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Advanced strategies for solid electrolyte interface design with MOF materials

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ABSTRACT

Emerging energy technologies, aimed at addressing the challenges of energy scarcity and environmental pollution, have become a focal point for society. However, these actualities present significant challenges for modern energy storage devices. Lithium metal batteries (LMBs) have gained considerable attention due to their high energy density. Nonetheless, their use of liquid electrolytes raises safety concerns, including dendritic growth, electrode corrosion, and electrolyte decomposition. In light of these challenges, solid-state batteries (SSBs) have emerged as a highly promising next-generation energy storage solution by leveraging lithium metal as the anode to achieve improved safety and energy density. Metal organic frameworks (MOFs), characterized by their porous structure, ordered crystal frame, and customizable configuration, have garnered interest as potential materials for enhancing solid-state electrolytes (SSEs) in SSBs. The integration of MOFs into SSEs offers opportunities to enhance the electrochemical performance and optimize the interface between SSEs and electrodes. This is made possible by leveraging the high porosity, functionalized structures, and abundant open metal sites of MOFs. However, the rational design of high-performance MOF-based SSEs for high-energy Li metal SSBs (LMSSBs) remains a significant challenge. In this comprehensive review, we present an overview of recent advancements in MOF-based SSEs for LMSSBs, focusing on strategies for interface optimization and property enhancement. We categorize these SSEs into two main types: MOF-based quasi-solid-state electrolytes and MOF-based all-solid-state electrolytes. Within these categories, various subtypes are identified based on the combination mode, additional materials, formation state, preparation method, and interface optimization measures employed. The review also highlights the existing challenges associated with MOF materials in SSBs applications and proposes potential solutions and future development prospects to guide the advancement of MOF-based SSEs. By providing a comprehensive assessment of the applications of MOFs in LMSSBs, this review aims to offer valuable insights and guidance for the development of MOF-based SSEs, addressing the key issues faced by these materials in SSBs technology.
1. Introduction

The global energy crisis, characterized by the scarcity of petroleum and other non-renewable resources, coupled with escalating environmental pollution, has significantly impacted human existence. In response, the scientific community has shown remarkable interest in the development of green, efficient, and environmentally friendly electrochemical technologies and energy storage devices (ESDs) [1–4]. The pressing need for high-energy-density batteries and high-capacity energy storage/conversion systems (ESCS) has surged, particularly in areas such as portable electronic devices, power transportation, 5G telecommunications, modern intelligent networks, and other related fields. Consequently, there is a growing demand for the advancement of next-generation ESCS with exceptional performance [5–7]. Lithium-ion batteries (LIBs), as a classical electrochemical ESD, have gained widespread popularity due to their high energy density, lightweight nature, extended cycle life, and cost-effectiveness. These batteries have found applications in various domains, including smartphones, electric vehicles, fixed and car chargers, military and medical equipment, digital cameras, and more [9–10]. For several decades, LIBs have demonstrated their efficacy across diverse sectors and have emerged as the most efficient and commercially successful environmentally friendly ESDs [11, 12]. The burgeoning trend of global vehicle electrification has created an enormous demand for power batteries that exhibit high energy density, extended cycle life, and absolute safety.

With the continuous progress and advancement of science and technology, there is an increasing demand for batteries that exhibit improved capacity, reduced weight, and compact volume [13,14]. Among these battery systems, lithium metal batteries (LMBs) have garnered significant attention as they offer ultra-high energy storage capacity and possess a theoretical specific capacity by utilizing Li metal as the anode. This characteristic makes LMBs highly promising for meeting the requirements of future ESDs [15–17]. The utilization of Li metal electrodes in LMBs provides several advantages, including an exceptionally high theoretical specific capacity (3860 mAh g⁻¹), an extremely low electrochemical reduction potential (−3.04 V vs. the standard hydrogen electrode), and low density (0.59 g cm⁻³), making it one of the most attractive anode materials for achieving high energy density [18–20]. Current commercial configurations of LMBs predominantly consist of positive (cathodes), negative (anodes), separators (membranes), and non-aqueous liquid electrolytes (organic electrolytes containing Li salts) [21]. However, the repeated charge/discharge cycles of LMBs lead to the formation of an unstable solid-electrolyte interphase (SEI) layer, which adversely affects the electrolyte polarity, triggers uncontrollable growth of Li dendrites, punctures the membrane due to the uneven accumulation of Li deposits, and results in the formation of non-functional “dead Li” masses. Furthermore, the prolonged cycling of Li electroplating/stripping causes the electrode to undergo infinite volume expansion [22,23]. These issues collectively contribute to the short cycle life, low Coulomb efficiency (CE), and pose severe safety concerns for LMBs [24,25]. Additionally, conventional electrolytes, such as carbonate-based electrolytes (e.g., LiPF₆-EC/DMC), are susceptible to combustion at high temperatures, leading to a significant decline in both battery safety and electrochemical performance. The reaction between LiPF₆ and even trace amounts of water present in the electrolyte produces detrimental HF, which further corrodes both the cathode and the metallic Li surface [26]. The dissolution of transition metal ions from the cathode, accelerated by HF, results in irreversible changes in the cathode structure and rapid degradation of the Li anode, ultimately leading to poor electrochemical performance and premature cell failure. These factors collectively limit the widespread commercial utilization of LMBs [27,28].

Despite the implementation of various strategies to enhance the performance of LMBs, such as employing electrospinning or non-solvent induced phase separation to fabricate high-porosity separators and inhibit the growth of Li dendrites [29–31], increasing the electrolyte uptake to facilitate Li-ion (Li⁺) transfer, creating artificial SEI layers on the anode surface to prevent direct contact between the electrolyte and Li metal, and incorporating additives to mitigate electrolyte decomposition, LMBs still encounter challenges such as intensified polarization, increased internal resistance, electrolyte decomposition, and volume changes in the electrode material during prolonged fast charge/discharge cycling [32]. To address these issues and mitigate the direct degradation of the electrolyte, efforts have been made to reduce polarization during the charge-discharge process or shorten the diffusion path of Li⁺, and improve conductivity without inducing side reactions [33,34]. Due to the limitations of liquid LMBs reaching a plateau in terms of development, the exploration of solid-state batteries (SSBs) has gained traction as a practical approach to enhance battery safety and energy density. SSBs employ solid-state electrolytes (SSEs) as separators and conductive media, replacing traditional insulating membranes and liquid electrolytes (LEs), thus forming the core of SSBs. These batteries are considered promising future ESDs due to their ability to enable the use of Li metal anodes with significantly improved safety [35,36]. By removing inherent safety and performance barriers in achieving high-energy and cost-effective electrical energy storage, SSEs facilitate the formation of stable passivating SEI films. SSEs offer enhanced safety through their non-volatile nature and slower chemical reactions with the Li electrode, as well as their inherent ability to mechanically suppress non-planar/dendritic growth of the Li anode during repeated charge/discharge cycles. However, the effective management of the SSEs interface is crucial for the successful application of SSBs, as it plays a key role in addressing the challenges associated with SSEs [37,38].

Conventional SSEs have been classified into three main categories: inorganic (e.g., ceramics, glass) solid electrolytes (ISEs), organic polymer solid electrolytes (PSEs), and hybrid organic-inorganic composite solid electrolytes (CSEs) [39]. ISEs exhibit remarkable ionic conductivity comparable to or even surpassing that of LEs, a wide electrochemical window, high Li⁺ transference number (t), and sufficient mechanical strength to inhibit Li dendrite growth. However, their inherent brittleness, limited processability, and high interfacial resistance impede their practical application in SSBs. It is necessary to address morphological changes and maintain the interfacial contact between SSEs and electrodes, which pose challenges for their implementation [40–42]. PSEs, composed of polymer matrices and Li salts, have been extensively investigated. They can be tailored to respond to stress and thermal fields, overcoming wettability challenges associated with SSEs. PSEs exhibit high flexibility, ultrathin thickness, seamless interfacial contact with electrodes, and ease of preparation compared to ISEs [43,44]. Additionally, they can be formulated to achieve low volatility and high chemical and electrochemical stability when in contact with Li metal, while maintaining satisfactory mechanical properties to suppress non-planar/dendritic growth of the Li metal electrode. Notably, significant progress has been made in this area over the past decade, resulting in numerous SSEs options [45–47]. However, PSEs still face challenges including low ionic conductivity at room temperature (RT), unsatisfactory mechanical properties, and poor interfacial contact and compatibility at the cathode side. There is a well-known tradeoff between Li⁺ conductivity and mechanical strength in PSEs [48,49]. Various approaches have been proposed to enhance the ionic conductivity of PSEs, such as reducing polymer crystallization or increasing the ionic transfer pathways through cross-linking, block copolymer formation, addition of plasticizers, or introduction of fillers [50]. However, the observed improvements are modest and fail to meet the demands. CSEs possess advantages inherited from both ISEs and PSEs, offering flexibility in operation, high ionic conductivity, excellent electrochemical performance, and compatible interface and stability [51–53]. Nevertheless, challenges persist concerning the mechanical properties and interface compatibility of CSEs. The interface between the inorganic and polymer matrix serves as a fast pathway for Li⁺ transport. However, the low Li⁺ conductivity of CSEs and the instability of the interface contact hinder the practicality of Li metal SSBs (LMMSSBs). Finding successful SSEs for LMMSSBs remains a complex and challenging task. These electrolytes
stabilize the electrolyte/electrode interface by facilitating Li⁺ transport and suppress the formation of Li dendrites through the formation of a particle-rich coating on the anode during repeated Li plating/stripping [54]. Key features of effective SSEs for LMSSBs include excellent electrochemical performance (high Li⁺ conductivity at RT and sub-ambient temperature, appreciable t1/2, and compatibility with electrodes), robust stability properties (thermal and electrochemical stability, mechanical strength), and reliable safety performance (environmental friendliness, nonflammable, and good electronic insulating properties) [55].

Metal organic frameworks (MOFs) represent a new class of hybrid materials composed of metal ions and organic ligands, known as coordination polymers. These materials exhibit diverse applications due to their multi-scale interactions between inorganic and organic components and the potential confinement effects within coordination channels [56, 57]. Their versatile functionalities include molecular recognition, ion exchange, nonlinear optics, gas storage/adsorption/separation, heterogeneous catalysis, energy storage, and more [29,30,58]. As classical porous materials, MOFs possess inherent advantages such as continuous transfer channels, tunable porosity, and high surface areas [59–61]. Their highly ordered pore structures and abundance of open metal sites (OMSs) make them promising candidates for addressing the limitations of SSEs and offering significant advantages over traditional inorganic nanoparticles as excellent modifiers for CSEs in SSBs [62]. To enable the application of MOFs in SSEs, it is crucial to utilize their abundant interconnected and highly ordered multi-stage cavity structures, ultra-high specific surface area, superior porosity, excellent thermochemochemical stability, and diverse alternative functional groups (e.g., terephthalic acid ligands). These features facilitate effective mitigation of volumetric expansion issues and a substantial increase in the electrode-electrolyte contact area [63,64]. Generally, Lewis acid-base (LAB) interactions are employed to combine the polymer matrix, Li⁺, and anions. Through judicious selection of ligands, MOFs can be custom-designed to achieve specific pore sizes and geometries, making them suitable SSEs materials [57,65]. MOFs offer unique advantages in optimizing the ionic conductivity of SSBs while simultaneously promoting the reversible stripping and plating of Li and suppressing undesired (electro)chemical side reactions [66]. The interfaces between MOF crystals have various effects on Li⁺ transport in LMSSBs, and they play a crucial role in improving SSEs characteristics. These interfaces can enhance Li⁺ transport by facilitating ion diffusion across the gaps between crystals. Additionally, nanoparticles derived from MOFs can enhance and dominate the interface connection between SSEs and electrodes. Moreover, they can influence the deposition of Li⁺ on the Li metal surface, stabilizing the interface and inhibiting Li dendritic growth. These aspects should be considered to ensure essential characteristics for improved SSEs performance.

In order to effectively advance the development of LMSSBs, two critical challenges need to be addressed: enhancing the ionic conductivity of the solid electrolyte at RT and optimizing the electrode-electrolyte interface. While numerous studies have explored the application of MOFs in ESCSs as fillers, substrates, or supports to improve interface properties and overall performance, few have thoroughly investigated MOF-based SSEs and the strategies for interface optimization [57,67–70]. This review aims to categorize and describe different types of MOF-based SSEs based on their combination with polymers and the current state of SSEs while highlighting the modifications and advantages achieved by incorporating MOFs. Here, the MOF-based SSEs are classified into two categories (Scheme 1): quasi-solid-state electrolytes (QSSEs) and all-solid-state electrolytes (ASSEs), depending on whether they include LEs and conduction modes. Within the QSSS category, four types are distinguished based on the MOF combination mode, presence of ILs, gel state, and other factors. The ASSEs are further divided into two types: generally mixed type and composite interface design type, based on the different strategies employed for interface optimization. Detailed discussions are presented on the interface-related challenges associated with SSEs for LMSSBs, highlighting the unique electrochemical properties introduced by MOF-based SSEs. Finally, the review outlines several challenges that need to be addressed in the application of MOF materials in SSBs. By providing an overview of recent advancements in MOF-based SSEs, this review aims to offer valuable insights and guidance for the development of SSEs utilizing MOFs.

2. MOFs-based optimization strategy for QSSEs

The interfacial properties, structure, and characteristics exert a direct influence on the efficient transport of Li⁺ and play a crucial role in stabilizing the Li anode. Therefore, an effective approach to achieving uniform Li deposition and constructing high-safety LMBs is to optimize the electrolyte structure, ensuring stable interface compatibility, a high t1/2, and robust mechanical strength [71–73]. A promising strategy in this regard involves designing electrolyte systems with a stable interface, where liquid components are confined within the nanofaipes of frameworks, while still maintaining solid-like mechanical properties, thus creating so-called “quasi-solid” systems [74,75]. To date, charged frameworks have been utilized to enhance the t1/2. However, the presence of a sufficient quantity of organic solvent is typically necessary to maintain a localized liquid-like environment and achieve high ionic conductivity [76]. The search for more advanced framework-based SSEs with superior single-ion conductivity and reduced or minimal solvent content remains a challenging task. QSSSs integrating the advantages of liquid and solid electrolytes, not only provide mechanical rigidity to impede dendritic growth but also offer a much safer operating environment (nonflammable) compared to conventional LEs [77,78]. MOFs can serve as the main body, supporter, carrier, cage, or bond in combination with LEs, ionic liquids (ILs), small organic molecules, and polymers to form SSEs, thereby enabling efficient Li⁺ conduction, transmission, and hopping [79].

2.1. MOFs as main body for QSSSs

Conventional PSEs are classified as dual-ion conductors, primarily comprising LAB oxygen-containing polymers, such as polyethylene oxide (PEO), blended with lithium salts. These polymers facilitate the mobility of both Li⁺ cations and counter anions, yet the t1/2 is typically below 0.5 due to the lower mobility of Li⁺ cations compared to LAB sites within the
polymer matrix. During the charging/discharging cycles of the cell, anions tend to accumulate at the anode side, resulting in polarization. This polarization adversely affects cell performance, including voltage loss, high internal impedance, and undesirable reactions, ultimately leading to inevitable cell failure. Notably, Li⁺ and counter-anions diffuse in opposite directions, with anions exhibiting a preference for concentration at the positive electrode during battery charge/discharge cycles, resulting in low t_Li and concentration polarization [80,81]. To address this issue, the theory proposed by Monroe and Newman suggests that eliminating the concentration gradient allows for the sufficient utilization of the active substance [82]. Therefore, a single-ion conduction mechanism has been proposed, wherein anions are immobilized through covalent interactions using anion-trapping agents to enhance the transference number and transport efficiency of Li⁺. In the development of single Li-ion conductors (SLICs), specific design strategies have been employed to immobilize anions, including their covalent attachment to polymeric backbones, incorporation into the inorganic framework, or through the utilization of trapping agents. These approaches allow SLICs to achieve a t_Li value as high as unity, eliminating concentration gradients as the design strategies have been employed for the recent MOFs as main body QSSEs. As a result, MOFs hold significant potential for reshaping the landscape of SLIC-based SEs. For instance, Yang et al. proposed an innovative SLIC design in which anions were covalently linked to the framework of a MOF, namely UIO-66-LiSS, leaving the Li ions free to migrate along the porous channels [80]. The ionic conductivity of Uio-66-LiSS was enhanced by the addition of ethylene carbonate (EC) and propylene carbonate (PC), which improved the transport properties of Li ions within the system. The SLIC exhibits an infinite t_Li (0.90, at 25 °C), ensuring efficient Li ion transport within the system. Moreover, the incorporation of confined organic carbones in nano-wetted interfaces enhances the contact between MOF electrolytes and electrodes. The resulting SLIC structure demonstrates an impressive ionic conductivity of 7.8 × 10⁻⁴ S cm⁻¹ at RT. Another MOF material, Uio-66-NH₂, is amino-functionalized, providing favorable conditions for

