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Mini Review of High-Performance Supercapacitors Derived Metal-Organic Frameworks: Current Challenges and Potentials

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Abstract: The persistent rise in fossil fuel consumption has heightened the greenhouse effect, posing a substantial threat to both human well-being and the environment. To counteract the global energy shortage and pollution crisis, there is an imperative to develop renewable and clean energy sources. Technological advancements in net-zero energy conversion and climate-neutral storage systems are gaining prominence. In recent decades, there has been a noteworthy surge in interest and significant efforts directed towards advancing new technologies, particularly in the realm of enhancing the efficiency of energy storage devices like batteries and capacitors. However, inherent drawbacks in batteries, such as low power density and limited charge/discharge cycles, and the low energy density of traditional capacitors, have restricted their utilization in high-technology applications. This limitation has spurred the emergence of the high-performance supercapacitor concept. Researchers in both industry and academia are keen on exploring energy conversion and storage systems characterized by exceptional stability and efficiency, presenting a substantial challenge in their construction and design. This mini review specifically delves into recent progress in supercapacitor applications derived from Metal-Organic Frameworks (MOFs), addressing both current challenges and its future potential.

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1. Introduction

Metal-organic frameworks (MOFs) have emerged as promising materials for supercapacitor applications due to their exceptional tunability and favorable porous properties. MOFs, characterized by metal centers interconnected by organic ligands, offer a unique advantage in their high-tunability. This tunability arises from the ease with which the electronic properties of MOFs can be adjusted by modifying the metal centers, organic ligands, or guest species within the pores [1]. MOFs offering a unique combination of crystalline structures and porous architectures for supercapacitor applications. However, the widespread adoption of MOFs in supercapacitors is impeded by a series of challenges that span the material's properties and applications [2].

The foremost challenge revolves around the low electrical conductivity inherent in MOFs, a characteristic that significantly hampers their effectiveness in supercapacitors. MOFs, typically comprised of metal ions or clusters intricately coordinated with organic ligands, exhibit a crystalline and porous framework. However, the insulating or semiconducting nature of these organic ligands introduces a limitation, as the overall electrical conductivity of MOFs remains inherently low. This limitation becomes particularly affect the performance of supercapacitors, where efficient electron transport is paramount for facilitating rapid charge and discharge cycles. Consequently, the movement of electrons within MOFs is impeded, adversely affecting the overall performance of the supercapacitor in terms of power density and charge/discharge rates [2]–[4].

Additionally, MOFs demonstrate a sensitivity to the electrolyte components commonly used in supercapacitors, which constitutes another layer of complexity. The introduction of organic electrolytes or ionic liquids can induce chemical transformations or structural changes in certain MOFs, leading to a compromise in structural stability over time. Furthermore, the concept of narrow electrochemical windows adds another dimension to the challenges. MOFs exhibit a limited range of stable operating voltages in electrochemical devices like supercapacitors, constraining their electrochemical performance compared to alternative materials used in energy storage devices [2], [5].

The significant approaches to optimize MOF properties for supercapacitor applications are needed. Tailoring the MOF structure and composition emerges as a critical strategy, with a focus on minimizing resistance at the interfaces between the MOF electrode and the electrolyte. Surface modifications and the incorporation of conductive coatings present avenues to enhance compatibility, thereby improving charge/discharge kinetics. The intricate synthesis procedures inherent in MOF production pose challenges to achieving large-scale and consistent manufacturing for supercapacitor applications. Elevated production costs, stemming from expensive starting materials, energy-intensive synthesis processes, and specialized equipment, create a significant barrier to the cost-effective integration of MOFs into commercial supercapacitors [6], [7].

This mini review will navigate through current challenges, shedding light on the intricacies that must be addressed for MOFs to unlock their full potential as materials for supercapacitors on a global scale in the pursuit of efficient and scalable energy-storage solutions.

2. Challenges in MOF-Derived Supercapacitors

Metal-organic frameworks (MOFs) show promising as supercapacitor materials. However, MOFs have some drawbacks that can affects its performances. The challenges are including lower low electrical conductivity, limited stability in electrolytes, narrow electrochemical windows, optimization of MOF properties and scalability and production costs as depicted in Fig. 1.

