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2D Vertically Conductive Metal–Organic Framework Electrolytes: Will They Outperform 3D MOFs for Solid State Batteries?

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Lithium-ion batteries are currently the mainstream for almost all portables, and quickly expand in electrical vehicles and grid storage applications. However, they are challenged by the poor safety regarding organic liquid electrolytes and relatively low energy density. Solid-state batteries, characterized by using solid-state electrolytes (SSEs), are recognized as the next-generation energy technology, owing to their intrinsically high safety and potentially superior energy density. However, developing SSEs is impeded by several key factors, including low ionic conductivity, interfacial issues, and high-cost in industrial scales. Recently, a novel category of SSEs, known as frameworked electrolytes (FEs), has emerged as a formidable contender for the transition to all-solid-state batteries. FEs exhibit a unique macroscopically solid-state nature and microscopically sub-nanochannels offering high ionic conductivity. In this perspective, the unique lithium-ion transport mechanisms within FEs are explored and 2D vertically conductive metal–organic framework (MOF) is proposed as an even more promising FE candidate. The abundant active sites in the 1D sub-nanochannels of 2D vertically conductive MOFs facilitate efficient ion transport, favorable interfacial compatibility, and scalable industrial applications. This perspective aims to boost the emergence of novel SSEs, promoting the realization of long-expected all-solid-state batteries and inspiring future energy storage solutions.

1. Introduction

Lithium-ion batteries (LIBs) have undergone extensive development and commercialization since their emergence in early 1990s, establishing themselves as the predominant power sources for portable electronic devices, electric vehicles, and now the large-scale stationary energy storage.[1,2] Despite their great success in the past and in the time being, further progress is constrained by the relatively low energy densities and high flammability risks associated with the use of organic liquid electrolytes. A transformative shift toward solid-state electrolytes (SSEs) has emerged, more recently, as a promising new avenue, giving rise to the rapid development of all-solid-state batteries (ASSBs) with much improved safety and energy densities, which have been considered as the next technological leap in battery development. The global market for ASSBs has witnessed remarkable growth, surging from \$0.34 billion in 2022 to \$0.49 billion in 2023, with a projected ascent to \$2.41 billion by 2027 at an impressive annual growth rate of 48.8%.[3] Given this rapid advancement, the Federal Consortium for Advanced Batteries in the United States has projected an energy density of 500 Wh kg^{-1} for ASSBs in production by 2030.[4] Both the rapidly expanding market and strategic initiatives underscore the pivotal role of ASSBs in shaping future energy systems.

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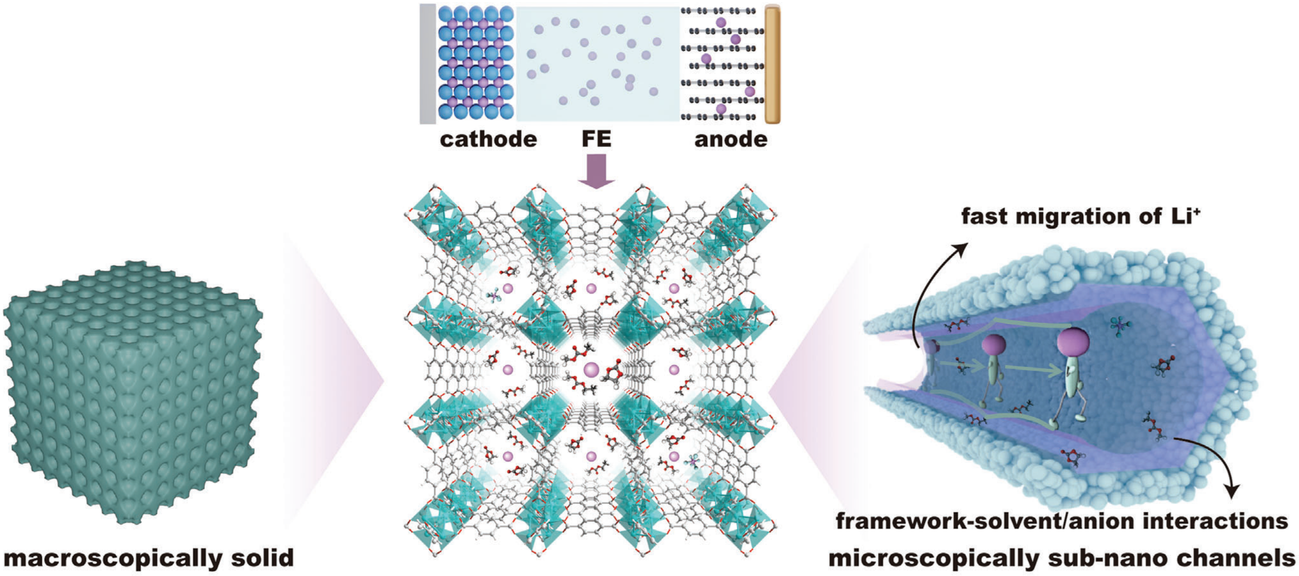

