Metal-Organic Frameworks for Next-Generation Lithium-Based Batteries: From Molecular Design to System Integration

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Abstract. The growing need for green power, particularly for electric vehicle, is driving up the need for high-energy-dense, safe, and life-extending lithium batteries. But the problem of the growth of lithium dendrites, the formation of the polysulfides, and the instability of the interface have hampered their actual use. Metal organic frameworks (MOFs), which are characterized by varying porosity, rich activation sites, and a variety of structures, have been proposed as a transition material to overcome those constraints. In this paper, MOFs are used in the next generation lithium-ion batteries, including lithium, lithium sulfur, and lithium air, with emphasis on their functions as electrodes, separators, and electrolyte modifiers. MOFs enhance ion transport uniformity, suppress dendrite formation, and improve redox kinetics through customized pore structures and conductive frameworks. The composite materials and derived materials derived from MOFs further demonstrate excellent cycling stability and high capacity. Despite the progress made, scalability and cost remain challenges, thus requiring strategies such as low-cost metal substitution and simplified synthesis. Future efforts should prioritize improving conductivity, mechanical robustness, and compatibility with industrial processes. By utilizing the multifunctionality and structural adaptability of MOFs, this work highlights their potential to achieve safer and higher performance lithium batteries, accelerating the transition to sustainable electric vehicle technology.

Keywords: Metal-organic frameworks, lithium-based batteries, structural design, dendrite suppression, energy storage.

1. Introduction

Along with the fast progress of modern society, there is an exponential increase in the need for green energy, particularly in the areas of electric vehicles (EVs) and fixed power networks. The development of effective and sustainable energy-storing technologies for electric vehicles is crucial in order to reduce GHG and fossil-fuel dependency. Due to the advantages of high-power density, low-cost, clean and light weight, lithium-based batteries are becoming more and more popular [1]. For example, lithium metal anodes have attracted much attention due to their small weight, the lowest standard potential, and the high theoretical specific capacity (3860 milliamperes/kWh) [2]. The actual use of lithium metal batteries (LMBs) in electric vehicles is, however, still confronted with serious problems. In the course of charging and discharging, the morphology of the liquid-crystal is reduced, and the Coulomb efficiency of LMBs is reduced, causing an internal short-circuit, causing significant security concerns [3]. In addition, the separation/electrolyte system, which is a vehicle for ionic transfer in the cell and significantly affects the electrochemical properties of LMBs, is restricted by their properties. Mechanical strength, wetting and ion conductivity are among the disadvantages of conventional separators that are mainly composed of polyolefins (e.g. poly (propylene) and poly (ethylene)). Therefore, complex electrode materials and separation devices need to be developed to improve the properties and security of lithium batteries in EVs [4].

Metal Organic Frameworks (MOFs), which are also called porous coordination polymers, are made up of metallic nodes connected by an organic bond. Due to their unique properties, MOFs are attractive in many applications, including separating, catalyzing, and storing gas. Recently, MOFs have been studied as a potential component for improving the capability of rechargeable cells. The addition of MOFs to a spacer may, for instance, enhance their mechanical strength, wetting ability,

and ion conduction at the same time as controlling ion transfer and preventing lithium dendrites from forming [5].

The purpose of this paper is to explore the use of MOFs in lithium-based batteries like LMBs, lithium-ion batteries (LIBs), lithium-sulfur batteries, lithium-air cells, and so on. In this paper, some outstanding performance or enhancement of MOFs are presented, such as the influence of MOFs onion transfer, inhibiting the growth of lithium dendrite and improving the efficiency of the cell. Furthermore, a summary of the applied conditions for a number of MOF materials was presented, and a summary was given on how MOFs could improve the properties of lithium-based batteries. The exploration of MOFs in lithium-based batteries will offer new ways to enhance their properties and security, which will greatly influence the next generation of electric vehicles.

