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REVIEW

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Hypercrosslinked porous and coordination polymer materials for electrolyte membranes in lithium-metal batteries

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Abstract

Rechargeable lithium-metal batteries (LMBs) hold great promise for providing high-energy density. However, their widespread commercial adoption has been inhibited by critical challenges, for example, the capacity fading from irreversible processes at electrolyte/electrode interfaces and safety concerns originating from the inhomogeneous lithium deposition. Polymer electrolytes benefiting from enhanced electrolyte/electrode contact and low interfacial impedance provide a variable solution to address these challenges and enable a high-energy and flexible battery system. Although promising, inefficient bulky ionic conductivity and poor mechanical stability confront the stable operation of polymer electrolytes in tangible batteries, which highly requires the development of innovative polymer electrolyte chemistries. Among various polymer materials, microporous polymers stand out due to their abundant porosity and customizable micropore structure, positioning them as promising candidates for next-generation electrolyte membranes. This review, therefore, summarizes recent advances in electrolyte membranes based on two new chemistries, hypercrosslinked polymers (HCPs) and porous coordination polymers (PCPs). Other microporous polymers, such as covalent organic polymers, porous organic cages, and polymers of intrinsic microporosity, are also discussed with an emphasis on their applications in LMBs. Most importantly, by reviewing the design strategies, synthesis protocols, and performance in LMBs, we gain insights into the design principles of high-performance electrolyte membranes based on HCPs and PCPs and highlight potential future research directions.

KEYWORDS
electrolyte membranes, hypercrosslinked polymers, lithium-metal batteries, polymer electrolytes, porous coordination polymers

1 | INTRODUCTION

The increasing growth of electric vehicles and portable electronics necessitates the development of high-energy density and durable storage systems, particularly in battery technologies.[1–5] Metallic lithium, benefiting from the high-energy density of 3860 mAh g^{-1}, emerges as a pivotal component enabling next-generation efficient battery technology.[6–10] However, the deployment of redox-active and chemically unstable lithium metal undesirably challenges the safety and stable operation of lithium-metal batteries (LMBs) along with unfavorable electrolyte/lithium-metal side-reactions and as-induced uncontrollable metallic dendrite.[11–14] To effectively tackle these challenges, there is a pressing need to develop new electrolyte membranes that incorporate not only innovative chemistries compatible with lithium metal but also possess ion-conductive and selective properties, ensuring regulation of Li^+ ion transport.[15–18]

Ideally, electrolyte membranes are anticipated to deliver high Li^+ ion conductivity and exceptional electro-/chemical stability and alleviate parasitic reactions on the electrolyte/electrode interface.[19–21] Although commercial polyolefin separators integrating liquid electrolytes (LEs) demonstrate appreciable ionic conductivity, this electrolyte membrane is flammable and highly reactive toward lithium metal, resulting in electrolyte degradation and uncontrolled lithium dendrite proliferation.[22,23] These challenges are driving the research focus toward safe and stable solid-state alternatives, for example, solid inorganic electrolytes (SIEs) and solid polymer electrolytes (SPEs).[24–29] Although SIEs display distinct ionic conductivities and admirable resilience toward mechanical and thermal abuses, their poor processability, inherent brittleness, and unstable electrolyte/electrode interfacing are challenging their large-scale applications. Conversely, flexible and solution-processible SPEs present inadequate ionic conductivity and compromised mechanical robustness at ambient conditions. Recent advances have emphasized the development of continuous microporous polymer electrolyte membranes that impregnant guest molecules, for example, LEs and ionic liquids (ILs). Alternatively, microporous polymer particles serve as fillers embedded in polymer matrixes to provide more ion channels and enhance the overall mechanical properties. Such approaches seek to exploit the synergistic potential of microporous polymers, SPEs, and guest molecules, merging their distinct strengths and offsetting inherent deficiencies.

Microporous polymer materials, particularly hypercrosslinked polymers (HCPs) and porous coordination polymers (PCPs), with intrinsic pore channels and ease of functionalization, have become crucial components in solid-state LMBs. Figure 1A compares the electrochemical windows of LEs-, HCP-, and PCP-based electrolyte membranes. HCP-based electrolyte membranes exhibit superior oxidation resistance and an extended electrochemical window in comparison to those based on polyolefin separators and PCPs. The radar chart presented in Figure 1B compares the critical properties of HCPs and PCPs against their counterparts using commercial LEs. Electrolyte membranes derived from HCPs and PCPs with their rigid and crosslinked frameworks demonstrate enhanced safety, superior cycling duration, and robust mechanical resilience relative to LEs in polyolefins. Of great note, HCPs and PCPs intrinsically furnish a plethora of coordination sites and ion transport channels, enabling fast Li^+ ion transport in electrolyte membranes. The structural design and porous attributes of HCPs and PCPs can be modulated by rationally selecting building blocks with linking units where the geometry of linking units determines the topological and porous architecture of HCPs and PCPs as well as the constructed ion channels.[30–33] According to protocols for establishing electrolyte membranes, the HCPs and PCPs can be classified into two categories: (1) *Free-standing electrolyte membranes*. Those membranes harness micropores to encapsulate guest molecules; (2) *Functional fillers*. HCPs and PCPs particles act as stiffened fillers to strengthen mechanical and thermal resilience.

Herein, this short review summarizes recent advancements in electrolyte membranes based on HCPs and PCPs, encompassing design strategies, synthesis methodologies, and their applications in LMBs. Cutting-edge materials, including covalent organic frameworks (COFs), porous organic cages (POCs), and polymers of intrinsic microporosity (PIMs) and their applications are also briefly reviewed in this article (as depicted in Figure 2). By summarizing and analyzing the latest research results, this review will shed light on the fundamental structure–property-function relationships crucial to electrolyte membrane innovation. Such understanding will guide the development of advanced electrolyte membranes for use in solid-state LMBs.

2 | HCPs

2.1 | Definition and design strategies as an electrolyte membrane

HCP-based electrolyte membranes are constructed from HCPs, where the permanent micropores and residual voids are generated via the high crosslinking among polymer chains. The building of HCPs predominantly revolves around Friedel–Crafts chemistry that facilitates rapid kinetics conducive to forming robust C–C bonds,

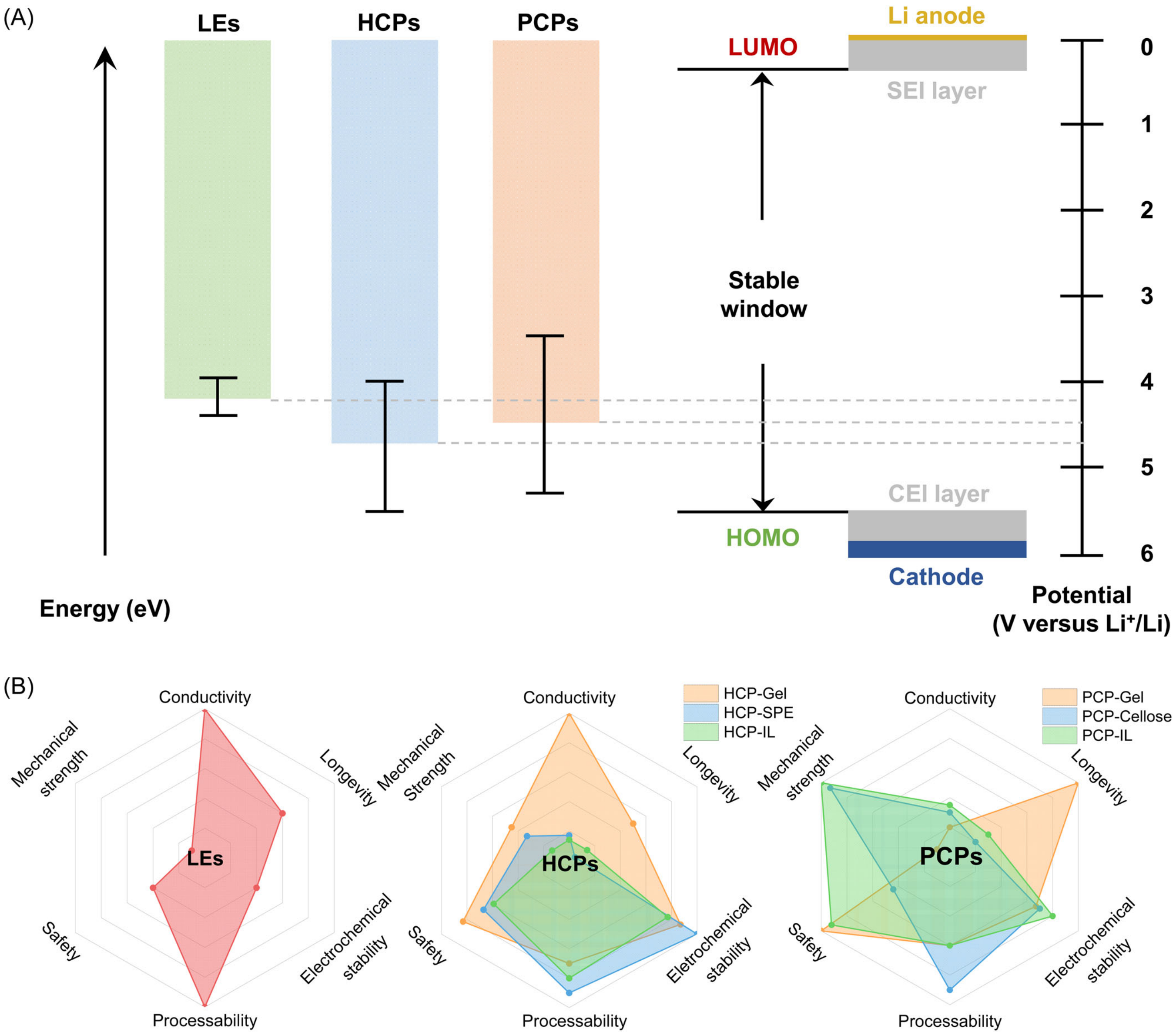

FIGURE 1 Comparisons of key properties for electrolyte membranes based on liquid electrolytes, hypercrosslinked polymers, and porous coordination polymers. (A) Electrochemical window. (B) Key metrics, including conductivity, longevity, electrochemical stability, processability, mechanical strength, and safety. HCP, hypercrosslinked polymer; LE, liquid electrolyte; PCP, porous coordination polymer.

culminating in a dense network characterized by marked porosity.[34–36] The rigorous crosslinking of aromatic moieties not only endows thermal and chemical stability but also prevents the polymer chains from collapsing, ensuring pronounced porosity and expansive surface areas. A discerning selection of appropriate monomers and crosslinkers, as well as optimized reaction parameters, culminate in a defined topology and customizable pore dimensions.[32,37,38]

Noteworthily, numerous and interconnected pores involved in HCPs can promisingly accommodate charge carriers and create highly conductive ion channels, which allow HCPs to serve as ion conductors in two manners, one by creating self-supporting porous membranes that confine guest molecules/charge carriers, the other by using their particle format to create more active channels in an existing and well-established electrolyte membranes, such as polyethylene oxide membranes. Distinct from other microporous framework materials, HCPs boast a compelling combination of economic viability and straightforward scalability, which arise from cost-effective reagents, brisk reaction kinetics, and benign reaction conditions. This amalgamation of durability, cost-effectiveness, and simplicity in upscale fabrication earmarks HCPs as potential frontrunners for electrolyte membrane applications.

