

# Engineering Porous Liquids for Enhanced Ion Mobility and Stable Battery Electrolytes

Mehran Arzani, Hamidreza Mahdavi,\* and Vikas Berry\*



Cite This: *ACS Energy Lett.* 2025, 10, 3259–3268



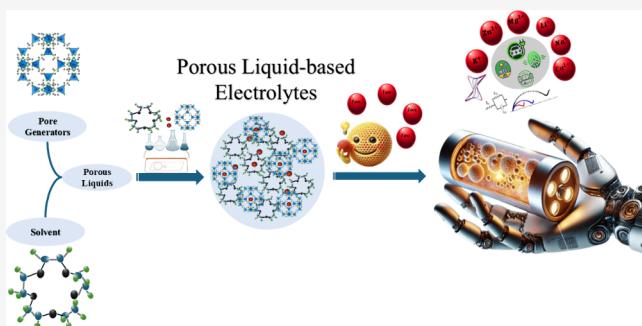
Read Online

ACCESS |

Metrics & More

Article Recommendations

**ABSTRACT:** Beyond traditional electrolytes, innovative electrolytes with molecular porosity to selectively embed ions can provide a protective shield to increase their mobility for enhanced battery efficiency. The molecular structure of these porous liquid-based electrolytes (PLEs) can be designed to provide permanent, empty, and selective porous media. In this Perspective, we show the potential and design principles of porous liquids (PLs) that can enable their incorporation into all ion batteries. The porous structure of PLs increases their surface area exposure to ions for their selective shielding from dendrite formation, enhancing their mobility/conductivity, thus also addressing challenges with thermal instability and safety risks associated with conventional electrolytes. This work proposes a roadmap for PLE development, emphasizing molecular design, target mechanisms, and computational studies aligned with specific battery chemistries to enhance the energy density and extended cycle life.



This work proposes a roadmap for PLE development, emphasizing molecular design, target mechanisms, and computational studies aligned with specific battery chemistries to enhance the energy density and extended cycle life.

Critical challenges in electrolyte design for batteries include limited thermal and electrochemical stability, low ionic conductivity and ion mobility,<sup>1</sup> safety,<sup>2</sup> and decomposition at high voltages or extreme temperatures.<sup>3</sup> Additionally, ensuring compatibility with various electrode materials while mitigating side reactions and preventing dendrite formation continues to be a significant barrier to energy efficiency.<sup>4,5</sup> Although the majority of reviews on porous liquids (PLs) have explored their synthesis and gas separation applications,<sup>6</sup> this perspective uniquely focuses on their potential as battery electrolytes.

Porous liquids offer a transformative platform for electrolyte design across different battery chemistries.

PLs with an accessible and selective molecular encasement for ions provide permanent porosity within the electrolyte, overcoming these limitations. PLs combine the fluidity of liquid electrolytes with selective, stable, and empty porosity, which can enhance electrochemical properties of electrolytes such as ion mobility, safety, and resistance to dendrite formation. Unlike solid-state electrolytes, they maintain processability, while their tunable pores provide selectivity unmatched by that of conventional liquid electrolytes. These properties position PLs as good candidates for new electrolyte

design, addressing the mentioned challenges.<sup>1,6,7</sup> In this perspective, we will discuss why and how PLs can be a great alternative to design electrolytes for all battery types to enhance their performance.

## ■ POROUS LIQUIDS

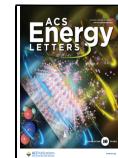
Unlike conventional liquids, PLs include a permanent and empty porous structure that remains stable in the liquid state.<sup>8</sup> Structural solids can maintain permanent, uniform cavities with precise size and shape due to their rigidity and robustness. On the other hand, regular liquids exhibit fluidity and dynamic structures where any “porosity” is a result of transient intermolecular cavities, most of which are smaller than typical molecules.<sup>9,10</sup> According to scaled particle theory, the solubility of a solute in a liquid is largely determined by the energy required to create cavities to accommodate the solute.<sup>11</sup> Consequently, introducing high concentrations of permanent, molecule-sized cavities into a liquid could significantly alter its solvating and solute-transporting properties.<sup>12,13</sup>

Received: May 12, 2025

Revised: June 5, 2025

Accepted: June 6, 2025

Published: June 16, 2025



## Integrating porous liquids with electrolytes would enhance ionic mobility, stability, and electrochemical performance.

Such internal permanent porosity can effectively contribute to a mobile network of voids or channels, which can pave the way for ion movement throughout the electrolytes.<sup>14</sup> These unique features of PLs make them promising candidates for different applications.<sup>13</sup> The cavities in PLs offer greater free volume compared to dense liquid phases.<sup>15</sup> Additionally, the chemical properties and structural characteristics of the porous host, liquid medium, and solid–liquid interface can play important roles in widening the application of these PLs beyond gas sorption.

As shown in Figure 1, PLs are generally divided into three categories based on their structure and pore accessibility (type

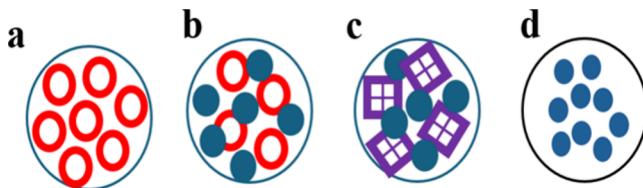


Figure 1. PLs vs conventional liquids: (a) type I, (b) type II, (c) type III, and (d) conventional liquid.

I, type II, and type III).<sup>16</sup> Type I consists of neat liquids with intrinsically porous molecules requiring no solvent; type II includes rigid, porous molecules dissolved in a bulky solvent that cannot enter the pores; and type III features porous solids such as metal organic frameworks (MOFs) dispersed in such solvents, forming stable colloids. The key differences lie in whether the pore generator is a liquid, dissolved molecule, or solid and whether a solvent is used but excluded from the pores. Some hybrid systems may exist but are classified by their dominant porosity mechanism.<sup>6,16</sup>

**Engineered pore generators in porous liquids can help protect the anode by reducing dendrite growth, volume changes, and surface damage.**

PLs are synthesized through various methods, such as physically mixing porous materials with a solvent such as ionic liquids (ILs), surface ionization, and surface modification techniques. These methods ensure that the pores remain open and empty.<sup>16</sup>

To synthesize the PLs, different solvents such as ILs and solid pore generators such as porous organic cages (POCs), MOFs, covalent–organic frameworks (COFs), etc., can be used.<sup>6</sup> Figure 2 shows selected pore generators and the structure of commonly selected solvents to synthesize the PLs. The stability and viscosity of the pore generator-solvent combination, along with the prevention of solvent penetration into pores, must be carefully optimized to achieve suitable capacities and kinetics for specific applications.<sup>17</sup> ILs are frequently employed as solvents in the synthesis of PLs due to their ability to act as nonpenetrating solvents when one or both

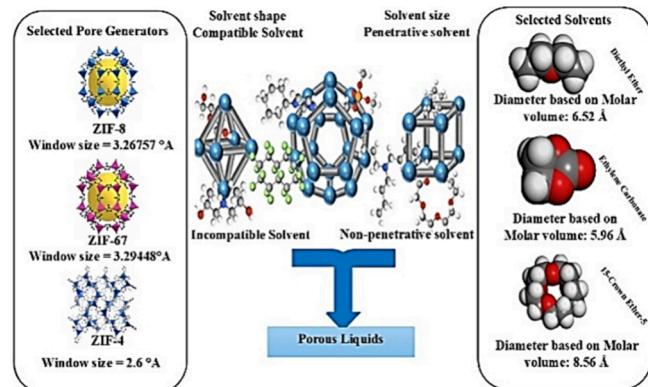


Figure 2. Selected solvents and pore generators used in PLs. Reproduced with permission from refs 20. Copyright 2021 American Chemical Society. Reproduced with permission from ref 21. Copyright 2021 Elsevier. Reproduced with permission from ref 22. Copyright 2023 American Chemical Society.

ion pairs are sterically hindered, preventing them from entering the pores.<sup>18,19</sup>

Figure 3a shows an example of the [M2070][IPA] solvent molecule with dimensions of 24 Å, 18 Å, and 20 Å, which

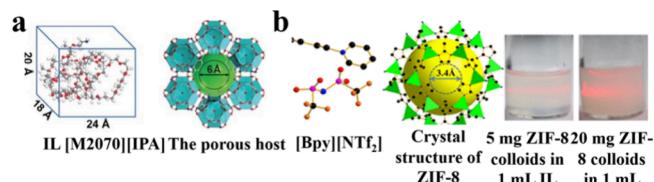


Figure 3. (a) Size of the [M2070][IPA] and the porous host. Reprinted with permission from ref 23. Copyright 2024 Wiley. (b) PL Type III. Reprinted with permission from ref 25. Copyright 2018 American Chemical Society.