2. Advantage of MOFs

2.1. Uniform Pore Structure

The uniform pore structure is one of the most remarkable characteristics of MOFs. The pores in MOFs are highly ordered and tunable by modifying the length of organic ligands around metal centers, enabling effective regulation of ion transport pathways in lithium-based batteries. This flexibility allows optimization for specific scenarios: smaller pores can restrict polysulfide shuttling in Li-S batteries, while larger pores facilitate fast ion diffusion. By precisely controlling the pore size, MOFs can achieve the selective conduction of lithium ions, thereby improve ionic conductivity and reduce unnecessary side reactions. Thin and uniform pore size MOFs are very promising in the protection of Li-S batteries and in enhancing their properties. Using Cu, Zhou and his colleagues developed a MOF-based membrane-1,3,5-tricarboxylate (HKUST-1) nanoparticles as construction blocks and PVDF-HFP as binder [6]. Even the pore diameter of the HKUST-1 nano-particles is critical to the promotion of the homogeneous lithium ion (Li^+) flux. Due to such uniformity, the growth of lithium dendrites is substantially suppressed, enabling a steady deposition and removal of lithium even at a high current density of 10 $mA \cdot cm^{-2}$. The performance of MOF-based material as a spacer in Li-S cells is exceptional. The Li-S cell having this type of separator has a remarkable reduction in its capacity of only 0.015 percent per cycle and has reached an extremely high cycle lifetime [7]. This shows that MOFs, especially ones that have a well-designed pore structure such as HKUST-1, are capable of protecting the cathode of Li-S batteries and improving its long-term stability and cyclic properties.

2.2. Abundant Metal Active Components

MOFs exhibit distinct advantages stemming from their "Abundant Metal Active Components," particularly through the role of open metal sites. The redox-active sites could be designed through selecting metal nodes (e.g., Cu, Fe) and organic linkers (or called ligands), tailoring MOF reactivity to favor electrochemical processes like lithium intercalation or oxygen reduction in LMBs. The surface chemical and electrical structure of MOFs can be adjusted by modifying the coordination elements to improve the oxidation-reduction kinetics and structural stability in the course of the cycle to satisfy the requirements of higher power [8]. MOF-based cathodes have garnered significant attention because of their design versatility, with structures adjustable by selecting different transition metals and organic linkers. The main advantage is that the MOFs are coordinated by metal-ligand binding to form an open metallic site with an organic linker, thereby increasing the total ion and electric conductivity of the MOFs. As shown in Fig. 1, such a conductive framework, in combination with their porous and conjugated electronic structures, allows high ionic/electrical conductivity, accelerates charge transfer and facilitates efficient metal-ion diffusion during the intercalation/deintercalation process [9].

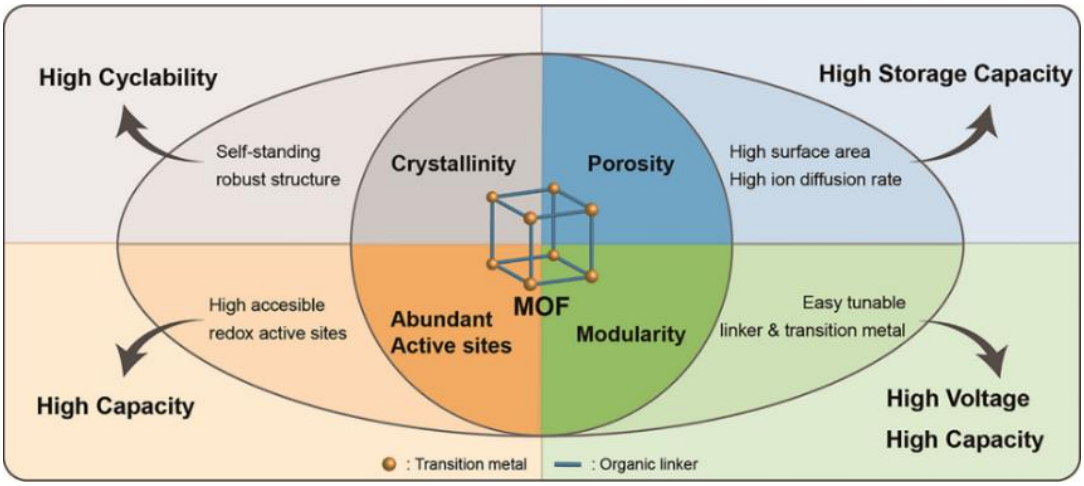

Figure 1. Advantages of MOF as a battery cathode material [9]