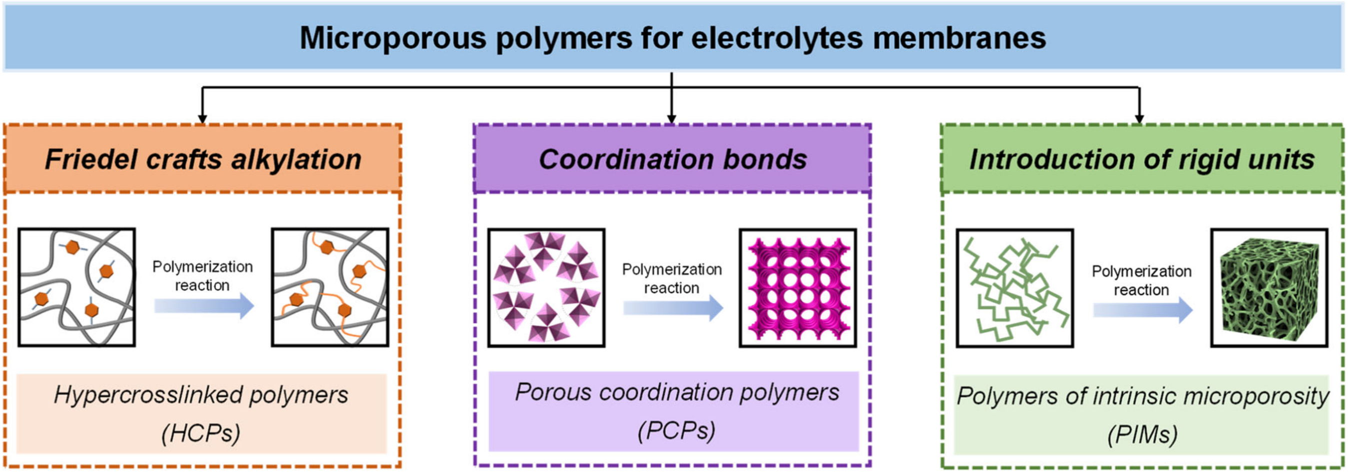

FIGURE 2 Schematic illustration of three typical microporous polymers, hypercrosslinked polymers (HCPs), porous coordination polymers (PCPs), and polymers of intrinsic microporosity (PIMs).

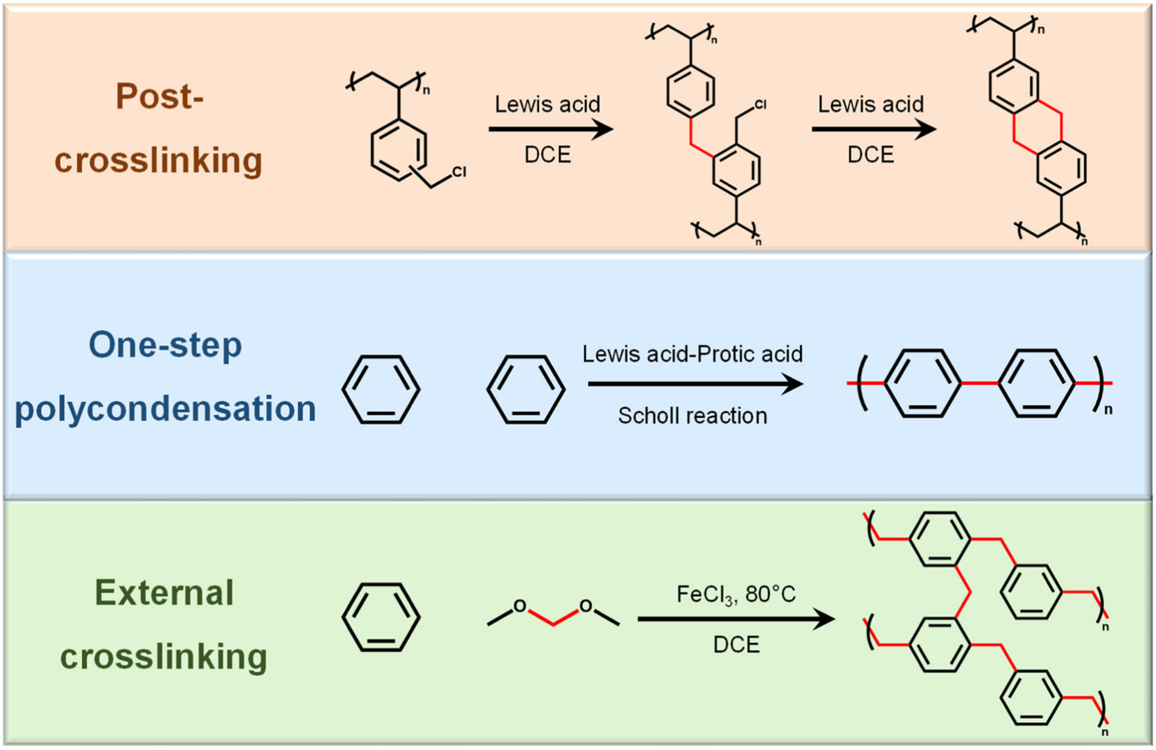

FIGURE 3 Three typical synthesis protocols for fabricating hypercrosslinked polymers. Reproduced with permission.[39] Copyright 2017, The Royal Society of Chemistry.

2.2 | Synthetic approach

The simplicity and versatility of current synthetic protocols permit a broad spectrum of aromatic monomers that can be employed in crafting porous and functional polymer networks.[38] HCPs are chiefly realized via three predominant strategies (Figure 3):

(1) Postcrosslinking involves the integration of benzene rings within the polymer matrix using an external crosslinking agent/electrophilic reagent in the presence of a Lewis acid catalyst and an appropriate solvent.[40,41] This method typically comprises two pivotal phases: (a) complete dissolution or swelling of polymer precursors; (b) an intensive postcrosslinking. Before crosslinking,

preformed polystyrene (PS) chains uniformly disperse in the solvent along with a stoichiometric bifunctional crosslinker and catalyst. The subsequent rapid reaction promotes the robust crosslinking of proximate phenyl rings through rigid bridges in myriad chain segments. Such structural rigidity confines the resultant network, preventing chain movement or collapse postsolvent removal, resulting in a highly porous and low-density material.[42]

(2) One-step polycondensation, pivoting on the Scholl coupling reaction, directly binds neighboring phenyl rings, removing two bound hydrogen atoms and initializing a new aryl–aryl bond. This occurs in the presence of an anhydrous $AlCl_3$ catalyst, and occasionally, a Brønsted acid like hydrogen chloride might be requisite.[43,44] The reaction extends conjugation from monomers across extended scales without external bridging. Owing to the heightened activity of the catalyst, plenty of monomers, such as high electron density (anisole, benzyl amine) or low electron density (tetraphenylporphyrin), acidic (benzoic acid), or alkaline (bipyridine) functional groups an aryl ring (TPB), a fused ring (naphthalene, pyrene), or even a heterocyclic ring (pyrrole), can take part in the reaction.

(3) External crosslinking employs potent external crosslinkers, for example, formaldehyde dimethyl acetal, associating basic aromatic entities such as benzene or biphenyl through rigid methylene bridges, facilitated by the anhydrous $FeCl_3$-catalyzed Friedel–Crafts reaction.[45,46] The proposed mechanism commences with a Lewis acid catalyst complexing with a crosslinker molecule, which can weaken the bonding strength between the methoxyl group and central carbon atom and then generate copious intermediate carbocations in the dichloroethane solvent. As the reaction unfolds, carbocations react with phenyl rings, incorporating multimethoxymethyl groups into aromatic molecules, subsequently releasing methanol. These highly reactive groups, upon interaction with other phenyl rings, are transformed into methylene linkages, thus sculpting highly structured crosslinked networks.

The diversity of building blocks, coupled with the extensive synthetic methodologies, render HCPs as quintessential scaffolds for innovating new electrolyte membranes with enormous potential to achieve high electrochemical performance of LMBs. Furthermore, the synthesis methods of HCPs leverage low-cost reagents, such as monomers, reaction mediums, and catalysts, as well as easy-to-handle and control reaction conditions resulting in the production of high-yield products, making them strong competitiveness in electrolyte membranes.

2.3 | Applications in LMBs

HCP-based electrolyte membranes can favor the operation of solid-state LMBs in various aspects. (1) *Avoiding side reactions*. Membrane microporous structures and rigid skeletons can allow fast ion transport while immobilizing organic LEs to minimize side reactions between organic liquid with chemically active lithium-metal anode, thus promoting the electrochemical stability and longevity of devices. (2) *Enhancing thermal performance*. The microporous structures can also confine volatile organic solvents to enhance thermal stability while avoiding electrolyte leakage. (3) *Maintaining ion-conductive framework*. These HCP-based electrolyte membranes effectively impede the reorganization of polymer chains, maintaining the geometry of ion channels and retaining a high Li^+ ion conductivity, which is beneficial for the electrochemical performance of solid-state LMBs. (4) *Ease of functionality*. Grafting suitable functional groups in the HCP configuration fosters strong intermolecular forces with certain flexible polymer substrates, such as poly(ethylene oxide) (PEO) and poly(1,3-dioxolane), which effectively addresses the interface compatibility challenges between the filler and the substrate.