theoretically does not diffuse into the nanopores of the selected MOF, which have an approximate size of 6 Å.<sup>23</sup> This highlights the critical importance of considering the molecular dimensions of components, such as the liquid phase and pore generators, materials creating and stabilizing the voids, during the design of PLs.<sup>24</sup> Furthermore, Figure 3b illustrates a PL type III structure, including [Bpy][NTf<sub>2</sub>] as the solvent (IL) and ZIF-8 as the pore generator. The pore window size of this PL is 3.4 Å, indicating that molecules larger than this dimension cannot penetrate the pores.<sup>26</sup> The interaction between the solid host and the liquid counterpart is important as well, with surface chemistry, solvation effects, and solid–liquid interface properties playing key roles in the stability and functionality of PL systems.<sup>14</sup> This chemistry and its molecular structure enable applications in gas storage, separation, and catalysis by leveraging the molecular sieving effect, selective sorption, and adjustable cavity sizes.<sup>16</sup>

An ideal PL is stable, nonvolatile, and low viscous for effective processing.<sup>8</sup> The evaluation of the solvent's physicochemical properties, molecular size, and capacity to penetrate pores is the main step in synthesizing the PLs. The solvation and interaction mechanisms of pore-generators, for example, ZIF-62 and ZIF-8 (Figure 4a and 4b), with specific solvents impact the formation of stable PL systems.<sup>17</sup>

Solvents such as hydrophobic TPB effectively solvate organic ligands such as imidazole and benzimidazole on the ZIF-62 surface (Figure 4a). This is because of the



**Figure 4.** Schematic of proposed mechanisms: (a) Chemical binding affinity and (b) solvation. Reproduced with permission from ref 17. Copyright 2022 Springer.

## Porous liquids can unlock new dimensions in electrolyte safety and long-term electrochemical stability through stable, empty and ion selective pores.

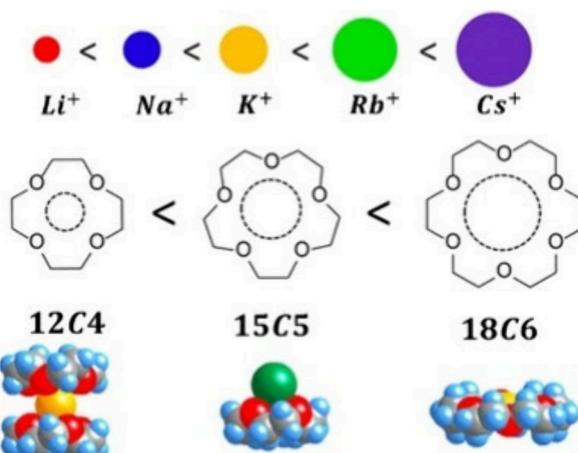
compatibility of both pore generators and the hydrophobic groups in the solvent. In this case, Solvation triggers charge density oscillations, leading to steric repulsion that blocks interpenetration. Meanwhile, weak van der Waals forces between  $Zn^{2+}$  ions and benzene electrons enhance dissolution.<sup>26–29</sup>

In contrast, hydrophilic solvents such as MIM interact with ZIF-8 (Figure 4b) by weakly solvating its 2-methylimidazole ligands; however, they form strong chemical bonds with ZIF-8 ions due to their nucleophilicity. These interactions create efficient van der Waals forces between  $Zn^{2+}$  ions and nitrogen atoms in MIM, leading to stable colloidal dispersions.<sup>25,28,29</sup> ZIF-62 and ZIF-8 particles maintain stable colloids due to van der Waals repulsion and strong chemical bonding with the solvent. While solvation helps, chemical bonding between ZIF ions and solvent molecules is the primary factor in preventing aggregation, ensuring long-term stability without sedimentation.<sup>29</sup> Comparatively, solvent interactions vary; ZIF-8 interacts more strongly with TEG than ZIF-7, while ZIF-7 shows better solvation with DPG than ZIF-8. These nuanced interactions significantly influence dissolution and stability in PL applications.<sup>19,29</sup>

These unique properties of PLs show great potential to contribute to electrolyte design to overcome the current challenges in batteries. However, the design of PLEs, their compatibility with battery electrodes, and their potential impact on battery performance need to be thoroughly evaluated and discussed.

### ■ PLES DESIGN AND COMPATIBILITY WITH BATTERY ELECTRODES

The relationship between metal ions ( $Li^+$ ,  $Na^+$ ,  $K^+$ ,  $Rb^+$ , and  $Cs^+$ ) and crown ethers 12-crown ethers-4 (12C4), 15-crown ethers-5 (15C5), and 18-crown ethers-6 (18C6)) is governed by the size matching between the ion and the cavity of the crown ether, as shown in Figure 5. When the ionic radius is



**Figure 5.** Simplified schematic of ions and crown ethers. Reproduced with permission from ref 30. Copyright 2021 American Chemical Society.

smaller than the crown cavity, for example  $Li^+$  with 18C6, the cation exhibits motional freedom within the cavity, while size compatibility, for example  $K^+$  with 18C6,  $Na^+$  with 15C5, leads to stable planar disc-type complexes. Conversely, when the ion is larger than the cavity,  $Cs^+$  with 15C5 as an example, the cation adopts a cone-shaped or sandwich-type coordination, affecting supramolecular structure, stability, and dynamic behavior in the resulting assemblies.<sup>30</sup>

PLs can be designed with specific pore sizes and chemical functionalities to selectively transport certain ions while blocking others.<sup>31</sup> The pore size in PLs can be adjusted during synthesis to match<sup>19</sup> the size of the desired ions (e.g.,  $Li^+ = 1 \text{ \AA}$ ,<sup>14</sup>  $Na^+ = 1.02 \text{ \AA}$ ,<sup>32</sup>  $Mg^{2+} = 1.44 \text{ \AA}$ ).<sup>14</sup>) This allows only ions of a certain size to pass through the porous network while blocking larger ions or molecules that might cause side reactions.<sup>16</sup> This selective ion transport can improve battery efficiency and prevent unwanted side reactions that could degrade the performance over time. Additionally, selective ion transport results in more efficient electrolytes, allowing higher ionic conductivity without the interference of unwanted products.<sup>31,32</sup> This mechanism is useful for maintaining ion balance during cycling and preventing unwanted ion accumulation in the electrolyte.<sup>33</sup> In lithium–sulfur batteries (LiS), PLEs can be designed to allow  $Li^+$  transport while blocking sulfur-containing species, which could otherwise lead to the shuttle effect and degrade performance.<sup>34</sup> This means PLEs can be designed to selectively block the diffusion of polysulfides that cause the shuttle effect while allowing  $Li^+$  ions to pass.<sup>35</sup> This prevents the degradation of the cathode material and improves the cycle life.

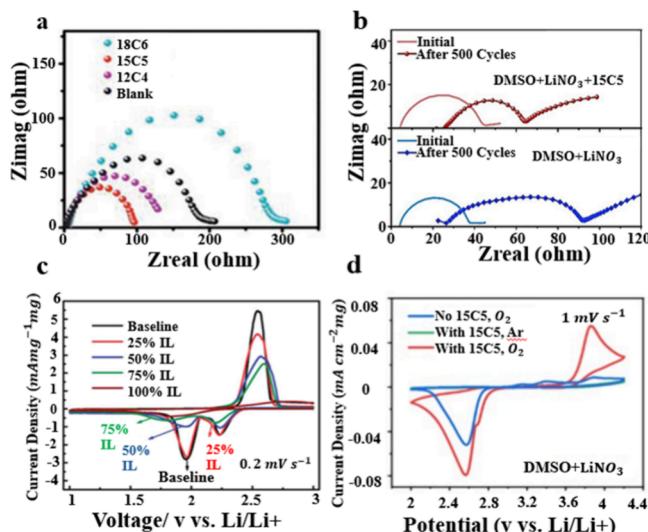
Liu et al. demonstrated that glycol-based slurries of ZIF-8 exhibited significantly enhanced carbon dioxide sorption selectivity, which was attributed to increased mass transfer resistance caused by the solvent layer adhering to the particle surface.<sup>36</sup> This can effectively control the environment for the electrochemical reaction of the  $Li\text{-CO}_2$  or  $Na\text{-CO}_2$  battery, for example.<sup>37</sup>

Although direct studies of the compatibility of PLs with battery electrodes are still lacking, foundational studies suggest strong potential. For example, Wang et al. reported that 15C5 molecules form stable complexes with  $Li^+$ , effectively regulating solvation structure and promoting uniform Li deposition. This

interaction facilitates dense, conductive solid electrolyte interphase (SEI) formation, significantly improving cycling performance and preventing dendrite growth in Li-metal batteries.<sup>38</sup> Moreover, Giri et al. demonstrated that crown-ether cages possess high thermal and structural stability under reactive conditions, which can be used for electrolytes.<sup>9</sup>

Moreover, components often found in PLs, such as MOFs and ILs, have shown notable compatibility with battery systems.<sup>5,39–41</sup> MOFs help prevent the polysulfide shuttle in Li–S batteries due to their high porosity, tunable chemistry, and chemical stability.<sup>42</sup> ILs such as [EMIM][TFSI] offer wide electrochemical windows and thermal stability, aiding SEI formation and supporting stable cycling with electrodes such as Li metal, sulfur, and silicon.<sup>40</sup> Qi et al. demonstrated that combining [EMIM][TFSI] with ZIF-8 in a membrane increased the  $\text{Li}^+$  transference number to 0.45 and enabled ionic conductivity of  $2.09 \times 10^{-4} \text{ S cm}^{-1}$  at 25 °C, enabling dendrite-free cycling and high-performance operation in full cells.<sup>43</sup> Hence, such studies clearly show the compatibility of PLs components with different electrodes, such as graphite, silicon, sulfur, sodium, and other active materials in battery electrodes.

