid electrolyte (HPILSE) was composed of PDDATFSI membrane and poly(C1-4TFSI) crosslink network.

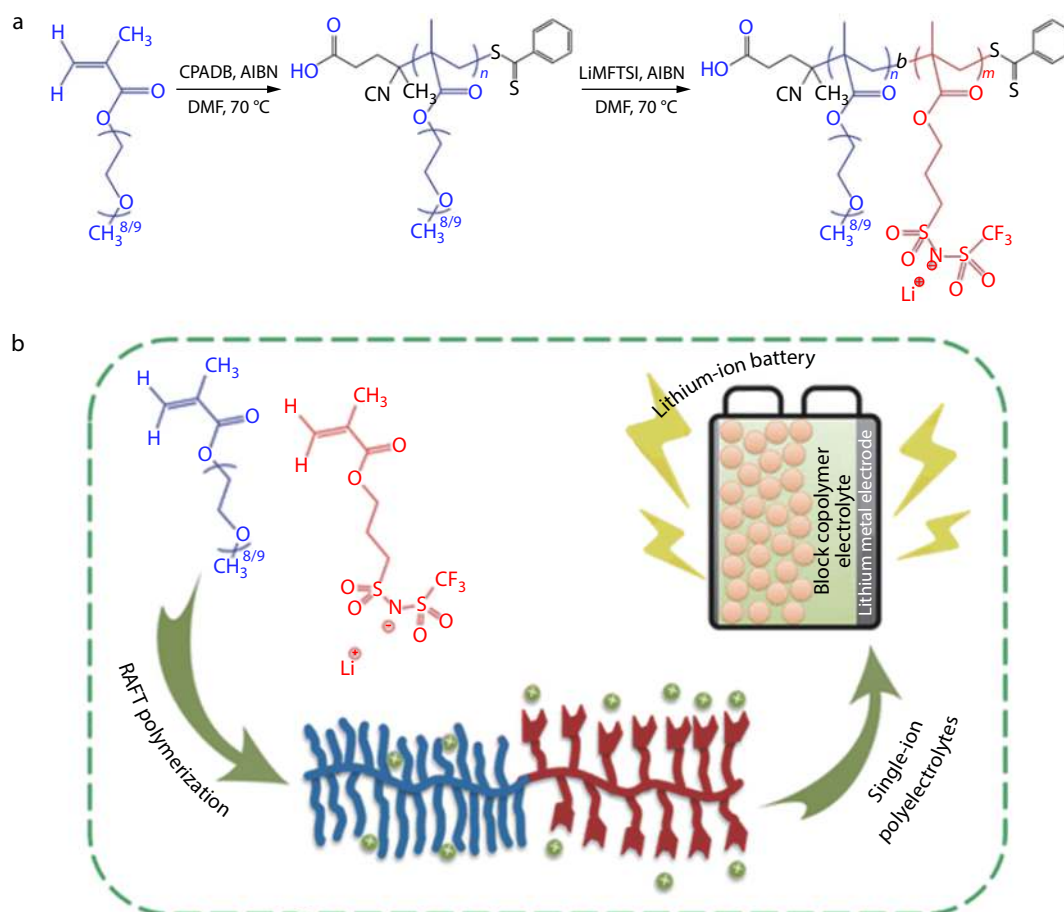


Fig. 7 (a) Preparation processes of PIL-based copolymers. (b) Schematic illustration of PIL-based single-ion conducting electrolytes for solid-state lithium-ion batteries. (Reprinted with permission from Ref. [61]; Copyright (2016) American Chemical Society).

LiFePO₄/Li-HPILSE/Li cell showed specific capacitance of 162.4 mA·h·g⁻¹ at 25 °C, offering a stable electrochemical window (4.4 V) and good electrolyte/electrode interfacial contact.

Single-ion Conducting Electrolytes

When anion is bonded to the polymer backbone, the cation becomes the only free movable ion of electrolyte, and thus single-ion conducting electrolytes are formed.^[57] Usually, lower glass transition temperature and higher polymer segment mobility can improve the ionic conductivity of single-ion conductors.^[57] High ionic conductivity and lithium ion transference number of single-ion conducting electrolytes could suppress the growth of lithium dendrites on electrodes.^[58] In 1984, Bannister *et al.* reported using anionic polymer to obtain single-ion conducting electrolytes.^[59] The purpose was to restrict anion from combining with lithium ion and therefore accelerate the transfer of lithium ion.

Mecerreyes *et al.* prepared a single-ion conducting triblock copolymer electrolyte,^[60] consisting of PEO and poly(lithium 1-[3-(methacryloyloxy)propylsulfonyl]-1-(trifluoromethylsulfonyl)imide) blocks, poly(LiMTFSI). The fabricated triblock copolymer electrolyte exhibited low glass transition temperature (–55 °C to 7 °C) and high ionic conductivity (about 10⁻⁴ S·cm⁻¹ at 70 °C).

Recently, a novel PIL-based single-ion conducting electrolyte for solid-state lithium-ion batteries prepared by RAFT polymerization was reported by Shaplov and co-workers (Fig. 7a).^[61] Single-ion conducting electrolytes could be used for solid-state lithium-ion batteries, exhibiting good conductivity of 2.3×10^{-6} S·cm⁻¹ at 25 °C and delivering high specific capacity to 130 mA·h·g⁻¹ (Fig. 7b). Controlling the molecular structure by RAFT polymerization, PIL-based single-ion conducting electrolyte achieved high ionic conductivity and high electrochemical stability, suggesting promising candidates for semi-solid state lithium-ion batteries.^[62] Zhou *et al.* presented a single-ion conducting electrolyte composed of LiPStTFSI and poly(ethylene oxide),^[63] which displayed low glass transition temperature of 44.3 °C and high Li-ion transference number, making it a promising semi-solid state electrolytes for lithium-ion batteries.

CONCLUSIONS

In summary, recent progresses on the application of IL/PIL-based electrolytes, including gel electrolytes, ionic plastic crystal electrolytes, hybrid electrolytes and single-ion conducting electrolytes, for semi-solid state lithium batteries are reviewed. Since the liquid nature of ILs still limits their applications in battery due to leakage problems, growing attention has been paid to IL/PIL-based semi-solid state electrolytes. Although the conductivity of electrolyte and electrolyte/electrode interface resistance should be improved, the IL/PIL-based semi-solid state electrolytes certainly have potential applications in flexible lithium batteries and wearable electronics.

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