Critical Applications of Metal-Organic Framework Materials in Redox Flow, Solid-State, and Lithium-Sulfur Batteries

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Abstract. The global energy landscape is undergoing a profound transformation, rendering the development of efficient electrochemical energy storage technologies an urgent imperative. Currently, redox flow batteries, solid-state lithium metal batteries, and lithium-sulfur batteries represent highly promising energy storage solutions; however, their practical implementation remains hindered by numerous obstacles. The fundamental bottlenecks are frequently attributed to the failure of mass transport regulation at membrane or interfaces, exemplified by poor ion selectivity or compromised interfacial mechanical integrity. The transition to sustainable energy demands efficient storage technologies. While redox flow, solid-state lithium metal, and lithium-sulfur batteries are promising, their performance is currently limited by mass transport and interfacial instability. Metal-Organic Frameworks offer a solution through their highly tunable pore structures. This review analyzes it utility across these systems: they act as ion sieves to curb cross-contamination and boost kinetics in redox flow batteries; reinforce electrolytes to balance conductivity and suppress dendrites in solid-state lithium cells; and mitigate the shuttle effect in lithium-sulfur batteries via physical and chemical trapping. Despite these technical advances, the paper identifies high manufacturing costs and long-term operational stability as key remaining hurdles for commercial viability.

1 Introduction

A radical shift is currently reshaping the global energy sector. With fossil fuel reserves dwindling and environmental damage intensifying, the move towards clean power has become unavoidable. although solar and wind technologies have expanded rapidly, their output remains notoriously unpredictable. This fluctuation threatens grid stability, making the creation of robust electrochemical storage systems a pressing priority.

In the landscape of storage solutions, Redox Flow Batteries (RFBs) stand out due to their exceptional safety records and longevity [1], qualities that are ideal for grid-scale applications. In parallel, academic focus has sharpened on high-energy-density alternatives such as Lithium-Sulphur (Li-S) and solid-state lithium metal batteries. However, widespread

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commercial adoption of these advanced systems is still hindered by significant technical barriers.

When examining why these diverse battery types need to be improved, there is a shared and apparent limitation, which is the inability to regulate mass transport effectively within the electrolyte or membrane. For instance, in RFBs, current membrane fail to reconcile the trade-off between conducting ions and filtering them. They cannot adequately prevent the migration of active species [2]. This will lead to swift capacity loss. Likewise, the persistent shuttle effect in Li-S cells occurs because of a failure of the membrane to act as a molecular sieve for polysulphides. Moreover, solid-state batteries struggle with the double demand of creating fast ion pathways while preserving mechanical stability at interface. Fundamentally, the improvement of precise control over ion transport mechanisms will largely reduce the conventional materials fall short.

The emergence of MOFs provides a novel paradigm for addressing the aforementioned difficulties. These are a class of porous materials assembled from metal nodes and organic ligands. Distinct from traditional inorganic or organic materials, MOFs possess highly ordered pore structures [3]. More significantly, both their chemical environments and pore dimensions are tunable. This implies that they can be engineered to function as specific 'ion sieves'. Such intelligent structures not only intercept harmful by-products via physical or chemical means but also provide low-impedance channels for charge carriers.

This paper aims to review the progress regarding the application of MOFs and their derivatives within the three aforementioned battery systems. Emphasis is placed on exploring how the structural characteristics of MOFs are utilised to optimise the ion selectivity of membrane and enhance the interfacial stability between electrodes and electrolytes. It is anticipated that through this systematic review of frontier research, theoretical references and practical pathways will be provided for the design of critical materials for the next generation of high-performance batteries.

2 Applications of MOF materials in redox flow batteries

RFBs occupy a pivotal position within the domain of large-scale energy storage. Their design philosophy is predicated on the decoupling of energy and power. Energy is stored within external reservoirs, whilst power output is contingent upon the scale of the reactor stack. This architecture endows the system with exceptional flexibility; should an increase in capacity be required, the expansion of reservoir volume suffices. Furthermore, owing to the characteristics of aqueous electrolytes, their safety profile is significantly superior to that of organic-based batteries.

Despite these benefits are obvious, the broader usage of RFBs is currently restricted by limitations in two critical areas. The first is the membrane. It acts as the battery's safety barrier by keeping positive and negative electrolytes apart. At the same time, it allows conductive ions to go through such as protons. Although commercial perfluorinated sulphonic acid membranes offer high proton conductivity, their ability to filter ions is poor [4]. Bulky active species, notably vanadium ions, can easily breach the membrane. This crossover leads to significant capacity loss over time. Secondly, the limiting factor is the electrode. Conventional carbon felt electrodes lack sufficient surface functional groups. This may demonstrate weak electrochemical activity [5]. This slow redox reaction rate lowers the battery's power output, particularly at high current densities. However, using MOF materials, which is a targeted strategy to overcome these special performance drawbacks.