Figure 1. Schematic of the macroscopic and microscopic structure of the FE and the unique "swing" effect of the lithium-ion transport mechanism. Solid-state FE materials possess numerous sub-nano channels that can confine solvent molecules, thereby reducing the migration energy barrier for lithium ions transport.

As the core component of ASSBs, SSEs have garnered widespread attention, especially in recent years, which can be broadly classified into inorganic solid electrolytes (ISEs), solid polymer electrolytes (SPEs), and composite-type solid electrolytes (CSEs), where different ionic transport mechanisms take place. In ISEs, for example, the transportation of lithium ions occurs through ion hopping between adjacent crystal defects.[5] Characteristically, ISEs possess relatively high ionic conductivity, thermal stability, and mechanical robustness. A notable example is the high-entropy-based $Li_{9.54}[Si_{1-0.4}Ge_{0.4}]_{1.74}P_{1.44}S_{11.1}Br_{0.3}O_{0.6}$ electrolyte, which has demonstrated an impressive ionic conductivity of 32 mS cm^{-1} at 25 °C.[6] However, ISEs often face challenges in forming adequate interfacial contact with solid electrodes, which is crucial for stable battery operation.[7,8] Poor interfacial contact can lead to increased internal resistance and reduced ion transport efficiency. In contrast, SPEs offer superior flexibility, electrode interface compatibility, and affinity in most cases. Lithium ions in SPEs migrate through the local segmental motion of polymer molecules, involving transitions between coordination sites along a polymer chain, and interchain transfers.[9] Nevertheless, SPEs commonly show relatively sluggish ion transport (10^{-8}–10^{-5} S cm^{-1}), as well as electrochemical instability under high-voltage conditions.[10,11] CSEs, on the other hand, amalgamating polymers with inorganic constituents, emerge as a formidable alternative. This includes the incorporation of inorganic fillers within an appropriate polymeric host (e.g., "ceramic in polymer") and embedding polymers within an ISE ("polymer in ceramic").[12–14] The transport paths of lithium ions in CSEs are thus intricate, for example involving the interactions of the polymer, ceramic phases, and their interfaces.[15] A recent groundbreaking development in CSEs, combining $Li_{0.95}Na_{0.05}FePO_4$ with poly(vinylidene fluoride) (PVDF), achieved an impressive ionic conductivity of 0.358 mS cm^{-1} at 25 °C, along with exceptional electrode compatibility.[16] Despite these technological strides, CSEs confront challenges in ensuring a homogeneous dispersion, optimizing interfacial compatibility among disparate components, scalable production at low cost, and also integration into large-sized pouch cells.[17]

While the mainstream SSEs have made an overall significant progress more recently, they still struggle to grapple with achieving a simultaneous trifecta: high ionic conductivity at around room temperature, efficacious electrode interface interaction, long-term cycling stability, and fabrication at low cost. To address these important issues, the authors' research group has proposed a class of frameworked electrolytes (FEs) more recently, which are derived from a large group of porous framework materials, aiming at marking a paradigm shift in SSE technology.[18,19] As shown in **Figure 1**, characterized by their macroscopic solidity and microscopic architecture of highly ordered sub-nanopore networks in continuation, FEs offer a distinctively new approach to lithium-ion transport, in contrast to those in both the inorganic and organic electrolytes that have been documented in literature. While they are macroscopically solid, those sub-nano framework channels within FEs confine a number of solvent molecules and render ions in condensed states via weak molecule-ion interactions, thereby effectively reducing the migration energy barrier for lithium ions. These confined solvent molecules act like "solid solvents" and facilitate rapid and orderly lithium-ion transport at room temperature.[20] They realize a "swing" mechanism for ion transport, as has been shown more recently.[21,22] Through meticulously selecting the mechanically, chemically, and electrochemically stable insulating porous frameworks and fine-tuning the sub-nano channel sizes, internal functional groups, and Lewis acid sites, one can precisely tailor the interactions within the framework, enhancing the dynamics of solvents and anions, leading to a high ionic conductivity. This approach holds great promise for producing SSEs with superior overall performance.