2.3.1 | Electrolyte membranes comprising HCPs-confined guest molecule composites

In this section, we reviewed the typical research work on HCPs with inherent mobile ions and potential solvents, for example, ethylene carbonate (EC), dimethylformamide (DMF), ILs for their applicability as electrolyte membranes for LMBs. Given the vast range of HCPs and advancements in nanotechnology, HCPs can be custom-designed with desired microporous structures and surface functionalities.

Goodenough et al. reported a micropores-in-macroporous HCP-based electrolyte membrane (Li-HCFu-PH) fabricated by integrating rigid microporous HCPs into the macropores of a flexible polymer host via in situ hypercrosslinking polymerization (Figure 4A).[47] This electrolyte membrane forms a consistent polymeric network that can entrap LEs, facilitating ion transport through “liquid pathways” throughout the membrane and thereby delivering a high ionic conductivity of $6.41 \times 10^{-3}\ \mathrm{S\,cm^{-1}}$. Due to a fast transport of lithium ions through the microporous

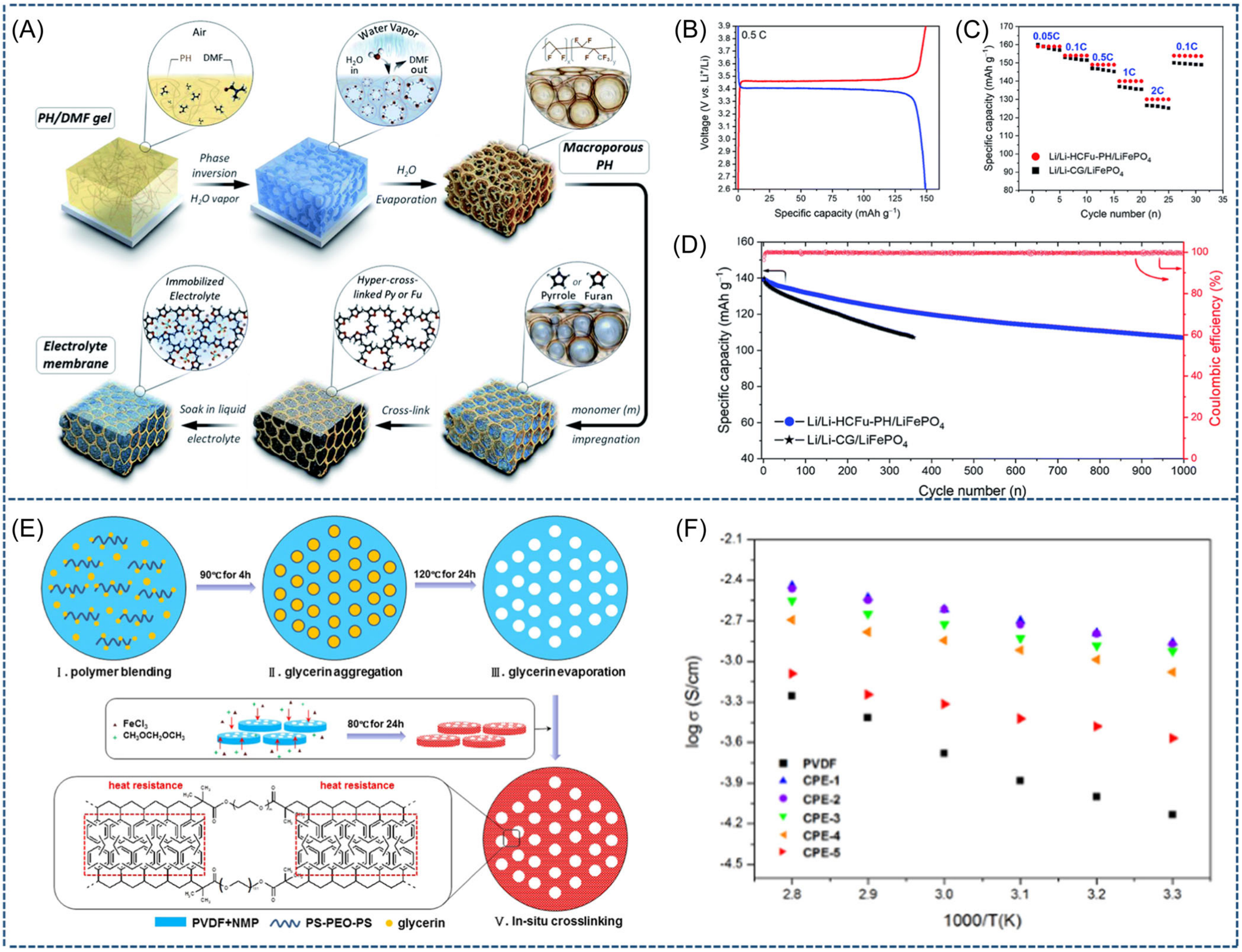

FIGURE 4 Hypercrosslinked electrolyte membranes and their applications in lithium-metal batteries. (A) Schematic representation of the synthesis strategy for Li-HCFu-PH electrolyte membranes. The electrochemical performance of Li/Li-HCFu-PH/LFP full cell: (B) charge-discharge curve, (C) rate performances, and (D) comparison of cycle life with Li/Li-CG/LFP full cell at 1 C. Reproduced with permission.[47] Copyright 2020, The Royal Society of Chemistry. (E) Schematic of the preparation and in-situ cross-linking process of porous electrolyte membranes. (F) Ionic conductivities of different composite polymer electrolyte membranes and PVDF electrolyte membranes. Reproduced with permission.[48] Copyright 2019, American Chemical Society. PEO, poly(ethylene oxide).

HCFu, the Li/Li-HCFu-PH/$LiFePO_4$ (LFP) full cells demonstrated smooth cycling with low overpotentials and remarkable rate performance (Figure 4B–D). Owing to the minimal volatility of LE components confined within the micropores, the Li-HCFu-PH displays commendable self-extinguishing properties. The enhanced thermal stability of the HCFu-PH leads to significantly reduced flammability compared to traditional electrolyte/separator systems, enhancing the safety of batteries using lithium metal. Likewise, Ren et al. employed a Friedel–Crafts reaction for in situ hypercrosslinking of the PS segments present in the triblock copolymers (PS-PEO-PS), as shown in Figure 4E.[48] This led to the creation of highly heat-resistant microporous HCP-based electrolyte membranes built on polyvinylidene fluoride (PVDF) matrices. The electrolyte membranes display considerably greater ionic conductivity (1.38×10^{-3} S cm^{-1}), surpassing that of the pure PVDF electrolyte membranes in electrochemical evaluations (Figure 4F).

2.3.2 | Electrolyte membranes integrating HCP-based fillers

The incorporation of HCP-based fillers in electrolyte membranes represents a burgeoning area of research. In contrast to traditional porous inorganic fillers, HCPs provide a platform to tune the properties as per the requirements of the devices. In addition, the precise design of HCP structures at the molecular level modulates the interaction between guest molecules and polymer matrices, which, in turn, improves the Li^+ ion transport and inhibits the nucleation growth of lithium dendrites. As a typical example, Ren et al. meticulously crafted the filler structures at a molecular scale to cultivate stable composite interfacial phases (Figure 5A).[49] The filler contains two components: the primary being a hypercrosslinked phosphorus ligand polymer called KAP1, which offers a porous structure and a hydrogen bonding network, and the secondary component being ILs encapsulated within the nanochannels of KAP1. This ILs@KAP1 composite filler that disperses in PEO matrices at a molecular level can enhance PEO chain mobility by destroying the ordered packing of PEO chains and also wet the electrode surface to ensure a compactable contact between electrolyte membranes and electrodes. Consequently, the ILs@KAP1-PEO electrolyte membranes exhibited a remarkable conductivity of $9.06 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at 60°C, significantly surpassing that of pure PEO. The LFP/Ils@KAP1-PEO/Li full cell shows the best electrochemical performance with a high-capacity retention of 78.07% after 300 cycles (Figure 5B). Following a similar concept, Ren et al. synthesized PEO-based composite SPEs (CSPE-HCPs), leveraging hypercrosslinked SiO_2@PMMA-co-PS nanoparticles for reinforcement (Figure 5C).[50] With the addition of SiO_2@PMMA-co-PS nanoparticles, the overall ionic conductivity is improved to $1.13 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at 30°C along with enhanced battery performance (Figure 5D,E), further proving functions of hypercrosslinked nanofillers, that is, enhancing chain mobility of PEO and stabilizing battery cycling.

In fact, due to the presence of more benzene rings, HCPs lack functional groups capable of conducting lithium ions, which hampers the potential application of this type of electrolyte membrane. Consequently, the use of HCPs is primarily confined to two applications: enhancing the mechanical strength of chain polymers (e.g., PEOs, etc.) and providing the mobility channels of ions and guest small molecules in three-dimensional consecutive channels. Despite some limitations, the relative ease of synthesizing and functionalizing HCPs positions them as highly competitive for large-scale production and applications in electrolyte membrane technology.

3 | PCPs

3.1 | Definition and design strategies as an electrolyte membrane

PCPs are a rapidly growing class of porous crystalline inorganic–organic materials assembled by metal ions/clusters and organic ligands, for example, metal-organic frameworks (MOFs).[51–54] Recognized for their versatility, PCPs serve as exceptional platforms for designing diverse functional materials through host–guest chemistry and reaction transformation and have been extensively explored across a variety of domains, including gas adsorption, drug delivery, catalysis, and energy storage, among others.[55–59] In recent years, a surge in interest has been observed regarding the use of PCP-based electrolyte membranes in LMB systems, attributed to their insulating nature combined with their intrinsic characteristics.[60–63] The flexibility in their chemical compositions, the adaptability of their pore structures, and the modifiability of their surface functionalities render PCPs highly customizable. This inherent designability presents a plethora of opportunities for tailoring the physicochemical properties of PCPs, thereby optimizing the performance of PCP-based electrolyte membranes. Following similar approaches for membrane engineering, PCPs have also been widely employed as self-supporting membranes for charge–carrier incorporation and functional electrolyte fillers.

3.2 | Synthetic approach

The synthesis of PCPs can be broadly categorized into two methods: top-down and bottom-up (Figure 6).[64–67] Both approaches impart distinctive physical and chemical characteristics to PCPs, influencing their size distribution, chemical composition, crystallinity, and thickness, among other attributes.