<table>
<thead>
<tr>
<th>MOF Material</th>
<th>Addition</th>
<th>Electrochemical Window (V)</th>
<th>σ (S cm⁻¹)</th>
<th>t_Li</th>
<th>Specific Capacity (mAh g⁻¹)</th>
<th>Cycles</th>
<th>Capacity Retaining (%)</th>
<th>Coulomb Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>UIO-66-LiSS</td>
<td>LiF  +  LiTFSI</td>
<td>5.20</td>
<td>7.80 × 10⁻⁴ (RT)</td>
<td>0.90</td>
<td>127.00 at 34.00 mA g⁻¹</td>
<td>100</td>
<td>88.10</td>
<td>99.20 (av.)</td>
<td>[80]</td>
</tr>
<tr>
<td>UIO-66-NH₂-M</td>
<td>LiBF₄  +  LiTFSI</td>
<td>5.40</td>
<td>5.65 × 10⁻⁴ (RT)</td>
<td>0.65</td>
<td>154.60 at 90.00 mA g⁻¹</td>
<td>200</td>
<td>95.75</td>
<td>99.40</td>
<td>[83]</td>
</tr>
<tr>
<td>UIO-66-NH-M</td>
<td>LiBF₄  +  LiTFSI</td>
<td>5.40</td>
<td>2.26 × 10⁻⁴ (25 °C)</td>
<td>0.44</td>
<td>143.70 at 90.00 mA g⁻¹</td>
<td>500</td>
<td>85.60</td>
<td>≥98.00 (av.)</td>
<td>[84]</td>
</tr>
<tr>
<td>Li-NOA</td>
<td>LiF  +  LiTFSI</td>
<td>\</td>
<td>1.09 × 10⁻⁵ (RT)</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>[88]</td>
</tr>
<tr>
<td>Li-InOF</td>
<td>LiF  +  LiTFSI</td>
<td>\</td>
<td>1.49 × 10⁻⁵ (25 °C)</td>
<td>0.078</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>[89]</td>
</tr>
<tr>
<td>Zn-MOF-COOLI</td>
<td>PTFE  +  LiPF₆</td>
<td>6.50</td>
<td>1.65 × 10⁻⁴ (RT)</td>
<td>0.77</td>
<td>139.40 at 17.00 mA g⁻¹</td>
<td>50</td>
<td>83.10</td>
<td>\</td>
<td>[90]</td>
</tr>
<tr>
<td>ZIF-67@ZIF-8</td>
<td>PTFE  +  LiPF₆</td>
<td>5.31</td>
<td>1.35 × 10⁻⁴ (25 °C)</td>
<td>0.82</td>
<td>116.00 at 38.00 mA g⁻¹</td>
<td>100</td>
<td>89.10</td>
<td>99.38</td>
<td>[97]</td>
</tr>
<tr>
<td>Hollow ZIF-8</td>
<td>PTFE  +  LiPF₆</td>
<td>6.50</td>
<td>7.36 × 10⁻⁴ (RT)</td>
<td>0.83</td>
<td>111.20 at 17.00 mA g⁻¹</td>
<td>100</td>
<td>85.10</td>
<td>≥98.00</td>
<td>[98]</td>
</tr>
<tr>
<td>H-ZIF-8/HTN</td>
<td>PTFE  +  LiPF₆</td>
<td>5.44</td>
<td>7.44 × 10⁻⁴ (25 °C)</td>
<td>0.84</td>
<td>123.64 at 17.00 mA g⁻¹</td>
<td>200</td>
<td>84.00</td>
<td>100.57</td>
<td>[104]</td>
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<tr>
<td>BF-MOF</td>
<td>PTFE  +  LiPF₆</td>
<td>4.50</td>
<td>1.27 × 10⁻⁴ (25 °C)</td>
<td>0.74</td>
<td>133.60 at 340.00 mA g⁻¹</td>
<td>4500</td>
<td>96.50</td>
<td>99.90</td>
<td>[105]</td>
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<tr>
<td>MIL-121</td>
<td>LiOH  +  PC</td>
<td>5.20</td>
<td>5.00 × 10⁻⁵ (25 °C)</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>[106]</td>
</tr>
<tr>
<td>HM-MIL-101</td>
<td>PTFE  +  LiPF₆</td>
<td>5.74</td>
<td>1.24 × 10⁻³ (RT)</td>
<td>0.86</td>
<td>128.56 at 17.00 mA g⁻¹</td>
<td>200</td>
<td>97.42</td>
<td>–100.00</td>
<td>[108]</td>
</tr>
<tr>
<td>MIL-101(C)_DETA-Li</td>
<td>PTFE  +  LiPF₆</td>
<td>4.70</td>
<td>7.13 × 10⁻⁴ (30 °C)</td>
<td>0.87</td>
<td>119.00 at 340.00 mA g⁻¹</td>
<td>700</td>
<td>92.00</td>
<td>–100.00</td>
<td>[82]</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>LiClO₄  +  PC</td>
<td>5.00</td>
<td>1.36 × 10⁻³ (RT)</td>
<td>0.72</td>
<td>128.56 at 17.00 mA g⁻¹</td>
<td>200</td>
<td>97.42</td>
<td>–100.00</td>
<td>[111]</td>
</tr>
<tr>
<td>HKUST-1</td>
<td>Cellulose fibers + LiClO₄ + PC</td>
<td>5.26</td>
<td>1.02 × 10⁻³ (30 °C)</td>
<td>0.56</td>
<td>117.00 at 170.00 mA g⁻¹</td>
<td>210</td>
<td>93.00</td>
<td>–100.00</td>
<td>[112]</td>
</tr>
<tr>
<td>808-LCE</td>
<td>LiClO₄  +  LiTFSI</td>
<td>5.00</td>
<td>3.50 × 10⁻⁴ (25 °C)</td>
<td>0.64</td>
<td>135.00 at 85.70 mA g⁻¹</td>
<td>&gt;900</td>
<td>80.00</td>
<td>≥97.00%</td>
<td>[113]</td>
</tr>
<tr>
<td>NiCo-MOF</td>
<td>LiClO₄  +  LiTFSI</td>
<td>5.27</td>
<td>7.41 × 10⁻⁴ (25 °C)</td>
<td>0.59</td>
<td>148.20 at 34.00 mA g⁻¹</td>
<td>200</td>
<td>94.70</td>
<td>–100.00</td>
<td>[117]</td>
</tr>
<tr>
<td>Zn-MOF-74</td>
<td>DME  +  LiTFSI + PPy⁺TFSI</td>
<td>5.20</td>
<td>1.74 × 10⁻⁴ (30 °C)</td>
<td>0.47</td>
<td>130.00 at 85.00 mA g⁻¹</td>
<td>&gt;500</td>
<td>–90.00</td>
<td>–100.00</td>
<td>[119]</td>
</tr>
</tbody>
</table>
subsequent derivatization. Its stable Zr-O bond within the metal cluster and the highest unit ligand coordination number contribute to its structural stability, rendering it a reliable material across the entire MOF family. Building upon this, Shang et al. introduced a double bond to UIO-66-NH2 and achieved copolymerization with aliphatic polycarbonate (UIO-66-NH2-MPC), leading to the formation of immobilized-anion MOF PSEs (MSPE) ([Fig. 1a] [83]). The combination of MSPE (immobilized-anion MOF PSEs) with azodisobutyronitrile (AIBN) and lithium bis(trifluoromethanesulfonylimide) lithium triflate (LiTFSI) exhibits a remarkable inhibitory effect on the formation of Li dendrites compared to traditional LE (LiPFSi). This effect was evaluated by analyzing the morphology of the Li metal surface using a Li/Li cell test after applying a constant current for 300 h. The synergistic effect of M-S-PEGDA, resulting from the chemical cross-linking of tetraakis(3-mercaptocarboxylic acid) pentanethyrrhol (PETMP), UIO-66-NH2, and long-chain poly(ethylene glycol) diacrylate (PEGDA), is enabled by the following mechanism [84]. M-S-PEGDA leverages the spatial stereo structure of MOFs and establishes a branched structure by connecting PEGDA to UIO-66-NH2 through PETMP. This design leads to Li⁺ conductivity as high as 2.26 × 10⁻⁷ S cm⁻¹ at RT. Moreover, the multiple -C–C- covalent bonds formed through the photopolymerization of thiols and olefins within the MOF PETMP, and PEGDA chains contribute to excellent overall mechanical properties, including high strength (9.4 MPa) and super toughness (≈500%). Consequently, this eliminates the tradeoff typically observed between ionic conductivity and mechanical properties in PSEs. Furthermore, by initiating in situ polymerization on the surface of electrodes using ultraviolet light or heat, a three-dimensional (3D) interpenetrating network of PSEs is formed. This network ensures seamless contact between the electrode and electrolyte, resulting in low interfacial resistance [85].

The incorporation of SSEs into MOFs architectures is facilitated by the combination of a 3D pore system and a highly connected crystalline structure that is constructed from strong bonds. The rich porous structure of MOFs provides well-defined pathways for cation diffusion while adsorbing impurities and byproducts to inhibit side reactions. Immersion of In₃⁺ body resistance values for Li⁺ conductivities of LiCl@HM-MIL, LiClO₄@HM-MIL, and LiTFSI@HM-MIL. Among these candidates, LiCl@HM-MIL exhibits the ability to store a higher quantity of Li⁺ ions [91–93]. The establishment of an efficient Li-bond network through segmental anion dynamics can enhance Li⁺ conductivity [94–96]. Balancing the high specific cavity structure of hollow MOFs allows for the storage and transmission of Li⁺ through the cavity walls, providing continuous transport channels for Li+. In this regard, a novel strategy was employed to synthesize a hollow ZIF-67/ZIF-8-based SSEs, which exhibited efficient ionic conductivity (1.35 × 10⁻⁷ S cm⁻¹, 25 °C) and high tₚ, (0.82), demonstrating excellent electrochemical performance over a wide temperature range (20–100 °C) [97]. To further enhance the ionic conductivity, Tian et al. employed an exterior template method to synthesize ZIF-8 with a hollow structure, sacrificing carbonyl-terminated polyethylene microspheres as a template, resulting in significant improvements in tₚ, and interface stability compared to non-hollow ZIF-8. The cavity diameter of the hollow ZIF-8 reached 1 μm [98,99]. In order to optimize the electrochemical performance of SSE materials, it is necessary to consider multiple influencing factors beyond morphology regulation [100]. Halloysite nanotubes (HNTs) possess a distinctive hollow nano-tube/inner tube structure, featuring an electropositive alumina octahedral inner layer and an electronnegative silica tetrahedral exterior surface [101–103]. To leverage the favorable characteristics of HNTs, a composite material called H-ZIF-8/HNT was developed by combining hierarchical porous ZIF-8 (H-ZIF-8) with HNTs. This composite material capitalizes on the electropositive tube wall properties of HNTs and the porosity of hollow MOFs. As a result, a significant portion of the anions can be immobilized within the structure, facilitating efficient storage and migration of Li⁺ ions [104]. The H-ZIF-8/HNT composite material exhibits exceptional performance as a SSE, demonstrating superior ionic conductivity of 7.74 × 10⁻⁷ S cm⁻¹ and a high tₚ, value of 0.84. In order to address the detrimental effects of limited ionic conductivity on battery performance, which leads to inferior electrochemical kinetics and weak mechanical strength unable to withstand the growth of Li dendrites in MOF materials, Mai et al. have proposed a novel SSE based on bifunctional MOFs (BF-MOFs) [105]. These BF-MOFs consist of mesoporous silica shells that greatly enhance mechanical robustness due to the superior toughness of silica, thereby suppressing dendrite growth. Additionally, the interior MOF cores possess unique pores that act as anionic regulator, facilitating uniform transport of Li⁺. The mesoporous shells provide rapid pathways for ionic transport and control the deposition of Li⁺ in a uniform manner. The presence of large gaps between the mesoporous shells and the MOF cores further enhances ionic conduction, leading to improved electrochemical kinetics and enabling fast-charging performance. Consequently, the BF-MOFs SSEs demonstrate a high ionic conductivity of 1.27 × 10⁻⁷ S cm⁻¹ at 30 °C and a high tₚ, value of 0.74. When assembled into LiFePO₄/Li cells, these SSEs exhibit excellent cycling stability, with a capacity retention of up to 96.5% after 4500 cycles.

The MIL-121 structure is characterized by its flexibility and the presence of aluminum (Al) centers. In this structure, only two out of the four carboxylic units of the linker are utilized for constructing the framework, leaving the remaining carboxylic units free. The protons associated with these free carboxylic units can undergo ion exchange with Li or sodium (Na) ions, thus imparting the MOFs with new ion conduction functionality. MIL-121 has been explored as a promising candidate for hybrid Li and Na SSE systems. Furthermore, a hollow mesoporous structure known as HM-MIL was obtained through surface-selective etching of a Cr, Al-bimetallic precursor called S-MIL [106,107]. HM-MIL exhibits the ability to store a higher quantity of Li⁺ and facilitate their rapid transport, resulting in enhanced ionic conductivity. To further optimize the electrochemical performance of HM-MIL, five different electrolyte materials were prepared by impregnating various Li⁺ salts into HM-MIL, namely LiNO₃@HM-MIL, LiBF₄@HM-MIL, LiCl@HM-MIL, LiCO₃@HM-MIL, and LiTFSI@HM-MIL. Among these materials, LiNO₃@HM-MIL demonstrated excellent ionic conductivity at RT, measuring 1.24 × 10⁻⁷ S cm⁻¹. Additionally, it exhibited a higher tₚ, value of 0.86, exceptional rate capability, stable Li plating/stripping.
Fig. 1. (a) Synthetic strategy and structure illustration of M-S-PEGDA. (Reproduced with permission from Ref. [84]. Copyright 2022, Wiley-Blackwell); (b) The crystal structure of InOF viewed along the crystallographic [110] direction and (c) Nyquist plots of Li$^+$, Na$^+$, K$^+$, and Zn$^{2+}$ for InOF-M at 25 °C. (Reproduced with permission from Ref. [89]. Copyright 2021, American Chemical Society); (d) Schematic illustration of the molecular-scale interface engineering strategy of MOF with long chain Lewis base. Red, gray, blue, white, and cyan balls indicate Cr, C, N, H, and Li atoms, respectively; (e) Photograph of SE-DETA-Li. (Reproduced with permission from Ref. [82]. Copyright 2020, Wiley-VCH Verlag); (f) Schematic illustrations of Li-MC QSSEs, locally amplified MC fiber with Li-ion migration, and the corresponding pathways in the pores or on the surface of the MOF. (Reproduced with permission from Ref. [111]. Copyright 2022, Wiley-Blackwell).
behavior, low interfacial resistance between the electrode and electrolyte, and good cycling stability. These modification strategies present a promising avenue for enhancing the safety and lifespan of ESSDs [108]. Specifically, the use of MOFs functionalized with diverse molecules, such as long alkyl chains (LACs), enables the optimization of interfaces and their impact on ion transport. In SSEs comprising an ionic conductor and a small amount of polymeric binder, the ion transport is significantly impeded by nanoscale gaps between crystals and the limited contact area between the SSEs and electrodes. Consequently, the overall capacity of the system is compromised [109]. To address these challenges, a molecular-scale interface engineering approach is employed to enhance the ion transport in SSEs based on ion-conductive MOFs. LAB is chemically anchored onto the OMSs of the MOF, resulting in the formation of MIL-101(Cr)-LAB hybrids (Fig. 1d). The LAB molecules, capable of interacting with Li⁺, facilitate improved ion transport within the MOF structure [110]. Additionally, the elongated molecular chains of LAB are expected to reduce the nanoscale gaps between crystals and enhance the contact between the SSEs and electrodes (Fig. 1e). Electrochemical evaluations show this strategy demonstrates its effectiveness in promoting ion transport, suppressing the formation of Li dendrites, and enhancing the performance of the SSBs [82].

Taking inspiration from the multi-layered structure of tree trunks, which possess inner mechanical strength and outer smooth species transportation, a flexible and robust organic QSSE with hierarchical ion channels, namely Li-MOF/cellulose (Li-MC), is constructed [111]. The MOF component in this configuration is commonly referred to as HKUST-1, Cu₃BTC₂ or Cu₃(C₆H₃O₆)₂ (Fig. 1f). Through the utilization of synchrotron X-ray tomography, the structure and morphology of Li dendrites at the electrode/electrolyte interfacial region are directly visualized, revealing dendrite-free Li metal deposition. Li-LE laden HKUST-1 (Li-LE@HKUST-1) QSSEs with a hierarchical pore structure were designed and realized by morphology control and different cold-pressing procedures [112]. The macropores and mesopores of Li-LE@HKUST-1 could construct a set of interconnected Li-LE networks with innate MOF channels and facilitate Li⁺ transfer in hybrid pathways. Thereinto, cuboctahedron Li-LE@HKUST-1 with most Li-LE-filled hierarchical pores exhibited an extraordinary ionic conductivity (1.02 mS cm⁻¹, RT). Moreover, the hierarchical hybrid ion-transport pathways design can be successfully applied in different systems (Na⁺, Mg⁺, and Al⁺), with high ionic conductivities (>10⁻⁴ S cm⁻¹) in all the cases. Else, inspired by the efficient proton conduction in protein molecules that embed single-file water chains, a biomimetic pseudo SLIC is developed, denoted as Liₓ[Zr₂(μ₃-O)₂O(BTC)₂(CI₂O₄)ₓ]16EC (808-LCE), where LiCI₂O₄·2 EC is immobilized within a unique Zr-carboxylate framework [113]. The SLIC exhibits high Li⁺ conductivity (0.35 mS cm⁻¹) and low activation energy (0.19 eV) simultaneously due to the presence of single-file Li⁺ chains. In contrast, succinonitrile (SN), a typical plastic crystal, displays rapid Li⁺ conduction (10⁻³ S cm⁻¹, RT) owing to its high molecular rotational motion and self-diffusion characteristics [114]. However, the high reactivity of SN leads to challenging corrosion of the Li anode, resulting in increased interfacial resistance and diminished battery capacity [115,116].

The chemical stability of MOF nanosheets contributes to the achievement of a stable laminar framework structure, enabling the incorporation of LiTFSI-SN into NiCo-MOF to form a laminar LSN-MOF CSE [117,118]. The interlayer nanochannels of LSN-MOF CSE provide storage sites for the LSN electrolyte, and the coordination interactions between metal sites (Co and Ni) and Ca²⁺ groups effectively anchor the LSN electrolyte, resulting in high Li⁺ conduction and a stable anode interface. Nanocrystalline MOFs with similar morphology but different topological structures serve as a platform for exploring the structure-property relationship of MOF-based SSEs for LMBs. A combined experimental and theoretical approach is employed to investigate the influence of pore apertures and OMS in MOFs on ion transport properties and electrochemical stability [75]. MOF-based electrolytes with non-redox-active metal sites exhibit a wider electrochemical stability window (0.2–5.2 V) compared to those with redox-active centers. The pore aperture of Zn-MOF-74, soaked in a LiTFSI solution in dimethoxyethane (DME) with a 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py₄TFSI) Li-ILs binder, determines the uptake of LiTFSI and governs the ionic conductivity of MOF-based electrolytes (1.73 × 10⁻⁴ S cm⁻¹ at 30 °C) [119]. Moreover, Li⁺ solid-state nuclear magnetic resonance (SSNMR) analysis reveals that solvated Li⁺ exhibit higher mobility than de-solvated ones, suggesting a vehicle-type mechanism for ion transport in MOFs. Molecular dynamics (MD) simulations demonstrate that the OMS of MOFs can facilitate the dissociation of Li salts and immobilize the anions of Li salts through interactions with LAB, thereby promoting Li⁺ mobility and achieving high 1Li⁺ values (up to 0.47).