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Indeed, the feasibility of the FE has been preliminarily validated in the $Ca_nNa_{12\text{-}2n}[(AlO_2)_{12}(SiO_2)_{12}]\cdot xH_2O$ zeolite system,[21] which is shown to exhibit a high ionic conductivity (0.113 mS cm^{-1} at room temperature), low activation energy (0.179 eV), and remarkable mechanical flexibility. When utilized as the electrolyte together with Li and $LiFePO_4$ electrodes, the constructed ASSB is shown to exhibit stable cycling at a 2 C rate over 450 cycles at room temperature, with an average energy density of 395 Wh kg^{-1}.

2. Comparison of the 2D Vertically Conductive MOF and 3D MOF for FE Applications

In spite of the high chemical stability of inorganic zeolites, challenges also arise in the precise manipulation of their Lewis acid sites.[23] In contrast, electrically insulating metal–organic frameworks (MOFs) appear as a class of more viable alternatives for FEs due to their exceptional tunability in chemistry and intrinsically low electrical conductivity. Comprising metal ions and organic ligands interconnected via well-coordination bonds, MOFs can be made to exist in a diverse array of structural configurations, including 0D, 1D, 2D, and 3D.[24]

Nevertheless, 0D and 1D MOFs are largely unsuitable for FE applications, owing to their absence of continuous charge transfer channels within the organic ligand matrices, and are therefore excluded further in this discourse. Both 2D and 3D MOFs are endowed with periodic sub-nano channels, which can provide well-defined pathways for lithium ions (also other ions), and be able to facilitate uniform cation plating and stripping. During the synthesis of MOFs, the properties of sub-nano pore channels, such as pore shape, size, polarity, and internal functional groups, can all be readily modulated through the strategic selection and combinations of metal ions and organic ligands, as well as processing conditions. Such versatility would permit a precise modulation in the framework interactions with various solvents and anions, paving the way for optimized electrolyte performance in solid battery technology applications.

Compared to their 3D counterparts, 2D vertically conductive MOFs not only preserve the inherent periodic sub-nano channels and high tunability characteristics, but they also manifest the distinct advantages of being mechanically flexible and can steadily be tuned in both thickness and chemistry in at least one direction. In addition, the 2D morphology offers shortened charge transfer spacing for ions between the two electrodes, an extensively high specific surface area, and an abundance of unsaturated metal coordination sites. Such properties arising from 2D vertically conductive MOFs would significantly augment their applicability as framework electrolytes in batteries and other diversified fields, including ionic transport, catalysis,[25] energy conversion,[26] optoelectronic devices,[27] and sensing.[28] For instance, 2D π–d conjugated MOF presents a graphite-like charge storage mechanism, which stands out as a highly advantageous material for secondary batteries.[29] A triptycene-based 2D vertically conductive MOF, rich in accessible active sites, has demonstrated exceptional electrocatalytic efficiency in the conversion of CO_2 to methane.[30]

When employed as thin FEs in solid batteries, 2D vertically conductive MOFs are positioned to surpass their 3D MOFs counterparts (**Figure 2**). First, instead of the 3D channels in bulk 3D MOFs with grain boundaries among the different MOF crystals, 2D vertically conductive MOFs provide 1D and highly oriented channels for lithium-ion transfer, which can apparently improve the ion transport efficiency and ionic conductivity. Second, the stratified structure of 2D vertically conductive MOFs offers an extensively high surface area, thereby exposing a large multitude of accessible open metal sites and the Lewis acid–base sites, rather than sealing them in the internal pores or channels in the 3D MOFs.[31–33] These plentiful active sites would assist in anchoring solvent molecules and anions, promoting lithium salt dissociation, and lowering the migration barrier for lithium ions, giving rise to high ionic transport. This set of unique properties has been exemplified in the applications reported for 2D vertically conductive MOFs. For instance, a 2D Mn-MOF shows a high energy barrier for the migration of SO_4^{2-} anions and H_2O molecules, while providing a low barrier for Zn^{2+} ions, thus accelerating their transport in the 2D framework structure.[34] In addition, the incorporation of positively charged functional groups, such as $\text{-}NH_2$, onto the MOF internal surface allows for the efficient trapping of anions, offering the potential of fully exploiting the MOF structure. Beyond these electrochemical advantages, 2D vertically conductive MOFs are inherently flexible in mechanical behavior,[35] which not only improves the interfacial contact with solid electrodes, but also bolsters their durability against external and internal straining during repeated charging/discharging. Finally, the synthesis of 2D vertically conductive MOFs can usually be conducted at low temperatures, through hydrothermal or self-assembly methods, and their malleability facilitates their processing into films or thin coatings. These traits grant 2D vertically conductive MOFs an edge over their 3D MOFs counterparts, particularly in scalability and integration with the battery manufacturing workflows, thereby contributing to the feasibility of their industrial applications at large scales.