The top-down approach encompasses methods that derive two-dimensional (2D) PCPs from their corresponding layered bulk PCPs by disrupting the interactions between contiguous layers. This disruption is typically achieved by targeting the weak forces that hold these layers together, such as van der Waals forces, hydrogen bonds, and π–π interactions. A significant proportion of 2D PCPs are synthesized using this method. Essentially, this approach is contingent upon the presence of existing layered PCP structures coupled with a variety of physical and chemical exfoliation techniques. In the physical exfoliation method, an appropriate external force is employed to exfoliate layered bulk PCPs into ultrathin 2D PCPs. Alternatively, in the chemical exfoliation method, when layered bulk PCPs are dispersed in a particular solvent, this solvent disrupts the weak bonds between the PCP layers, yielding multilayer or even mono-layer PCP nanosheets.

The bottom-up approach pertains to the direct synthesis of PCPs via coordination interactions between metals and organic ligands. Generally, surfactants, capping solvents, or confined spaces are employed to control grain growth, thereby facilitating the production

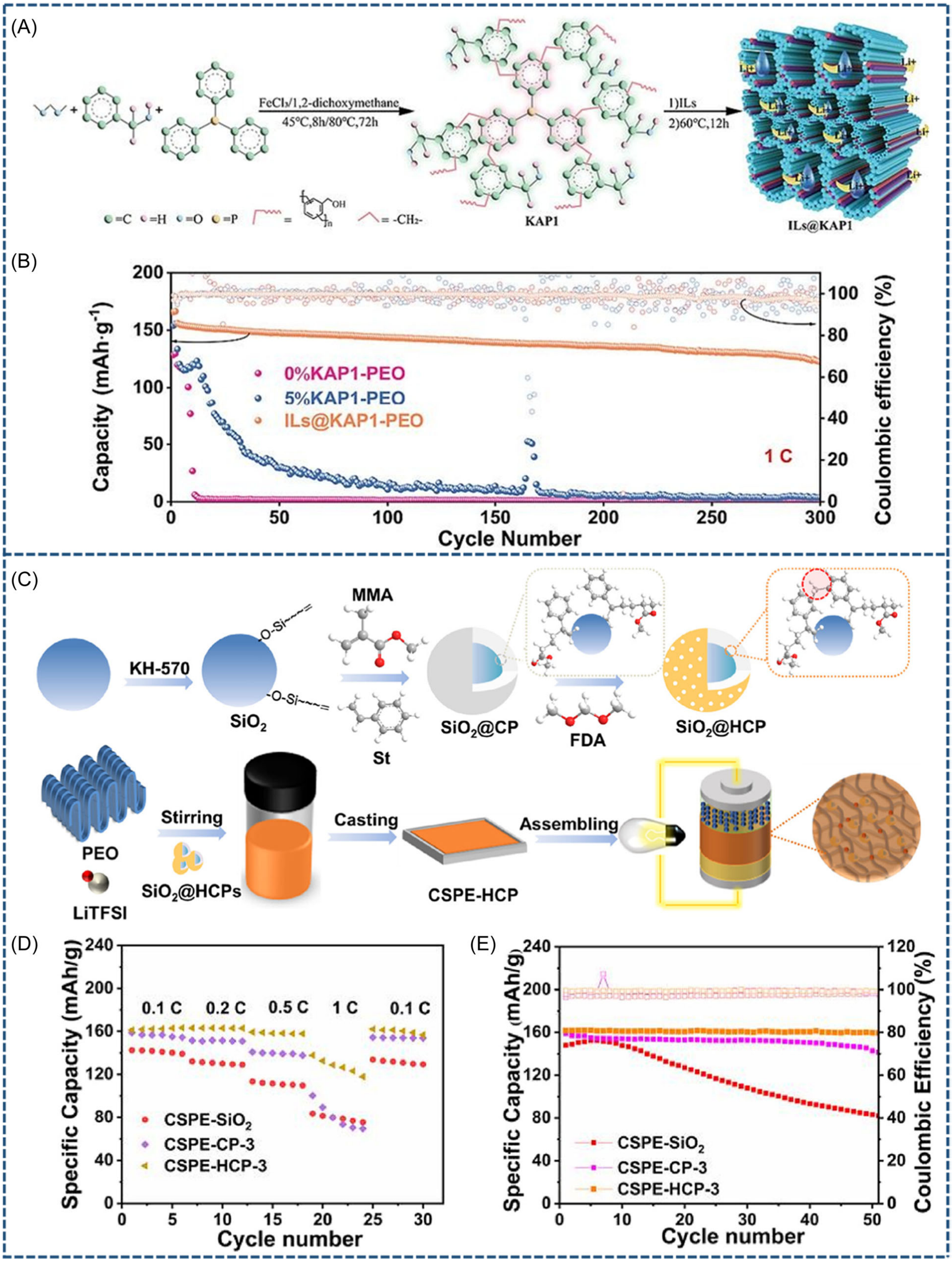

FIGURE 5 Hypercrosslinked electrolyte fillers and their applications in lithium-metal batteries. (A) Synthesis procedure of ILs@KAP1-poly(ethylene oxide) (PEO). (B) Cycling performance of LFP/Li batteries with different electrolyte membranes at 60°C, 1.0 C (1 C = 170 mAh g^{-1}). Reproduced with permission.[49] Copyright 2023, Elsevier B.V. (C) Synthesis process of the SiO$_2$@HCP and CSPE-HCP. The electrochemical performance of LFP/Li cells using CSPE-SiO$_2$, CSPE-CP-3, and CSPE-HCP-3 electrolyte membranes, respectively. (D) Rate performance. (E) Cycling performance. Reproduced with permission.[50] Copyright 2023, American Chemical Society.

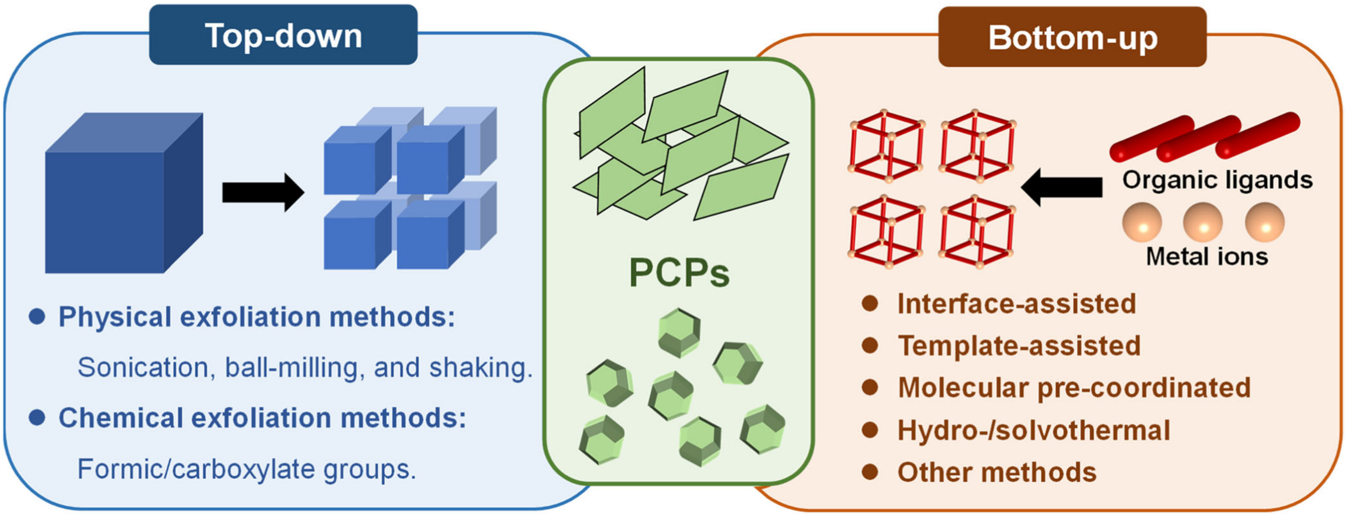

FIGURE 6 Two typical protocols for fabricating porous coordination polymers. PCP, porous coordination polymer.

of PCPs with diverse morphologies and sizes. The key to manufacturing PCPs from the bottom-up method is to control the growth rate of PCP grain in a specific direction. Compared to top-down methods, bottom-up strategies are typically more efficacious in generating PCPs, permitting the synthesis of zero- to three-dimensional PCPs. Depending on their synthesis mechanisms, bottom-up approaches can be further subcategorized into interface-assisted methods, surfactant-assisted methods, template-assisted methods, molecular precollocation methods, and hydro-/solvothermal methods.

The versatility in the design and synthesis of PCPs, especially through the strategic selection of organic ligands and metal centers, as well as the modulation of surface polarity, metal types, and pore structures, presents many opportunities for the systematic enhanced electrochemical performance of PCP-based electrolyte membranes.

3.3 | Applications

The exceptionally high surface area of PCPs facilitates sufficient contact with other components, while their adjustable surface polarity allows for precise modulation of Lewis acid–base interactions within the composite electrolyte membranes. Moreover, due to the inherent high surface energy and robust adsorption capabilities of PCPs, they can effectively trap LEs and ILs. The periodic crystalline structure and meticulously arranged pores of PCP-based electrolyte membranes provide uniformly distributed sites and well-defined pathways for ion diffusion, promoting the uniform deposition of Li^+-ion. Overall, PCP-based electrolyte membranes, with their adjustable porous configurations (in terms of pore size, shape, and polarity), enable the selective dissociation of Li-salt, thereby enhancing Li^+-ion transfer.