As shown in Figure 6a, EIS for different crown ethers after 150 cycles, the Li|Li cell using the 15CS additive exhibits the



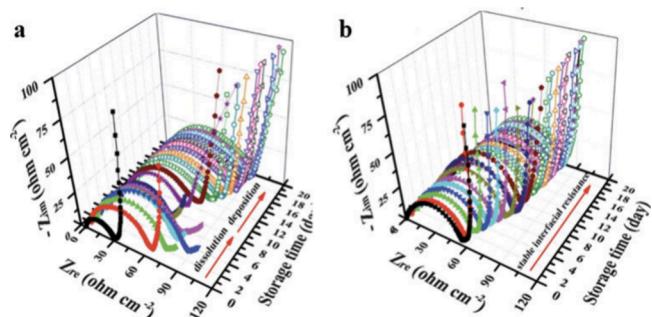
**Figure 6.** (a) EIS of all electrolytes after 150 cycles with the current density of  $1 \text{ mA cm}^{-2}$  and a capacity of  $0.5 \text{ mAh cm}^{-2}$ . Reproduced with permission from ref 38. Copyright 2021 Wiley. (b) Nyquist plots of the Li|Li symmetrical cells with DMSO +  $\text{LiNO}_3 + 15\text{CS}$  and DMSO +  $\text{LiNO}_3$  electrolytes before and after 500 cycles at  $0.1 \text{ mA cm}^{-2}$ . Reproduced with permission ref 44. Copyright 2024 American Chemical Society. (c) CV of Li–S cells with electrolytes with different amounts of IL ( $\text{Py}_{14}\text{TFSI}$ ). Reproduced with permission from ref 45. Copyright 2013 RSC. (d) CV curves in the electrolyte with and without 15CS, under Ar and  $\text{O}_2$  atmospheres. Reproduced with permission from ref 44. Copyright 2024 American Chemical Society.

lowest impedance compared to cells with 12C4, 18C6, and the blank electrolyte. The smaller semicircle for 15CS indicates a much lower interfacial resistance, meaning that it more effectively suppresses side reactions between the electrolyte and Li metal. This suggests that 15CS provides better stabilization of the electrode interface, leading to improved long-term cycling performance.<sup>38</sup> These results show how

these ILs can effectively decrease the charge transfer resistance ( $R_{ct}$ ) and improve battery performance.

Similarly, Figure 6b confirms that DMSO+ $\text{LiNO}_3+15\text{CS}$  maintains a much lower interfacial resistance after 500 cycles, attributed to enhance  $\text{NO}_3^-$  dissociation and stable SEI formation via  $\text{Li}_2\text{O}$  layers because of the presence of 15CS.<sup>38</sup> Moreover, cyclic voltammetry (CV) in Figure 6c demonstrates that increasing  $\text{Py}_{14}\text{TFSI}$  IL content (up to 100%) in Li–S cells protect the conversion of  $\text{Li}_2\text{S}_4$  to  $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$ , as seen by diminished cathodic peak intensities around 2.0 V. While high IL content slows polysulfide kinetics, it also stabilizes intermediates and enhances SEI integrity. As a result, ILs are able to play an important role in controlling the shuttle effects in Li–S and stabilizing the SEI layer.<sup>45</sup> Figure 6d indicates that 15CS enhances ORR/OER kinetics in Li–O<sub>2</sub> battery by promoting reactions and maintaining active sites, with stronger redox peaks under  $\text{O}_2$  and negligible current under Ar, confirming its electrochemical stability.<sup>44</sup>

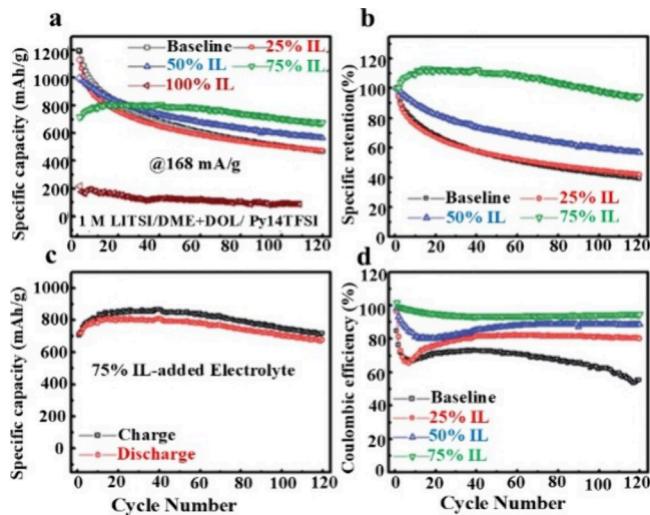
The incorporation of IL ( $\text{Py}_{14}\text{TFSI}$ ) into the electrolyte has demonstrated a significant effect on the electrochemical stability of the Li–S battery. Compared to the baseline electrolyte (without IL), Figure 7b, EIS reveals that cells with



**Figure 7.** EIS spectra of Li–S battery, electrolyte (a) without IL and (b) With 50% IL. Reproduced with permission from ref 45. Copyright 2013 RSC.

50% IL exhibit a significantly lower impedance growth during storage. Without an IL, Figure 7a, the impedance increases sharply over time, reflecting interfacial degradation due to polysulfide dissolution, shuttle effects, and reactions with the lithium metal anode. These changes are characterized by broad, disordered semicircles in the Nyquist plots and higher  $Z$ , indicative of unstable SEI formation and growing resistance. In contrast, the hybrid electrolyte containing 50% IL shows a more stable and gradual impedance profile over the same storage duration. The IL stabilizes by preventing polysulfide dissolution, reducing parasitic reactions at the lithium surface and maintaining a more stable SEI. This results in lower  $R_{ct}$  and enhanced interfacial stability.

Figure 8 demonstrates that increasing the IL content in the electrolyte significantly enhances the cycling performance of Li–S batteries. The IL-free electrolyte, the battery exhibits significant capacity fading (39.1% retention after 120 cycles), indicating poor cycle stability. With the addition of 25% IL, a slight improvement is observed, which becomes more pronounced as the IL concentration increases. At 75% IL, the sulfur electrode achieves an impressive 94.3% capacity retention after 120 cycles. Interestingly, an initial increase in discharge capacity is observed, reaching a maximum around the 20th cycle. This is attributed to the high viscosity of the



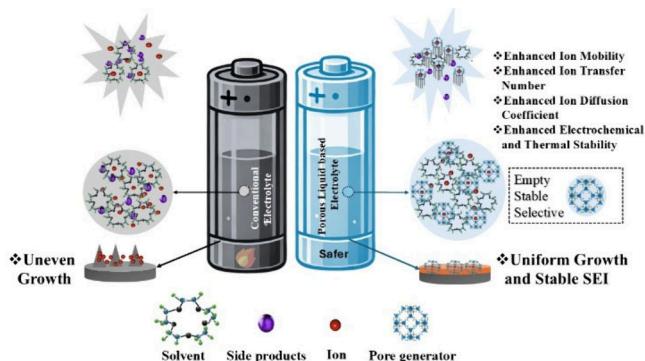
**Figure 8.** (a) Capacity lost, (b) capacity retention during cycling, (c) capacity retention after 120 cycles (IL: containing 75%), and (d) Coulombic efficiency in Li–S battery (electrolyte: 1 M LiTFSI/(DME–DOL+Py<sub>14</sub>TFSI) at 0.1 C). Reproduced with permission from ref 45. Copyright 2013 RSC.

75% IL electrolyte, which delays full wetting of the sulfur composite and gradually activates previously inaccessible sulfur. This activation process accounts for the early stage capacity growth. Moreover, the Coulombic efficiency is significantly improved by the presence of IL. The initial efficiency increases from 84.5% in the baseline to nearly 100% in electrolytes with 50% IL or higher. This stability is maintained throughout long-term cycling, further demonstrating the beneficial effect of ILs. Similar trends were confirmed under different current rates, highlighting the robustness of IL-enhanced electrolytes.<sup>45</sup>

These findings highlight that integrating pore generators into solvents, PLs, not only is compatible with battery electrodes but also provides considerable benefits in enhancing electrode stability, improving redox performance, and advancing electrolyte design for all batteries.