To validate the above hypothesis, MIL-125[36] and MIP-207[37] were selected to investigate the ion migration process in FEs. Both MOFs incorporate titanium metal clusters and linkers containing aromatic rings and carboxylic groups (–COOH) (**Figure 3a**). MIL-125 features a 3D structure with tetrahedral cages (pore size 6.13 Å) and octahedral cages (pore size 12.55 Å), indicating that the aperture size of MIL-125 is 6.13 Å. Whereas MIP-207 possesses a 2D layered structural arrangement with a pore size of about 6 Å. More detailed crystal structure information can be obtained from the aforementioned work. Given their similar compositions and pore sizes, we can explore the excellent opportunity to examine how 3D and 2D structural characteristics influence ion transport in these MOFs. The adsorption energies of both MOFs for Li^+ are higher than those for DME and DOL (Figure 3b), which are typical solvents of LIBs. This difference can be attributed to the chemical bonding interaction between the MOF and Li^+, compared to the van der Waals interaction between the MOF and solvent molecules. Subsequently, the energy landscapes of Li^+ migration within the MOFs are calculated (Figure 3e). For MIL-125 and MIP-207, the energy barriers are 0.51 and 0.25 eV, respectively, confirming that the 2D vertically conductive framework facilitates a higher ionic conductivity. When both Li^+ ions and the DME molecule are present (Figure 3f), the energy barriers in MIL-125 and MIP-207 turn out to be 0.83 and 0.07 eV, respectively. The significant reduction