3.3.1 | Electrolyte membranes comprising PCP-confined guest molecule composites

Due to the diversity of building blocks and the functionalized frameworks of PCPs, the as-derived electrolyte membranes potentially contain various families that can be classified according to the metal clusters, such as Zr, Zn, Fe, and Al. As a typical example, Kang et al. reported the use of a PCP-based electrolyte membrane fabricated from a MOF gel as a separator for organic batteries (Figure 7A).[68] The homogeneous micropores intrinsic to PCPs combine with an ether-based electrolyte, achieving an ionic conductivity of $\sim 1 \times 10^{-4}\ \mathrm{S\,cm^{-1}}$ at room temperature (Figure 7B). Such high ionic conductivity is comparable to traditional electrolyte membranes using commercial Celgard separators. This PCP electrolyte membrane demonstrates high rejection toward soluble redox active molecules and delivers high-capacity retention for Li-organic batteries. A battery employing this membrane with 5,5′-dimethyl-2,2′-bis-p-benzoquinone (Me_2BBQ) as the cathode demonstrates a high cycling stability of 82.9% capacity retention after 2000 cycles at a current density of $300\ \mathrm{mA\,g^{-1}}$. Polar solvent molecules confined and immobilized in the micropores can surprisingly assist the transport of transport ions by providing anchored polar units, that is, slightly negatively charged moieties. For instance, unlike free LEs, electrolytes confined in MOF channels with ~6.5 Å apertures demonstrate

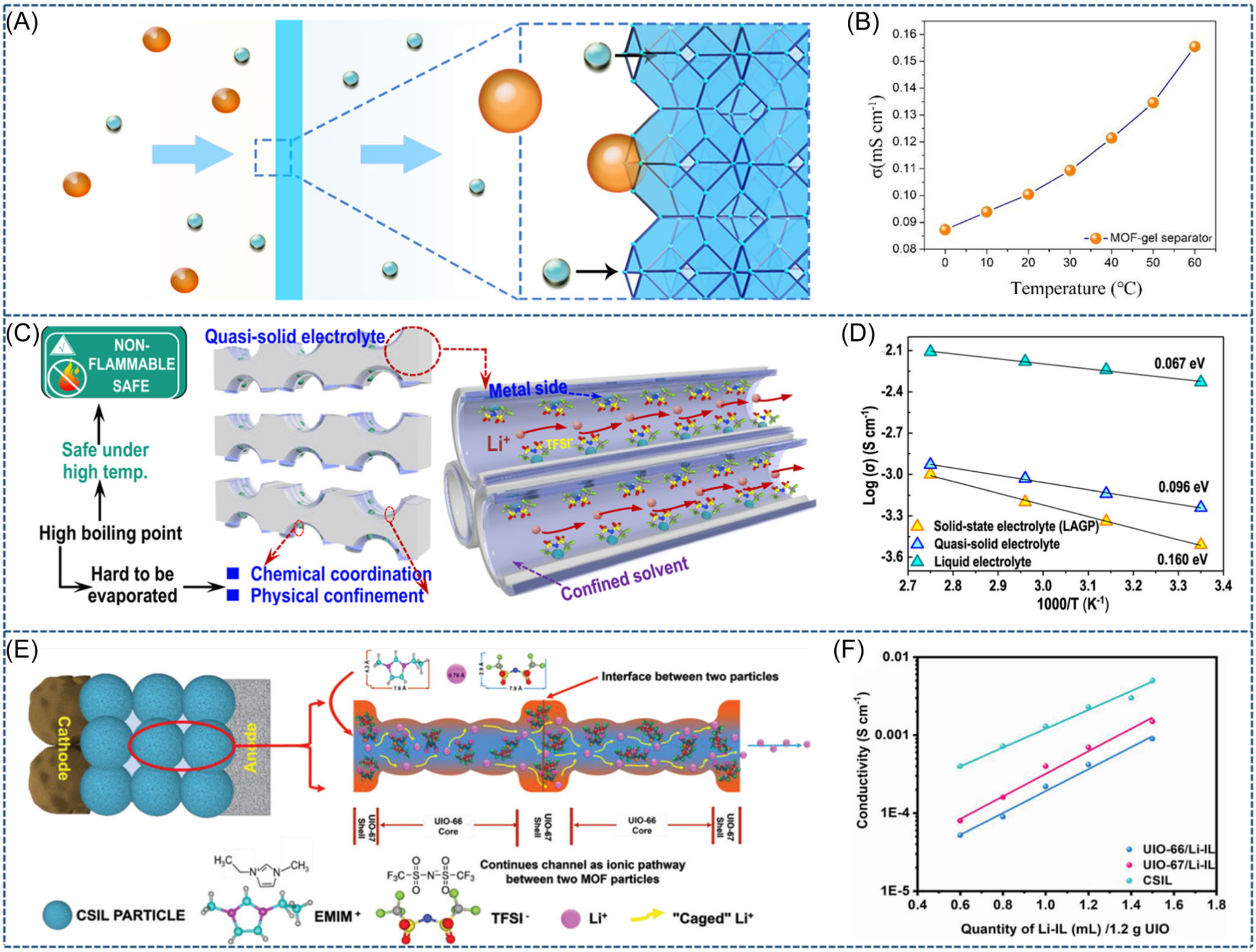

FIGURE 7 Metal-organic framework (MOF)-based electrolyte membranes and their applications in lithium-metal batteries. (A) Schematic illustration of the molecular and ionic sieving process of the MOF-gel separator. (B) Ion conductivity of the MOF-gel separator. Reproduced with permission.[68] Copyright 2021, Springer Nature. (C) Schematic representation of advantages of porous coordination polymer-based electrolyte membranes confined electrolyte. (D) Ion conductivities of the solid-state electrolyte, quasi-solid electrolyte, and liquid electrolyte. Reproduced with permission.[69] Copyright 2022, Springer Nature. (E) Schematic of ion transportation in a continued channel of CSIL. (F) Ion conductivities of UIO-66/Li-IL, UIO-67/Li-IL and CSIL. Reproduced with permission.[70] Copyright 2021, Wiley-VCH GmbH.

an impressive lithium-ion conductivity of about 4.67×10^{-3} S cm^{-1} (Figure 7C,D).[69] When these electrolyte membranes are paired with high-voltage $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$//Li pouch cells, the resulting batteries maintain superb electrochemical performance, even at elevated operating temperatures of 90°C or after damage (yielding 164 mAh g^{-1} after 100 cycles). Additionally, Mai et al. introduced a core-shell MOF-in-MOF nanopore, UIO-66@67, with a unique bifunctional host of IL to develop a core-shell IL–solid electrolyte named CSIL (Figure 7E).[70] In this CSIL design, the shell structure (UIO-67) features a large pore size and a high specific surface area, enhancing the absorption of the ionic LE and, meanwhile, the core structure (UIO-66) has smaller pores relative to the IL, confining larger ions to selectively facilitate Li^+ ion transport. Compared to the low Li^+ ion conductivity of the homogeneous porous host, UIO-66 (4.2×10^{-4} S cm^{-1}) and UIO-67 (5.8×10^{-4} S cm^{-1}), the PCP-based electrolyte membranes (CSIL) demonstrate a notable improvement in Li^+ ion conductivity (2.1×10^{-3} S cm^{-1}) (Figure 7F). Additionally, at the current density of 3 C, the Li/CSIL/LFP solid-state batteries can retain 90% initial specific capacity after 500 cycles.

Anions can bind to PCP frameworks, serving as negatively charged sites and promoting the transport of lithium ions within the porous channels. Therefore, free cations can become the main charge carriers that dominate ionic conductivity. Dincă et al. present two kinds of Cu-azolate PCP-based electrolyte membranes, MIT-20 and $Cu_4(ttpm)_2$ (H_4ttpm = tetrakis(4-tetrazolylphenyl)-methane), for Li^+, Na^+, and Mg^{2+} conduction (Figure 8A,C).[71,72] These electrolyte membranes contain traces of residual propylene carbonate (PC) solvent, which can facilitate Li-salt dissolution and Li^+ ion transport. When Cu-azolate PCPs are treated with metal halide salts (e.g., LiCl, LiBr, and LiI), the skeleton of PCPs will undergo a reversible transition from neutral to anionic, producing derivatives with varying ionic conductivities and transference numbers. The transference number of MIT-20-LiCl was as high as 0.66, which obviously surpassed the values for LEs, typically less than 0.4, proving the Li^+-dominated ionic conduction. Compared with MIT-20-LiCl, MIT-20-LiBr, with less Li^+ ion content, exhibited much higher ionic conductivity due to the less electronegative Br^- and weaker interactions with Li^+ ion (Figure 8B). A similar phenomenon can be found in $Cu_4(ttpm)_2$ PCPs that the ionic conductivities of MOF-LiCl, MOF-LiBr, and MOF-LiI were in the range of 10^{-4}–10^{-5} S cm^{-1}, depending on the anion identity (Figure 8D). The Li^+ ion transference number for MOF-LiCl was as high as 0.69, which was competitive with many electrolyte membranes and a remarkable enhancement upon LEs. Comparatively, MOF-LiBr and MOF-LiI showed a lower transference number of 0.42 and 0.36, revealing the weaker interaction of Cu^{2+} centers with Br and I. The results suggested that the anion softness was an important factor, which not only impacted the ionic conductivity but also dominated the transference number via the ion-pairing and grafting interactions. The anion species also affected the electrochemical performance of SSEs to some degree. MOF-LiCl had a higher potential window of 4.5 V compared to that of MOF-LiBr (3.5 V), which could be attributed to the partial oxidation of Br. In other representative works, Hu et al.