## BENEFITING FROM THE STRUCTURE OF PLs TO IMPROVE THE ELECTROLYTES

Figure 9 shows a comparison between conventional electrolyte and PLEs in batteries. PLs can offer a transformative advantage in battery technology by enhancing performance across several



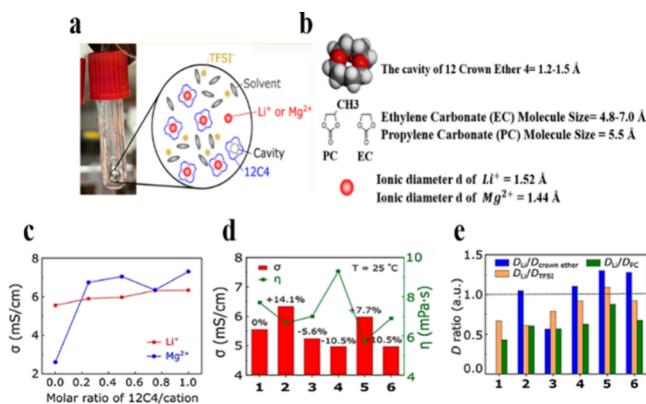
**Figure 9.** Schematic comparison between a conventional electrolyte and PLEs in batteries.

dimensions, such as improved ion mobility, increased surface area for ion interaction, selective ion channels, enhanced safety features (nonflammability), improved thermal stability, and resistance to dendrite formation. This makes them a sustainable solution for designing next-generation electrolytes in batteries.

**Ionic Conductivity, Viscosity, and Ion Diffusion Coefficient.** Unlike conventional electrolytes, PLEs feature a permanent porous structure that remains stable and empty<sup>8</sup> in the electrolytes. This provides a continuous network of voids or channels,<sup>6</sup> which can facilitate the efficient movement of ions<sup>16</sup> throughout the electrolyte. This means that porous media in PLEs can effectively improve the ion transfer mechanism by enhancing the diffusion coefficient via the porous structure. This results in higher ionic conductivity compared to peer electrolytes, which offer limited ion mobility.<sup>29</sup>

By enabling selective ion transport via the porous structure, PLEs incorporated in a battery will be able to diminish the ion migration resistance, leading to faster charge and discharge cycles. The chemical structure of PLs, such as imidazole, or other nitrogen-rich frameworks<sup>29</sup> facilitates ion transport by improving the interaction with different ions such as Li<sup>+</sup>, Na<sup>+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, or other charge carriers, reducing the resistance of the electrolyte. In addition, MOF, as a pore generator in PLs, with its tunable porous structure,<sup>46</sup> enhances ion transport by creating fast diffusion pathways.<sup>46,47</sup> Moreover, ILs, as a common solvent in PLs, show an effective impact on conductivity and ion mobility and ameliorate the mechanism.<sup>48</sup> The nanowetting interfaces formed within the MOFs allow ions to move freely, while larger anions are immobilized at Lewis acidic metal sites, reducing polarization and improving ion mobility.<sup>41</sup> This selective ion transport porous structure increases the ion transference number, boosting battery efficiency and preventing dendrite formation, which is crucial for enhancing battery performance and stability.<sup>49</sup> Therefore, with the combination of these as PLs, we can expect the advantages of both in battery electrolyte design.

The high surface area associated with the porous structure<sup>50</sup> allows for greater ion adsorption and interaction, leading to more effective ion transport as well. This property is particularly beneficial in high-capacity batteries, where rapid and efficient ion movement is important.<sup>51</sup> When ions come into contact with the surface, they can be absorbed into the surface more effectively. This allows for better utilization of the ions, reducing the distance they need to move within the electrolyte or between the electrodes and the electrolyte.<sup>52</sup> Additionally, it accelerates electrochemical reactions that occur during the charging and discharging cycle.<sup>53</sup> For example, PLs where crown ethers are used to provide internal porosity and coordinate metal ions enhance ion transport in Li<sup>+</sup> and Mg<sup>2+</sup> systems, as shown in Figure 10. This could increase ionic conductivity due to its cavity size matching Li<sup>+</sup> ions and facilitating the dissociation of Li<sup>+</sup>–TFSI<sup>-</sup> ion pairs.<sup>14</sup> The addition of crown ether-based PLs, particularly 12C4, significantly improves electrolyte performance in Li-based systems by enhancing ionic conductivity, Li<sup>+</sup> mobility, and solvation structure. With 12C4 (Li<sup>+</sup>/12C4 = 1), conductivity increased from 5.55 to 6.33 mS cm<sup>-1</sup>, and the Li<sup>+</sup> diffusion coefficient rose from  $1.72 \times 10^{-10}$  to  $2.12 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ . NMR and PFG measurements revealed the formation of stable Li–12C4 complexes, weakening Li<sup>+</sup>–TFSI<sup>-</sup> interactions and enabling vehicle-type transport ( $D_{\text{Li}^+}/D_{12\text{C}4} \approx 1$ ). Molecular



**Figure 10.** (a) Simplified schematic 12C4-based electrolyte, (b) components' size and structure, and (c) ionic conductivities of 12C4-based electrolytes containing LiTFSI and Mg(TFSI)<sub>2</sub>, measured at 25 °C. (d) Ionic conductivities and viscosities of the crown ether-based liquid electrolytes (2–6) with different functional groups and cavity sizes containing LiTFSI measured at 25 °C (1 = 1 M LiTFSI, 2 = 1 M LiTFSI with 1 M 12C4, 3 = 1 M LiTFSI with 1 M 12C4-OH, 4 = 1 M LiTFSI with 1 M 12C4-Benz, 5 = 1 M LiTFSI with 1 M 15CS, and 6 = 1 M LiTFSI with 1 M 15CS-OH. (e) The ratio of diffusion coefficients of  $D_{\text{Li}}/D_{\text{crownether}}$ ,  $D_{\text{Li}}/D_{\text{TFSI}}$ , and  $D_{\text{Li}}/D_{\text{PC}}$  for the electrolytes (1–6). Reproduced with permission ref 14. Copyright 2022 American Chemical Society.

dynamics simulations (MD) confirmed strong Li<sup>+</sup> coordination within 12C4, with minimal TFSI<sup>-</sup> interaction, lowering desolvation and enhancing transport. These findings highlight the potential of PLs' contribution to engineering high-performance electrolytes in batteries.<sup>14</sup>

High viscosity in concentrated electrolytes generally hinders ion mobility and electrode wetting.<sup>54</sup> The incorporation of PLs, facilitating ion movement through structured diffusion mechanisms, allows for improved ion transport without sacrificing electrolyte viscosity.<sup>14</sup> This can also enhance the electrodes' wetting, facilitating the penetration of the electrolyte into porous electrode materials, and ensuring efficient ion transport throughout the cell as well as the cell's stability. Figure 10 illustrates the minimal effect of 12C4 in the electrolyte's viscosity, including PC and EC as solvents and LiTFSI as the salt.<sup>14</sup>

PLs can be chemically modified with functional groups (such as sulfonates, carboxylates, or metals) that are selective for certain ions based on charge, polarity, or coordination chemistry. Functional groups with specific charges can attract or reject certain ions.<sup>55</sup> For example, negatively charged functional groups can attract cations such as Li<sup>+</sup>, while rejecting larger anions, preventing their movement through the electrolyte. Some functional groups can bind selectively to particular ions, enabling preferential transport. For instance, crown ethers or other ionophoric groups can be used to selectively bind Li ions while excluding other ions.<sup>44</sup> S. H. R. Shin et al. showed that the crown ether-based Liquid effectively bound Li<sup>+</sup> and Mg<sup>2+</sup> ions, creating a favorable solvation environment for enhanced ion mobility by molecular dynamics simulation results. Moreover, the experimental data from NMR and FTIR, combined with MD, revealed that the improved ion transport in crown ether-based liquid electrolytes is due to two main mechanisms: as vehicle mechanism and the hopping mechanism. In the first mechanism, Li<sup>+</sup> ions form complexes with a crown, which diffuse through the electrolyte

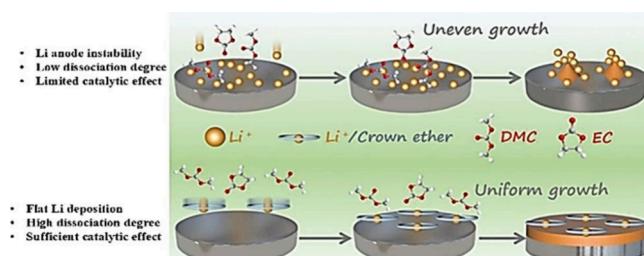
as a unit. In the second mechanism, in some functionalized crown ether systems, Li<sup>+</sup> ions hop between different coordination sites, enhancing mobility.<sup>14</sup> Nicola Giri et al. prepared a stable crown ether-based PL type II.<sup>9</sup> Crown ethers are well-known for their ability to coordinate with cations like Li<sup>+</sup>. The oxygen atoms in the crown ether can donate single pairs of electrons to Li ions, forming a coordination complex.<sup>56</sup> This interaction helps stabilize the Li ions in the solution and can enhance Li-ion transport.<sup>38</sup> The organic cage molecules in these PLs have functional groups (such as ether, carbonyl, or nitrogen-based groups)<sup>9</sup> that can coordinate with ions, they may also facilitate interaction with ions. These cages provide a controlled environment that could selectively host specific ions, improving ion mobility without a significant reaction or degradation of the liquid.