Different from conventional cathode materials, which are prone to structural collapse at high energy densities, MOFs leverage their open metal sites to maintain robust redox activity. For example, transition metal nodes in MOFs (e.g., Co and Fe) create pathways for rapid electron transport via metal-ligand interactions, addressing the diffusion limitations common in bulk active materials [10]. Morphological engineering of MOFs further impacts performance by optimizing the exposure of active sites and the interactions of ion-electrolyte. Nanostructured MOFs, for example, increase accessible surface area and reduce ion diffusion paths, boosting rate capability. This feature can support high-power performance whilst mitigates capacity fading by enabling ions to participate in redox reactions more completely. Therefore, such metal-rich active components position MOFs as promising candidates to overcome the limitations of traditional cathodes, offering a balance of high conductivity, structural stability, and enhanced redox kinetics [11].

2.3. Chemical Stability

The chemical stability of MOFs is vital for its application in lithium metal batteries. High chemical stability of MOF materials enables structural integrity to be maintained during the lithium-ion insertion/extraction processes. For instance, Ogihara et al. developed an intercalated metal-organic framework (iMOF) for high-voltage bipolar batteries [12]. Fig. 2 shows the bipolar charging mechanism of iMOF [13]. The key benefit of this architecture was its ability to maintain structural integrity during the lithium-ion intercalation process, thus facilitating the unimpeded transport of lithium and contributing to favorable cyclic stability. This work underscores how the chemical stability of MOFs directly enables sustained structural robustness, which is essential for maintaining efficient ion migration and long-term performance in lithium-ion battery systems [8].

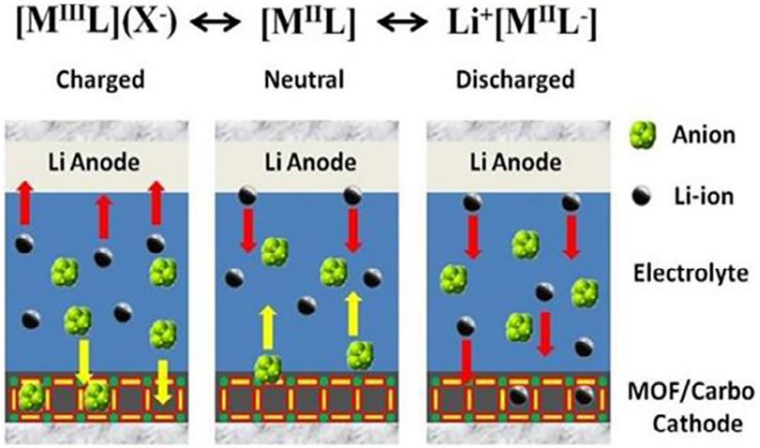

Figure 2. Lithium-ion batteries: the "Bipolar Charging" mechanism and the solid-state electrochemical process of MOF used as active materials [13]

2.4. Multifunctionality

The versatility of MOFs enables them to serve as electrodes, separators, or electrolyte framework. For example, conductive MOFs (c-MOFs) leverage their inherent large specific surface area, porous architecture, and high conductivity to generate abundant active sites and lithium storage sites. This structural advantage could boost the energy density of LMBs, whilst supporting the rapid charging capability by minimizing diffusion resistance [14]. In Li-S batteries, conductive MOFs (c-MOFs) serve dual roles as both cathode components and separator materials. The porous frameworks of c-MOFs can effectively adsorb polysulfide intermediates produced in the redox reactions, which are notorious for causing the shuttle effect—where soluble polysulfides migrate between electrodes, degrading capacity and cycle life. By capturing these species physically and chemically, c-MOFs stabilize the electrolyte environment and maintain the integrity of the cathode, thus improving the long-term recyclability of Li-S systems [14].

Collectively, these unique features—surface area, pore size, redox activity and morphology—make MOFs versatile platforms to address the challenges in lithium-based batteries (e.g., low conductivity and structural decay), driving innovations in energy density, cycle life, and operational stability [8].