In conclusion, there are two main types of MOFs used in QSSEs: MOFs-based SLICs derived from functional MOF materials, and MOFs serving as large containers for Li⁺-containing LEs. Both types require the assistance of polymer or organic liquid ionic transporters to achieve excellent electrochemical performance. The former type of QSSEs takes advantage of the designability and tunability of MOFs’ molecular structure. By introducing functional groups that covalently immobilize anions to the MOFs, more free Li⁺ are produced, enabling their movement along the porous channels and participation in conduction [81]. MOFs-based SLICs typically exhibit high 1Li⁺ values close to unity, and their high mechanical strength helps suppress dendrite formation [120]. The flexibility of functional groups allows for further derivatization and prevents MOF nanoparticles from agglomerating. The latter type of QSSEs utilizes MOFs as reservoirs and containers, capitalizing on their special cavity structures designed to store and transmit Li⁺. The addition of LEs alleviates the rigid lattice of MOFs, and MOF nanoparticles improve the interface contact between electrolyte and electrode. The porous structure of MOFs provides continuous transport channels for Li⁺, and the abundance of electronegative sites facilitates the hopping of Li⁺ ions in the channels, resulting in highly efficient ion conductivities and superior voltage platforms through molecular-scale interface engineering [121]. Both types harness the properties of MOFs as the main body, leveraging functionalization, grafting, crosslinking, hollow design, and tunable pore channels to achieve remarkable ion conductivity and electrochemical properties. However, the design and synthesis processes tend to be complex and inconvenient for practical applications, warranting further investigation. Furthermore, excessive addition of transporters can negatively impact the performance of SSBs during cycling, presenting significant challenges for the further development of SSEs. Therefore, it is crucial to focus on novel synthetic methods, ideal architectural models, a clear understanding of interaction mechanisms, and the exploration and utilization of superior materials for future advancements in this field.

2.2. MOFs with ILs for QSSEs

Ionic liquids (ILs) are characterized by their thermal stability and high ionic conductivity, making them attractive candidates for enhancing the electrochemical performance of SSBs at elevated temperatures. Their use in PSEs has proven to be a promising strategy to improve ionic conductivity and establish reliable interface contacts [122]. In comparison to the conventional organic liquid electrolytes, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) stands out due to its robust ionic conductivity, excellent electrochemical and thermal stability, and compatibility with Li, thereby enhancing the Coulombic Efficiency (CE) [123,124]. The combination of porous materials with ILs has emerged as a crucial approach in the development of SSEs, offering enhanced conductivity and improved interface compatibility [125]. The porous structure of MOFs facilitates the encapsulation of ILs, and the aligned one-dimensional (1D) channels within MOFs serve as effective transport pathways for Li⁺. Li-ILs, a type of functional ILs containing Li salt (e.g., LiTFSI in EMIM-TFSI), with TFSI⁻ size of 0.79 nm and EMIM⁺ size of 0.76 nm, exhibit excellent adsorption capacity for Li⁺. The exploration of ILs@MOFs gained momentum following the discovery...
that impregnating Mg-MOF-74 with Li isopropoxide forms a conductive solid-like electrolyte, leading to further research on ILs@MOFs for SSBs [86]. ILs-decorated MOFs have been employed as ion-conductive fillers to develop CSEs with high ionic conductivity. The interaction between MOFs and ILs, as well as the influence of MOF types, requires greater attention, as understanding the role of Li-ILs@MOF in ion transport mechanisms will advance the practical application of SSBs. The conductivity of ILs@MOF-pellet composite materials was found to significantly differ between the surface ILs before and after removal. The observed increase in conductivity is attributed to the augmented presence of excess ILs between MOF crystals within the particles, forming a “nanowetted interface” [126]. Table 2 summarizes the property of the recent MOFs with ILs auxiliary QSSEs.

Wang et al. conducted a study involving the design of HKUST-1(Cu), a well-known MOF with exceptional chemical stability and large pore size, as the host material for accommodating Li-ILs [127]. Leveraging the remarkable absorption capability of HKUST-1, Li-ILs were encapsulated within the 3D channels of the host structure, which possess a pore diameter of approximately 0.8 nm, slightly larger than the dimensions of TFSI− ions. The interaction between Li-ILs and the OMS of HKUST-1 resulted in the formation of stable ion-conductive solid hybrids, denoted as Li-ILs@HKUST-1. To isolate flexible CSEs, Li-ILs@HKUST-1 was uniformly dispersed into a precursor solution containing a PEO-based polymer using a solution-casting method. The incorporation of Li-ILs@HKUST-1 effectively reinforced the polymer matrix and established an ion-conductive network, thereby improving the electrochemical performance of the CSEs. The resulting CSEs exhibited an enhanced ionic conductivity of 1.20 × 10⁻⁴ S cm⁻¹ at 30 °C, and the corresponding SSBs achieved a high reversible capacity of 136.2 mA h g⁻¹ with a capacity retention of 92%. In a similar vein, the angstrom-scale pores of HKUST-1 restricted the movement of TFSI− and EMIM⁺ ions, creating a modified coordination environment that enhanced the mobility of Li⁺. Direct encapsulation of Li-ILs within HKUST-1 (referred to as HKUST-1@Li-ILs) preserved the dynamic mobility of Li-ILs, resulting in high ionic conductivity. Furthermore, the 3D nanochannels of HKUST-1@Li-ILs provided numerous direct contact points between the electrolyte and the electrode, facilitating atomic-scale wetting of the interface. This transformation of the primitive solid-solid contact into “nanowetted interfaces” effectively reduced interfacial resistance, ensured stable Li metal plating/stripping, and suppressed the formation of Li dendrites [128]. Subsequently, Vazquez et al. employed MD simulations to investigate the mobility of Li-ILs within MOF nanopores and elucidate the underlying conduction mechanism [128].

The investigation focused on the conduction behavior of ILs with the composition [Li0.2BMIM0.8] [TFSI] within the framework of HKUST-1. To provide reference systems, [BMIM] [TFSI] and LiTFSI in HKUST-1 were also examined. The study revealed that the ion mobility and conduction of [BMIM][TFSI] in HKUST-1 significantly decreased as the pores became increasingly filled due to mutual pore blocking by the larger organic ions [129]. In contrast, the conduction of [Li0.2BMIM0.8] [TFSI] only exhibited a slight decrease with the increasing pore filling. MD simulations were performed, and they qualitatively reproduced the experimental findings, demonstrating that Li conduction follows a Grotthuss-like mechanism. Interestingly, despite representing only 10% of the ions, Li contributed to 26%–37% of the total conductivity. Two distinct conduction regimes were unveiled: at low and medium concentrations, the Grotthuss-like Li conduction was constrained by the proximity of the [TFSI] anions. At high loadings, the relatively large organic cations and anions exhibited field-induced bunching and immobilization behavior, akin to the Li-free reference system. However, the formation of charge-neutral LiTFSI cation-anion complexes mitigated the bunching effect since they were not accelerated by the electric field. Consequently, compared to the Li-free ILs, the collapse of conduction caused by ion bunching at full loading was averted, resulting in a conductivity of approximately two orders of magnitude larger.

In order to address the limitations of ILs, such as low t¹, and restricted Li⁺ diffusion at the electrolyte and electrode/electrolyte interfaces, various MOFs with different pore sizes and specific surface areas have

Table 2
The property of MOFs with ILs for QSSEs.

<table>
<thead>
<tr>
<th>MOF Material</th>
<th>Addition</th>
<th>Electrochemical Window (V)</th>
<th>σ (S cm⁻¹)</th>
<th>t¹ (°C)</th>
<th>Specific Capacity (mAh g⁻¹)</th>
<th>Cycles</th>
<th>Capacity Retaining (%)</th>
<th>Coulombic Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1</td>
<td>Li-ILs</td>
<td>1.20 × 10⁻⁴</td>
<td>0.13 (30 °C)</td>
<td>136.2 at 170 mA g⁻¹</td>
<td>100</td>
<td>92.00</td>
<td>−100.00</td>
<td>[127]</td>
<td></td>
</tr>
<tr>
<td>HKUST-1</td>
<td>Li-ILs</td>
<td>0.68 × 10⁻⁴</td>
<td>0.46 (25 °C)</td>
<td>144.0 at 85 mA g⁻¹</td>
<td>100</td>
<td>92.00</td>
<td>99.00</td>
<td>[126]</td>
<td></td>
</tr>
<tr>
<td>UIO-67</td>
<td>Li-ILs+PVDF-HFP</td>
<td>4.8</td>
<td>4.30 × 10⁻⁴ (RT)</td>
<td>0.45 (RT)</td>
<td>149.0 at 17 mA g⁻¹</td>
<td>300</td>
<td>94.00</td>
<td>99.86 (av.)</td>
<td>[131]</td>
</tr>
<tr>
<td>UIO-66</td>
<td>Li-ILs+PVDF-HFP</td>
<td>5.0</td>
<td>1.10 × 10⁻³ (30 °C)</td>
<td>0.72 (30 °C)</td>
<td>145.2 at 170 mA g⁻¹</td>
<td>500</td>
<td>97.70</td>
<td>&gt;99.00</td>
<td>[135]</td>
</tr>
<tr>
<td>UIO-66</td>
<td>Li-ILs+PEO+LiTFSI</td>
<td>5.2</td>
<td>1.47 × 10⁻⁴ (30 °C)</td>
<td>0.47 (30 °C)</td>
<td>140.2 at 17 mA g⁻¹</td>
<td>100</td>
<td>96.58</td>
<td>−100.00</td>
<td>[136]</td>
</tr>
<tr>
<td>UIO-66</td>
<td>Li-ILs+PEO+LiTFSI</td>
<td>5.4</td>
<td>2.20 × 10⁻⁴ (25 °C)</td>
<td>0.35 (25 °C)</td>
<td>115.5 at 170 mA g⁻¹</td>
<td>1000</td>
<td>98.00</td>
<td>−100.00</td>
<td>[137]</td>
</tr>
<tr>
<td>UIO-66@67</td>
<td>Li-ILs</td>
<td>2.10 × 10⁻³ (RT)</td>
<td>0.63 (RT)</td>
<td>158.0 at 34 mA g⁻¹</td>
<td>100</td>
<td>99.00</td>
<td>−100.00</td>
<td>[138]</td>
<td></td>
</tr>
<tr>
<td>UIO-66@66</td>
<td>Li-ILs+PEO+LiTFSI</td>
<td>5.5</td>
<td>9.20 × 10⁻⁴ (RT)</td>
<td>0.74</td>
<td>155.0 at 34 mA g⁻¹</td>
<td>200</td>
<td>99.00</td>
<td>−100.00</td>
<td>[136]</td>
</tr>
<tr>
<td>UIO-66</td>
<td>Li-ILs+PAN</td>
<td>1.08 × 10⁻³ (25 °C)</td>
<td>0.52 (25 °C)</td>
<td>131.8 at 34 mA g⁻¹</td>
<td>100</td>
<td>90.00</td>
<td>−100.00</td>
<td>[140]</td>
<td></td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Li-ILs+PEO</td>
<td>5.0 (60 °C)</td>
<td>1.41 × 10⁻⁴ (25 °C)</td>
<td>0.41 (60 °C)</td>
<td>182.5 at 20 mA g⁻¹</td>
<td>100 (NCM)</td>
<td>73.00 (60 °C)</td>
<td>99.00</td>
<td>[141]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Li-ILs+PVDF+30 PI</td>
<td>5.2</td>
<td>4.08 × 10⁻⁴ (30 °C)</td>
<td>0.64 (30 °C)</td>
<td>152.6 at 85 mA g⁻¹</td>
<td>500</td>
<td>96.00</td>
<td>99.61</td>
<td>[142]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>Li-ILs+PP</td>
<td>4.7</td>
<td>2.09 × 10⁻⁴ (25 °C)</td>
<td>0.45 (25 °C)</td>
<td>157.9 at 34 mA g⁻¹</td>
<td>450</td>
<td>91.23</td>
<td>−100.00</td>
<td>[143]</td>
</tr>
<tr>
<td>ZIF-89SiO₂Co/HPCNs</td>
<td>Li-ILs</td>
<td>5.5</td>
<td>2.34 × 10⁻⁴ (30 °C)</td>
<td>0.60 (30 °C)</td>
<td>155.6 at 34 mA g⁻¹</td>
<td>100</td>
<td>965.00</td>
<td>−100.00</td>
<td>[144]</td>
</tr>
<tr>
<td>MIL-101 [Dinim][BF₄][Amin] [N(CN)₂]</td>
<td>5.2</td>
<td>3.73 × 10⁻³ \</td>
<td>2.69 × 10⁻³ \</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>[148]</td>
<td></td>
</tr>
</tbody>
</table>

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been employed as SSEs [75,130]. To gain further insight into the mechanism of Li⁺ transport within the voids of MOFs, a strategy was developed to incorporate ILs as guest electrolytes within the nanoporous structure of UIO-67 MOF, thereby creating a Li⁺ conductor [131]. UIO-67, composed of Zr₆(IV)(VO₂)(OH)₄ clusters and bipyphenyl-4,4',5,5'-dicarboxylic acid (BDPC) linkers, was chosen to encapsulate nonvolatile and nonflammable Li-ILs, resulting in the formation of Li-ILs@UIO-67. The estimated pore size of each octahedral cage in UIO-67 is approximately 1.2 nm, making it suitable for accommodating the Li-ILs segment [132]. The smaller Li⁺ (ionic radius: 0.059 nm) can freely diffuse within this framework. As the SSE layer, UIO-67-Li exhibits a strong ability to immobilize anions due to its abundant OMS and numerous Li⁺ transport channels, thereby enabling high ionic conductivity. Additionally, UIO-67-Li demonstrates low electronic conductivity, excellent chemical and electrochemical stability, as well as exceptional compatibility with Li metal.

The use of a dense UIO-67-Li SSE layer on the Li anode side provides an effective barrier against the infiltration of Li dendrites, ensuring enhanced safety and stability [133]. Incorporating Li-ILs@UIO-67 into a Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix results in the formation of a continuous ion transport network, exhibiting an impressive ionic conductivity of 4.3 × 10⁻⁴ S cm⁻¹ and a wide electrochemical window of 4.8 V (vs. Li⁺/Li) at RT. The electrolyte demonstrates stable Li plating/stripping at a current areal capacity of 0.3 mA cm⁻² for over 350 h. The prepared SSNs exhibit a sustained discharge capacity of 149 mA h g⁻¹ for 300 cycles at a rate of 0.1 C, with highly reversible Li plating/stripping throughout the cycling process. Considering that each individual MOF possesses its own advantages and limitations, it becomes challenging to identify a single MOF with a homogeneous structure that simultaneously enhances both ionic conductivity and selective Li⁺ transport. Density functional theory (DFT) calculations reveal that the adsorption energy of TFSI⁻ anions on the surface and inside the channels of UIO-66 is ~1.70 eV and ~0.63 eV, respectively. Therefore, UIO-66 is selected as the functional filler to construct a three-dimensional interconnected MOF network-based SSE [134]. By filling ILs into the nanoporous channels of UIO-66 and immobilizing them within a polymer matrix (Poly-ILs@UIO-66@PVDF-HFP), TFSI⁻ anions form complexes with Li⁺ solvates, enabling efficient translocation of Li⁺ with high tLi⁺ and achieving elevated ionic conductivity (Fig. 2a) [135]. Alternatively, when Li-containing liquid-state ion-electrolytes (Li-Ils) are encapsulated within the UIO-66 framework and incorporated into a PEO matrix, they facilitate Li⁺ transport, exhibit high ionic conductivity, effectively suppress the growth of Li dendrites, and display low interfacial resistance with the electrodes and Li metal [136].

The utilization of UIO-66, with its well-defined conductive tunnels, holds significant potential for regulating ion transport and ensuring the long-term stability of Li plating/stripping at an ultrahigh current density of 4 mA cm⁻². Liu et al. employed a straightforward approach by blending UIO-66 particles with a solvate ionic liquid (SIL) (Li(G4)³⁻) (TFSI⁻) to construct QSSEs. The uniform 3D channels and pores of UIO-66 serve as a confinement structure for the SIL (SIL@UIO-66) [137]. The interaction between Li⁺ and TFSI⁻ within the UIO-66 framework weakens the coordination environment of Li⁺, resulting in increased ionic conductivity and tLi⁺. The incorporation of SIL within the porous structure of UIO-66 contributes significantly to the creation of a plentiful nanowetted interface. This arrangement facilitates the establishment of a 3D network for Li⁺ transport, thereby enhancing the kinetics of Li⁺ movement. SIL@UIO-66 demonstrates remarkable compatibility with Li metal and exhibits excellent suppression of dendritic growth. This beneficial effect is attributed to the confinement of anions within the MOF framework, which enables the provision of a uniform Li⁺ flux. Furthermore, the dense structure of the QSSE impedes the occurrence of undesirable side reactions. As a result, Li symmetric batteries employing SIL@UIO-66 at various current densities exhibit consistent and stable behavior during Li plating and stripping processes (Fig. 2b). Additionally, UIO-66 effectively restrains TFSI⁻, facilitating the release of more Li⁺ and improving ion transport. This homogeneous Li⁺ flux production suppresses the formation of Li dendrites and enables stable Li deposition [69]. Furthermore, heterogeneous MOF-in-MOF structures are employed to enhance ionic conductivity and selectively transport Li⁺. The fabrication of core-shell MOF-in-MOF nanopores (UIO-66@67) is achieved using H₂-bpyridine as a linker. The shell structure (UIO-67) possesses a large pore size and high specific surface area, enabling increased absorption of the IL electrolyte. On the other hand, the core structure (UIO-66) possesses a small pore size that can effectively confine the larger ions present in the ILs, selectively enhancing the transport of Li⁺ (Fig. 2c) [138].