PLs in electrolytes can play the role of selective catalyst materials in batteries. MOFs or MOCs integrated into PLs are redox-active, which can act as catalysts for specific electrochemical reactions or improve the efficiency of charge transfer processes. Selecting transition metal-based structures within the PLs can offer redox centers that contribute to more stable cycling performance.<sup>12,57</sup> Moreover, PLs can improve oxygen evolution processes, particularly by incorporating MOFs or zeolites into the liquid phase.<sup>15</sup> PLs can capture oxygen molecules and deliver them at a controlled rate, and improve the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), thus enhancing the cycle life and charge voltage of batteries like Li-air and zinc-air batteries. Moreover, PLs can affect the products in the batteries. For instance, in Li-air batteries, crown ethers stabilize intermediate Li peroxide (Li<sub>2</sub>O<sub>2</sub>) formation and reduce the overpotentials during charging. This leads to the amorphization of Li<sub>2</sub>O<sub>2</sub>, which enhances the cycling stability and lifespan of the battery.<sup>58</sup>

Sodium-ion batteries (SIB) have received a huge amount of attention today because of the abundance and low cost of sodium. However, SIBs suffer from lower energy densities and slower ion transport.<sup>59</sup> PLs can ameliorate this situation by providing an electrolyte with higher sodium ion mobility and improved stability.<sup>39</sup> By adjustment of the pore size of the PL host material, as shown in Figure 5, the selective transport of sodium ions can be enhanced, leading to better performance in terms of charge/discharge rates and cycling stability.

**Dendrite Mitigation and SEI Stabilization.** Dendrite growth is a major cause of short circuits and thermal runaway in batteries.<sup>58</sup> By providing a more uniform ion distribution and reducing localized concentration gradients, PLs can prevent dendrite growth and enhance the overall safety of the battery. Moreover, this helps in regulating the flow of ions, ensuring that they are deposited more evenly during charging. This reduces the likelihood of dendrite formation and minimizes the risk of short circuits, which can lead to catastrophic failures, such as battery fire. By decreasing dendrite formation, PLs enhance the long-term stability and safety of batteries.

Crown ethers, such as 15CS, as an example, as shown in Figure 11, enhanced Li metal battery performance by regulating Li-ion solvation and stabilizing the SEI. By forming complexes with Li-ions, 15CS minimizes solvent decomposition, promotes smooth SEI, suppresses dendrite growth, and ensures uniform Li deposition, leading to improved cycle life and stability. As a result, symmetric Li|Li cells achieved excellent cycling stability for 170 cycles at 1.0 mA cm<sup>-2</sup> with a



**Figure 11.** Schematic of the effect of 15C5 on the decomposition process of solvents. Reproduced with permission ref 38. Copyright 2021 Wiley.

capacity of  $0.5 \text{ mAh cm}^{-2}$ , and improved cycling and rate performance was also observed in LiLNCM622 full cells by using 15C4.<sup>38</sup>

**Safety and Electrochemical Stability.** Safety has always been a paramount concern in batteries. Conventional electrolytes often suffer from thermal instability, degrading at high temperatures and leading to reduced battery life and efficiency.<sup>60</sup> Moreover, these electrolytes typically have a limited electrochemical stability window, restricting their use in high-voltage applications.<sup>61</sup> Beyond this window, the electrolyte can decompose, leading to performance degradation and the formation of harmful byproducts.<sup>62</sup> Furthermore, chemical incompatibility between the electrolyte and electrode materials can result in unwanted reactions, forming resistive layers that increase impedance and decrease battery efficiency over time.<sup>63</sup>

PLs can be engineered to optimize the SEI composition by carefully controlling the ion environment and facilitating the formation of stable, conductive interphases. The controlled structure of PLs minimizes undesired solvent-anion interactions, enhancing SEI stability and contributing to a longer cycle life.

One of the significant safety benefits of PLEs is their potential to be nonflammable, particularly when designed with ionic liquids or other nonvolatile components for thermal stability and improved safety.<sup>6</sup> This reduces the risk of fires or explosions, a common concern with traditional organic liquid electrolytes.<sup>64</sup> Unlike traditional organic electrolytes (e.g., those containing volatile and flammable solvents)<sup>65</sup> ILs are inherently nonflammable and have been used for PLs to synthesize.<sup>9</sup> PLEs are generally more thermally stable than conventional electrolytes, meaning that they can maintain their chemical and electrochemical properties over a wider range of temperatures because of their chemistry and structure.

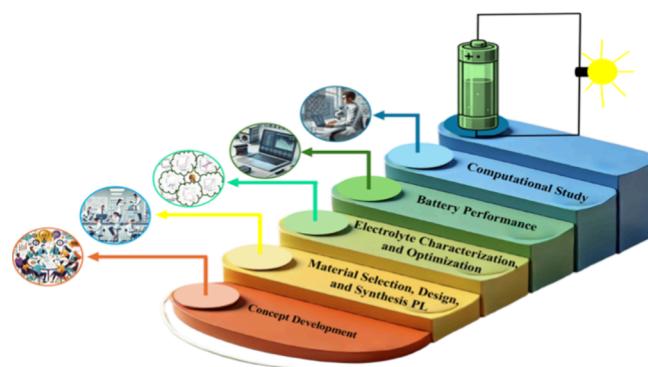
**Pore-Driven Ion Mobility in PLEs.** One question that should be answered in future studies of PLEs is how PLs can affect the ion mobility in batteries. In this section, we present the possible role of PLs in the PLE mechanism, and it should be studied by experiments and computational studies to confirm. When pore sizes exceed the hydrated or solvated diameter of the cation, pores serve as efficient pathways for ion movement, reducing diffusion barriers and enhancing cation mobility. Optimized pore architectures for the pore generator play an effective role in the ionic mobility and conductivity for battery electrolytes. In such systems, cations can enter the pores under the influence of electric fields or concentration gradients. This will be able to enhance mobility, which directly translates to improved rate capability and energy density, particularly in thick electrodes where minimized ion transport losses lead to better performance. Conversely, when pores are too small or restrictive, ions are excluded and forced to

navigate around voids, increasing diffusion path lengths and reducing overall mobility. Such effects are common in microporous materials with pore diameters near or below the solvated ion size, where mobility loss can lower the cation transference number and inadvertently increase anion mobility, detrimental for cation-dependent systems like Li-ion batteries.<sup>66–68</sup>

Beyond size effects, the nature of the pore wall interactions plays a critical role in determining whether voids enhance or hinder cation transport. Pores with nonpolar or weakly interacting surfaces act as low-resistance channels, enabling efficient diffusion. However, strong interactions such as those from negatively charged surfaces or Lewis basic sites can immobilize cations via strong coordination, thereby preventing cation motion and promoting anion-dominated conduction. This duality is evident in systems like crown ether-based PLs, where moderate  $\text{Li}^+$ -12C4 complexation promotes vehicle-type transport, but overfunctionalization traps cations and limits mobility. Similarly, in IL-MOF electrolytes, excessive functionalization or a mismatch between pore size and ion solvation structure can lead to cation trapping. Thus, achieving high cation transference numbers and effective ion mobility requires a delicate balance of pore size, coordination energy, and surface chemistry concepts validated through MD and experimental studies across membranes, MOFs, and PL systems.<sup>69–72</sup>

## ■ PLE/PLGE DESIGN AND DEVELOPMENT ROADMAP

As shown in Figure 12, the design and performance of PLEs include 5 phases as follows.



**Figure 12.** PLE design and development roadmap.

**Concept Development:** Identify the battery chemistry (e.g.,  $\text{Li}^+$  ion, LiS) and clarify the required properties of PLs based on electrolyte components such as salts, solvents, polymers, and additives. Determine which ions (e.g.,  $\text{Li}^+$ ,  $\text{Na}^+$ ) should be moved and which species must be blocked.

**Material Selection, Design, and Synthesis of PLs:** Select a porosity generator, such as the MOF, with tunable pore sizes, ion selectivity, chemical compatibility, and thermal stability to form the PL scaffold. Choose the solvent, such as ILs, with high conductivity, wide stability windows, and nonvolatility, ensuring compatibility with electrode materials (e.g., graphite or sulfur) and electrolytes. Consider surface functionalization to enhance the ion selectivity and stability.

**Electrolyte Characterization and Optimization:** Measuring conductivity, ion diffusion, viscosity, and ion transfer numbers

helps optimize the electrolyte design. Additional required electrochemical techniques, such as employment information system (EIS), oxygen ORR, OER, linear sweep voltammetry (LSV), and CV, should be done to evaluate the performance of PLEs.

**Battery Performance:** Energy density, cycle life, Coulombic efficiency, capacity, dendrite growth, and overall electrochemical performance should be evaluated via a battery test. These tests can provide direct insights into the advantages of using PLEs in real-world battery applications.