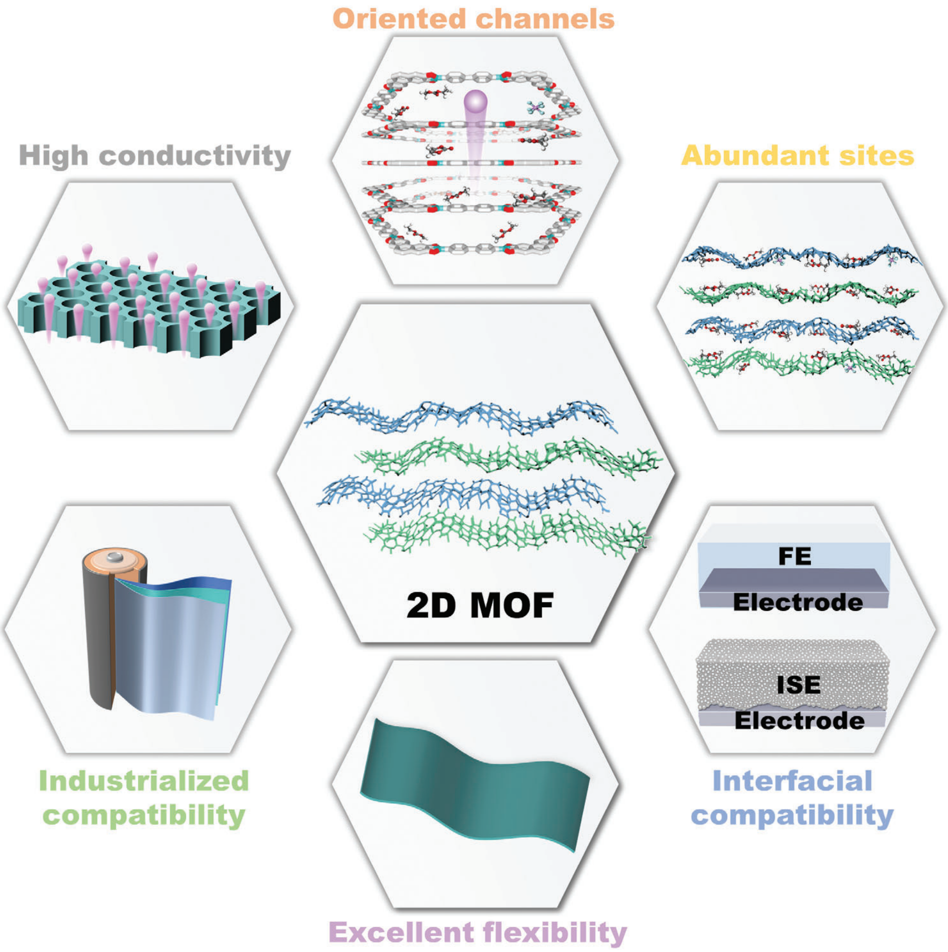

Figure 2. Schematic representation of a 2D vertically conductive MOF and its advantages in FE applications, including oriented channels, high conductivity, abundant active sites, excellent flexibility, and industrial and interfacial compatibility. These attributes make 2D vertically conductive MOFs as a promising selection for high-quality FEs.

in the Li^+ migration barrier in MIP-207 can well be attributed to DME being anchored in the continuous hydrogen-bonding network of the 2D vertically conductive MOFs, which would weaken the interactions between Li^+ and the frameworks. Using ab initio molecular dynamics (AIMD) simulations, we further calculated the mean square displacement (MSD) of Li^+ over 5000 fs in both the MIL-125 and MIP-207 (Figure 3d).[38] The results reveal that the migration rate of Li^+ in the 2D MOF (MIP-207) is significantly faster than in the 3D MOF (MIL-125). During the initial 2500 fs, the MSD curve appears approximately linear, with the lithium-ion diffusion coefficients D_{Li+} in MIP-207 and MIL-125 estimated at 8.50×10^{-8} and 4.67×10^{-8} $cm^2\ s^{-1}$, respectively. Additionally, we also evaluated the migration of Li^+ ions in combination with other components (Figure 3c). The results indicate that DOL and $TFSI^-$ hinder the movement of Li^+ ions within the MOF framework. This finding also underscores the importance of selecting appropriate organic molecules when using 2D vertically conductive MOFs as FEs. To fully utilize the ion migration advantages of the 2D vertically conductive MOF system, the organic molecules should interact strongly with the framework and weakly with Li^+.

Based on DFT and AIMD simulation results, lithium-ion migration is more efficient in MIP-207 compared to MIL-125. Specifically, the mobility barriers for Li^+ migration in MIP-207 and MIL-125 are 0.25 and 0.51 eV, respectively, while the Li^+-DME mobility barriers are 0.07 and 0.83 eV, respectively. The corresponding lithium-ion diffusion coefficients are 8.50×10^{-8} and 4.67×10^{-8} $cm^2\ s^{-1}$. Since MIP-207 and MIL-125 share similar metal clusters, linkers, and pore sizes, the primary distinction lies in their dimensionality: the metal clusters and linkers in MIP-207 are assembled in a 2D mode, while those in MIL-125 adopt a 3D configuration. Therefore, the differences in lithium-ion migration energy barriers between these two MOFs can be attributed to their structural differences. The 2D MOF features unidirectional sub-nanometer channels, which are expected to shorten the migration pathways for lithium ions between the anode and cathode. In contrast, the 3D MOF exhibits multidirectional sub-nanometer channels, resulting in disordered migration pathways that slow down lithium-ion transport and increase energy barriers. In summary, the DFT and AIMD calculation results demonstrate that 2D MOFs exhibit significant advantages in enhancing lithium-ion migration rates compared to their 3D