2.1 MOF-based ion-sieving membrane

Effective sieving is significant to solving cross-contamination. Ideally, a membrane requires molecular-level recognition capabilities. This enables small protons to permeate while blocking larger metal ions. MOFs are naturally suited to this task because of their ordered, continuous internal pore channels. Crucially, the aperture size of these pores can be finely changed at the Ångström scale.

Researchers have designed various modification methods. Most of them focus on using MOFs as functional fillers. When MOF nanoparticles are evenly dispersed in a polymer matrix, they create ion pathways via their own pores. Due to the size-exclusion effect, bulky vanadium ions are blocked. However, protons pass through without hinderance. This significantly boosts the selectivity of the membrane's ion.

Another direct method is to grow a dense, continuous MOF film in situ on a porous substrate to act as a physical shield. Experimental evidence shows that membrane treated with ZIF- or UIO-series materials offer significantly improved vanadium resistance. This leads to a notable rise in the battery's coulombic efficiency [6]. During extended charge-discharge cycles, capacity retention remains high, which confirms that cross-contamination is effectively inhibited. Additionally, MOF-derived carbon materials are known for their high specific surface areas and rich active sites. They are widely used to modify graphite felt electrodes. This modification lowers overpotential and accelerates redox reaction kinetics.

Beyond physical steric hindrance, chemical interactions also play a pivotal role. Researchers can apply functionalised modifications to the MOF framework. Following the introduction of positively charged groups, the framework exerts electrostatic repulsion against similarly positively charged metal ions via the Donnan exclusion effect [7]. This synergistic mechanism of 'physical sieving plus electrostatic repulsion' further reinforces the barrier efficacy of the membrane.

2.2 Optimisation of electrode kinetics via MOF-derived materials

Regarding the electrode, the core strategy for enhancing carbon felt activity lies in the introduction of efficient catalytic sites. MOF materials serve as ideal precursors for the preparation of such electrocatalysts.

High-temperature calcination of MOFs under an inert atmosphere induces a unique structural evolution. Organic ligands transform into a conductive porous carbon framework, whilst metal nodes are converted *in situ* into metal oxides or elemental metals. These active species are uniformly embedded within the carbon substrate, forming a nanocomposite structure.

These derived materials have two distinctive advantages. Firstly, they possess an ultra-high specific surface area and preserve the porous architecture of the original MOF. This significantly expands the three-phase boundary where the electrode meets the electrolyte. The reaction sites increase directly quickens the charge transfer process. Secondly, these materials exhibit excellent catalytic properties. Metal species generated in situ successfully reduce the energy barrier in redox reactions. Electrochemical data show that notably higher voltage efficiency can be achieved by using electrodes modified with these derivatives. Even under demanding high-current density conditions, the battery maintains a steady voltage. This indicates that the previous limitation of slow reaction kinetics has been effectively resolved.

In short, MOF materials have great value to redox flow batteries. They act as precise ion sieves within the membrane and serve as effective reaction boosters at the electrode. This versatility makes them serve as a main material for the next generation of high-performance flow batteries.

3 MOF-based composite electrolytes for solid-state lithium metal batteries

Solid-state lithium metal batteries are widely seen as promising candidates for the next generation of high-energy storage. Unlike standard liquid-based systems, these batteries replace flammable organic electrolytes with solid alternatives. This replacement removes the danger of leaks and explosions. It also enables the use of high-capacity metallic lithium anodes.

However, in practice, solid electrolytes still face a critical challenge. This conflict comes from the tension between ionic conductivity and mechanical resilience [8]. Polymer electrolytes offer excellent flexibility and contact at the interface, but their conductivity at room temperature is not often enough. Moreover, they lack the structural toughness to effectively prevent lithium dendrites. What is more, while inorganic ceramic electrolytes provide superior strength and conductivity, they suffer from brittleness and high resistance at the interface [9]. Consequently, creating composite electrolytes that successfully combine rapid ion transport with robust mechanical strength has become a primary research goal.

MOFs provide an ideal scheme for resolving this performance trade-off. The rigid MOF skeleton can serve as a reinforcing filler to enhance the mechanical modulus of the composite membrane. Simultaneously, its abundant pore structure is capable of accommodating lithium salts or ionic liquids, thereby constructing rapid ion transport channels.