**Computational study and validation:** Theoretical and computational methods, particularly molecular dynamics (MD) and density functional theory (DFT), play an important role in advancing the electrolyte design in batteries. MD simulations offer atomistic insights into diffusion coefficients, ion mobility, and solvation dynamics, while DFT enables an accurate prediction of reaction pathways, energy barriers, and interfacial stability. There are a variety of modeling techniques offering different scales, such as kinetic Monte Carlo simulates long-time behavior, classical force fields model large non-reactive systems, and reactive force fields capture both transport and chemistry with moderate accuracy. Machine-learning potentials and semiempirical methods provide trade-offs in transferability, computational cost, and chemical fidelity. DFT remains the standard for studying reaction mechanisms but is restricted by high computational demand and small system sizes.<sup>73,74</sup>

These techniques are now being extended to PLEs to offer the design of next-generation electrolytes. MD is especially beneficial for modeling ion transport through nanoconfined porous domains, the dynamic formation of the SEI layer, and growth, while Monte Carlo techniques can predict gas uptake and validate porosity effects using NMR and adsorption isotherms. DFT will allow detailed analysis of interactions between ions and porosity, electrolyte decomposition pathway, and charge-transfer kinetics and define the possible mechanisms. This integrated modeling framework supports the design of PLEs with empty, stable, and selective architectures and optimized and bridging theoretical insight with experiments to engineer stable, high-performance battery electrolytes.<sup>75,76</sup>

PLs hold transformative potential for overcoming critical limitations in conventional battery electrolytes. By combining stable, selective, and empty porosity with fluidity, they provide a unique pathway to enhance electrochemical properties of electrolytes such as ionic conductivity, prevent side reactions at electrode interfaces, stabilize redox mediators, and enable selective ion transport, all while maintaining the processability of liquids. These properties position PLs as promising candidates to address challenges such as limited cycle life, poor electrode–electrolyte compatibility, and poor ion mobility that currently hinder advanced battery systems, including Li–S, Li–O<sub>2</sub>, sodium-ion, Zn-ion, and so on. However, important challenges must be addressed to realize their full potential. Key research priorities include the synthesis of chemically and thermally stable PLs with tunable pore sizes and surface chemistries, ensuring long-term electrochemical and mechanical stability under cycling conditions and optimizing pore–solvent interactions to avoid pore blockage or collapse over time. Comprehensive experimental studies on ion transport mechanisms, electrolyte decomposition pathways, and interfacial stability, coupled with computational modeling, are essential to pave the way for PLs in batteries. By

addressing these scientific and engineering challenges, PLs can unlock new electrolyte designs and open new opportunities in batteries for the future.

## ■ AUTHOR INFORMATION

### Corresponding Authors

**Hamidreza Mahdavi** — Department of Chemical and Biological Engineering, Monash University, Clayton, VIC 3800, Australia;  [orcid.org/0000-0001-8175-4303](https://orcid.org/0000-0001-8175-4303); Email: [hamidreza.mahdavi1@monash.edu](mailto:hamidreza.mahdavi1@monash.edu)

**Vikas Berry** — Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States;  [orcid.org/0000-0002-1102-1996](https://orcid.org/0000-0002-1102-1996); Email: [vikasb@uic.edu](mailto:vikasb@uic.edu)

### Author

**Mehran Arzani** — Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607, United States;  [orcid.org/0000-0001-5603-7775](https://orcid.org/0000-0001-5603-7775)

Complete contact information is available at:  
<https://pubs.acs.org/10.1021/acsenergylett.5c01446>

### Author Contributions

M.A. led the project administration, conceptualization, interpretation of discussions, and writing the draft. V.B. and H.M. contributed to the project administration, conceptual, supervision, and interpretation of the results. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

### Biographies

Mehran Arzani is a Ph.D. candidate in Chemical Engineering at the University of Illinois at Chicago. His research focuses on advanced materials, including metal–organic frameworks (MOFs), 2D materials, porous liquids, membranes, and catalysts for battery electrode design.

Hamidreza Mahdavi is a postdoctoral fellow in Chemical Engineering at Monash University. His expertise lies in materials science, nanomaterials, and porous liquids, with a focus on developing solutions for environmental applications.

Vikas Berry is Dr. Satish C. & Asha Saxena Professor and Head in chemical engineering at University of Illinois at Chicago, leads innovations in 2D nanomaterials, metal–organic frameworks (MOFs), optoelectronic devices, and energy storage systems.

## ■ ACKNOWLEDGMENTS

V.B. and M.A. thank University of Illinois at Chicago for financial support.

## ■ REFERENCES

- (1) Meng, Y. S.; Srinivasan, V.; Xu, K. Designing Better Electrolytes. *Science* (1979) **2022**, 378 (6624), eabq3750.
- (2) Abouali, S.; Yim, C.-H.; Merati, A.; Abu-Lebdeh, Y.; Thangadurai, V. Garnet-Based Solid-State Li Batteries: From Materials Design to Battery Architecture. *ACS Energy Lett.* **2021**, 6 (5), 1920–1941.
- (3) Tian, X.; Yi, Y.; Fang, B.; Yang, P.; Wang, T.; Liu, P.; Qu, L.; Li, M.; Zhang, S. Design Strategies of Safe Electrolytes for Preventing Thermal Runaway in Lithium Ion Batteries. *Chem. Mater.* **2020**, 32 (23), 9821–9848.