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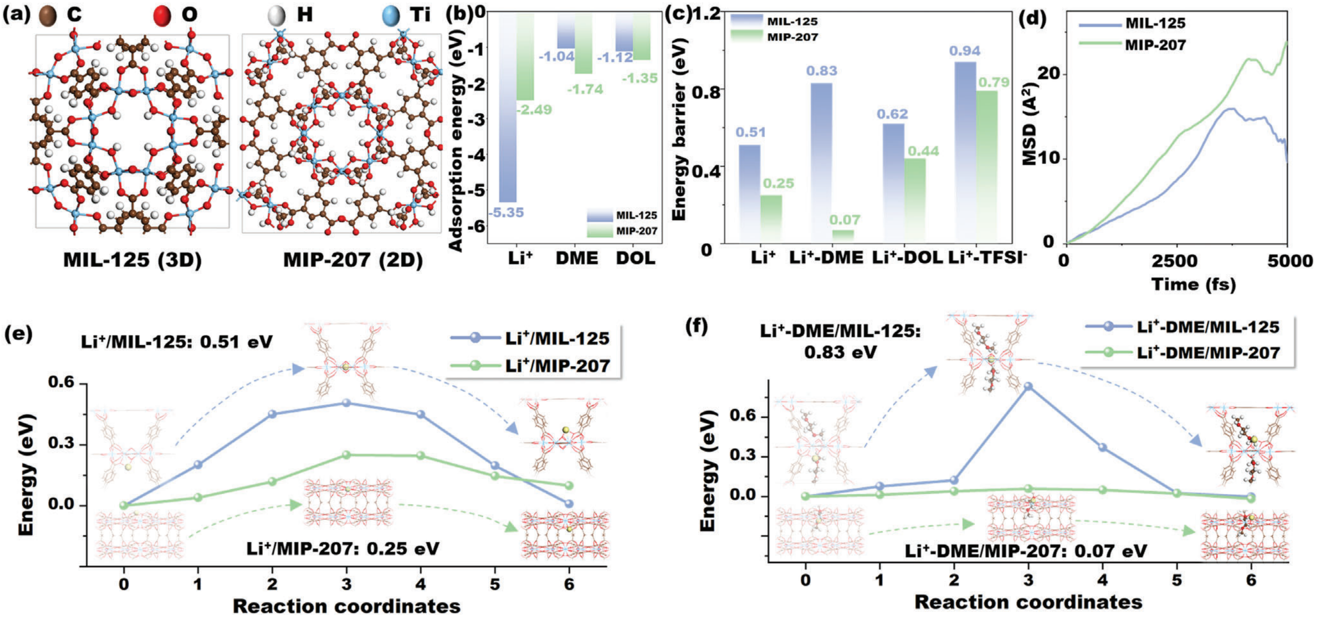

Figure 3. Ion migration in the 3D and 2D framework is shown by density functional theory (DFT) calculations. a) Crystal structures of MIL-125 (3D MOF) and MIP-207 (2D MOF). b) The adsorption energies of ions/molecules. c) The migration energy barriers of Li^+. d) The corresponding MSD curves of MIL-125 (3D MOF) and MIP-207 (2D MOF). e) The energy landscapes of Li^+ migration in the MIL-125 and MIP-207. f) The energy landscapes of Li^+ migration with the DME molecule in the MIL-125 and MIP-207.

counterparts. Further experimental validation shall be conducted in future studies.

3. Design Principle for 2D Vertically Conductive MOF FEs

For practical applications on large scales, the successful deployment and maximization of the efficacy of 2D vertically conductive MOFs hinge on a set of considerations. These factors can be summarized as the "2A2C" principle, which stands for "aspect ratio", "aperture", "coordination", and "chemical modification" (see **Figure 4**).

3.1. High Aspect Ratio

To fully leverage the structural advantages of 2D vertically conductive MOFs, a critical strategy involves the maximization of their aspect ratio. An enlarged aspect ratio in 2D would expose a greater number of accessible active sites, efficiently anchoring the solvent molecules and anions, and consequently improving the mobility of metal ions, such as Li^+, Na^+, and Zn^{2+}. There are various experimental approaches that can be used to achieve this objective, for example by regulating reaction temperatures, employing suitable templates, and implementing suitable post-processing methods. To be specific, as an example, the temperature at which the MOF is synthesized can significantly impact the growth and morphology of the 2D vertically conductive MOFs. By fine-tuning the reaction conditions, such as temperature, it would be possible to control the rate of crystallization and the subsequent layer formation, thereby impacting the aspect ratio of the final MOF product. Besides, the selection of appropriate templates can help dictate the thickness, uniformity, and layering of the MOF, thereby enabling the achievement of a desired aspect ratio for 2D vertically conductive MOFs.