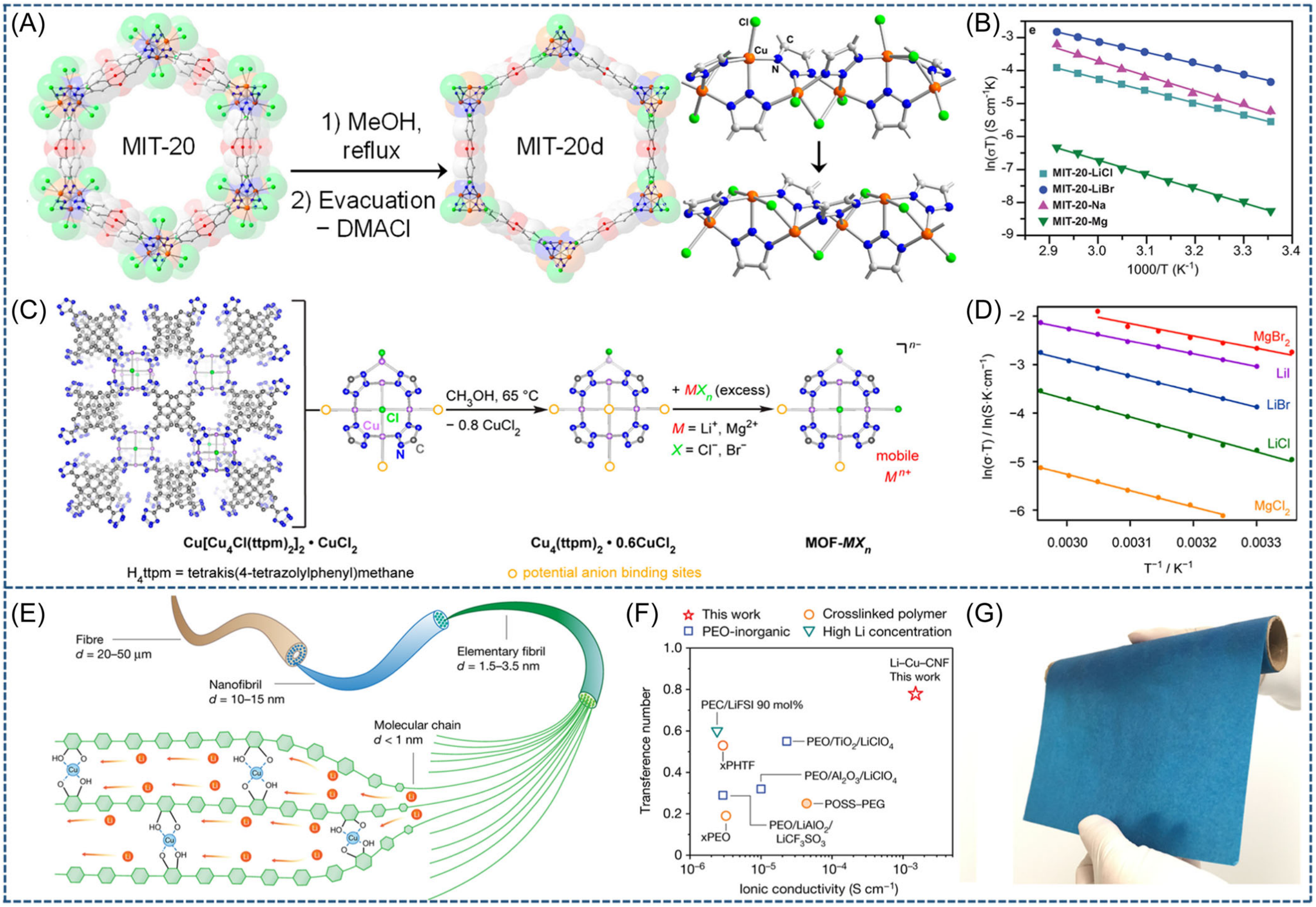

FIGURE 8 Ion-conductive polymer–metal coordination polymers. (A) Schematic of crystal structures of MIT-20 and MIT-20d, formed by the process of DMACl losing. (B) Ion conductivities of MIT-20-LiCl, MIT-20-LiBr, MIT-20-Na, and MIT-20-Mg. Reproduced with permission.[71] Copyright 2017, American Chemical Society. (C) Schematic representation of the synthesis of $Cu[Cu_4Cl(ttpm)_2]_2{\cdot}CuCl_2$, $Cu_4(ttpm)_2{\cdot}0.6CuCl_2$ and MOF-MX_n. M = Li^+ or Mg^{2+}, $X = Cl^-$ or Br^-, and $n = 1$ or 2. (D) Ion conductivities of MOF-LiCl, MOF-LiBr, MOF-LiI, MOF-$MgCl_2$, and MOF-$MgBr_2$. Reproduced with permission.[72] Copyright 2019, American Chemical Society. (E) Schematic illustration of the hierarchical structure of CNFs. (D) Li^+ ion transference number versus ion conductivities plot for Li-Cu-LNF and other solid polymer electrolytes. (F) Digital photograph of Li-Cu-CNF electrolyte membranes. Reproduced with permission.[73] Copyright 2020, Springer Nature.

prepared novel PCP-based electrolyte membranes through copper ion (Cu^{2+}) coordination with one-dimensional cellulose nanofibrils (CNF), termed Cu-CNF (Figure 8E).[73] Subsequent studies prove that expanding the intermolecular polymer structure and decoupling the Li^+ ion transport from the polymer segmental relaxation enable rapid transport of Li^+ ion along the polymer chains. This expanded intermolecular polymer structure, combined with residual solvents like H_2O and DMF, enabled high Li^+ ion conductivity ($1.5 \times 10^{-3}\ S\ cm^{-1}$) and transference number (0.78) at room temperature (Figure 8F). Due to a simple and reproducible synthesis method, Li–CNF–Cu electrolyte membranes have the potential for scaled-up production (Figure 8G). The full battery assembled with this electrolyte membrane and $LiFePO_4$ cathode can be stably cycled at 0.2 C for 100 cycles. In addition, the electrolyte membrane also shows good compatibility with the NMC811 cathode.

Although PCPs incorporating guest molecules have shown potential in achieving enhanced ionic conductivity, the integration of flammable solvents must compromise the safety and mechanical robustness of electrolyte membranes. The inclusion of ILs, while beneficial, might elevate the manufacturing cost, potentially hindering their economic feasibility ion commercial applications. Furthermore, elucidating the ion transport dynamics within the PCP matrix, whether inside porous or at interfacial levels, demands a synergy of sophisticated in situ characterization techniques and rigorous computational analyses. A summary of objective rules is essential to delineate the interaction of metal ions, molecular structures, sizes, and morphologies in governing ionic transport within PCPs. Such insights will be invaluable for advancing the next-generation PCP-based electrolyte membranes. A meticulous investigation into the intrinsic thermal and electrochemical stability of PCPs is imperative. Doubts arise regarding the resilience of PCPs when exposed to extreme conditions, such as solvent evacuation at high temperatures or variances in metal ions oxidation/reduction states during cell cycling. These aspects highlight the necessity to assess the reliability and longevity of PCP-based electrolyte membranes in LMBs.

3.3.2 | Electrolyte membranes integrating PCP-based fillers

PCP-based particles have been demonstrated to be effective fillers, boosting ionic conductivity and mechanical strength for parent electrolyte membranes, as evidenced by the MOF-5 fillers in PEO-LiTFSI electrolyte membranes (Figure 9A).[74] PEO-LiTFSI/MOF-5 attained a high Li^+ ion conductivity of $3.16 \times 10^{-5}\ S\ cm^{-1}$ at room temperature, surpassing those of traditional PEO-LiTFSI electrolyte membranes. However, this electrolyte membrane remains challenging of operating at ambient temperature due to its large interfacial resistance. The PCP-based electrolyte membranes suitable for room temperature LMBs were developed by polymerizing vinyl functionalized MOF (UiO-66-NH_2), poly(ethylene glycol) diacrylate (PEGDA), and LiTFSI (Figure 9B).[75] Noteworthily, robust chemical interactions between MOF nanoparticles and polymer chains were formed through the UV photopolymerization of vinyl-functionalized UiO-66-NH_2 with carbon–carbon double bonds, PEGDA, and LiTFSI. The as prepared electrolyte membranes possessed high ionic conductivity of $4.31 \times 10^{-5}\ S\ cm^{-1}$ at 30°C, as well as commendable interfacial compatibility with electrodes. Recently, Li et al. incorporated an amorphous infinite coordination polymer (ICP) nano-network of Ce-coordinated polyphenol ellagic acid ($EACe_2$) into a PEO matrix, aiming to realize more durable LMBs (Figure 9C).[76] The ICP network with extensive interconnectivity and self-assembly capability, facilitates improved filler penetration and multiscale interaction within PEO. Additionally, the $EACe_2$ nano-filler enhances the ionic conductivity and Li-ion transference number of PCP-based electrolyte membranes. As a result, this development paves the way for ultrastable and kinetically favorable Li/Li cells, which shows mitigated dendrite formation even after cycling for over 8800 h. The electrolyte membranes, CSPE-0.1$EACe_2$, achieve high ionic conductivities, $2.03 \times 10^{-5}\ S\ cm^{-1}$ at 30°C and $2.76 \times 10^{-4}\ S\ cm^{-1}$ at 60°C, respectively.

4 | APPLICATIONS OF OTHER MICROPOROUS POLYMERS

In addition to HCPs and PCPs, other microporous polymers such as PIMs, POCs, and COFs also hold considerable promise for use as electrolyte membranes in LMBs. Likewise, these covalently bonded porous materials feature a series of promising attributes, such as large surface areas and tunable pore sizes, easy processability, and readily adaptable functionalities. By rationally designing their molecular structures, these features can be tuned to meet the specific ionic conductivity and electrochemical stability needs of electrolyte membranes.

4.1 | COF-based electrolyte membranes

Electrolyte membranes based on COFs are distinctively crystalline, formed either by the direct growth of COFs or through the self-assembly of 2D COF nanosheets. COFs connected by robust covalent bonds between organic linkers generally exhibit a regular and periodic pore structure with a narrow pore size distribution, which are