The objective of this study is to utilize the UIO-66@67 composite structure as a multifunctional host for electrolytes, enhancing ionic conductivity, tLi⁺, and interface stability of SSEs. Taking inspiration from interwoven and intercommunicating structures found in various scientific fields, a novel approach was developed to create CSNs with fast ion transport by incorporating MOF-in-MOF spherical nanoparticles into a PEO-LiTFSI matrix [139]. In the context of polymer-MOF-based electrolytes, Sun et al. employed electrospinning and electrochemical spraying techniques to fabricate a 3D MOF-based flexible composite membrane (PAN/UIO-66@Li-ILs, referred to as PUIE) [140]. The polyacylonitrile (PAN) component, known for its excellent mechanical performance, was chosen as a self-supporting polymer skeleton. The incorporation of UIO-66 within the composite structure effectively restricts the transference of ILs ions, mitigates the formation of large concentration gradients of Li⁺, prevents the inhomogeneous deposition of Li⁺ at the Li anode side, and ultimately inhibits the growth of Li dendrites. This comprehensive approach results in outstanding performance characteristics for SSNs (Fig. 2d).

The core-shell structure of the fillers in this study offers distinct advantages, including an insulating shell that inhibits the growth of Li dendrites and an inner cavity that enables the storage of an ample amount of Li-ILs while enhancing Li diffusivity. To achieve this, ZIF-8 nanofibers encapsulating ILs (referred to as ILs@ZIF-8) were incorporated into a PEO matrix to form CSNs. ZIF-8, known for its low cost, facile synthesis, and superior electrochemical stability, possesses abundant pores that can confine ILs within a restricted space. Its micro-channeled structure serves as an insulating and Li⁺-transporting scaffold. Furthermore, an acid etching method was employed to create a hollow structure within ZIF-8, enabling the accommodation of Li-ILs. This design expectation is aimed at boosting Li⁺ conductivity and maintaining long-term cycling stability [141]. The fabrication of ILs@ZIF-8@PEO CSNs, utilizing a tape casting method, resulted in a core-shell structure that enhances ionic conductivity, improves interface resistance, promotes the stability of the LiF layer, and enhances thermal and electrochemical stability. This was achieved through the precise control of surface roughness and filler dispersion. It is of great significance to fabricate 3D ion conductors with well-ordered structures and high mechanical strength to enable continuous ion transport while simultaneously enhancing the resistance against dendrite growth. A hierarchically self-assembled MOF network was constructed by growing continuous MOF nanocrystals on a 3D cross-linked network composed of 1D polyimide fibers. These fibers provide spatial guidance for the self-assembly of MOF nanoparticles. Additionally, a surface-etching strategy was employed to create carboxylated polyimide, which offers abundant and uniform nucleation sites for well-ordered MOF growth (Fig. 2e). The resulting MOF@ILs composite combines micro-scale MOF LAB with the benefits of MOF@ILs transport. The MOF network is impregnated with a polyvinylidene fluoride (PVDF) polymer, resulting in a composite that exhibits high ionic conductivity [142]. In another approach, a ZIF-8/PP composite membrane was prepared using a facile in-situ growth method, with ZIF-8 nanoparticles uniformly distributed on the surface and within the interior of the porous PP membrane. The unique distribution of ZIF-8 nanoparticles in the composite membrane enhances its affinity for Li⁺ conductors and inhibits dendrite growth. Subsequently, the ZIF-8/PP composite membrane was
impregnated with nonflammable and nonvolatile Li-ILs to create a Li-ILs@ZIF-8/PP electrolyte, which exhibited improved ionic conductivity, $t_{Li^+}$, mechanical strength, excellent nanowetted interfaces, and an appropriate electrochemical window [143]. Furthermore, three different composite modes of ZIF-8 and mesoporous SiO$_2$ (ZIF-8@SiO$_2$), with mesoporous SiO$_2$ spheres adsorbed on the surface of ZIF-8 (ZIF-8/SiO$_2$), and with a mesoporous SiO$_2$ shell deposited on the surface of ZIF-8 (ZIF-8@SiO$_2$), were investigated through mechanical mixing [144]. ZIF-8@SiO$_2$/ILs composite was obtained by encapsulating Li-ILs within the hierarchical pore structure of ZIF-8@SiO$_2$, and when used as filler with PEO-LiTFSI, the resulting CSEs exhibited excellent performance. They demonstrated high ionic conductivity ($2.35 \times 10^{-4}$ S cm$^{-1}$) at 30
During battery operation, transport limitations can lead to local depletion of Li-ILs into the material (Fig. 2f) [145]. By dispersing Li-ILs into a functionalized MIL-121 MOF, followed by the investigation of ion dynamics using 7Li nuclear magnetic resonance (NMR) spectroscopy, sheds light on the ionic conduction properties of these materials [146]. The results indicate that the ILs exhibit limited penetration into the pores of MIL-121. In contrast, MIL-101, known for its large pore volume, pore size, and width size [147], was employed to synthesize two ILs@MOF composites: [Dmim][BF4]@MIL-101(Cr) and [Anim][N(CN)2]@MIL-101(Cr) [148]. The ionic conductivity of both composites shows linear Arrhenius behavior and low conductivity activation energies, indicating that these two composites exhibit fast ionic conduction. Thorough analysis from both thermodynamic and kinetic perspectives provides insights into the superior ionic conductivity of these composites.

The confinement of ILs within nanoporous MOFs (ILs@MOFs) has attracted considerable attention as SSEs due to their tunable functionality and favorable electrochemical properties. ILs offer several advantages over conventional LEs, including low flammability, low volatility, thermal stability, and an electrochemical window of up to 6.0 V. The unique porosity of MOFs restricts the mobility of ILs, and the presence of nanosized ILs within MOFs’ micropores prevents freezing transitions and mitigates liquid leakages [149]. ILs@MOFs exhibit higher ionic conductivity and enhanced security compared to bulk ILs, primarily attributed to the ion hopping mechanism. The excellent ionic transport is governed by factors such as the size of the anion, the pore width within MOFs, and the loading of ILs. Additionally, the mechanical stability of ILs@MOFs plays a significant role in the formation of interfaces between SSEs and cathodes, as the occurrence of chemical reactions can lead to severe interface impedance [150]. Therefore, the development of ILs@MOFs SSEs requires a focus on several aspects, including 1) the potential blockage of MOFs’ pores hindering ionic transport due to anion size mismatch, 2) distinct charge transfer dynamics for different anions within MOFs, 3) the diffusion dynamics of Li+ ions, 4) considerations regarding the working potential window, t21 values, and resistance to dendrite growth, and 5) the exploration of essential electrochemical properties and addressing the challenge of the high cost associated with ILs when assembling them in cells.

2.3. MOFs for GT-QSSEs

Conductors of this nature typically rely on the presence of a liquid solvent or confined small molecules within their pores to facilitate ion transport. In the absence of a mobile solvent, the geometry and large size of the pores result in significantly slower ionic conduction. Therefore, these conductors are more appropriately classified as hybrid SSEs, similar to the relation between gel polymer electrolytes (GPEs) and PSEs [151–153]. GPEs, which combine relatively high ionic conductivity and good interfacial compatibility, have emerged as promising alternatives for overcoming obstacles in SSEs and expanding their practical applications [154,155]. Various polymers such as PVDF-HFP, PVDF, PAN, PEO, and poly(methyl methacrylate) (PMMA) have been extensively investigated as polymer matrices in GPEs for SSEs. These polymers possess desirable properties such as low crystallinity, chemical resistance, thermal stability, self-extinguishing behavior, and flexibility [156–161]. During battery operation, transport limitations can lead to local depletion of Li+ ions, exacerbating concentration polarization and compromising interfacial stability and cycle life. However, unlike Li+ conducting GPEs, MOF ion conductors are considered true solids from a rheological standpoint. Therefore, incorporating MOFs into GPEs results in a new class of electrolytes called gel-type QSSEs (GT-QSSEs). Table 3 summarizes the property of the recent gel-type QSSEs. Through post-synthetic modifications, a Zr-based MOF is endowed with charged ligands to immobilize anions, and the resulting MOF-laden PSEs exhibit superior t21 (>0.7) [162]. In this context, a Zr-based MOF with OMSs serves as the microporous filler in GT-QSSEs. These thermally generated OMSs with ligand-anchoring capabilities facilitate Li+ conduction, leading to high ionic conductivity on the order of 10⁻⁶ S cm⁻¹, high t21 (0.66), and low activation energy (<0.1 eV). This straightforward treatment of a Zr-based MOF imparts desirable ion transport properties to GT-QSSEs, ensuring the safe and durable operation of batteries (Fig. 3a) [163].

Cellulose possesses desirable attributes such as good mechanical strength, thermal stability, and excellent matrix properties for electrolytes due to its abundance of hydroxyl groups. These hydroxyl groups facilitate strong binding with Li+ and electrolyte solvents, inhibiting anion motion and thereby enhancing both ionic conductivity and t21 [164]. In this regard, Fu et al. have introduced a composite aerogel consisting of ionic-regulating and high-voltage compatible bacterial cellulose (BC) combined with mesoporous Zr-based MOFs as the matrix for GT-QSSEs [100]. By incorporating anionic organic linkers, such as UO₂-66-NH₂ nanofillers, into the BC skeleton, a synergistic effect is achieved, resulting in high ionic conductivity (≈1×10⁻² mS cm⁻¹), high t21 (0.82), and a wide electrochemical stability window (4.9 V). Moreover, HKUST-1, a copper-based MOF, has demonstrated potential as a multifunctional filler for enhancing the electrochemical performance of PEO-based electrolytes. To further improve the properties of GT-QSSEs, the photoinitiator benzophenone (BP) was introduced into the PEO matrix via ultraviolet (UV) curing, resulting in HKUST-1@BP-PEO composites [165]. These composites, when combined with the corresponding liquid electrolyte, exhibited favorable interfacial contact and enhanced stability during the electrochemical reactions of Li/Na batteries (Fig. 3b).

The utilization of 1D Cu-MOF fibers has been proposed as a promising filler to leverage the synergistic benefits of high mechanical strength and high Li⁺ conductivity in GT-QSSEs [166]. The design rationale behind Cu-MOF fibers lies in their unique 1D fibrous structure, which intertwines with each other to form a 3D interlinked matrix. This architecture serves as a mechanical barrier against the penetration of Li dendrites, while the abundant nanochannels within the Cu-MOF facilitate the uptake of LEs during the gelation process. To further enhance the suitability of GT-QSSEs for practical applications, the incorporation of multilayered structures becomes necessary to establish a stable interface with reduced diffusion barriers, while simultaneously regulating ion transport. In this context, a heterostructured GT-QSSEs configuration, referred to as ZIF-8@Al₂O₃@GPEs, has been developed. This configuration involves the modification of one side of the polymer matrix (PVDF-HFP), cellulose acetate (CA), and SN with a ZIF-8 layer and atomic layer-deposited Al₂O₃ [167]. The introduction of Al₂O₃ as an electrolyte additive improves the physical and chemical properties of SSEs. The ZIF-8 and Al₂O₃ layers act as “traffic commanders” that regulate a uniform Li⁺ flux, contributing to ion transport, and imparting high mechanical strength to inhibit the growth of Li dendrites. The ZIF-8 particles exhibit a nucleophilic effect that enables binding with Li⁺, prolonging the Li nucleation time, while the defined nanosized channels within ZIF-8 restrict the free migration of anions. Additionally, the Al₂O₃ nanocoating obtained through atomic layer deposition not only enhances the affinity of the lithium anode but also actively participates in the formation of the SEI film and reduces the diffusion barrier for lithium ions.

GT-QSSEs benefit from the incorporation of ionically conductive gel polymers along with plasticizers or organic compounds. This combination provides good flexibility and facilitates excellent interfacial contact with the Li metal anode. The introduction of MOFs materials in GT-QSSEs addresses the limitations of conventional GPEs, such as relatively low ionic conductivity, narrow operating windows, and insufficient dendrite inhibition ability. Additionally, MOFs-based GT-QSSEs exhibit excellent...
Sieving capabilities, effectively preventing the migration of specific intermediate impurities within the battery. This characteristic results in lower polarization and exceptional reversibility, indicating that MOFs-based GT-QSSEs have the potential to suppress Li dendrite formation and growth, consequently enhancing the effectiveness and high-temperature durability of SSBs [168]. However, there is an urgent need to develop advanced technologies for fabricating high-quality, pure, and free-standing MOFs-based GT-QSSEs, as practical batteries require durability and stability. Furthermore, the selection of a compatible polymer with suitable plasticizers and organic compounds is crucial for ensuring the usefulness of the MOFs-based GT-QSSEs.

### 2.4. MOFs for other QSSEs

QSSEs have emerged as a promising solution for addressing certain challenges. These QSSEs not only offer comparable interfacial compatibility to LEs but also maintain favorable mechanical strength. To enhance the interfacial compatibility of MOF-based QSSEs, it is crucial to establish close contacts and create ion transport channels between MOF particles. Table 4 summarizes the property of the recent other QSSEs. In this regard, a strategy was employed to modify the surfaces of UIO-66-2OH particles with cross-linking nodes, followed by the in-situ ring-opening reaction to polymerize MOFs (PMOFs). By incorporating...
Electronegative -OH groups, the resulting PMOFs were expected to bind Li⁺ and facilitate the formation of transport pathways between MOF particles through covalent bonding with an ionic conductive polymer. This chemical connection between MOF particles enabled the direct utilization of the synthesized membrane as SSEs [169]. These SSEs exhibited desirable ion conductivity, high \( t_{\text{li}} \) values, reduced interfacial resistance, and improved performance in assembled SSBs. In a study conducted by Hou et al., a combination of MD simulations, quantum chemistry, and grand canonical Monte Carlo methods elucidated the dominant pathway for Li⁺ conduction in MOF-688 materials. Solvent-assisted hopping was identified as the critical mechanism in QSSSEs, highlighting the pivotal role of the solvent in facilitating ion conduction [170]. This theoretical model provides valuable atomistic insights into the ionic conduction mechanism of QSSSEs, which are challenging to obtain solely from experimental results. Furthermore, the synthesis of MOF-688 (one-fold) with a larger pore size than MOF-688 (Mn) necessitates the use of large and appropriately sized template guests or cations to support the reticulation of organic and inorganic building blocks (Fig. 3c). In the pursuit of suitable SSE options, hollow MOFs have also been explored. For instance, hollow UIO-66 structures with biomimetic ion channels have been prepared for use in QSSSEs. These hollow UIO-66 materials exhibit the capability to selectively transport Li⁺ and can accommodate a higher loading of Li salts, resulting in exceptional ionic conductivity (1.15 × 10⁻³ S cm⁻¹ at 25 °C) and high \( t_{\text{li}} \) values (0.70) [171]. The unique characteristics of these hollow MOFs make them a promising choice for solid-state electrolyte applications.

A simple and innovative approach is essential for the development of highly ionic-conductive MOF-based electrolytes. Among the plastic materials, SN has demonstrated exceptional characteristics as an organic solvent for Li salts due to its relatively high dielectric constant (\( \varepsilon = 55 \), RT) and excellent solvent capacity. When combined with LiTFSI, SN-based electrolytes exhibit outstanding ionic conductivity (10⁻³ S cm⁻¹, RT) [173,174]. However, SN's limited compatibility with Li metal can result in undesired side reactions and compromise the electrolyte/electrolyte interfaces, thereby affecting electrochemical performance. Typically, SN-based electrolytes require the addition of fluoroethylene carbonate (FEC), an effective film-forming electrolyte additive, to enhance interface stability. FEC promotes the formation of amine LiF inorganic salts on the surface of the Li metal, mitigating the polymerization of nitriles upon contact with Li and mitigating the formation of an incompatible interface between the electrode and the electrolyte [175–177]. In this study, SSEs were fabricated using a rolling technology and a simple dipping method at elevated temperature, combining SN and ZIF-8 electrolyte. The MOF, acting as an ionic sieve, restricts the movement of large electrolyte anions and facilitates homogeneous Li⁺ flux during electrochemical cycling. The interaction between ZIF-8 and SN significantly promotes rapid Li⁺ migration, while the FEC additive is utilized to improve interfacial compatibility between the electrolyte and Li anode [178]. By employing MOFs with appropriate windows/channels, it is possible to achieve aggregative SN-based electrolytes by removing excess solvent molecules from the solution sheaths of solvated Li⁺. Specifically, the MOF material ZIF-69 (pore size: 4.4 Å) was employed to extrude additional solvent molecules from the solvated Li⁺ in SN (1 M LiTFSI-SN), resulting in QSSSEs with an over-saturated electrolyte configuration within ZIF-69 channels [179]. The designed SN-ZIF-69 electrolyte successfully addresses the inherent incompatibility issue of SN towards Li metal. It exhibits a significantly extended electrochemical voltage stability window of approximately 5.4 V, higher \( t_{\text{li}} \) (0.67), and satisfactory ionic conductivity (1.37 × 10⁻³ S cm⁻¹ at 25 °C). MOF glasses have attracted scientific interest due to their unique characteristic of lacking grain boundaries [180]. This feature makes them a promising candidate for producing high-performance QSSSEs, considering their remarkable ionic conductivity and isotropy without grain boundaries [181]. To achieve good processability and favorable interface properties, MOF glasses can be employed to fabricate monolithic network SSEs [182]. In this context, the incorporation of glassy ZIF-4 combined with LiTFSI as QSSSEs has been explored, demonstrating notable ion conductivity, excellent dendrite suppression, and interface compatibility [183].