3.2. Aperture Adjustment for Sub-Nano Channels

Tuning the 1D sub-nano channels in 2D vertically conductive MOFs can substantially boost lithium-ion transport efficiency. The modulation encompasses both the size and orientation of pore apertures, which are closely related to the configuration of ligands and the coordination environment of transition metal ions. Excessively small pores will impede the mobility of ions, whereas overly large pores will weaken the interactions between solvents, anions, and FEs, which affects the efficiency of ion transport. 2D vertically conductive MOFs can be obtained using both top-down and bottom-up methods.[39–44] To enhance the uniform orientation of pores, it is crucial to optimize a set of controlled guidances in the growth of 2D vertically conductive MOFs, employing/controlling techniques such as crystal seed induction and external field effects. By carefully selecting and positioning crystal seeds, for example, it would be possible to tune the direction and orientation of the MOF crystallization process. Such control would be crucial for ensuring that the resulting 2D vertically conductive MOFs possess well-organized, 1D sub-nano channels, which shall be optimal for lithium-ion transport. Additionally, the application of an external field, such as magnetic or electric fields, during the MOF synthesis process can also direct the crystalline growth, where these external fields can align the structure developed in a particular orientation, which in turn affects the orderly arrangement of the sub-nano channels. By focusing on these advanced synthesis and fabrication techniques, it would be possible to produce 2D vertically conductive MOFs

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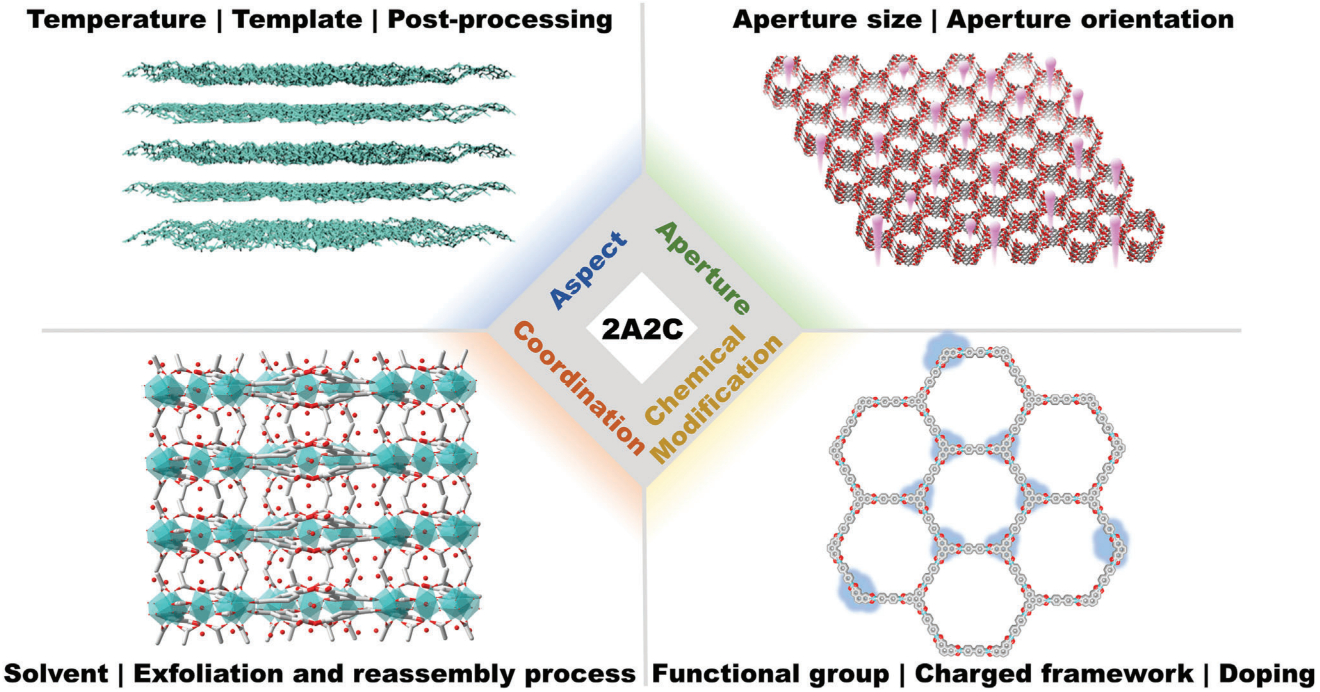

Figure 4. The "2A2C" rule is to be followed in designing FEs based on 2D vertically conductive MOFs. For 2D vertically conductive MOFs, it is recommended to maximize the aspect ratio to leverage structural advantages, optimize apertures of sub-nano channels for ions transport, select appropriate interlayer coordination modes, and perform chemical modifications to further accelerate dynamics.

with highly organized sub-nano channels, thereby unlocking their full potential in enhancing lithium-ion transport efficiency.