- (4) Lee, B.; Paek, E.; Mitlin, D.; Lee, S. W. Sodium Metal Anodes: Emerging Solutions to Dendrite Growth. *Chem. Rev.* **2019**, *119* (8), 5416–5460.
- (5) Vishnugopi, B. S.; Kazyak, E.; Lewis, J. A.; Nanda, J.; McDowell, M. T.; Dasgupta, N. P.; Mukherjee, P. P. Challenges and Opportunities for Fast Charging of Solid-State Lithium Metal Batteries. *ACS Energy Lett.* **2021**, *6* (10), 3734–3749.
- (6) Mahdavi, H.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Practical Considerations in the Design and Use of Porous Liquids. *Mater. Horiz.* **2022**, *9* (6), 1577–1601.
- (7) Pierotti, R. A. The Solubility of Gases in Liquids I. *J. Phys. Chem.* **1963**, *67* (9), 1840–1845.
- (8) Fulvio, P. F.; Dai, S. Porous Liquids: The next Frontier. *Chem.* **2020**, *6* (12), 3263–3287.
- (9) Giri, N.; Del Pópolo, M. G.; Melaugh, G.; Greenaway, R. L.; Rätzke, K.; Koschine, T.; Pison, L.; Gomes, M. F. C.; Cooper, A. I.; James, S. L. Liquids with Permanent Porosity. *Nature* **2015**, *527* (7577), 216–220.
- (10) Pohorille, A.; Pratt, L. R. Cavities in Molecular Liquids and the Theory of Hydrophobic Solubilities. *J. Am. Chem. Soc.* **1990**, *112* (13), 5066–5074.
- (11) Pierotti, R. A. A Scaled Particle Theory of Aqueous and Nonaqueous Solutions. *Chem. Rev.* **1976**, *76* (6), 717–726.
- (12) Mahdavi, H.; Eden, N. T.; Doherty, C. M.; Acharya, D.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Underlying Polar and Nonpolar Modification MOF-Based Factors That Influence Permanent Porosity in Porous Liquids. *ACS Appl. Mater. Interfaces* **2022**, *14* (20), 23392–23399.
- (13) Melaugh, G.; Giri, N.; Davidson, C. E.; James, S. L.; Del Pópolo, M. G. Designing and Understanding Permanent Microporosity in Liquids. *Phys. Chem. Chem. Phys.* **2014**, *16* (20), 9422–9431.
- (14) Shin, S. H. R.; Lim, H.-S.; Han, K. S.; Robinson, A. J.; Hollas, A.; Sivakumar, B. M.; Johnson, S. I.; Chun, J.; Wang, W.; Murugesan, V.; Thallapally, P. K. Porous Liquids as Electrolyte: A Case Study of Li<sup>+</sup> and Mg<sup>2+</sup> Ion Transport in Crown Ether-Based Type-II Porous Liquids. *ACS Mater. Lett.* **2023**, *5* (2), 330–335.
- (15) Li, E.; Siniard, K. M.; Yang, Z.; Dai, S. Porous Liquids: An Integrated Platform for Gas Storage and Catalysis. *Chem. Sci.* **2024**, *15* (43), 17720–17738.
- (16) Wang, D.; Xin, Y.; Yao, D.; Li, X.; Ning, H.; Zhang, H.; Wang, Y.; Ju, X.; He, Z.; Yang, Z.; Fan, W.; Li, P.; Zheng, Y. Shining Light on Porous Liquids: From Fundamentals to Syntheses, Applications and Future Challenges. *Adv. Funct. Mater.* **2022**, *32* (1), 2104162.
- (17) Mahdavi, H.; Zhang, H.; Macreadie, L. K.; Doherty, C. M.; Acharya, D.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Underlying Solvent-Based Factors That Influence Permanent Porosity in Porous Liquids. *Nano Res.* **2022**, *15*, 3533–3538.
- (18) Costa Gomes, M.; Pison, L.; Červinka, C.; Padua, A. Porous Ionic Liquids or Liquid Metal–Organic Frameworks? *Angew. Chem.* **2018**, *130* (37), 12085–12088.
- (19) Shan, W.; Fulvio, P. F.; Kong, L.; Schott, J. A.; Do-Thanh, C.-L.; Tian, T.; Hu, X.; Mahurin, S. M.; Xing, H.; Dai, S. New Class of Type III Porous Liquids: A Promising Platform for Rational Adjustment of Gas Sorption Behavior. *ACS Appl. Mater. Interfaces* **2018**, *10* (1), 32–36.
- (20) Mahdavi, H.; Burdloff, J.; Robin, A.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Accelerated Systematic Investigation of Solvents Suitability for Type II/III Porous Liquids. *ACS Mater. Lett.* **2023**, *5* (2), 549–557.
- (21) Liu, Y.; Cheng, H.; Cheng, M.; Liu, Z.; Huang, D.; Zhang, G.; Shao, B.; Liang, Q.; Luo, S.; Wu, T.; Xiao, S. The Application of Zeolitic Imidazolate Frameworks (ZIFs) and Their Derivatives Based Materials for Photocatalytic Hydrogen Evolution and Pollutants Treatment. *Chem. Eng. J.* **2021**, *417*, 127914.
- (22) Song, J.; Frentzel-Beyme, L.; Pallach, R.; Kolodzeiski, P.; Koutsianos, A.; Xue, W.-L.; Schmid, R.; Henke, S. Modulating Liquid–Liquid Transitions and Glass Formation in Zeolitic
- Imidazolate Frameworks by Decoration with Electron-Withdrawing Cyano Groups. *J. Am. Chem. Soc.* **2023**, *145* (16), 9273–9284.
- (23) Xu, Y.; Ren, Y.; Zhou, G.; Feng, S.; Yang, Z.; Dai, S.; Lu, Z.; Zhou, T. Amide-Engineered Metal–Organic Porous Liquids Toward Enhanced CO<sub>2</sub> Photoreduction Performance. *Adv. Funct. Mater.* **2024**, *34* (19), 2313695.
- (24) Mahdavi, H.; Sadiq, M. M.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Underlying Potential Evaluation of the Real-Process Applications of Magnetic Porous Liquids. *J. Mater. Chem. A Mater.* **2023**, *11* (31), 16846–16853.
- (25) Liu, S.; Liu, J.; Hou, X.; Xu, T.; Tong, J.; Zhang, J.; Ye, B.; Liu, B. Porous Liquid: A Stable ZIF-8 Colloid in Ionic Liquid with Permanent Porosity. *Langmuir* **2018**, *34* (12), 3654–3660.
- (26) Liu, H.; Liu, B.; Lin, L.-C.; Chen, G.; Wu, Y.; Wang, J.; Gao, X.; Lv, Y.; Pan, Y.; Zhang, X.; Zhang, X.; Yang, L.; Sun, C.; Smit, B.; Wang, W. A Hybrid Absorption–Adsorption Method to Efficiently Capture Carbon. *Nat. Commun.* **2014**, *5* (1), 5147.
- (27) Annapureddy, H. V. R.; Nune, S. K.; Motkuri, R. K.; McGrail, B. P.; Dang, L. X. A Combined Experimental and Computational Study on the Stability of Nanofluids Containing Metal Organic Frameworks. *J. Phys. Chem. B* **2015**, *119* (29), 8992–8999.
- (28) Atilhan, M.; Cincotti, A.; Aparicio, S. Nanoscopic Characterization of Type II Porous Liquid and Its Use for CO<sub>2</sub> Absorption from Molecular Simulation. *J. Mol. Liq.* **2021**, *330*, 115660.
- (29) Zhang, H.; Dasbiswas, K.; Ludwig, N. B.; Han, G.; Lee, B.; Vaikuntanathan, S.; Talapin, D. V. Stable Colloids in Molten Inorganic Salts. *Nature* **2017**, *542* (7641), 328–331.
- (30) Sambe, K.; Hoshino, N.; Takeda, T.; Nakamura, T.; Akutagawa, T. Crystal Structures and Physical Properties of (M<sup>+</sup>)(Crown Ethers)<sub>x</sub>(TCNQ)<sub>y</sub> Salts with M<sup>+</sup> = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup>. *Cryst. Growth Des.* **2021**, *21* (10), 5928–5942.
- (31) Stenina, I.; Golubenko, D.; Nikonenko, V.; Yaroslavtsev, A. Selectivity of Transport Processes in Ion-Exchange Membranes: Relationship with the Structure and Methods for Its Improvement. *Int. J. Mol. Sci.* **2020**, *21* (15), 5517–5550.
- (32) Wang, S.; Fu, J.; Liu, Y.; Saravanan, R. S.; Luo, J.; Deng, S.; Sham, T.-K.; Sun, X.; Mo, Y. Design Principles for Sodium Superionic Conductors. *Nat. Commun.* **2023**, *14* (1), 7615.
- (33) Adigun, B.; Thapaliya, B. P.; Luo, H.; Dai, S. Ionic Liquid-Based Extraction of Metal Ions via Polymer Inclusion Membranes: A Critical Review. *RSC Sustainability* **2024**, *2* (10), 2768–2780.
- (34) Zhao, Y.; Zhang, Y.; Gosselink, D.; Doan, T. N. L.; Sadhu, M.; Cheang, H.-J.; Chen, P. Polymer Electrolytes for Lithium/Sulfur Batteries. *Membranes (Basel)* **2012**, *2* (3), 553–564.
- (35) Singh, S.; Arzani, M.; Berry, V. Li-Ion Delivery Via Molecular Cages in Porous Liquid Type-II Electrolytes: Lithium-Sulfur Batteries. In *2023 AIChE Annual Meeting*; AIChE, 2023.
- (36) Liu, H.; Liu, B.; Lin, L.-C.; Chen, G.; Wu, Y.; Wang, J.; Gao, X.; Lv, Y.; Pan, Y.; Zhang, X.; Zhang, X.; Yang, L.; Sun, C.; Smit, B.; Wang, W. A Hybrid Absorption–Adsorption Method to Efficiently Capture Carbon. *Nat. Commun.* **2014**, *5* (1), 5147.
- (37) Mu, X.; Pan, H.; He, P.; Zhou, H. Li–CO<sub>2</sub> and Na–CO<sub>2</sub> Batteries: Toward Greener and Sustainable Electrical Energy Storage. *Adv. Mater.* **2020**, *32*, No. 1903790.
- (38) Wang, H.; He, J.; Liu, J.; Qi, S.; Wu, M.; Wen, J.; Chen, Y.; Feng, Y.; Ma, J. Electrolytes Enriched by Crown Ethers for Lithium Metal Batteries. *Adv. Funct. Mater.* **2021**, *31* (2), No. 2002578.
- (39) Arzani, M.; Mahdavi, H.; Berry, V. Unveiling the Potential of Porous Liquid-Based Electrolytes in Battery Applications: Improved Conductivity and Ion Mobility in Lithium and Sodium-Based Batteries. In *2024 AIChE Annual Meeting*; AIChE, 2024.
- (40) Macfarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A. Energy Applications of Ionic Liquids. *Energy and Environmental Science* **2014**, *7*, 232–250.
- (41) Zhu, H.; Li, S.; Peng, L.; Zhong, W.; Wu, Q.; Cheng, S.; Xie, J. Review of MOF-Guided Ion Transport for Lithium Metal Battery Electrolytes. *Nano Energy* **2024**, *125*, No. 109571.