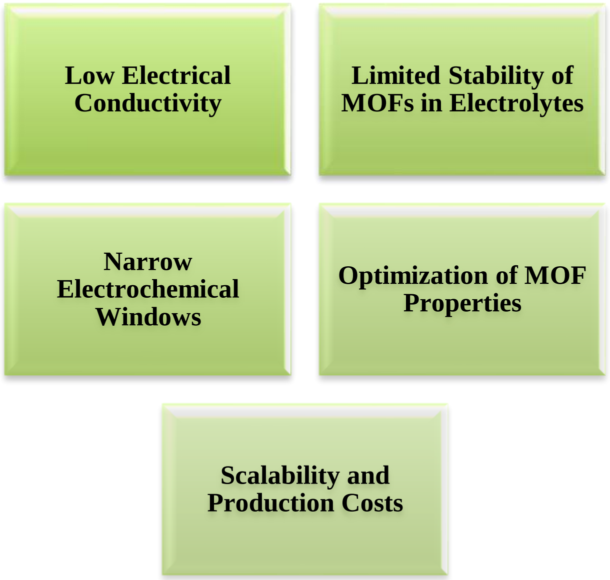

Fig. 1 - Challenges in MOF-Derived Supercapacitors

2.1 Low Electrical Conductivity

The low electrical conductivity of metal-organic frameworks (MOFs) is a significant challenge when considering their application in supercapacitors. This issue can limit their effectiveness in supercapacitors where efficient electron transport is crucial. MOFs are often composed of metal ions or clusters coordinated to organic ligands, resulting in a crystalline and porous structure. However, the organic ligands, which contribute to the framework, are typically insulating or semiconducting in nature. As a result, the overall electrical conductivity of MOFs is inherently low. In supercapacitors, efficient electron transport is crucial for rapid charge and discharge cycles. The low electrical conductivity of MOFs can impede the movement of electrons within the material. This limitation affects the overall performance of the supercapacitor, particularly in terms of power density and charge/discharge rates [2], [8].

Supercapacitors rely on rapid charge transfer between the electrode material and the electrolyte. The low electrical conductivity of MOFs can create barriers to effective charge transfer processes, leading to slower kinetics and reduced overall efficiency. Researchers are actively exploring strategies to enhance the electrical conductivity of MOFs. One approach involves incorporating conductive additives or incorporating highly conductive components into the MOF structure. For example, the addition of conductive polymers or carbon-based materials can help improve the overall conductivity of the MOF. Creating hybrid materials or composites by combining MOFs with other conductive materials is a common strategy to address the conductivity issue. This can involve incorporating carbon nanotubes, graphene, or conducting polymers into the MOF structure to enhance electron transport pathways [3], [9], [10].

Achieving a balance between maintaining the unique properties of MOFs and improving their electrical conductivity is a challenge. Modifying MOF structures to enhance conductivity can sometimes result in alterations to other desirable properties, such as porosity or specific surface area. The electrical conductivity of the electrode material significantly influences the overall performance of supercapacitors. In MOF-based supercapacitors, efforts to improve conductivity aim to maximize the utilization of the MOF's capacitance while ensuring efficient charge transport. Therefore, improving conductivity is crucial for optimizing charge transfer processes and realizing the full potential of MOFs in energy storage devices [9], [11].

2.2 Limited Stability of MOFs in Electrolytes

The limited stability of MOFs in electrolytes can result in a reduced life cycle for supercapacitors. Structural changes or chemical reactions occurring at the interface between the MOF electrode and the electrolyte can contribute to the gradual degradation of the MOF material. In some cases, the exposure of MOFs to certain electrolyte conditions can lead to the leaching of metal ions from the MOF structure. This can result in a loss of active material and diminish the overall capacitance of the supercapacitor [8].

MOFs can be sensitive to the components of the electrolyte used in supercapacitors. Commonly, organic electrolytes or ionic liquids are employed, and some MOFs may undergo chemical transformations or structural changes in the presence of certain ions or solvents. MOFs are crystalline materials with well-defined structures. The introduction of certain electrolyte components, such as ions or solvents, can lead to structural degradation of the MOF. This degradation can compromise the overall stability and performance of the supercapacitor over time [10].

The interaction between the solvent and ions present in the electrolyte and the MOF structure can be complex. Some solvents or ions may interact unfavorably with the organic ligands or metal nodes in the MOF, leading to changes in the MOF's chemical composition or morphology [2]. Researchers are actively working on strategies to enhance the stability of MOFs in electrolytes. This includes the design of MOFs with improved chemical stability, the development of protective coatings or encapsulation techniques, and the exploration of alternative electrolyte formulations that are less detrimental to MOF structures. Aqueous electrolytes are often considered more environmentally friendly than organic electrolytes. However, MOFs may face challenges in terms of stability in aqueous environments. Research is ongoing to identify MOFs that are compatible with aqueous electrolytes or to develop strategies to mitigate stability issues in water-based systems [9].