The MIL-100(Al) structure, composed of Al octahedra trimers with capping terminals and trimesic acid (BTC) ligands, represents a new family of solid-like electrolytes. The ion-conduction principles of MOF-infused electrolytes, consisting of various perchlorate salts and PC, have been systematically investigated [184]. The MIL-100(Al)-like microscopic structure of the metal-organic network (MON) with Al-BTC tetrahedra as building blocks (referred to as Al-MON) features mobile anionic molecular chains exhibiting high Li⁺ conductivity and single-ion conduction behavior. These anionic aminosulfonate molecules, with tunable length, reside in the pore channels of the MON and are linked to the unsaturated Al sites [172]. Solid-state nuclear magnetic resonance (SSNMR) experiments have revealed the hemilabile nature of the anionic chains, enabling localized molecular rotation and vibration within the rigid metal-organic skeletons. Such dynamic molecular motion facilitates rapid Li-ion transport under solvent-free and low-solvent conditions (Fig. 3d). The development of new MOFs and optimization of interfaces are crucial for enhancing ion transport. Interfacial optimization based on functionalized UIOs (-COOH, -OH, and -SO₃H) has shown some improvement in ion transport [169,185]. MOFs hold the potential for confining organic electrolytes within their pores and enabling single-ion transport [186]. Therefore, the development of new MOFs with well-regulated channels and an exploration of their ion conduction

### Table 4

<table>
<thead>
<tr>
<th>MOF Material</th>
<th>Polymer</th>
<th>Electrochemical Window (V)</th>
<th>( \sigma ) (S cm⁻¹)</th>
<th>( t_{\text{li}} )</th>
<th>Specific Capacity (mAh g⁻¹)</th>
<th>Cycles</th>
<th>Capacity Retaining (%)</th>
<th>Coulombic Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uio-66 2OH</td>
<td>γ-GPS   + DDPP + PC</td>
<td>4.60</td>
<td>1.70 × 10⁻³</td>
<td>0.800</td>
<td>138 at 170 mA g⁻¹</td>
<td>500</td>
<td>92.03</td>
<td>−100.0</td>
<td>[169]</td>
</tr>
<tr>
<td>Uio-66 PVDF + PTFE</td>
<td>4.72</td>
<td>1.15 × 10⁻³</td>
<td>0.700</td>
<td>115 at 170 mA g⁻¹</td>
<td>800</td>
<td>98.00</td>
<td>−100.0</td>
<td>[171]</td>
<td></td>
</tr>
<tr>
<td>ZIF-8</td>
<td>SN + FEC</td>
<td>4.90</td>
<td>7.04 × 10⁻⁴</td>
<td>0.680</td>
<td>161 at 17 mA g⁻¹</td>
<td>100</td>
<td>98.90</td>
<td>−100.0</td>
<td>[178]</td>
</tr>
<tr>
<td>ZIF-69</td>
<td>SN + PTFE + PC</td>
<td>5.40</td>
<td>1.37 × 10⁻³</td>
<td>0.670</td>
<td>143.8 at 170 mA g⁻¹</td>
<td>800</td>
<td>89.10</td>
<td>99.4</td>
<td>[179]</td>
</tr>
<tr>
<td>ZIF-4</td>
<td>PC</td>
<td>4.00</td>
<td>1.61 × 10⁻⁴</td>
<td>0.885</td>
<td>101 at 170 mA g⁻¹</td>
<td>500</td>
<td>100.00</td>
<td>−100.0</td>
<td>[183]</td>
</tr>
<tr>
<td>MIL-100(AI)</td>
<td>H₂NCH₂CH₂SO₃H + PC + LiO₂⁻</td>
<td>4.40</td>
<td>1.10 × 10⁻³</td>
<td>0.750</td>
<td>147.8 at 170 mA g⁻¹</td>
<td>300</td>
<td>\</td>
<td>−100.0</td>
<td>[172]</td>
</tr>
<tr>
<td>Zr-Ma</td>
<td>PC</td>
<td>4.60</td>
<td>6.62 × 10⁻⁴</td>
<td>0.630</td>
<td>106 at 340 mA g⁻¹</td>
<td>700</td>
<td>84.90</td>
<td>−100.0</td>
<td>[187]</td>
</tr>
<tr>
<td>CuBTC</td>
<td>PSS + PC</td>
<td>5.40</td>
<td>\</td>
<td>\</td>
<td>171 at 20 mg cm⁻²</td>
<td>300</td>
<td>89.00 (90 °C)</td>
<td>−100.0</td>
<td>[74]</td>
</tr>
</tbody>
</table>

---

**Table 4**

The property of MOFs for other QSSSEs.
Table 5
The property of MOFs mix with polymer ASSEs.

<table>
<thead>
<tr>
<th>MOF Material</th>
<th>Polymer and Additive</th>
<th>Electrochemical Window (V)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$\theta_{Li}$</th>
<th>Specific Capacity (mAh g$^{-1}$)</th>
<th>Cycles</th>
<th>Capacity Retaining (%)</th>
<th>Coulombic Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIF-8</td>
<td>PEO + LiTFSI</td>
<td>5.20</td>
<td>$2.20 \times 10^{-3}$ (30 $^\circ$C)</td>
<td>0.360 (60 $^\circ$C)</td>
<td>130.5 at 85 mA g$^{-1}$</td>
<td>350</td>
<td>85 (60 $^\circ$C)</td>
<td>-100</td>
<td>[194]</td>
</tr>
<tr>
<td>ZIF-8-EMIM$<em>{3}$-IL$</em>{4}$ + TFSI</td>
<td>PEO + LiClO$_4$</td>
<td>&gt;5.20</td>
<td>$4.26 \times 10^{-4}$ (30 $^\circ$C)</td>
<td>0.670 (70 $^\circ$C)</td>
<td>167.0 at 155 mA g$^{-1}$</td>
<td>120</td>
<td>76.80</td>
<td>95</td>
<td>[195]</td>
</tr>
<tr>
<td>ZIF-90-g-IILa</td>
<td>PEO + LiTFSI</td>
<td>4.80</td>
<td>$7.20 \times 10^{-3}$ (30 $^\circ$C)</td>
<td>0.440 (60 $^\circ$C)</td>
<td>142.3 at 340 mA g$^{-1}$</td>
<td>500</td>
<td>71 (60 $^\circ$C)</td>
<td>-100</td>
<td>[196]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>PVDF + LiTFSI + NiC$_6$O$_4$</td>
<td>4.80</td>
<td>$1.50 \times 10^{-4}$ (RT)</td>
<td>0.833 (RT)</td>
<td>155.0 at 170 mA g$^{-1}$</td>
<td>500</td>
<td>98.20</td>
<td>-100</td>
<td>[199]</td>
</tr>
<tr>
<td>ZIF-8</td>
<td>MXene + PEO + PVDF-HFP</td>
<td>4.50</td>
<td>$4.40 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>0.195 (60 $^\circ$C)</td>
<td>132.0 at 170 mA g$^{-1}$</td>
<td>200</td>
<td>92</td>
<td>-100</td>
<td>[202]</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>PEO + LiTFSI + GF</td>
<td>5.20</td>
<td>$1.78 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>0.185 (25 $^\circ$C)</td>
<td>153.7 at 85 mA g$^{-1}$</td>
<td>100</td>
<td>90.17</td>
<td>-100</td>
<td>[207]</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>PEO + LiTFSI</td>
<td>5.20</td>
<td>$1.51 \times 10^{-4}$ (25 $^\circ$C)</td>
<td>0.627 (60 $^\circ$C)</td>
<td>102.7 at 1700 mA g$^{-1}$</td>
<td>1000</td>
<td>87.10</td>
<td>99.2</td>
<td>[209]</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>PSEO + PEO</td>
<td>5.00</td>
<td>$1.07 \times 10^{-4}$ (30 $^\circ$C)</td>
<td>0.510 (30 $^\circ$C)</td>
<td>152.1 at 85 mA g$^{-1}$</td>
<td>150</td>
<td>94</td>
<td>-100</td>
<td>[211]</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>PEO + LiTFSI</td>
<td>5.00</td>
<td>$5.74 \times 10^{-4}$ (25 $^\circ$C)</td>
<td>0.204 (25 $^\circ$C)</td>
<td>155.6 at 34 mA g$^{-1}$</td>
<td>100</td>
<td>95</td>
<td>=100</td>
<td>[212]</td>
</tr>
<tr>
<td>ZIF-NH$_2$</td>
<td>PEO + LiTFSI</td>
<td>4.70</td>
<td>$3.40 \times 10^{-5}$ (60 $^\circ$C)</td>
<td>0.360 (60 $^\circ$C)</td>
<td>138.3 at 85 mA g$^{-1}$</td>
<td>650</td>
<td>79.50</td>
<td>-100</td>
<td>[216]</td>
</tr>
<tr>
<td>UIO-66</td>
<td>PEO + LiClO$_4$</td>
<td>4.90</td>
<td>$4.80 \times 10^{-5}$ (25 $^\circ$C)</td>
<td>0.390 (25 $^\circ$C)</td>
<td>160.0 at 170 mA g$^{-1}$</td>
<td>200</td>
<td>83</td>
<td>=100</td>
<td>[220]</td>
</tr>
<tr>
<td>UIO-66</td>
<td>PEO + LiTFSI</td>
<td>4.90</td>
<td>$3.00 \times 10^{-5}$ (25 $^\circ$C)</td>
<td>0.365 (25 $^\circ$C)</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>\</td>
<td>[221]</td>
</tr>
<tr>
<td>UIO-66-NH$_2$</td>
<td>PEO + LiTFSI</td>
<td>4.50</td>
<td>$2.56 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>0.200 (60 $^\circ$C)</td>
<td>164.0 at 17 mA g$^{-1}$</td>
<td>110</td>
<td>89.80</td>
<td>99</td>
<td>[222]</td>
</tr>
<tr>
<td>UIO-66-NH$_2$</td>
<td>SiO$_2$ + PEO + LiTFSI</td>
<td>4.20</td>
<td>$8.10 \times 10^{-5}$ (60 $^\circ$C)</td>
<td>0.680 (60 $^\circ$C)</td>
<td>151.0 at 17 mA g$^{-1}$</td>
<td>\</td>
<td>\</td>
<td>99.6</td>
<td>[223]</td>
</tr>
<tr>
<td>UIO-66-NH$_2$</td>
<td>S-ZrO$_2$ + LiTFSI + PVDF-HFP</td>
<td>5.00</td>
<td>$1.05 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>0.430 (60 $^\circ$C)</td>
<td>158.0 at 34 mA g$^{-1}$</td>
<td>55</td>
<td>\</td>
<td>-100</td>
<td>[224]</td>
</tr>
<tr>
<td>UIO-66-NH$_2$</td>
<td>PEO + BE@CM + LiTFSI</td>
<td>5.29</td>
<td>$1.04 \times 10^{-4}$ (90 $^\circ$C)</td>
<td>0.590 (60 $^\circ$C)</td>
<td>145.5 at 34 mA g$^{-1}$</td>
<td>30</td>
<td>\</td>
<td>96</td>
<td>[225]</td>
</tr>
<tr>
<td>UIO-66-2COOH</td>
<td>PVDF-HFP + LiTFSI</td>
<td>4.50</td>
<td>$1.06 \times 10^{-3}$ (25 $^\circ$C)</td>
<td>0.580 (25 $^\circ$C)</td>
<td>157.0 at 170 mA g$^{-1}$</td>
<td>500</td>
<td>95.50</td>
<td>-100</td>
<td>[185]</td>
</tr>
<tr>
<td>UIO-66-(F)$_3$</td>
<td>PEO + HPEI + LiTFSI</td>
<td>4.30</td>
<td>$2.01 \times 10^{-3}$ (30 $^\circ$C)</td>
<td>0.540 (30 $^\circ$C)</td>
<td>141.4 at 34 mA g$^{-1}$</td>
<td>200</td>
<td>\</td>
<td>=100</td>
<td>[217]</td>
</tr>
<tr>
<td>UIO-66-NH$_2$@67</td>
<td>PVDF-HFP + LiTFSI</td>
<td>=5.00</td>
<td>$2.09 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>$0.670$ (60 $^\circ$C)</td>
<td>143.5 at 34 mA g$^{-1}$</td>
<td>80</td>
<td>98.13</td>
<td>-100</td>
<td>[218]</td>
</tr>
<tr>
<td>UIO-66-NH$_2$@UIO-66-COOH</td>
<td>PEO + LiTFSI</td>
<td>5.00</td>
<td>$5.20 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>0.360 (60 $^\circ$C)</td>
<td>152.3 at 170 mA g$^{-1}$</td>
<td>100</td>
<td>98.45</td>
<td>-100</td>
<td>[228]</td>
</tr>
<tr>
<td>MOF-5</td>
<td>PTFEMA-ran-P(PEGMA) + LiTFSI</td>
<td>5.38</td>
<td>$1.44 \times 10^{-3}$ (30 $^\circ$C)</td>
<td>0.510 (60 $^\circ$C)</td>
<td>116.0 at 17 mA g$^{-1}$</td>
<td>25</td>
<td>92.20</td>
<td>-100</td>
<td>[230]</td>
</tr>
<tr>
<td>Ni-MOF</td>
<td>PEO + LiTFSI</td>
<td>4.90</td>
<td>$1.66 \times 10^{-3}$ (25 $^\circ$C)</td>
<td>0.378 (25 $^\circ$C)</td>
<td>130.0 at 17 mA g$^{-1}$</td>
<td>50</td>
<td>96.20</td>
<td>=100</td>
<td>[234]</td>
</tr>
<tr>
<td>Al-MOF</td>
<td>PEO + LiTFSI</td>
<td>4.70</td>
<td>$7.11 \times 10^{-4}$ (60 $^\circ$C)</td>
<td>0.460 (60 $^\circ$C)</td>
<td>167.3 at 17 mA g$^{-1}$</td>
<td>100</td>
<td>87.10</td>
<td>99</td>
<td>[235]</td>
</tr>
</tbody>
</table>

(continued on next page)
mechanisms are of great significance for advanced solid-state electrolytes [81]. These endeavors aim to achieve ion conductors with enhanced ion conductivity and solid-state batteries with improved performance. The presence of functional groups within MOFs plays a vital role in increasing their spatial density within the pores and reducing the distance between functional groups. By functionalizing the smaller pores of MOFs with -SH groups, the presence of functional groups within MOFs plays a vital role in increasing conductivity and solid-state batteries with improved performance. The -SH functionalized MOF (Zr-MA, MA: mercaptosuccinic acid), Zn2⁺, Na⁺, K⁺, Li⁺, Cs⁺, and Cu2⁺. These ionic conductors exhibited excellent ionic conductivity, with Zr-Ma-Li⁺-based SSEs demonstrating a high tLi⁺ (0.63), a wide electrochemical window (4.6 V), and the ability to suppress the growth of Li dendrites [187]. The concept of confining small amounts of LE within a host matrix with a nanoporous or sub-nanoporous structure holds promise for the development of QSSEs that meet the requirements of good electrode contact, low volatility, stability, and safe operation at high temperatures (Fig. 3e). Consequently, QSSEs were prepared to function normally and remain stable in harsh working conditions (90 °C), even after sustaining damage such as bending and cutting. These QSSEs were confined within the sub-nanochannels of flexible and porous MOFs (6.5 Å), offering the advantage of reduced weight compared to a typical pouch cell assembled with a lean electrolyte (3.5 mg cm⁻² vs. 4.5 mg cm⁻²). The developed QSSEs exhibited favorable Li⁺ conductivity comparable to ISE (Li₁₃Al₀.₃Ge₁.₇(PO₄)₃, LAGP) and typical LE (Fig. 3f) and demonstrated a wide electrochemical stability window [74].

QSSEs serve as an intermediate state between LEs and SSEs, offering advantages from both while avoiding their respective shortcomings. The incorporation of MOFs in QSSEs as SSEs provides several beneficial properties, including good thermal stability, high ionic conductivity, superior interfacial characteristics, and mechanical stability. These advantages stem from the electrically insulating nature, facile processability, and porous structure of MOFs, which allow for the confinement of small amounts of LEs within a host matrix. However, some limitations persist in MOFs-based QSSEs. The inclusion of a sufficient quantity of organic solvent is typically necessary to maintain a localized liquid-like environment, ensuring high ionic conductivity. Nonetheless, excessive amounts of Li salt and solvent can increase costs, reduce mechanical strength, and compromise ESDs. Furthermore, MOFs-based QSSEs significantly reduce interfacial resistance and enhance the performance of assembled SSBs compared to SSEs that consist of MOFs mechanically mixed with polymer binders. However, the presence of small amounts of LEs introduces risks and can impact the robustness of QSSEs, requiring extensive study as this transition state poses ongoing challenges.

### 3. MOFs-based optimization strategy for ASSEs

MOFs, possessing porous framework structures with open pore channels, offer the potential to accommodate Li salts and organic solvents, thereby exhibiting promising ionic conductivity at ambient temperature. However, the incorporation of Li salt and relatively large amounts of organic solvents introduces safety risks and deviates from the concept of SLLs. To address these challenges, ideal PSEs need to simultaneously meet several essential criteria, including high ionic conductivity, high tLi⁺, low interfacial resistance, excellent electrochemical/thermal stability, and mechanical properties. Among various PSEs, those based on PEO have garnered significant attention due to their favorable interfacial contact with electrodes, ease of fabrication, low cost, and strong solvation ability towards Li salts. However, the low ionic conductivity (<1 × 10⁻⁶ S cm⁻¹, RT), low tLi⁺ (~0.2), and inherent softness of PEO matrices limit their application in LMBs [188]. Numerous approaches have been explored to enhance the electrochemical and mechanical performance of PEO-based PSEs, including copolymerization, polymer blending, plasticizer addition, and incorporation of inorganic fillers [189].