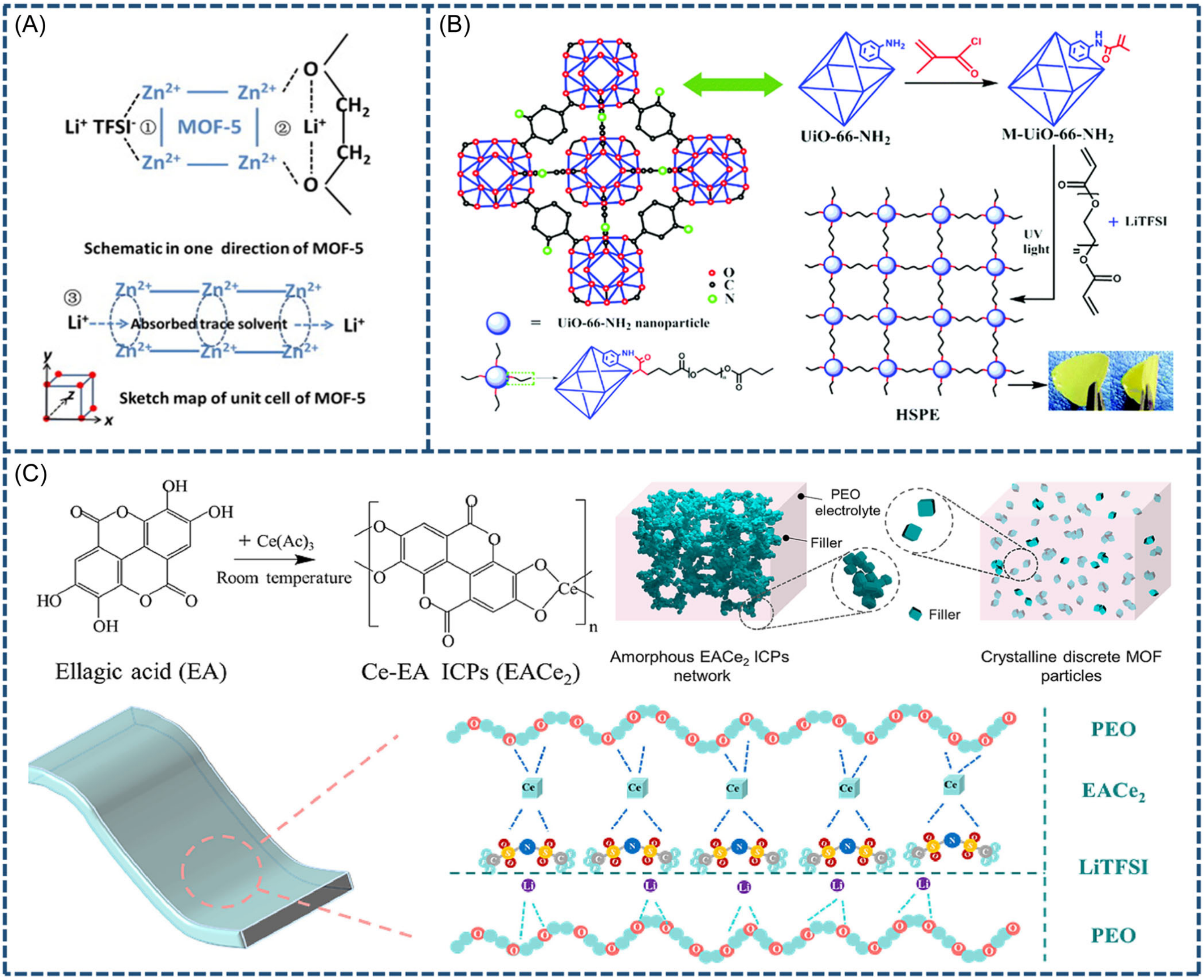

FIGURE 9 Metal-organic framework (MOF)-based electrolyte fillers and their applications in lithium-metal batteries. (A) Schematic processes of Li-salt dissociation and Li^+ ion transportation. Reproduced with permission.[74] Copyright 2013, Elsevier B.V. (B) Synthesis of the covalently linked MOF–poly(ethylene glycol) diacrylate electrolyte membranes. Reproduced with permission.[75] Copyright 2018, The Royal Society of Chemistry. (C) Schematics of synthesis procedure of $EACe_2$, composite electrolyte membranes, and Li^+ ion transport mechanism. Reproduced with permission.[76] Copyright 2021, Elsevier B.V. ICP, infinite coordination polymer; PEO, poly(ethylene oxide).

adjustable by altering the organic linkers.[77,78] Given these advantageous characteristics, these membranes have intrigued significant interest for their potential in LMBs. Xu et al. prepare COFs by introducing electron-withdrawing triazine and polyfluorobenzene groups into the skeleton of imine-linked COF and further converting the reversible imine linkage into more lithophilic and stable quinoline aromatic ring linkages via Povarov reaction. These COFs exhibit a large band gap with an ultralow highest ocuupied molecular orbital value (−6.2 eV under vacuum) and impressive oxidative stability up to 5.6 V (vs. Li^+/Li) as well as an outstanding ionic conductivity of $1.5 \times 10^{-4}\ S\ cm^{-1}$ at 60°C when used as electrolyte membranes (Figure 10A,B).[79] Additionally, the organic nature of COFs also allows the integration of various functional groups onto their pore wall, thus facilitating Li-salt dissociation and rapid Li^+ ion migration by introducing ion-conducting polymer chains in pores or constructing Lewis acidic/basic pore structures.[82] Guo et al. harnessed the electron-absorbing effect of nitro groups to regulate the donor–acceptor structure in COFs, achieving the construction of directional Li^+ transport channels. During the charging and discharging process, nitro can be reduced to NO_2^- and further react with Li metal to form Li_3N and LiN_xO_y with high ionic conductivity. This process synergistically accelerates the homogeneous deposition of Li^+ ions, and ultimately obtains a dendrite-free lithium battery with a long life of 6000 h.[83] Kim et al. prepared a diethylene glycol-modified pyridinium COF (DEG-PMCOF) with a

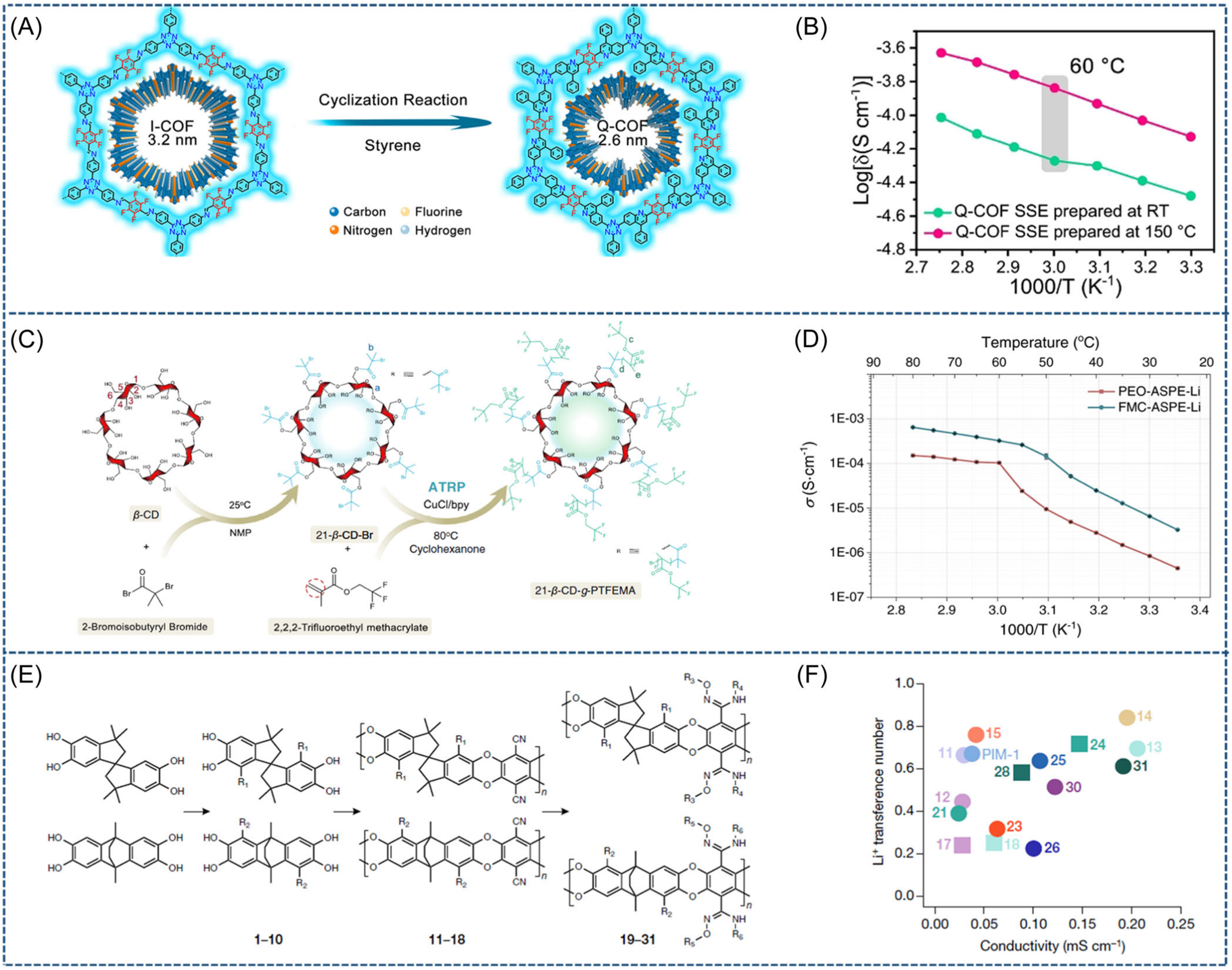

FIGURE 10 Electrolyte membranes based on other typical microporous materials. (A) Schematic synthesis process from I-covalent organic framework (COF) to Q-COF. (B) Ion conductivity curves of Q-COF electrolyte membranes prepared at room temperature and 150°C. Reproduced with permission.[79] Copyright 2021, Wiley-VCH GmbH. (C) Synthesis of 21-*β*-CD-g-poly(2,2,2-trifluoroethyl methacrylate) electrolyte membranes. (D) Ion conductivity verse temperature plots of poly(ethylene oxide)-ASPE-Li and FMC-ASPE-Li electrolyte membranes. Reproduced with permission.[80] Copyright 2022, Springer Nature. (E) Synthesis for a various library of polymers of intrinsic microporosity. (F) Plot of Li^+ ion transference verse ion conductivity. Reproduced with permission.[81] Copyright 2019, Springer Nature.

well-defined periodic structure, which is a multi-component electrolyte membrane with a highly polar cationic molecule, a flexible ion-transporter, and an ordered ionic channel. The electrolyte membrane achieves high ionic conductivity (1.71×10^{-4} S cm^{-1}) and transference number (0.61) at room temperature.[84]