2.3 Headings Narrow Electrochemical Windows

The concept of narrow electrochemical windows in the context of metal-organic frameworks (MOFs) refers to the limited range of voltages over which these materials can operate stably in electrochemical devices like supercapacitors. The electrochemical window refers to the range of voltages within which a material can undergo reversible redox reactions without suffering from irreversible chemical changes or structural degradation. In the case of MOFs, the electrochemical window is often limited compared to some other materials used in energy storage devices [1].

Researchers are exploring various strategies to widen the electrochemical window of MOFs. This includes modifying the MOF structure to enhance its stability, designing new ligands with improved redox properties, and investigating alternative electrolyte systems that can better accommodate the electrochemical characteristics of MOFs. The narrow electrochemical window influences the overall performance of MOF-based supercapacitors, including their power density, energy density, and cycle life. Efforts to widen this window are aimed at improving the competitiveness of MOFs in comparison to other materials used in supercapacitors [1], [2].

The electrochemical stability of MOFs is highly dependent on their composition, including the metal ions and organic ligands used. Some combinations may exhibit a wider electrochemical window than others, and the challenge lies in finding optimal combinations that balance stability and electrochemical performance. The narrow electrochemical window affects the charge storage capacity of MOF-based supercapacitors. A limited voltage range constrains the amount of charge that can be stored in the device, impacting both specific capacitance and overall energy storage capacity [7].

MOFs, due to their specific composition and structure, may have a narrow operating voltage range in electrochemical devices. This limitation impacts the potential window within which the supercapacitor can efficiently and reversibly store and release energy. The electrochemical window directly affects the energy density of a supercapacitor. The energy stored in a capacitor is proportional to the square of the operating voltage. Therefore, a narrow electrochemical window limits the energy density of the supercapacitor compared to materials that can operate over a wider voltage range [4], [12].

2.4 **Optimization of MOF Properties**

The optimization of metal-organic framework (MOF) properties for supercapacitor applications involves tailoring the MOF structure and composition to enhance its electrochemical performance. Optimization efforts focus on minimizing the resistance at the interfaces between the MOF electrode and the electrolyte. Surface modifications or the introduction of conductive coatings can help enhance the compatibility between the MOF and the electrolyte, improving charge/discharge kinetics [2], [9].

Considering the limitations related to MOF stability in certain electrolytes, optimization involves designing MOFs that are more robust in the presence of commonly used electrolytes. This may include exploring alternative electrolyte formulations or developing protective coatings to mitigate degradation. The choice of metal ions and organic ligands in MOF synthesis plays a crucial role in determining its electrochemical properties. Researchers work on selecting metal nodes and ligands with favorable redox characteristics and stability, considering the specific requirements of supercapacitor operation [3].

Combining MOFs with other materials, such as conductive polymers or carbonaceous materials, can create hybrid structures that leverage the strengths of each component. This approach aims to enhance the overall electrochemical performance and stability of MOFs in supercapacitor applications. Aqueous electrolytes are preferred for environmental reasons, and optimizing MOF properties for compatibility with water-based electrolytes is a focus of research. This includes selecting MOF components that are stable in aqueous environments and exploring strategies to enhance water stability [8].

Supercapacitor performance is influenced by the specific surface area and porosity of the electrode material. Optimizing MOF properties involves tuning the pore size and maximizing the surface area to enhance the accessibility of electrolyte ions to the MOF surface, thereby improving charge storage capacity. Researchers explore novel MOF architectures, such as hierarchical structures or MOF-derived materials, to improve electrochemical performance. These architectures can provide additional active sites, shorten diffusion paths, and enhance the overall charge storage capabilities of MOFs [9].

2.5 **Scalability and Production Costs**

Please The complex and intricate synthesis procedures involved in metal-organic framework (MOF) production pose a challenge to scalability, hindering the ability to achieve large-scale and consistent manufacturing for supercapacitor applications. Elevated production costs for MOFs, attributed to the use of expensive starting materials, energy-intensive synthesis processes, and specialized equipment, present a significant barrier to their cost-effective integration into supercapacitors on a commercial scale [11].

MOFs face strong competition with conventional materials, such as activated carbons, which have well-established, cost-effective production processes. The ability of MOFs to compete in terms of production costs is crucial for their practical adoption in supercapacitor technology. The overarching challenge lies in developing strategies to overcome these scalability and production cost hurdles, ensuring that MOFs can be manufactured at a scale and cost that enables their widespread use in supercapacitors, contributing to advancements in energy storage technology [12].

Difficulty in achieving economies of scale in MOF production arises from the intricate nature of the synthesis process and the need for specialized conditions, limiting the cost advantages typically associated with larger production volumes and impeding widespread adoption in supercapacitor technology. The limited availability and high cost of certain MOF precursors, including specific metal ions and organic ligands, contribute to the overall production cost challenge, making it imperative to explore alternative, more cost-effective sources [13].