- (42) Qiu, S.; Zhang, J.; Liang, X.; Li, Y.; Cui, J.; Chen, M. Tunable MOFs Derivatives for Stable and Fast Sulfur Electrodes in Li-S Batteries. *Chem. Eng. J.* **2022**, *450*, No. 138287.
- (43) Qi, X.; Cai, D.; Wang, X.; Xia, X.; Gu, C.; Tu, J. Ionic Liquid-Impregnated ZIF-8/Polypropylene Solid-like Electrolyte for Dendrite-Free Lithium-Metal Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14* (5), 6859–6868.
- (44) Liu, F.; Xue, M.; Hu, T.; Yao, T.; Xu, C.; Sheng, L.; Dou, H.; Zhang, X. Promoted Reaction Reversibility by Dual-Effect 15-Crown-5 Ether Additive for High-Performance Li–O<sub>2</sub> Batteries. *J. Phys. Chem. Lett.* **2024**, *15* (21), 5738–5746.
- (45) Zheng, J.; Gu, M.; Chen, H.; Meduri, P.; Engelhard, M. H.; Zhang, J. G.; Liu, J.; Xiao, J. Ionic Liquid-Enhanced Solid State Electrolyte Interface (SEI) for Lithium-Sulfur Batteries. *J. Mater. Chem. A Mater.* **2013**, *1* (29), 8464–8470.
- (46) Mahdavi, H.; Robin, A.; Eden, N. T.; Khosravianian, A.; Sadiq, M. M.; Konstas, K.; Smith, S. J. D.; Mulet, X.; Hill, M. R. Engineering Insights into Tailored Metal–Organic Frameworks for CO<sub>2</sub> Capture in Industrial Processes. *Langmuir* **2024**, *40* (33), 17387–17395.
- (47) Baumann, A. E.; Burns, D. A.; Liu, B.; Thoi, V. S. Metal-Organic Framework Functionalization and Design Strategies for Advanced Electrochemical Energy Storage Devices. *Commun. Chem.* **2019**, *2* (1), 86.
- (48) Li, W.; Xiao, W.; Luo, Q.; Yan, J.; Zhang, G.; Chen, L.; Sun, J. Ionic Liquids Promoted Synthesis, Enhanced Functions, and Expanded Applications of Porous Organic Frameworks. *Coord. Chem. Rev.* **2023**, *493*, No. 215304.
- (49) Lin, R.; Jin, Y.; Li, Y.; Zhang, X.; Xiong, Y. Recent Advances in Ionic Liquids—MOF Hybrid Electrolytes for Solid-State Electrolyte of Lithium Battery. *Batteries* **2023**, *9* (6), 314.
- (50) Jie, K.; Zhou, Y.; Ryan, H. P.; Dai, S.; Nitschke, J. R. Engineering Permanent Porosity into Liquids. *Adv. Mater.* **2021**, *33* (18), No. 2005745.
- (51) Boz, B.; Dev, T.; Salvadori, A.; Schaefer, J. L. Review—Electrolyte and Electrode Designs for Enhanced Ion Transport Properties to Enable High Performance Lithium Batteries. *J. Electrochem. Soc.* **2021**, *168* (9), 090501.
- (52) Gerdroodbar, A. E.; Alihemmati, H.; Safavi-Mirmahaleh, S.-A.; Golshan, M.; Damircheli, R.; Eliseeva, S. N.; Salami-Kalajahi, M. A Review on Ion Transport Pathways and Coordination Chemistry between Ions and Electrolytes in Energy Storage Devices. *J. Energy Storage* **2023**, *74*, No. 109311.
- (53) Fletcher, D. *A First Course in Electrode Processes*; Royal Society of Chemistry, 2019.
- (54) Giffin, G. A. The Role of Concentration in Electrolyte Solutions for Non-Aqueous Lithium-Based Batteries. *Nat. Commun.* **2022**, *13* (1), 5250.
- (55) Qu, C.; Zhao, B.; Jiao, Y.; Chen, D.; Dai, S.; deglee, B. M.; Chen, Y.; Walton, K. S.; Zou, R.; Liu, M. Functionalized Bimetallic Hydroxides Derived from Metal–Organic Frameworks for High-Performance Hybrid Supercapacitor with Exceptional Cycling Stability. *ACS Energy Lett.* **2017**, *2* (6), 1263–1269.
- (56) González-Pérez, R.; Adams, S.; Dowling, A. W.; Phillip, W. A.; Whitmer, J. K. Thermodynamics of Li+–Crown Ether Interactions in Aqueous Solvent. *J. Phys. Chem. A* **2023**, *127* (21), 4624–4631.
- (57) Abitha, M.; Viswanathan, C.; Ponpandian, N. Oxide Derivatives of Metal–Organic Frameworks for Water Splitting: A Concise Review. *Sustainable Energy Fuels* **2025**, *9* (4), 921–941.
- (58) Hong, Z.; Viswanathan, V. Phase-Field Simulations of Lithium Dendrite Growth with Open-Source Software. *ACS Energy Lett.* **2018**, *3* (7), 1737–1743.
- (59) Huang, Y.; Zheng, Y.; Li, X.; Adams, F.; Luo, W.; Huang, Y.; Hu, L. Electrode Materials of Sodium-Ion Batteries toward Practical Application. *ACS Energy Lett.* **2018**, *3* (7), 1604–1612.
- (60) Hou, J.; Lu, L.; Wang, L.; Ohma, A.; Ren, D.; Feng, X.; Li, Y.; Li, Y.; Ootani, I.; Han, X.; Ren, W.; He, X.; Nitta, Y.; Ouyang, M. Thermal Runaway of Lithium-Ion Batteries Employing LiN(SO<sub>2</sub>F)<sub>2</sub>-Based Concentrated Electrolytes. *Nat. Commun.* **2020**, *11* (1), 5100.
- (61) Wan, H.; Xu, J.; Wang, C. Designing Electrolytes and Interphases for High-Energy Lithium Batteries. *Nat. Rev. Chem.* **2024**, *8* (1), 30–44.
- (62) Bordes, A.; Marlair, G.; Zantman, A.; Chesnaye, A.; Lore, P.-A. Le; Lecocq, A. Safety Evaluation of a Sodium-Ion Cell: Assessment of Vent Gas Emissions under Thermal Runaway. *ACS Energy Lett.* **2022**, *7* (10), 3386–3391.
- (63) Tran, Y. H. T.; An, K.; Vu, D. T. T.; Song, S.-W. High-Voltage Electrolyte and Interface Design for Mid-Nickel High-Energy Li-Ion Batteries. *ACS Energy Lett.* **2025**, *10* (1), 356–370.
- (64) Jeevarajan, J. A.; Joshi, T.; Parhizi, M.; Rauhala, T.; Juarez-Robles, D. Battery Hazards for Large Energy Storage Systems. *ACS Energy Lett.* **2022**, *7* (8), 2725–2733.
- (65) Yang, A.; Yang, C.; Xie, K.; Xin, S.; Xiong, Z.; Li, K.; Guo, Y.-G.; You, Y. Benchmarking the Safety Performance of Organic Electrolytes for Rechargeable Lithium Batteries: A Thermochemical Perspective. *ACS Energy Lett.* **2023**, *8* (1), 836–843.
- (66) Liu, B.; Zhuo, S.; Li, L.; Zhou, Y.; Li, Z. Molecular Dynamics Simulations of Li+/Mg<sup>2+</sup> Separation Using Metal-Organic Frameworks. *J. Membr. Sci.* **2024**, *702*, No. 122759.
- (67) Bao, S.; Ma, Z.; Yu, L.; Li, Q.; Xia, J.; Song, S.; Sui, K.; Zhao, Y.; Liu, X.; Gao, J. Randomly Oriented Covalent Organic Framework Membrane for Selective Li<sup>+</sup> Sieving from Other Ions. *Nat. Commun.* **2025**, *16* (1), 3896.
- (68) Pramanik, K.; Sau, K.; Kumar, P. P. Role of Framework Flexibility in Ion Transport: A Molecular Dynamics Study of LiM2IV(PO<sub>4</sub>)<sub>3</sub>. *J. Phys. Chem. C* **2020**, *124* (7), 4001–4009.
- (69) Warnock, S. J.; Sujanani, R.; Zofchak, E. S.; Zhao, S.; Dilenschneider, T. J.; Hanson, K. G.; Mukherjee, S.; Ganeshan, V.; Freeman, B. D.; Abu-Omar, M. M.; Bates, C. M. Engineering Li/Na Selectivity in 12-Crown-4-Functionalized Polymer Membranes. *Proc. Natl. Acad. Sci. U.S.A.* **2021**, *118* (37), No. e2022197118.
- (70) González-Pérez, R.; Adams, S.; Dowling, A. W.; Phillip, W. A.; Whitmer, J. K. Thermodynamics of Li + -Crown Ether Interactions in Aqueous Solvent. *J. Phys. Chem. A* **2023**, *127* (21), 4624–4631.
- (71) Farina, M.; Duff, B. B.; Tealdi, C.; Pugliese, A.; Blanc, F.; Quartarone, E. Li<sup>+</sup> Dynamics of Liquid Electrolytes Nanoconfined in Metal-Organic Frameworks. *ACS Appl. Mater. Interfaces* **2021**, *13* (45), 53986–53995.
- (72) Zhu, S.; Ramsundar, B.; Annevelink, E.; Lin, H.; Dave, A.; Guan, P. W.; Gering, K.; Viswanathan, V. Differentiable Modeling and Optimization of Non-Aqueous Li-Based Battery Electrolyte Solutions Using Geometric Deep Learning. *Nat. Commun.* **2024**, *15* (1), 8649.
- (73) Wan, S.; Zhao, S.; Ma, W.; Chen, S. Computational Approaches to Electrolyte Design for Advanced Lithium-Ion Batteries. *Chem. Commun.* **2025**, *61*, 7019.
- (74) Nair, M. R.; Roy, T. Role of Artificial Intelligence in the Design and Discovery of Next-Generation Battery Electrolytes. *Chemical Physics Reviews* **2025**, *6* (1), No. 011311.
- (75) Bin Jassar, M.; Michel, C.; Abada, S.; De Bruin, T.; Tant, S.; Nieto-Draghi, C.; Steinmann, S. N. A Perspective on the Molecular Modeling of Electrolyte Decomposition Reactions for Solid Electrolyte Interphase Growth in Lithium-Ion Batteries. *Adv. Funct. Mater.* **2024**, *34* (30), No. 2313188.