#### 3.1. MOFs mixed with polymer for ASSEs

PEO is widely utilized as a polymer matrix for SSEs in Li batteries due to its excellent compatibility with Li salts, low interfacial resistance with anodes, ease of preparation, and cost-effectiveness [190]. However, one drawback of PEO, which is a highly successful SPE, is its semicrystalline nature. It tends to crystallize within a temperature range of 60–65 °C. To
overcome this limitation, CSEs have been developed by incorporating high ion-conductive inorganic fillers into PEO matrices. These composite electrolytes effectively enhance Li⁺ transport, interface wettability, thermal stability, and mechanical integrity through the synergistic combination of organic and inorganic components. Despite these advantages, batteries assembled with CSEs still face challenges associated with the growth of lithium dendrites within the polymer matrix and at the grain boundaries of inorganic ceramic electrolyte fillers during long-term cycling, which can lead to short-circuits and battery failure [191]. Table 5 summarizes the property of the recent MOF mix with polymer ASSEs.

Incorporating MOFs with active groups into CSEs can yield several beneficial effects. Through nucleophilic substitution, these MOFs fillers can introduce cationic groups, thereby enhancing the absorption of anionic species from Li salts through electrostatic interactions. This, in turn, improves the \( t_{\text{Li}} \) within the electrolyte. Additionally, polar functional groups can be grafted onto the surface of MOFs fillers to provide protection for the ether oxygen atoms in PEO chains via hydrogen bonding. These functional groups also aid in removing impurities at the interfaces, thereby extending the electrochemical stability window of the electrolyte [192]. Moreover, the presence of MOFs fillers with LAB sites on their surfaces can promote anion attraction, facilitating the dissolution of Li salts and resulting in the release of more free Li⁺. This phenomenon contributes to enhanced ionic conductivity and an improved \( t_{\text{Li}} \) value [193]. MOFs are highly promising fillers characterized by a range of exceptional properties. They exhibit favorable compatibility with PEO, facilitating the uniform dispersion of inorganic fillers within the polymer matrix. Additionally, they possess strong coordination capabilities with negative ions, thereby promoting the dissociation of Li salts. The exceptional adsorption ability of MOFs towards micro-molecules enhances interfacial stability and safety. Furthermore, the presence of numerous Li⁺ conducting channels in MOFs contributes to increased ionic conductivity. In a previous study, Wang et al. employed ZIF-8 as a plasticizer in PEO to reduce the glass \( T_g \) of the PEO electrolyte [194]. The incorporation of ZIF-8 resulted in the formation of Li⁺ conducting pathways within the PEO matrix, thus enhancing the ionic conductivity. Moreover, the high porosity and LAB sites of ZIF-8 offered benefits in terms of stabilizing the interfaces between the electrolyte and electrodes, further improving ionic conductivity. To enhance ion transport and improve the design of polymer networks, cross-linked copolymer electrolytes have been proposed as a feasible and effective strategy. This approach enables the creation of high-performance electrolytes with excellent thermal stability and enhanced wettability of the polymer matrix. In line with this, a novel UV cross-linked copolymer electrolyte based on ZIF-8, PEO-LiTFSI, and EMIM-TFSI was developed [195]. The porous structure of ZIF-8 serves as a stable three-dimensional framework capable of absorbing EMIM and TFSI, effectively restricting the migration of EMIM⁺ and TFSI⁻. The interactions between the ZIF-8 host and anions further contribute to enhanced ionic conductivity and the transport of Li⁺. Additionally, the UV irradiation process reduces the crystallization of the polymer, thereby increasing the amorphous region. The resulting cross-linked polymer matrix restricts the migration of larger anions and provides the copolymer electrolytes with excellent electrochemical and mechanical stability. This unique Li⁺ transport mechanism occurs at the solid-liquid transport interface of the polymer chains and ZIF-8, transitioning from a “chain-chain” configuration to a “chain-ZIF-8-chain” configuration, as depicted in Fig. 5a. Moreover, the unique polymer matrix-PEDOT with ILs and electrolytes can lead to synergistic effects. To achieve a more uniform distribution of nanofillers in polymer-BCS, ILs containing siloxane groups were chemically decorated onto a MOF called ZIF-90 through a dehydration condensation reaction at high temperature, resulting in the formation of ZIF-90-g-IL nanofillers [196]. The incorporation of PEO/ZIF-90-ILs in CSEs exhibited several advantages, including a wider electrochemical stability window, higher ionic conductivity, and increased \( t_{\text{Li}} \). In comparison to PEO, PVDF possesses a relatively wide electrochemical window and superior thermal and mechanical properties. However, Li⁺ cannot migrate through segmental motion in PVDF, unlike in PEO at RT [197,198]. To address this limitation, the surface of PVDF-based SSES is modified by introducing Nickel Oxalate, resulting in a smoother surface similar to PEO. Moreover, the dissociation of LiTFSI is facilitated by the presence of LAB in ZIF-8, leading to the generation of more free Li⁺ [199].

While MOFs and MXene materials exhibit excellent flame resistance properties, MOF nanoparticles and MXene layers often suffer from issues such as agglomeration and restacking [193,200,201]. To overcome these challenges and achieve synergistic enhancements in CSEs, an ordered combination of MOFs and MXene is proposed. Hybrid nanosheets were fabricated by horizontally extending MOFs on the MXene skeleton, resulting in two-dimensional (2D) ZIF-8 modified Ti₃C₂-MXene (ZIF-8@MXene) nanosheets. These nanosheets, along with CSEs consisting of PEO and PVDF-HFP, demonstrated several improvements. The ZIF-8@MXene nanosheets formed hydrogen bonds with polymer molecules, enhancing the tensile strength of the electrolyte. Additionally, the nanosheets provided abundant functional groups and large accessible surface areas, facilitating the dissociation of Li salts and increasing Li⁺ conductivity by creating channels for Li ion transport [202-204].

Glass fiber (GF) membranes have gained significant attention as separators for liquid LIBs due to their notable features, including high porosity, excellent absorption capacity, remarkable mechanical strength, and thermal/chemical stability [205]. To enhance their performance, a strategy involving the \textit{in-situ} growth of zeolitic imidazolate framework-67 (ZIF-67) on GF membranes (GF@ZIF-67) was employed, followed by the infiltration of a precursor solution of a PEO-based polymer matrix. This resulted in the successful construction of anion-immobilized and fiber-reinforced CSEs (GF@ZIF-67@PEO) [206]. The 3D skeleton provided by GF@ZIF-67 enhances the mechanical strength, while the OMS of ZIF-67 immobilizes free anions within the polymer matrix, promoting ion migration and facilitating long-term cycling stability. Zhao et al. synthesized ZIF-77 with different morphologies and incorporated them into PEO to form reinforced CSEs [207]. The resulting electrolytes exhibit an ionic conductivity (1.51 \( \times \) \( 10^{-5} \) S cm⁻¹ at 25 °C) approximately five times higher than that of pure PEO-based PSEs. They also demonstrate a wider electrochemical window, higher \( t_{\text{Li}} \), and improved compatibility with Li metal compared to PEO-based electrolytes. Lithium alginate (LA), a natural and cost-effective polymer with environmental benefits, was utilized as an electrospinning substrate material. It was employed in \textit{in-situ} composite ZIF-67 onto an electrospray composite membrane composed of polyacrylamides (PAM) [208]. The resulting modified electrolyte matrix (ZIF-67@LA-PAM) forms a 3D network structure that enhances the required mechanical strength of the electrolyte (Fig. 4b) [209].

Previous study has demonstrated that electrospray membranes have the capability to form a stable interfacial layer, thereby increasing the contact between the electrode and the electrolyte. This leads to a more uniform distribution of Li⁺ flux, enabling the homogeneous deposition of Li⁻ and effectively suppressing dendrite proliferation [210]. The combination of ZIF-67 and porous electrosprinning membranes provides a network of ion transport pathways that facilitate fast ion conduction and uniform Li⁺ deposition. The presence of abundant polar functional groups in modified LAB enables strong hydrogen bond interactions, enhancing the mechanical strength and suppressing the formation of Li dendrites. Incorporating MOFs into polymer nanofibers not only improves the mechanical strength but also guides the nanofibers to form a long-range 1D structure. This attachment of nanoparticles to the polymer fibers results in a significant increase in the nanoparticle content (Fig. 4c). Sulfonated polyethersulfone (PES), known for its high mechanical strength and excellent heat resistance, can serve as a transition site for Li⁺ due to the electronegativity and Coulomb force of the sulfonate groups on the polymer chain. By anchoring ZIF-67 \textit{in-situ} within PSES and combining it with a PEO matrix, a 3D framework CSEs (ZIF-67-PSES-PEO) is fabricated (Fig. 4d) [211]. The robust nature of this
CSE, facilitated by MOFs, promotes the dissociation of Li salts through interactions with LABs, leading to the release of more free Li\(^+\). Moreover, the attachment of MOFs on PSES nanofiber membranes creates a continuous 3D organic-inorganic ion transport pathway, reducing particle agglomeration and significantly improving ionic conductivity. The prepared 3D-ordered organic-inorganic ion transport path facilitates the uniform deposition of Li\(^+\), thereby minimizing the formation of Li dendrites (Fig. 4e). Among various 3D printing (3DP) methods, direct ink writing (DIW) has garnered considerable attention due to its simplicity and cost-effectiveness. Li et al. developed a universal RT 3DP strategy to create PEO-MOFs hybrid SSEs that effectively inhibit dendrite formation (Fig. 4f). This strategy utilizes DIW to fabricate the hybrid SSEs, providing enhanced dendrite suppression capabilities [212]. The Li\(^+\) diffusion coefficient of a LFP||Li cell was determined using the galvanostatic intermittent titration technique (GITT) method (Fig. 4g). The incorporation of ZIF-67 nanopores as a filler promotes the migration of Li\(^+\), resulting in significantly enhanced Li\(^+\) diffusion coefficients. Specifically, during the charging and discharging processes, the diffusion coefficients were measured to be approximately $10^{-11.5}$ cm\(^2\) s\(^{-1}\) and $10^{-11}$ cm\(^2\) s\(^{-1}\), respectively. These findings highlight the excellent electrochemical performance of the system, indicating a high level of ionic conductivity. ZIF-67 has emerged as a prominent research subject.
particularly in the context of 3D printed ZIF-67@PEO/LiTFSI hybrid SSEs, which exhibit exceptional performance in inhibiting the formation of Li dendrites. The formation of a LiF-rich SEI layer offers significant advantages in terms of Li$^+$ transport and electrochemical performance [213]. Constructing artificial LiF-rich SEI film represents an effective strategy to suppress the nucleation of Li dendrites and minimize side reactions by optimizing the composition and enhancing ionic conductivity [214]. The design of functional MOFs, involving ligand selection and the choice of secondary building units for metal ions, holds promise for achieving high porosity, homogenous doping of heterogeneous atoms, and adjustable morphology, which could facilitate the generation of LiF-rich SEI [215]. In the realm of organic molecular catalysis, fillers such as ZIF-NH$_2$ and ZIF-CH$_2$ have been synthesized to promote the formation of LiF-rich SEI in PEO-based systems [216]. Compared with the Van der Waals force, the hydrogen-bond interaction between -NH$_2$ and PEO chains is more powerful to interrupt the ordered arrangement and reduce the crystallinity of PEO. Furthermore, the organic catalytic interphase formed between Li metal and the electrolyte by ZIF-NH$_2$ helps to mitigate side reactions and stabilize the plating/stripping process of Li metal at the electrolyte/Li interface, thereby improving the cycling performance of the CSEs cells.

Zirconium-based MOFs, known for their exceptional stability and microporous structure, have attracted significant attention. However, the analysis of the interaction mechanism between the open-framework structure of MOFs and polymers remains an active area of research [219]. Gaining a comprehensive understanding of the intermolecular interactions within the system and their influence on performance is crucial for the development of high-performance CSEs. In this context, a functional filler, Uio-66, characterized by its monodispersed size and porous structure, has been introduced to modify the properties of PSEs (PEO-LiClO$_4$), leading to improvements in both physicochemical and electrochemical properties [220]. Similarly, nano-sized Uio-66 has been incorporated into PEO-LiTFSI [221]. By loading amine-functionalized Uio-66 onto PEO (Uio-66-NH$_2$@PEO), the electronic effect and corresponding pore polarity were tuned, effectively preventing Li electrodeposition and ensuring stability over hundreds of charge-discharge cycles and more than 1500 operating hours. This approach has demonstrated a tenfold increase in cyclability compared to conventional PEO-based SSEs [222]. The addition of fillers generally disrupts the crystalline phase of the polymeric host, promoting the segmental motion of the polymer chains and enhancing ionic conductivity. To this end, Zhou et al. employed Uio-66-NH$_2$ anchored on silica (SiO$_2$) microparticles (Uio-66-NH$_2$@SiO$_2$) as a microporous functional additive in a PEO matrix. This composite exhibited pronounced microporosity, chemical stability, and abundant chemical functionalities within its cages, including hydroxyl and amine groups. The cages and channels of Uio-66-NH$_2$@SiO$_2$ provided efficient diffusion pathways for Li$^+$ [223]. Furthermore, Uio-66-NH$_2$ and surface-functionalized metal oxide particles (S-ZrO$_2$) were incorporated into a PVDF-HFP polymer matrix, enabling anion trapping through LAB interactions and facilitating abundant channels for Li$^+$ migration [224]. The hydrogen bonds formed between the F atoms of PVDF-HFP chains and -NH$_2$ groups reinforced the structural stability, while the incorporation of S-ZrO$_2$ offered a cost-effective means of inducing anions.

The presence of ionogenic chemical groups in transmembrane proteins has been demonstrated to facilitate metal ion transport. Similarly, MOFs possess ionogenic chemical groups capable of binding and transporting Li$^+$. DFT calculations have indicated that MOFs can act as favorable relay centers for Li$^+$, and a higher density of these centers correlates with improved ionic conductivity. Enhancing the interfacial compatibility between SSEs and electrodes requires the design of microscale interfacial architectures that effectively increase the contact area between the two components and promote Li$^+$ transport across the interface. To achieve this, a well-dispersed form of Uio-66-COOH was developed by decelerating its nucleation process [185]. Furthermore, to further improve the dispersion of MOFs within the polymer matrix, the surface of Uio-66-NH$_2$ was decorated with polycaprolactone (PCL) through ring-opening polymerization of ε-caprolactone, induced by the amino groups (MOF-PCL). This modification enables uniform dispersion of MOFs and enhances their compatibility with the polymer matrix. The resulting CSEs, fabricated using a combination of poly(ethylene glycol) diacrylate (PEGDA), boron ester monomer (BEM), LiTFSI, and MOF-PCL, were synthesized through UV-light photopolymerization [225]. Specifically, the double-network structure formed by PEGDA and BEM through effective cross-linking provides sufficient mechanical strength to impede the growth of Li dendrites. Simultaneously, the dispersion of MOF-PCL within the matrix further improves ion conduction and mechanical properties. Another approach involves the facile synthesis of a composite composed of cross-linked hyperbranched polymer matrix polyethylene glycol (PEG)-hyperbranched poly(ethylene imine) (HPEI), LiTFSI, and a fluorine-containing MOF, namely Uio-66-(F)$_3$ (Fig. 4b) [217].

The PEG-HPEI matrix is synthesized through a Schiff’s base reaction between aldehyde-terminated PEG and HPEI, offering a straightforward method for its preparation. The resulting hyperbranched cross-linked PEG-HPEI electrolyte matrix possesses a hyperbranched structure that facilitates a higher number of EO units for Li$^+$ conduction compared to a linear PEO matrix, thereby contributing to enhanced ionic conductivity. In the context of solidification, the use of spherical nanoparticles (SNs) with smooth edges holds great promise in reducing stress and deformation during the solidification process of PSEs, indicating their potential in fabricating highly uniform CSEs. SNs exhibit a notable reduction in the crystallinity of PSEs, while their larger surface area, relative to other nanoparticle shapes, enhances the contact area with the polymer matrix, leading to the improved mechanical strength of the resulting CSEs. Moreover, the surface roughness of SNs plays a crucial role in enhancing Li$^+$ transport by increasing the effective contact area between the electrolyte and electrodes. Although Uio-67 possesses high ionic conductivity, it is limited by its low t$_{1/2}$, which hampers its practical applicability [226]. In contrast, Uio-66-NH$_2$, featuring a smaller pore size, exhibits the ability to enhance t$_{1/2}$ and effectively restrict the mobility of relatively larger ions [227]. Taking advantage of the strengths of both MOFs, the design of a Uio-66-NH$_2$@67 core-shell structure presents a promising solution to overcome the limitations associated with low specific surface area and relatively low ionic conductivity (Fig. 4j) [218]. The Uio-67 shell structure possesses a high specific surface area and large pore size, contributing to improved ionic conductivity but reduced t$_{1/2}$. Conversely, the Uio-66-NH$_2$ core structure restricts the mobility of larger ions and further enhances t$_{1/2}$ due to its smaller pore size. Uio-66-NH$_2$@67 was added PVDF-HFP showed a high ionic conductivity (2.09 × 10$^{-4}$ S cm$^{-1}$, 60 °C) and t$_{1/2}$ (0.67). Additionally, a novel MOF material, MOF-2, is synthesized by combining two functionalized Uio-66 materials, namely Uio-66-NH$_2$ and Uio-66-COOH, which are subsequently used as additives in the fabrication of novel PEO-based CSEs [228]. The inclusion of amino and carboxyl groups in Uio-66 imparts excellent LAB interactions, contributing to improved performance of the resulting CSEs. The CSEs showed high ionic conductivity (5.20 × 10$^{-4}$ S cm$^{-1}$), wider electrochemical potential window (5.0 V), and excellent cycling performance with 98.45% capacity retention at 149.92 mA h g$^{-1}$ after 100 cycles operation (1.0 C, 60 °C).