3. Application of MOFs in EV Batteries

3.1. Pure MOF Materials

Pure MOF materials have shown significant potential in enhancing the performance of lithium-ion batteries, such as being used as high-performance anodes. Mn-benzene tricarboxylate (Mn-BTC), a typical Mn-based MOF, has been directly utilized as an anode material for lithium-ion batteries. When tested in a Li/Li half-cell with a potential window of 0.01-2.0 V, Mn-BTC exhibited a reversible specific capacity ranging from 694 to 400 $mAh \cdot g^{-1}$ at current densities of 0.1 and 1.0 $A \cdot g^{-1}$, respectively [15]. Excellent cyclic stability is preserved in this material, whose volume retention is a reflection of the structural integrity of the MOF frame when lithium ions are inserted/withdrawn. Mn-1,4-BDC@200 is an additional example, and it also exhibits exceptional electrochemical performance. Mn-1,4-BDC can be manufactured by solvothermal process by means of 1,4-BDC (1,4-benzenedicarboxylic acid) and $MnCl_2$ as feedstock. After processing at 200 ℃, Mn-1,4-BDC@200 can be obtained by removing the coordinating solvent. This MOF is employed as an anode in LIB and the Mn-1,4-BDC@200 electrode is kept at $100mA \cdot g^{-1}$ for 100 cycles, which shows superior electrochemistry properties compared to Mn-1,4-BDC [16]. The findings demonstrate that the electrochemical performance of Mn-BDC has been adversely affected by the coordination solvent pairs present in its structure. Importantly, Mn-1,4-BDC exhibits excellent electrochemistry when it is used as an anode, matching reported manganese oxide electrode materials derived from Mn-MOFs. This shows the potential of unmodified MOFs in lithium-ion battery technologies.

Beyond Mn-based MOF, ZIF is rich in N-elements, and dimethylimidazole is an organic ligand. N doped porous carbon materials can be manufactured on site when used as a self-sacrificing template for carbonization at high temperatures. For instance, ZIF-8 may be pyrolyzed to generate a porous carbon substance having as much as 17.72 % by mass [17]. The performance of this electrode is exceptional, and it is much higher than that of graphite carbon materials with a specific volume of 2,132 $mAh \cdot g^{-1}$ for 50 cycles at a condition of 100 $mA \cdot g^{-1}$. To facilitate such an ultra-high specific volume, it is shown in theory that pyridinium N and pyridinium N are able to absorb more Li ions from the surface of the graphite, acting as the active site.

Furthermore, the charge density difference between heteroatoms can be exploited by using organic ligands with different functional groups in different positions. This enhances charged transport by bringing heteroatoms to the interface, which creates a difference in potential and an inherent electric field. For example, when UiO-66 is used as the matrix, through a series of reactions, an N, P gradient heterogeneous doped composite material can be obtained. A gradient band structure and a potential

difference within the particles are created when heteroatoms undergo gradient doping, which causes charge rearrangement. This improves reaction kinetics, speeds up charge transport, and greatly increases the intrinsic conductivity of the derived carbon materials.

3.2. MOF-Based Composite Materials

MOF composite materials have been extensively explored to further enhance the performance of Li-S batteries. For example, a mesoporous copper-based spindle-like MOF was used as a template to synthesize a new electrode. This kind of electrode delivered a high capacity of 789 $mAh \cdot g^{-1}$ after 200 cycles at 100 $mA \cdot g^{-1}$ [18]. The excellent performance of this electrode in electrochemistry can be attributed to its special structure and compositional properties, including a hollow interior structure, small size, and porous characteristics [19]. Compared to other CuO-based hybrid anode materials, this anode demonstrates superior electrochemical performance, which benefits from its advantageous structural and compositional attributes—specifically, a hollow interior architecture, nanoscale dimensions, and porous features. These properties collectively enhance ion transport kinetics and electrode-electrolyte contact, optimizing charge storage efficiency. The hollow structure mitigates volume changes during cycling, while the porous nature increases accessible surface area for lithium-ion adsorption, and the reduced particle size shortens diffusion pathways. Together, these structural and compositional advantages drive the anode's enhanced rate capability and cycle stability compared to conventional CuO-based counterparts [19]. Similarly, the hollow CuO octahedron fabricated by Wu's group with $[Cu_3(btc)_2]$ MOFs as templates also showed good cyclic stability. Even in the case of deep circulation at 5000 $mA \cdot g^{-1}$, the charge capability was completely restored to near its original state when it was restored to the low density of 100 $mA \cdot g^{-1}$. This robust performance emphasizes the porous CuO hollow octahedra's great potential as a high-rate anode material for LIBs, combining superior speed preservation and structure resistance in heavy electrochemical cycles. Furthermore, these structures have been verified in iron-based materials, for example, the Fe_2O_3 multi-axis fabricated by Xu and his group with Fe MOF as the template. When 50 cycles were set, running at 0.2 C, the volume remained at 950 $mAh \cdot g^{-1}$ and even kept 424 $mAh \cdot g^{-1}$ at the high 10 C speed [20].