3.1 The synergistic enhancement strategy of "MOF + ionic liquid" [10]

Recent research has proposed a flexible composite solid electrolyte membrane based on PVDF-HFP, UIO-66, and ionic liquids. This design ingeniously utilises the synergistic effect between the MOF and the ionic liquid. In this system, UIO-66 nanoparticles function not merely as physical fillers but also as microscopic ion reservoirs.

UIO-66 possesses a rich microporous structure; these pores are capable of adsorbing and locking the ionic liquid. This effect resolves the issues of phase separation or leakage to which ionic liquids are prone within a polymer matrix. The ionic liquid confined within the MOF pores constructs a continuous and unobstructed ion transport path. This significantly lowers the transport energy barrier for lithium ions and facilitates the dissociation of lithium salts.

3.2 Dual breakthrough in electrochemical performance and mechanical stability

Experimental findings validate the success of this dual-approach design [11]. The composite electrolyte demonstrated superior electrochemical behaviour. It achieves room-temperature ionic conductivity levels that far surpass those of pure polymer versions. Most importantly, the lithium-ion transference number rose to 0.52. This means anion movement is being limited. This reduction in concentration polarisation at the electrode surface improves a more uniform deposition of lithium ions.

In terms of mechanical resilience, adding the MOF framework could greatly strengthen the membrane. The mixture of stiffness and flexibility gives the electrolyte a strong ability to block lithium dendrite growth. During extended lithium stripping and plating cycles, the cell maintains a steady overpotential with no signs of short-circuiting. Furthermore, the electrolyte offers a broad electrochemical window of 4.3 V. This ensures compatibility with high-voltage cathodes.

To sum up, using the pore confinement effect of MOFs to catch ionic liquids is a highly effective method for boosting overall performance of solid electrolytes. This approach successfully strikes the necessary balance between conductivity and physical strength. Moreover, it makes solid-state lithium metal batteries closer to practical use.

4 Multifunctional roles of mofs in lithium-sulfur batteries: from shuttle inhibition to thermal safety management

Li-S batteries boast an impressive theoretical specific capacity reaching 1675 mAh/g. This impressive performance enables them to be positioned as the candidate to overtake current lithium-ion batteries [12]. Despite this promise, their path to commercialisation has been blocked by two persistent electrochemical flaws. One key issue is the shuttle effect. The intermediate polysulphides dissolve easily into the electrolyte and migrate across the membrane to the anode. This causes an irreversible loss of active material. Simultaneously, the lithium anode also suffers from interfacial instability. Uneven lithium deposition leads to the formation of dendrites. This process not only runs out of the electrolyte but also puncture the membrane to trigger short circuits. In order to address these problems, researchers are turning to MOF-based membrane modifications and innovative electrolyte designs as effective countermeasures.

4.1 Dual breakthrough in electrochemical performance and mechanical stability

Traditional polypropylene or polyethylene membrane have large pore sizes and chemical inertness. These render them unable to effectively intercept polysulfides. To resolve this problem, the construction of composite membrane possessing 'adsorption-catalysis' functions has become a predominant strategy [13].

Recent research reports a polyacrylonitrile (PAN) nanofiber membrane modified with a copper-nickel bimetallic MOF (Cu-Ni MOF). This design is not merely a simplistic physical coating but rather the construction of a complex reactive interface. The PAN nanofibers serve as the skeleton and provide superior electrolyte wettability. At the same time, the in situ grown Cu-Ni MOF nanoparticles serve as the core functional units.

The function of this modified layer relies on three different mechanisms: physical blocking, chemical adsorption, and catalytic conversion. Firstly, packing MOFs densely creates complex and winding channels. These extend the diffusion path of polysulphides and acts as a physical sieve effectively. Furthermore, the inner Cu and Ni sites serve as Lewis acid centres. They strongly coordinate with the sulphur atoms which are found in polysulphides. Through this chemical adsorption, the polysulphides are tightly sticked to the cathode. Particularly, these bimetallic sites are also seen as catalysts. They can speed up polysulphide conversion kinetics and thereby cutting down the time these species stay in the electrolyte. Tests confirm that this combined protective strategy boosts the battery's cycling stability. It also preserves high capacity retention even when it comes to heavy loads [13].