The formation of a flexible, free-standing, and film-forming polymer matrix, P(TFEMA-ran-PEGMA), is achieved through the free radical copolymerization of trifluoroethyll methacrylate (TFEMA) and poly(ethylene glycol) methacrylate (PEGMA). MOF-5, an isoreticular MOF-1 (IRMOF-1), exhibits a cubic structure with ZnO$_4$ groups located at the corners. These ZnO$_4$ units are interconnected through [O$_2$C-C$_6$H$_4$CO$_2$] (1,4-benzenedicarboxylate, BDC) groups, forming a chemically robust benzene-linked framework [229]. The solution-casting method is employed to fabricate composite films using a well-dispersed solution of P(TFEMA-ran-PEGMA), MOF-5 particles, and LiTFSI in tetrahydrofuran (THF). This approach leads to enhanced electrochemical performances and thermal stability [230]. The addition of polarizing additives, such as
MOF-5-like nanoparticles, to PEO-LiTFSI structures results in increased ionic mobility by facilitating the release of Li cations from TFSI⁻ and PEO chains [231]. Molecular dynamics simulations are employed to investigate the effects of interactions within the MOF-5 with the PEO-LiTFSI system on ionic conductivity. The presence of LAB on the MOF-5 surface enhances ionic conductivity by promoting the separation of Li⁺ from TFSI⁻ anions and enabling the release of Li⁺ from regions between PEO chains [232]. Furthermore, nickel-based ultrathin MOF nanosheets (Ni-MOF) with good stability are synthesized using a simple ultrasonic strategy and incorporated into a PEO electrolyte. The Ni-MOF nanosheets consist of Ni nodes and aromatic benzenedicarboxylic acid (BDC)₂-organic ligands, exhibiting an inorganic-organic hybrid property that enhances the miscibility with PEO and improves the mechanical integrity [233]. The ultrathin nanosheet structure of Ni-MOF facilitates shorter and continuous ion transfer paths at the interfaces between the CSEs and Ni-MOF. Additionally, the central metal ions in Ni-MOF, with smaller coordination numbers, further enhance the interaction with the CSEs. These exceptional structural properties of Ni-MOF contribute to the significant improvement in t_{lf} and ionic conductivity of the resulting CSEs [234].

The synthesis of Al-MOF (Al(OH)(1,4-NDC)) incorporated into a PEO matrix was achieved using a straightforward solution-casting method to fabricate Al-MOF-PEO CSEs [235]. The Al-MOF particles exhibit spherical/quasi-spherical 1D nanorod morphology with an average length of approximately 1.6 μm. Upon embedding in the polymer matrix, they form a 3D network, reducing the crystallinity of the PEO matrix. The microporous nature of Al-MOF facilitates the transportation of Li⁺ while impeding the movement of bulky TFSI⁻ anions. As a result, the Al-MOF-PEO system demonstrates significant improvements in key electrochemical properties, including ion conductivity, electrochemical window, thermal stability, and t_{lf} [235]. Zn-MOF, characterized by its high mechanical strength, serves to prevent Li dendrite puncture. The Zn-MOF layer exhibits excellent electrolyte wettability, effectively reducing surface concentration gradients and screening ions, thus hindering anion migration. These characteristics contribute to an enhanced t_{lf} by promoting a uniform Li⁺ flux and inhibiting Li dendrite formation. The development of a SEI film with appropriate toughness, simple preparation process, good interfacial contact, and high Li⁺ conductivity is crucial. Polyvinyl alcohol (PVA), an environmentally friendly polymer organic material, possesses desirable attributes such as insolubility in organic solvents, favorable film formation, and absence of toxic side effects on the human body [236]. The addition of LiTFSI increases the viscosity and ionic conductivity of PVA [237]. PVA acts as a “glue” to form an artificial SEI film by cementing the Zn-MOF sheet. In-situ construction of Zn-MOF on a Cu foil ensures high ion conductivity, and the abundant polar bonds (O-H, Zn-N) on its surface facilitate Li⁺ adsorption and rapid diffusion to the artificial SEI film. Spin-coating enables the penetration of PVA into the surface of the Zn-MOF layer, cementing it without affecting Li⁺ conduction throughout the film layer and providing exceptional flexibility [238]. The resulting artificial SEI film effectively accommodates volume changes during cycling, significantly enhancing the stability of Li metal anodes and extending battery cycle life. Li-MOFs have also been designed and utilized in PEO-based SSEs. Their pore structure and interconnection effect create a pathway for Li⁺ (Fig. 5a) [239]. Additionally, the N(CH₃)₂ functional group may react with Li metal, forming a stable SEI layer that suppresses Li dendrite formation.
The incorporation of CeO$_2$ particles into a PEO matrix allows for the development of CSEs. The presence of defective or catalytic sites on the surface of CeO$_2$ likely plays a role in enhancing the interaction behavior and improving ion conductivity [240]. Ce-MOF, possessing abundant OMSs, can reinforce CSEs and enhance the electrochemical and mechanical performance of SSBs. The distribution of 3D structured grains as crosslinking centers within the PEO matrix prevents polymer reorganization, reduces the crystalline phase ratio, and enhances polymer chain motion, ultimately resulting in high ion conductivity [241]. These sites facilitate strong interactions with both PEO and Li salt, leading to high t$_{Li}^+$ and conductivity. In this study, Cu-MOF-74 particles (Fig. 5d) with abundant OMSs were used as fillers in PEO (Cu-MOF-74@PEO). The high-density exposed Cu$^{2+}$ sites coordinate with TFSI$^-$ and release free Li$^{+}$, as confirmed by DFT calculations (Fig. 5b). Cu-MOF-74@PEO (Fig. 5c) exhibits improved t$_{Li}^+$ (0.3) and high ion conductivity (5.5 $\times$ 10$^{-5}$ S cm$^{-1}$ at 30 $^\circ$C) [242]. Fe-MIL-88B MOF (Fe-MOF) was employed as fillers to modify PEO polymer electrolytes with high thermal stability, which facilitates the formation of LAB on the surface [243]. The LAB interaction between PEO and Fe-MOFs increases the concentration of mobile lithium ions, resulting in significantly improved ionic conductivity and t$_{Li}^+$ [244]. A straightforward solution-casting method was used to prepare CSEs by incorporating MIL-100 (Fe) MOFs with PEO, LiTFSI, and PVDF. PVDF acted as an auxiliary adhesive binder for MIL-100 (Fe), and the unsaturated metal sites in the MOFs promoted Li disassociation through LAB interactions with anions, as confirmed by DFT calculations (Fig. 5e) [245]. Furthermore, the PEO chains were threaded into the pores of amino-functionalized porous MOF (NH$_2$-MOF) nanosheets through hydrogen-bonding interactions between EO and -NH$_2$ groups. The subsequent low-pressure filtration process facilitated the threading of PEO chains into the pores, resulting in the assembly of free-standing, thin laminar CSEs. This threading of PEO chains improves chain motility and ensures a strong lock between adjacent MOF nanosheets, leading to enhanced microstructures and electrochemical properties [246].

The construction of a transport path for Li$^+$ between MOF particles and the reduction of interfacial resistance between MOFs and electrodes are vital mechanisms for utilizing MOFs in high-performance LMBs (Fig. 5g). A novel strategy to fabricate cross-linked chains of MOFs using a network of BC has been proposed to eliminate the interface between MOF particles and establish a continuous path for ion transport. MOFs functionalized with high-density electronegative groups, such as Zr-BPDC-2SO$_3$H, can facilitate ion transport along the pore channels. This modification leads to significantly improved ionic conductivities, particularly in the case of Li$^+$ (as shown in Fig. 5h) [62]. The HKUST-1 MOF demonstrates good compatibility with the polymer substrate, enabling even dispersion and preventing agglomeration. The MOF's OMSs effectively capture anions and release more Li$^{+}$, enabling their free conduction. Additionally, HKUST-1 exhibits certain flame-retardant properties [247]. The possible mechanism for its performance enhancement in PEO-based PSES involves a combination of thermal barrier effects, making it an effective multifunctional additive that enhances both the electrochemical performance and fire safety of the system [248]. By incorporating activated HKUST-1 as a reinforcing phase, the glass transition temperature (T$_g$) is reduced with captured TFSI$^-$, leading to improved t$_{Li}^+$, enhanced mechanical properties, and overall enhanced electrochemical performance.

In general, a wide range of commonly used polymers can be combined with MOFs possessing specific diameters and functional groups to form a variety of MOF composites. These composites inherit the advantages of MOFs, such as stability, plasticity, increased active metal sites, and high porosity, among others. Moreover, they exhibit interactions with the liquid electrolyte, benefiting from the transfer routes provided by the MOF particles. This promotes both ion conduction and polymer motion segments, thereby significantly enhancing the electrochemical performance of batteries [249,250]. Therefore, CSEs composites with MOFs hold great potential as SSSEs [251]. However, the exact mechanisms underlying the interactions between these components remain unclear. Many coordinatively unsaturated cationic metal sites or functionalized cationic groups within MOFs effectively anchor anions, while the OMSs or functional groups on MOFs mainly facilitate selective ion transport in SSSEs. Most MOF-based SSSEs rely on such an ion transport mechanism, which leverages the intrinsic properties of MOFs to achieve a homogeneous ionic flux, uniform plating behavior, and dendrite-free electrodeposition. Notably, the introduction of MOFs has been observed to significantly improve t$_{Li}^+$ in most MOF-based SSSEs. Nevertheless, further investigation is required to gain a comprehensive understanding of their functional mechanisms, especially with regards to the effects of MOF fillers’ morphologies, pore sizes, metal centers, and ligands on battery properties. Additionally, several key considerations must be taken into account for the application of MOFs. Firstly, MOFs should possess channels that facilitate ion transport, as low ionic conductivity and restricted electrochemical windows can limit the suitability of SSSEs. Secondly, MOF-based SSSEs should exhibit sufficient Young’s modulus to prevent dendrite growth, as only adequate mechanical strength can effectively mitigate this issue. Lastly, MOF attachments must maintain stability at the electrode interface to ensure stable cycling and prevent the inhomogeneous deposition of ions.

3.2. MOFs with composite interface structure for ASSEs

CSEs have emerged as promising candidates for advanced energy storage systems, offering a combination of higher ionic conductivity, mechanical robustness, and electrochemical stability. To enhance the performance of CSEs, various approaches have been explored, including the incorporation of low-dimensional inorganic electrolyte fillers, oxide nano-fillers, novel functional materials, and internal structure design, aiming to improve ionic conductivity, t$_{Li}^+$, and expand the electrochemical window. However, challenges associated with the solid-solid interface between CSEs and electrodes, such as inherent gaps and unstable connections, remain unresolved. Table 6 summarizes the properties of the recent MOF composite interface structure design for ASSEs. In order to address these challenges, a bilayer heterostructure electrolyte consisting of a soft-humid composite gel and a tough ion-conductive matrix has been proposed as a solution [252]. The robust matrix is composed of a uniform mixture of PVDF-HFP, LiTFSI, and garnet nanowires, providing flexibility and high voltage stability against the cathode. The gel-like component, formed by the fusion of HKUST-1 and PEO/PVDF-HFP, promotes good interfacial contact and stabilizes the electrochemical reaction at the Li anode. This heterointerface solid-state electrolyte enables fast and uniform Li$^{+}$ transmission, thanks to its electrochemically and chemically stable interface, allowing long-term plating/striping for Li anodes, as well as efficient capacity output and cycling stability for SSSEs. To address interface-related issues, the introduction of a buffer interlayer between the electrolyte and electrodes has been proven effective [253,254]. Polymeric films have been utilized as physical barriers to establish reaction-free contact with the Li anode, although they often exhibit moderate ionic conductivities and poor cycling stability. The incorporation of solid fillers within the polymeric film represents an effective approach to improving overall properties [37,255]. The choice of MOF materials and their physicochemical characteristics play a crucial role in interlayers/coating layers, influencing interfacial performance. For instance, an ionic conductive MOF (ZIF-67)-incorporated polymeric interlayer with high flexibility and excellent adhesiveness has been developed as a coating layer for Li$_{1.5}$Al$_0.5$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) [256]. This interlayer ensures intimate and conformal contact between the electrode and electrolyte, facilitating fast ion migration, uniform Li$^{+}$ flux, and long-term cycling stability. Fluorinated electrolytes have shown promise for forming stable anion-derived SEIs due to weak Li-F interactions, favoring the negative electrode side, while also providing prominent oxidation resistance to the positive electrode [257]. To restrain Li dendrite deposition and prevent interfacial parasitic reactions, an interfacial layer rich in fluorinated UO$_2$-66 was
prepared and applied to enhance the interfacial performance of SSBs. This interfacial layer, consisting of Li2La2Zr2O12 (LLZO), LiTFSI, and PVDF-HFP as the electrolyte, shares the same polymer substrate as the interfacial layer, aiming to reduce the interfacial impedance between the interfacial layer and the CSEs [258] (Fig. 6a).

In order to address the issue of Li dendrite growth, various types of fillers have been introduced to enhance the mechanical modulus and ionic conductivity of PSEs. However, the presence of fillers often leads to aggregation within the matrix, resulting in phase separation and the deterioration of well-defined ion-conducting paths. As a consequence, the ionic conductivity and energy density of batteries are significantly reduced [174]. To overcome these challenges, multilayer or the ionic conductivity and energy density of batteries are significantly deteriorated. To address this problem, a designed 3D asymmetric SPE structure, the ZIF-8 layer with high porosity (rt) is fabricated as a protective layer on the Li electrode side, thus inhibiting side reactions between SN and Li metal [269]. The PEO@ZIF-8 system exhibits outstanding cycle performance [265]. To improve the ionic conductivity of PEO-based electrolytes, plastic crystal SN has been widely used as a coupling agent. SN reduces the crystallinity of PEO and enhances the solubility of the Li salt [174,266]. Li-TFSI and PVDF-HFP are commonly used as the main component of the 3D flame-retardant skeleton. This skeleton incorporates environmentally friendly halogen-free aluminum diethylphosphinate (ADP) flame retardant (PVDF-HFP/ADP, 3DPA) [262,263]. ADP, containing Al and P elements, has been proven to modify and optimize the SEI layer. The 3DPA composite effectively prevents the accumulation of ADP particles, provides mechanical support, and enhances flame retardancy [264]. The addition of Li-ILs absorbed by the pore structure of ZIF-8, resulting in Li-ILs@ZIF-8, together with the incorporation of 3DPA into the PEO matrix, leads to synergetic effects, excellent overall performance, and outstanding cycle performance [265]. To improve the ionic conductivity of PEO-based electrolytes, plastic crystal SN has been widely used as a coupling agent. SN reduces the crystallinity of PEO and enhances the solubility of the Li salt [174,266–268]. However, PEO/SN-based electrolytes suffer from poor mechanical properties and the instability of SN within the PEO-based electrolyte [176]. The inclusion of MOFs helps in the uniform deposition of Li+ on the anode side, thus inhibiting side reactions between SN and Li metal [234,252]. The addition of ZIF-67 filler to PEO/SN-based SSEs increases the ionic conductivity and efficiently suppresses Li dendrite growth, reducing the side reactions between SN and Li metal [269]. Furthermore, maximizing the intrinsic functionality of MOFs to regulate Li+ distribution and enhance the thermal stability of separators is considered an effective strategy for enhancing safety. One such strategy involves the fabrication of a functional constructed called MOFs/polymer/MOFs separator (MPMS). This involves the in-situ growth of a continuous rigid MOF layer (ZIF-67) on both sides of a dopamine pre-modified high-temperature resistant poly-arylene ether nitrile (PEN) porous membrane (PEN@PDA). The homogenous MOF surface layer is formed by tuning the solvent composition of the MOF precursor solution, resulting in fine morphology and surface coverage (Fig. 6c) [270]. The MPMS facilitates uniform diffusion of Li+ transport channels and fast electrolyte diffusion. The anionophilic