3.3. Derivative Materials Based on MOF

Beyond MOF-based composites, metal organic frameworks can be converted into metal compounds, nano-structured porous carbon and their composites [7]. This kind of material made from MOFs has many polar or catalytic sites, excellent electrical conductivity, and hierarchically porous architecture, all of which greatly improve the performance of Li-S batteries or LIBs [21]. For instance, a study by Bai et al. demonstrated the use of MOF glass to stabilize cathodes with high-voltage cathodes in LMBs. Li-ion desolvation and transport were greatly accelerated by the MOF glass coating on NCM-811 cathodes, which also reduced interfacial resistance. The Li||Glass@NCM-811 battery demonstrated excellent speed and cyclic stability, with a capacity of more than 80 percent at 1,000 cycles at the cut-off voltage of 1 C and 4 V [22]. This advantage is more apparent at 4.8 V, where the naked Li||NCM-811 cell does not have an MOF glass coating, but the Li||Glass@NCM-811 battery still operates with a specific capacity of 180 $mAh \cdot g^{-1}$ for 400 cycles, which is quite a good performance level [22]. In addition, the MOF glass successfully inhibited gas production and the dissolution/migration of transition metals, resulting in a dendritic-free Li anode and enhanced battery safety in general [22]. Furthermore, MOF-derived mesoporous Mn_3O_4/C microsphere with Mn-PBA MOF was prepared by the construction of 5-(4-pyridin-3-yl-benzoylamino)-isophthalic acid. This material shows a high capacity of 1032 $mAh \cdot g^{-1}$ over 500 cycles [23], more highlighting excellent electrochemical performance and stability of derivative materials.

4. Conclusion

MOFs have shown extraordinary potential in revolutionizing LMBs for EVs, addressing key challenges such as lithium dendrite growth, polysulfide shuttle, and interface instability. Their unique

structural and functional characteristics, including uniform pore adjustability, abundant redox active metal sites, chemical stability, and multifunctionality, can precisely regulate ion transport, enhance lithium storage capacity, and improve electrode electrolyte interactions.

Despite these advances, there are still challenges in expanding the comprehensive scale of MOFs and reducing costs. The current reliance on expensive metals such as Zr and energy intensive solvothermal methods limits commercialization. Strategies such as using low-cost metals (Fe, Cu), simplifying synthesis (e.g., one pot method), and utilizing the multifunctional effects of MOFs (membranes, electrodes, additives) can reduce costs. Meanwhile, the multifunctionality of MOFs, such as serving as separators, electrodes, and electrolyte additives simultaneously, can reduce the demand for material types and indirectly lower system costs. If scale production is achieved, the cost of MOFs is expected to compete with traditional materials such as graphite and polymer membranes.

Future research needs to focus on improving the conductivity, mechanical strength, and compatibility with industrial processes of MOFs. In addition, exploring the universality of MOFs in other metal batteries such as sodium and zinc will further share research and development costs and promote their widespread application. Although challenges still exist, the structural tunability and multifunctionality of MOFs provide unique opportunities for their innovation in lithium-based batteries. MOFs are expected to drive the development of high-energy, safe, and cost-effective lithium-based batteries, accelerating the global transition to sustainable electric vehicle technology.

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