4.2 Dual breakthrough in electrochemical performance and mechanical stability

Beyond traditional elemental sulfur cathodes, sulfurized polyacrylonitrile (Li-SPAN) has emerged as a novel cathode material. Although it mitigates the shuttle effect to a certain extent, it continues to face challenges regarding lithium dendrites and safety. Particularly under high-temperature operating conditions, traditional membrane are prone to thermal shrinkage, leading to internal battery short circuits.

Targeting the Li-SPAN system, a novel polymer electrolyte named ZIF-67/PMIA@PVDF-HFP (abbreviated as MOF-PPH gel) has been developed. The innovation of this research lies in the incorporation of highly thermally stable poly (m-phenylene isophthalamide) (PMIA) and ZIF-67 into an electrospun skeleton.

The composite membrane demonstrates outstanding thermal safety. By leveraging the high-temperature resilience of PMIA and ZIF-67, the material retains its structural integrity at 200 ℃ with negligible shrinkage which is a critical indicator for preventing thermal runaway in batteries. Microscopically, the addition of ZIF-67 improves the deposition behaviour of lithium ions. The porous MOF serves to homogenise the lithium-ion flux [14], whilst its own lithiophilicity lowers the nucleation overpotential. Consequently, lithium ions are forced to spread uniformly across the electrode surface instead of accumulating vertically into sharp dendrites. Experimental data confirms that the lithium anode remains smooth and planar after extended cycling [14]. Ultimately, this regulation of deposition significantly enhances both the longevity and safety of the battery [14].

5 Challenges and outlook

Despite the exhilarating prospects demonstrated by MOF-based materials in advanced battery systems, the transition from 'laboratory prototypes' to 'industrial products' necessitates a lucid recognition of the following remaining obstacles.

5.1 The trade-off between cost and mass preparation

The primary concern is economic viability. Current laboratory synthesis of MOFs and their derivatives frequently relies on costly organic ligands and metal salts, often employing solvothermal methods with high energy consumption. Such small-batch preparation methods are ill-suited to satisfy the tonnage-level demands of the battery industry. Future research foci must shift towards low-cost, green synthesis routes. For instance, the development of aqueous phase synthesis methods or the utilisation of waste plastics as ligand sources represents a viable pathway for cost reduction.

5.2 Long-term stability in harsh environments

Chemical stability presents a secondary, yet formidable, challenge. Effectively acting as a complex electrochemical reactor, a battery’s internal environment forces MOF materials to endure prolonged exposure to aggressive acids, alkalis, or organic solvents, whilst simultaneously weathering thousands of redox cycles. In such extremes, specific carboxylate-based MOFs are prone to the severance of coordination bonds, resulting in structural pore collapse. Consequently, safeguarding stability over the full lifecycle demands critical engineering strategies, such as the synthesis of metal nodes with high coordination numbers—exemplified by high-valence Zr-based MOFs or the incorporation of hydrophobic groups for surface modification.

5.3 The trade-off between cost and mass preparation

Most pristine MOF materials are inherently insulators or semiconductors. Low electronic conductivity restricts their performance under high-rate charge/discharge conditions. Although the preparation of derivatives via high-temperature carbonisation can resolve this issue, this process frequently sacrifices the unique ordered pore structure of the MOF. How to endow materials with superior conductivity whilst retaining their pore advantages—for example, by developing novel conductive MOFs or constructing conductive network composites—remains a scientific conundrum awaiting resolution.

6 Conclusion

This paper has systematically reviewed the latest research progress regarding MOFs and their derivatives in redox flow batteries, solid-state lithium metal batteries, and lithium-sulfur batteries. Based on an analysis of the literature, the following conclusions are drawn:

Firstly, structure dictates function. The unique pore confinement effects and tunable chemical environments of MOFs render them an ideal platform for addressing specific issues within critical battery materials. In redox flow batteries, the precise interception of active ions is achieved via physical sieving and electrostatic repulsion; in solid-state batteries, the contradiction between electrolyte ionic conductivity and mechanical strength is balanced; and in lithium-sulfur batteries, a dual line of defence is constructed to suppress the shuttle effect and lithium dendrites.

Secondly, functional design is paramount. Whether through chemical modification via the introduction of functional groups or by functioning as precursors for the preparation of nanocomposites, customised design targeting the specific pain points of different battery systems is key to unlocking the potential of MOFs.

Looking ahead, with advancements in synthesis technology and a deepening understanding of structure-activity relationships, it is reasonable to posit that MOF-based advanced materials will play an irreplaceable role in the next generation of high-performance electrochemical energy storage systems, thereby propelling the further development of clean energy technologies.

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