<table>
<thead>
<tr>
<th>MOF and Material</th>
<th>Polymer</th>
<th>Electrochemical Window (V)</th>
<th>ρ (Ω cm⁻¹)</th>
<th>ionic conductivity (cm² s⁻¹)</th>
<th>Specific Capacity (mAh g⁻¹)</th>
<th>Cycles</th>
<th>Retaining (%)</th>
<th>Coulombic Efficiency (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HKUST-1 + LLZN</td>
<td>PEO + PVDF-LLZO</td>
<td>4.92</td>
<td>2.00 × 10⁻⁴ (25 °C)</td>
<td>0.62</td>
<td>130.1 at 170 mA g⁻¹</td>
<td>200</td>
<td>89.50</td>
<td>~100.0</td>
<td>[252]</td>
</tr>
<tr>
<td>ZIF-67 + LAGP</td>
<td>PEO</td>
<td>4.00</td>
<td>2.60 × 10⁻⁴ (60 °C)</td>
<td>\</td>
<td>138.0 at 17 mA g⁻¹</td>
<td>60 (60 °C)</td>
<td>79.70</td>
<td>\</td>
<td>[256]</td>
</tr>
<tr>
<td>UIO-66(F) + LLZO</td>
<td>PVDF-HFP</td>
<td>5.13</td>
<td>4.90 × 10⁻⁴ (RT)</td>
<td>0.51</td>
<td>150.7 at 85 mA g⁻¹</td>
<td>960</td>
<td>90.71</td>
<td>99.2</td>
<td>[258]</td>
</tr>
<tr>
<td>PI-ZIF-8</td>
<td>PEGDA + BMA</td>
<td>4.90</td>
<td>4.70 × 10⁻⁴ (RT)</td>
<td>0.68</td>
<td>135.0 at 100 mA g⁻¹</td>
<td>100 (25 °C)</td>
<td>95.60</td>
<td>~100.0</td>
<td>[193]</td>
</tr>
<tr>
<td>EMI-TFSI @ZIF-8</td>
<td>ZIF-8@PEO</td>
<td>4.90</td>
<td>9.02 × 10⁻⁴ (60 °C)</td>
<td>\</td>
<td>150.4 at 40 mA g⁻¹</td>
<td>100 (60 °C)</td>
<td>83.20</td>
<td>~100.0</td>
<td>[261]</td>
</tr>
<tr>
<td>Li-ILs</td>
<td>PEO + PVDF-LLZO</td>
<td>4.80</td>
<td>9.10 × 10⁻⁴ (55 °C)</td>
<td>0.40</td>
<td>150.6 at 85 mA g⁻¹</td>
<td>300 (55 °C)</td>
<td>90</td>
<td>\</td>
<td>[265]</td>
</tr>
<tr>
<td>ZIF-67</td>
<td>HFP/APD</td>
<td>4.50</td>
<td>1.78 × 10⁻⁵ (RT)</td>
<td>0.65</td>
<td>156.8 at 34 mA g⁻¹</td>
<td>70 (60 °C)</td>
<td>92.30</td>
<td>\</td>
<td>[269]</td>
</tr>
<tr>
<td>ZIF-67</td>
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<td>4.89</td>
<td>1.57 × 10⁻⁵ (25 °C)</td>
<td>0.81</td>
<td>154.0 at 85 mA g⁻¹</td>
<td>240</td>
<td>96.30</td>
<td>\</td>
<td>[270]</td>
</tr>
<tr>
<td>3D-UIO-66 + PAN</td>
<td>PEO + PC</td>
<td>4.70</td>
<td>2.89 × 10⁻⁴ (25 °C)</td>
<td>0.52</td>
<td>152.0 at 34 mA g⁻¹</td>
<td>300</td>
<td>86</td>
<td>99.8</td>
<td>[134]</td>
</tr>
<tr>
<td>UIO-66-NH2 + PAN</td>
<td>PVDF-HFP + SiO2</td>
<td>5.68</td>
<td>2.23 × 10⁻⁵ (60 °C)</td>
<td>0.80</td>
<td>152.6 at 85 mA g⁻¹</td>
<td>120 (60 °C)</td>
<td>98.30</td>
<td>99.0</td>
<td>[274]</td>
</tr>
<tr>
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<td>5.00</td>
<td>4.90 × 10⁻⁴ (25 °C)</td>
<td>0.72</td>
<td>160.0 at 34 mA g⁻¹</td>
<td>110</td>
<td>\</td>
<td>~100.0</td>
<td>[277]</td>
</tr>
<tr>
<td>HKUST@Pi</td>
<td>PVDF</td>
<td>4.50</td>
<td>2.38 × 10⁻⁴ (RT)</td>
<td>0.56</td>
<td>152.8 at 40 mA g⁻¹</td>
<td>500 (30 °C)</td>
<td>90 (NMC)</td>
<td>99.5</td>
<td>[271]</td>
</tr>
<tr>
<td>2D Cu(BDC)</td>
<td>PVDF + NWF</td>
<td>5.00</td>
<td>2.40 × 10⁻⁴ (30 °C)</td>
<td>0.61</td>
<td>164.0 at 20 mA g⁻¹</td>
<td>80 (30 °C)</td>
<td>99.4</td>
<td>\</td>
<td>[272]</td>
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<tr>
<td>NH2-MIL-101(Fe)</td>
<td>PEO + PVDF</td>
<td>5.10</td>
<td>5.70 × 10⁻⁴ (60 °C)</td>
<td>0.35</td>
<td>159.4 at 34 mA g⁻¹</td>
<td>100</td>
<td>\</td>
<td>\</td>
<td>[270]</td>
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</table>
characteristic and well-defined intrinsic microporous structure of the MOF layer on the PEN@PDA membrane promote Li\(^{+}\) transport. DFT calculations confirm the restriction of anion migration by the MOF layers. The sandwich structure of ZIF-67/PEN@PDA/ZIF-67, abbreviated as MPMS, with its large specific surface area and uniform microporous size, enables homogeneous Li dendrite growth and highly stable Li plating-stripping.

Simultaneously achieving fast ion transport, homogeneous Li\(^{+}\) flux, excellent interfacial compatibility, and enhanced mechanical strength is crucial for the development of CSes. In this regard, a rational approach involves the construction of 3D interconnected MOFs network-based CSes through electrospinning, followed by backfilling with polymer/Li salt. The 3D interconnected MOF/PAN network provides a continuous and fast Li\(^{+}\) transport pathway between MOFs, effectively increasing the ionic conductivity and significantly enhancing the mechanical strength of the CSes, which also demonstrated excellent cycling stability, maintaining a uniform distribution of Li\(^{+}\) flux. This leads to increased \(t_{\text{T}}\), homogeneous Li\(^{+}\) deposition, and inhibition of Li dendrite growth. Instead of dispersing nanofillers into a polymer electrolyte, the CSes involve impregnating the polymer electrolyte into a 3D continuous porous framework structure to establish continuous ionic conductive pathways with fast ion transport [273]. To create a novel single-ion polymer composite electrolyte (SIPCE), single-ion polymer monomers (PEGMEA and AMPSLi) were in-situ photopolymerized within porous MOF/polymer electrospun fibrous membranes [274]. The resulting single-ion polymer electrolytes (SIPEs) exhibit high \(t_{\text{T}}\) and good interfacial compatibility with Li metal anodes. The immobilization of anions in the SIPEs suppresses Li dendrite growth and reduces anionic concentration polarization, leading to low internal impedance and high discharge voltage [275]. The porous interconnected MOF fibrous membrane, prepared via electrospinning, provides a 3D ion-conducting pathway, serving as long-range ionic transfer channels that cannot be achieved with isolated nanofiller distributions in polymer electrolytes. The organic functional groups decorated on the surface of fillers contribute to enhanced ionic conductivity and interfacial effects in MOF-laden electrolytes, where the chemical and thermal stability of the system is influenced by the nature of weak
outstanding structural stability and ultrahigh porosity, along with the
this study, HKUST nanocrystals are grown
and thermal stability for high-voltage and high-safety applications. In
transport while maintaining mechanical robustness, oxidative tolerance,
respectively addresses the challenge of particle agglomeration and achieves a
uniform distribution of MOF particles.

A 3D ion-conducting network is crucial for SSBs to facilitate fast ion
transport while maintaining mechanical robustness, oxidative tolerance,
and thermal stability for high-voltage and high-safety applications. In
this study, HKUST nanocrystals are grown in-situ on a 3D polyimide (PI)
fiber network (HKUST@PI), where the PI fiber network serves as the
MOF growing skeleton, providing excellent mechanical strength, high
oxidative stability, and superior thermal and chemical stability (Fig. 6e).
Subsequently, the HKUST@PI structure is infiltrated with PVDF to form
CSEs (Fig. 6f) [271]. The HKUST nanocrystals, possessing appropriate
porous size and abundant OMS, are expected to restrict the migration of
Li⁺ and promote fast Li⁺ transport. The 3D continuous filler scaffolds
with large specific areas and sufficient mechanical strength are develope-
to further enhance Li⁺ conductivity based on their intrinsic fea-
tures. Utilizing these scaffolds, the LCM/|Li SSBs demonstrated superior
cycling performance and exhibited excellent interfacial compatibility, as
evidenced by a negligible increase in voltage polarization (Fig. 6g). The
3D continuous MOF network offers a large filler/polymer interface,
enabling effective interaction with the LE and facilitating fast 3D Li⁺
pathways along the interface [278]. Another approach involves the
construction of thin 2D laminar membranes with robust structural sta-
ibility and efficient conduction for SSEs. Analogously, 2D MOFs with large
specific surface areas and sufficient accessible active sites are employed,
providing fast ionic channels at the molecular level. Specifically, a
layered Cu(BDC) MOF, constructed from Cu(II) nodes and BDC ligands, is
in-situ grown on a nonwoven fabric (NWF) substrate to form a 3D con-
tinuous structure, followed by embedding in PVDF and LiClO₄
(Fig. 6g) [272]. The OMS within the MOF structure can anchor ClO₄⁻
anions and release free Li⁺ [75,81]. The CSEs are prepared using a
straightforward solution-casting method with PEO, PVDF, LiTFSI, and
activated NH₂-MIL-101(Fe) [279]. The addition of a small amount of
high-viscosity binder (PVDF) significantly improves the film-forming
properties of PEO, while NH₂-MIL-101(Fe), which possesses -NH₂
groups with OMS, is selected as the filler [280].

Therefore, the focus lies in exploring innovative approaches that
leverage the unique characteristics of multiple materials to address the
critical challenges associated with ASSEs, particularly related to ionic
conductivity and the electrode-electrolyte interface. The design of
asymmetric or multilayered MOFs-based SCEs incorporates distinct
layers with specific functions. The polymer layer offers high flexibility,
facilitates good contact interfaces, and enables convenient production.
The MOFs layer effectively suppresses Li dendrite formation and en-
hances the smoothness of Li⁺ transport, thereby improving safety and
stability. Additionally, the inorganic layer contributes to achieving su-
perhigh ionic conductivity. Moreover, the inherent high surface polarity
of MOFs enables control over LAB interactions, resulting in improved
electrochemical properties. The incorporation of MOFs-based scaffolds
within the polymer matrix facilitates facile modulation, grafting, and
functionalization, enabling the formation of a 3D network structure
through in-situ or electrostatic spinning. This approach significantly
enhances interfacial interaction and provides efficient pathways for rapid Li⁺
transport. Furthermore, MOFs can form specialized ion screens that
promote cation transfer and enhance the uniformity of ion migration.
However, the use of costly ligands and complex fabrication techniques
poses significant cost challenges that require careful consideration. The
multilayered and multi-dimensional structures also introduce complexity
in terms of their configuration and operating mechanisms. The precise
mode of Li⁺ transport in electrolytes remains to be fully elucidated, and
further research is needed to understand the mechanisms underlying the
reduction of interfacial resistance and the enhancement of Li⁺ transport
in certain solid-solid contact interfaces. Moreover, the conductivity of
many MOFs and their derivative materials is not yet optimal, and
increased internal charge transfer resistance may impact battery heat
dissipation and cycle stability. The development of composite structure
electrolytes with exceptional properties still requires extensive explora-
tion and investigation.

4. Outlook and summary

Conventional LMBs face several challenges, such as flammable elec-
trolytes, uncontrollable Li dendrite formation, unstable SEI layer, and
electrode corrosion. Extensive efforts have been dedicated to the devel-
opment of a stable and robust SEI layer to protect the Li metal anode from
dendrite growth and volumetric strain issues. Strategies include adjust-
ing electrolyte concentration or composition, designing artificial SEI films, and modifying the surface of the Li anode [281]. MOFs have
emerged as promising materials for LMB applications due to their
exceptional capacity, remarkable cycling stability, high Li⁺ conductivity,
excellent mechanical properties, and notable rate capability. Moreover,
porous MOF materials possess tunable components and unsaturated sites,
future enhancing their appeal for LMBs. This review focuses on the
research progress of MOFs and their derivatives in SSEs for LMSSBs.
These MOF-based SSEs offer flexibility and mechanical robustness,
optimizing the electrode-electrolyte interface and enhancing LMSSB
performance. Notably, MOF-based SSEs serve as multifunctional SSEs,
combining QSSEs and ASSEs, demonstrating impressive performance.
Generally, MOFs have been utilized as nanofillers in SSEs due to their
intrinsic electrical insulation properties, well-defined porous structures,
and controllable surface functionality [282]. Additionally, they can act as
reservoirs for LEs/ILs, providing a continuous supply for ion conduction.
MOFs employed in QSSEs can be categorized into four distinct classes:

1) MOFs serve as the primary host material containing LEs in SSEs. The
uniform pore structure of MOFs provides well-ordered channels for
ionic transport, enabling the injection and entrapment of LEs as carriers
to facilitate ion transport. Additionally, this structure allows for the
uniform deposition of Li⁺ during the charging and discharging process,
effectively inhibiting Li dendrite growth. MOF-based SSEs with a main body configuration typically exhibit higher \( \tau_L \) and
broader electrochemical windows, albeit with a more intricate fabrication process [168].

2) MOFs incorporating ILs as an auxiliary component offer SSEs with an
extended working temperature range (20–150 °C) due to the non-
flammability and non-volatility of ILs. The finely tuned open
framework structure of MOFs restricts the behavior of ILs, similar
to that of LEs, thereby enhancing interfacial wettability. However, the
optimization of transference numbers in IL-loaded SSEs remains a
subject of further investigation [150].

3) QSSEs combine the benefits of relatively high ionic conductivity and
good interfacial compatibility, making them a promising solution to
overcome the challenges associated with SSEs. The polymer matrix in
GPEs exhibits low crystallinity, chemical resistance, thermal stability,
self-extinguishing properties, and flexibility. The incorporation of
MOF-based materials with OMS immobilizes anions, facilitating the
smooth and rapid movement of cations within the porous structure and
ensuring \( \tau_L \) [283].

4) Mixed-type QSSEs employ MOFs as plasticizers to reduce the crys-
tallinity of polymer matrices. The presence of linker and LAB groups
on the MOF surface enhances the dissociation of Li salts, thereby
improving the ionic conductivity of the electrolyte [194].

The design of MOFs in ASSEs encompasses various strategies,
including ordinary mixing, stem grafting, hierarchical structure design,
and multi-component approaches. PSEs offer advantages such as low cost
and high flexibility, making them suitable for large-scale industrial production. However, their application in high-voltage and high-performance SSBs is limited by their low oxidation potential and ionic conductivity at RT, which requires further improvement. To address these challenges, MOFs are chosen as ideal materials to mitigate common issues, ensuring improved thermal stability and higher safety compared to unmodified PSEs. Additionally, MOF-based SSEs exhibit favorable mechanical properties, maintaining strength while enhancing flexibility to improve interface contact performance with the electrode. Ultimately, MOF-based SSEs hold promise for achieving high-performance SSBs. Hierarchical structure design and multi-component approaches facilitate a deeper understanding of the electrolyte interface mechanism and enable the construction of a robust composite interface. This promotes high ionic conductivity, cyclic stability, rate capability, and mechanical properties, maintaining strength while enhancing other desirable properties. So far, it represents the most promising avenue for future development in this field.

The role of MOFs in SSEs can be summarized as follows [57,284]:

i. The substantial specific surface area exhibited by MOFs can potentially facilitate enhanced contact between the MOF material and the electrolyte and electrode interfaces. This advantageous feature allows for improved interaction and control of the surface polarity between LABs. As a result, the electrochemical performance of SSEs can be optimized through the regulation of these interactions at the interface.

ii. The ordered crystal structure and high porosity of MOFs offer unique advantages over conventional materials, providing uniformly dispersed sites and well-defined pathways for ion diffusion. This exceptional structural feature is unmatched by many conventional materials, enhancing the overall ion transport properties of MOF-based SSEs.

iii. MOFs serve as ion sieves within SSEs, promoting efficient cation transfer through their abundant pore structure. This capability improves the uniformity of cation deposition during charge and discharge cycles, leading to enhanced performance stability and optimized interface characteristics in MOF-based SSEs.

iv. The high surface energy and strong adsorption capacity of MOF materials enable them to capture by-products generated during the electrochemical cycling process. However, despite these advantages, the utilization of MOFs in SSEs remains relatively limited.

Despite significant advancements in the development of MOFs, their application in SSEs is still in its early stages, presenting several unresolved problems and challenges. To further advance the research and development of MOFs in electrolyte applications, it is crucial to shift attention towards addressing and overcoming the following aspects:

(a) MOFs exhibit notable thermal and electrochemical stability, particularly due to their porous structure, ordered crystalline nature, and well-coordinated environment, making them promising materials for LMBs. However, the long-term stability of MOFs in complex electrochemical environments remains uncertain. During the charge/discharge process, MOFs can irreversibly decompose or transform into amorphous phases, which limits the rate capability and cycle stability of MOF-based SSEs and hinders their widespread adoption in SSEs. Pre-/post-modification techniques can be explored to enhance the stability of MOF materials and fulfill the requirements of SSEs for SSBs.

(b) The intrinsic ionic conductivity of MOFs and MOF derivatives relies on their porous structure, which necessitates improvements to enhance SSEs’ conductivity. Extensive research is required to develop new MOF materials and effective modification methods. The effects of MOF structural properties, such as pore size, nanoparticle morphology, crystallite size, and Framework topology, on ion transport properties should be thoroughly investigated. Furthermore, the behavior of SSEs is influenced by factors such as the choice of Li salt cations and anions, solvent polarity, and compatibility with cathode materials.

(c) The lack of efficient approaches for the large-scale production of MOFs poses a challenge, as most MOFs are synthesized using specialized organic ligands. The cost associated with synthesizing MOFs and the use of expensive ligands, along with the labor-intensive fabrication processes, impede the mass production of MOFs and MOF-based SSEs. Current methods for SSE fabrication, such as casting and hot-pressing, suffer from drawbacks such as extended processing times, sensitivity to temperature, excessive film thickness hindering Li⁺ transport, and difficulties in stabilizing interfacial contacts. Alternative techniques like 3DP, in-situ growth, and sputtering deposition can be explored for SSE production.

(d) It is crucial to conduct in-depth studies on the electrochemical mechanisms of MOFs in SSEs. This includes investigating the compatibility of MOFs with polymers, the coordination abilities of MOFs with ILs, and the role of OMS and LAB in ionic conduction. Fillers play a significant role in reducing the crystallinity of polymers to enhance ion transport. By adjusting parameters such as pore size or grain boundaries, the crystallinity of polymers can be effectively reduced while improving compatibility. Furthermore, the introduction of highly electronegative groups can enhance ion coordination sites, thus increasing ionic conductivity and \( t_{\text{Li}^+} \).

(e) The design of multifunctional MOFs warrants further investigation and development. For instance, incorporating nano-porous MOF particles into battery systems can mitigate the risks associated with trace gas generation during in-situ polymerization. Additionally, functionalized MOFs can facilitate the integration of metallic cations and LABs. Furthermore, detailed safety tests, including thermal runaway, electrolysis, and membrane puncture, should be conducted to expand the application scope of such SSEs.

In summary, the integration of functional materials into MOF composites has significantly impacted the field of EES by improving the electrochemical performance of MOFs. Despite remaining challenges, research on MOF composites has witnessed rapid progress in recent years, and the development of novel functional materials appears promising. This review contributes to the understanding of the application of MOF composites as potential materials in energy storage applications and offers a valuable reference for future research endeavors.

Declaration of competing 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.

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