4.2 | POC-based electrolyte membranes

Electrolyte membranes based on POCs are fabricated from the self-assembly or interfacial polymerization of organic cage molecules. These encompass not only synthetic organic cage molecules but also macrocycles and cage-like structures, including cyclodextrin, polyhedral oligomeric silsesquioxanes (POSS), and Noria, which feature permanent voids inside a rigid structure, as well as windows granting access to these voids.[85–87] Consequently, the micropores within POC-based electrolyte membranes are derived from the inherent cavities of the synthetic organic cage molecules.[88] One key distinction between synthetic organic cage molecules and the extended networks found in COFs and MOFs is that they are discrete organic molecules and can be dissolved in many solvents, because organic cage molecules are held together by relatively weak intermolecular forces, such as van der Waals forces or hydrogen bonds, rather than covalent, ionic, or coordinative bonds. This feature makes it possible to postmodify organic cage molecules during the fabrication of POC-based electrolyte membranes, thus enhancing compatibility with polymer matrices or improving electrochemical performances. Currently, POCs primarily serve as crosslinking agents and centers in electrolyte membranes, facilitating the creation of polymer electrolyte membranes with topological network structures. Hu et al. introduce a top-down design approach, devising 21-arm fluoropolymers (21-β-CD-*g*-PTFEMA) anchored on a postmodified β-cyclodextrin (β-CD) core with 21 poly (2,2,2-trifluoroethyl methacrylate) (PTFEMA) arms, which are designed and synthesized through atom transfer radical polymerization (Figure 10C). Due to the synergistic effects of supramolecular interactions between 21-β-CD-g-PTFEMA and PEO, the characteristics of PTFEMA, and the multi-arm topological constructs of the β-CD core, these POC-based electrolyte membranes exhibit remarkable high-voltage stability, transference number (0.88) and ionic conductivity of $6.43 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$ at 80°C (Figure 10D).[80] Furthermore, both Li et al. and Yang et al. have shown the favorable physical and electrochemical properties imparted by the topological structure of POSS within POC-based electrolyte membranes.[89,90]

4.3 | PIM-based electrolyte membranes

Electrolyte membranes based on PIMs can be fabricated through solution-casting of amorphous PIMs composed of stiff and contorted polymer chains. Due to steric hindrance arising from these chains, the micropores within PIMs predominantly emerge from the concave configuration of their monomeric units. Unlike HCPs, the formation of these pores does not need crosslinking steps.[91,92] Typically, PIMs exhibit high solubility in a variety of common organic solvents, making them highly amenable for electrolyte membrane fabrication. The convenience of this solution processing approach makes PIM-based electrolyte membranes particularly desirable for high electrochemical performance in LMBs. Moreover, the pore architecture within PIMs can be adjusted by strategically engineering their rigid backbones, which might include bulky pendant groups or specific contortion sites.[93,94] After studying a series of PIM-based electrolyte membranes, Helms et al. illustrate that the topology of free volume elements (FEVs) within PIMs evolves in response to changes in the functional groups coordinating with $\mathrm{Li^+}$ ion, thus affecting the overall microporous network, as well as the solvation structure, dynamics and transport of $\mathrm{Li^+}$ ion in the polymer matrix (Figure 10E).[81] Notably, PIM-13, with its distinct FVEs, exhibited enhanced $\mathrm{Li^+}$ ion conductivity ($2.06 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$ at 25°C) and a higher transference number (0.7) in comparison to PIM-1, attributing to the FVEs acting as solid solvent cages for $\mathrm{Li^+}$ ion (Figure 10F). Remarkably, the self-diffusion of $\mathrm{Li^+}$ is essentially the same in PIM-13 and PIM-1, except that self-diffuses of $\mathrm{Li^+}$ ion are faster than the $\mathrm{PF_6^-}$ in PIM-13. This phenomenon results from the $\mathrm{Li^+}$ ion being ensconced within the solid solvation cage along the polymer chain, which creates a double-layer structure. This configuration curtails the self-diffusion of $\mathrm{PF_6^-}$ more than that of $\mathrm{Li^+}$ ion, leading to a higher activation energy requirement for ion transport in PIM-13 relative to PIM-1. Additionally, the enhanced ionic conductivity witnessed in PIM-13, as opposed to PIM-1, stems more from amplified solubility (i.e., heightened incorporation of $\mathrm{LiPF_6}$ into the membrane due to complexation within the ionic solvation cage) than from any alterations in the mobility of $\mathrm{Li^+}$ within the pores. A full battery with PIM-13 as an intermediate layer should have better cycling performance, higher capacity, and lower cell impedance than a battery with PIM-1 as an intermediate layer or no interlayer at all. Given these insights, integrating functional groups that are nonionic yet capable of coordinating with $\mathrm{Li^+}$ ion into the porous matrix of PIMs shows promising potential in realizing high-performance PIM-based electrolyte membranes for LMBs. Recently, Xu et al. reported a highly ion-conducting electrolyte membrane was obtained by using a glassy, microporous, trapezoidal polymer with a highly rigid and twisted backbone structure. The polymer was modified with amidoxime functional groups. Compared to conventional polymer electrolyte materials, PIMs electrolyte membranes exhibit high ionic conductivity, electrochemical stability, environmental adaptability, and mechanical stability attributed to their excellent size-sieving properties.[95]

As aforementioned, microporous polymer electrolyte membranes consist of rigid moieties (e.g., benzene ring), which intrinsically exhibit poor ionic conductivity. When these polymers are employed as the primary scaffold of electrolyte membranes, integration with an external LE becomes indispensable to achieve the requisite ionic conductivity for LMBs working. Consequently, the physicochemical characterizations and electrochemical performances of the electrolyte membrane are mainly determined by the specific composition and nature of these liquid mediums. Intriguingly, while the inherent microporosity might confer advantages for the dissociation of Li-salt, the existing pieces of literature provide cursory insights into this aspect. This highlights the imperative to further probe the underlying mechanisms that drive the impact of microporous structures on Li-salt dissociation, thereby guiding the accurate design and fabrication of high electrochemical performance microporous electrolyte membranes.

5 | CHALLENGES AND OUTLOOKS

This review focuses on the design strategies, synthesis methods, and applications of electrolyte membranes based on HCPs and PCPs for LMBs. Table 1 summarizes four key indicators for different synthetic protocols of HCPs and PCPs. The modifiable microporous structures and robust frameworks of HCPs and PCPs have facilitated distinct design strategies, including their amalgamation with LEs or ILs, as well as integration with polymer matrices. Furthermore, other microporous polymer-based electrolyte membranes, such as COFs, POCs, and PIMs, are also succinctly discussed in this review. Each category possesses distinct merits and challenges, as delineated in Table 2. Currently, leveraging microporous polymers for high electrochemical performance in electrolyte membranes for LMBs is an area of emerging research. The large surface area of HCPs and PCPs allows for the introduction of densely packed charged species within minuscule pores to create closely packed cation-hopping sites, potentially reducing the activation energy required for ion transport and thereby augmenting ionic conductivity. Moreover, the pronounced porosity of HCPs and PCPs modulates Li^+ ion transport, fostering uniform Li^+ ion deposition and preventing dendrite formation. The rigid skeleton attribute of HCPs and PCPs also endows superior mechanical and thermal stability upon the electrolyte membranes, which serves to further curtail Li-dendrite proliferation, enhancing the safety of LMBs.

Despite the myriad advantages presented by the compositional and structural adaptability of HCPs and PCPs, challenges persist in crafting HCP- and PCP-based electrolyte membranes. There are concerns regarding the Li^+ ion conductivity of HCP-based electrolyte membranes. The prevalence of numerous benzene structures, which are nonconductive to Li, hinders the advancement of HCP-based electrolyte membranes. With respect to PCPs, the requisition of costly ligands or complex fabrication methodologies obstructs the large-scale production of both PCPs and their derivative electrolyte membranes. Moreover, the inherent multi-valence states of metal ions in PCPs might cause structural deterioration during charge and discharge cycles, thereby undermining the electrochemical stability of PCP-based electrolyte membranes.

In the quest for superior electrolyte membranes for LMBs, prospective research on HCPs and PCPs could be conducted by the following aspects:

1. Enhancing ionic conductivity at ambient temperatures by amplifying the density of mobile lithium ions and diminishing the associated energy barrier.
2. Recognizing that the dimensions and chemical environments of the micropores in HCPs and PCPs profoundly influence the Li^+ ion conductivity and transference within the electrolyte membrane.
3. Introducing suitable functional groups to the polymer surface can foster potent intermolecular bonds with polymer substrates, effectively addressing the interface compatibility challenges between HCPs/PCPs and polymers.

TABLE 1 Comparison of different synthetic protocols of HCPs and PCPs.

Types	Methods	Principle	Advantages	Disadvantages
HCPs	Postcrosslinking	Polymer precursors are polymerized again with Lewis acid catalyst	Low cost Simple procedure Mass production	Time-consuming Limited functional monomers
	One-step polycondensation	Monomers are polymerized directly under Lewis acid catalyst	Simple procedure Mass production Controllable pore size	Toxic by-product Strict reaction conditions
	External crosslinking	Monomers are directly polymerized with external linkers and $FeCl_3$ catalyst	Mass production Controllable pore size Mild reaction condition	Uncertain structure
PCPs	Top-down	The intermolecular interactions within the bulk materials are destroyed by external forces	Simple procedure	Lack of precise Low production rate
	Bottom-up	Metal ions interact directly with organic ligands	Uniform size Highly designable structure	High cost Strict reaction conditions

Abbreviations: HCP, hypercrosslinked polymer; PCP, porous coordination polymer.

TABLE 2 Comparison of different types of electrolyte membranes.

Types	Conductivity (S cm^{-1})	Advantages	Disadvantages
HCP	10^{-5}–10^{-3}	Stable with Li Ease of fabrication High mechanical strength High oxidation voltage	Lacking of Li$^+$ conducting functional group
PCP	10^{-6}–10^{-3}	High safety Good compatibility High mechanical strength	Low flexibility Limited thermal stability Tedious fabrication process
COF	10^{-8}–10^{-3}	Stable with Li High mechanical strength Ease of functionalization	Tedious fabrication process Relatively low oxidation potential
POC	10^{-5}–10^{-3}	High flexible Fine interfacial contact	Low mechanical strength Low oxidation potential
PIM	10^{-6}–10^{-3}	Ease of fabrication High oxidation potential High mechanical strength	Lacking of Li$^+$ conducting functional group

Abbreviations: COF, covalent organic framework; HCP, hypercrosslinked polymer; PCP, porous coordination polymer; PIM, polymer of intrinsic microporosity; POC, porous organic cage.

(4) A comprehensive exploration of the Li$^+$ ion conduction mechanisms both internally and at the interfaces of HCP- and PCP-based electrolyte membranes is crucial. This can be achieved through in situ techniques paired with theoretical computations.

(5) Advanced synthesis approaches of HCPs and PCPs need to be further explored. The fabrication of HCPs takes into account the reduction of pollution, while the manufacture of PCPs requires more efficient synthesis techniques to achieve mass production.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

Data will be made available on request.

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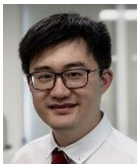

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