3.3. Engineering Interlayer Coordination

The intrinsic propensity of 2D materials to aggregate highlights the crucial role of interlayer interactions in their functional performance. This phenomenon is particularly relevant in 2D vertically conductive MOFs. During the fabrication of 2D vertically conductive MOFs via solvent exfoliation, for example, the chosen solvent plays a dual role in facilitating the delamination and stabilization of the formed 2D vertically conductive MOFs.[45] Given this dual functionality, the selection of an appropriate solvent would be paramount important for FE designed as electrolytes in ASSBs, in order to avoid the components that can induce unwanted chemical reactions (e.g., water).[37] Additionally, optimizing the reassembly procedures would be important to maintain stable interlayer coordination, which is the key to preserving the unique properties of 2D vertically conductive MOFs.

3.4. Chemical Modification

Strategic chemical modification of 2D vertically conductive MOFs can enhance the interaction with anions and solvents in their internal structures, thereby facilitating the transport of metal ions. For instance, grafting functional groups with specific chemical functionalities into 2D vertically conductive MOFs, either to linkers, or metal nodes or both, can improve the thermal, chemical, and electrochemical stability of the MOF system, enhance the interface compatibility with electrodes, and increase the efficiency of ion migration. Designing anionic or cationic frameworks contributes to the regulation of electrostatic interactions within the framework and the selective transport of ions. Additionally, doping 2D vertically conductive MOFs with certain metal ions can introduce localized charge centers for ion coordination, reduce the energy barrier for cation movement, and enhance the ionic conductivity of FEs. Finally, the proper incorporation of long molecular chains in the MOF system also promotes ion migration and improves the electrolyte efficiency.[12,13,46]

4. Conclusion

In summary, FEs embody a groundbreaking trajectory in the new domain of SSEs. Among the various candidates poised for impactful applications, the 2D vertically conductive MOF stands out with significant promise, as briefly mentioned above. By applying the "2A2C" rule, there is a strong anticipation that the unique attributes of 2D vertically conductive MOFs can be fully harnessed and optimized for SSEs. Such adherence to the "2A2C" rule is instrumental in maximizing the inherent strengths of 2D vertically conductive MOFs, involving a meticulous focus on the aspect or physical attributes for optimal ion transport and active site accessibility, the coordination chemistry for structural stability and functionality, and the ion-transport mechanism to ensure an efficient ion mobility within the framework. Simultaneously, the integration of 2D vertically conductive MOFs into ASSBs is not only just a step toward enhancing the energy density of these batteries, but also toward addressing the poor safety issue. The superior structural stability of 2D vertically conductive MOFs with chemical tunability, coupled with the optimized ion transport

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behavior, presents a unique opportunity to overcome some of the key challenges faced by the on-going development of SSEs and their applications in ASSBs. In essence, the exploration and development of 2D framework electrolytes under the "2A2C" principle shall be a promising avenue for propelling the new type of solid electrolytes and the next generation of ASSBs, marking a pivotal shift in the rapidly changing landscape of energy storage technologies.

5. DFT and AIMD Calculations

All spin-polarized first-principle calculations were conducted in the Vienna Ab initio Simulation Package (VASP) with the projector-augmented wave approach.[47–49] The generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE) functional was applied to the exchange–correlation interaction and an empirical van der Waals interaction correction was applied using DFT-D3.[50,51] The convergence tolerances for energy and force were 10^{-5} eV and 0.02 eV Å^{-1}, respectively. To obtain the energy barriers for the diffusion of ions/molecules, the climbing image nudged elastic band (CI-NEB) calculations were adopted.[52] The inserted images were optimized until the energies and forces converged to 10^{-5} and 0.03 eV Å^{-1}, respectively. AIMD simulations were performed with different ratios of solvents to salt under the NVT ensemble and Nosé thermostat at 300 K. The time step was set to 1 fs. The number of solvents and salts was determined by the size of zeolite and volume ratio of DME:DOL = 1:1.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D metal–organic framework, all-solid-state batteries, frameworked electrolytes, lithium-ion batteries

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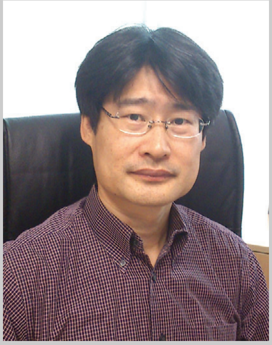

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