Energy-intensive synthesis methods required for some MOFs increase the environmental footprint and contribute to higher production costs, raising concerns about sustainability and diminishing the appeal of MOFs for large-scale supercapacitor applications. Post-synthesis processing steps, such as activation or purification, introduce additional complexity and cost to the production process, posing challenges in maintaining efficiency and cost-effectiveness when scaling up MOF production for supercapacitors [11], [14]. Other challenges and recommendations in addressing issues related to MOF materials-based electrodes are listed in the Table 1.

Table 1. Other challenges and recommendations in MOF materials-based electrodes

Challenges	Author/s	Recommendations
Limited mass loading and uniform distribution in electrodes	[15]	Explore MOF-based nanostructures derived from a single precursor; optimize mass balancing; improve electrode assembly
Mismatched electrochemical performance in supercapacitors	[16]	Investigate appropriate mass balancing and electrode matching; explore MOF-based nanostructures from a single precursor
Limited options for binder-free electrodes	[17]	Focus on developing more self-supported MOFs for binder-free electrodes; enhance MOF crystal design and assembly techniques
Lack of conductivity, processability, and catalytic activity in harsh conditions	[18]	Explore new strategies and techniques for optimizing MOF conductivity without compromising intrinsic properties

3. Potential in MOF-Derived Supercapacitors

Metal-organic frameworks (MOFs) have garnered significant attention in energy storage, particularly in supercapacitors, owing to their distinctive structural characteristics. MOFs are renowned for their exceptional surface area and porosity, attributes arising from the precisely organized crystalline structures they exhibit. This intricate arrangement results from the coordination of metal nodes with organic linkers during self-assembly, forming a highly ordered framework [7].

The high surface area of MOFs surpasses conventional materials, offering an expansive interface for electrochemical interactions. This notable feature stems from the porous nature intrinsic to MOF structures. The pores, with tunable sizes and structures, provide a versatile platform for accommodating ions during electrochemical processes [1]. Within the MOF structure, the metal nodes and organic linkers create a myriad of active sites distributed across the surface and within the pores. These active sites serve as loci for electrochemical reactions, particularly the adsorption and desorption of ions during charge and discharge cycles. The abundance of active sites plays a pivotal role in facilitating efficient charge storage, contributing to the high capacitance observed in MOF-based supercapacitors [19].

Moreover, the porous architecture of MOFs enhances ion accessibility to the active sites, ensuring effective utilization of the entire surface area. This heightened accessibility reduces diffusion limitations, leading to improved kinetics of electrochemical reactions. MOFs, exhibiting capacitive behavior, capitalize on the electrostatic adsorption of ions at the surface and within the pores, further bolstering their suitability for applications demanding rapid energy storage and release, characteristic of supercapacitors. The versatility of MOFs extends to their tunability for specific applications. By selecting appropriate metal-ligand combinations and optimizing synthesis conditions, researchers can tailor MOF structures to meet the requirements of supercapacitor applications. This tailoring ensures maximum performance in diverse electrochemical environments [8], [19].

The ability to tailor the pore size of MOFs is a consequence of the modular nature of their synthesis. By judiciously choosing the metal nodes and organic ligands, researchers can finely adjust the dimensions of the pores within the MOF structure. This tunability holds significant implications for optimizing ion transport dynamics, addressing diffusion limitations, and ultimately elevating the overall electrochemical performance of supercapacitors. When the pore sizes are strategically tailored, the transport of ions within the MOF structure becomes more efficient. Optimized pore dimensions enable a more facile movement of ions to and from the active sites, reducing the likelihood of diffusion-related bottlenecks. This improvement in ion transport kinetics has a profound impact on the charging and discharging processes of the supercapacitor, leading to enhanced charge storage and faster response times [20].

Previous studies [21] has suggested that minimization of diffusion limitations is particularly crucial in supercapacitors, where rapid charge and discharge cycles are essential. Tunable pore sizes in MOFs allow for the creation of an environment where ions can readily access the active sites, promoting a more effective utilization of the available surface area. This not only contributes to increased capacitance but also ensures that the supercapacitor can efficiently handle the high-frequency cycling characteristic of these energy storage devices. the optimization of ion transport through tunable pores in MOFs aligns with the broader goal of advancing the electrochemical performance of supercapacitors. By tailoring the pore size to suit specific applications or electrolytes, researchers can design MOFs that outperform traditional materials in terms of energy density, power density, and cycle life as illustrated in Fig. 2.

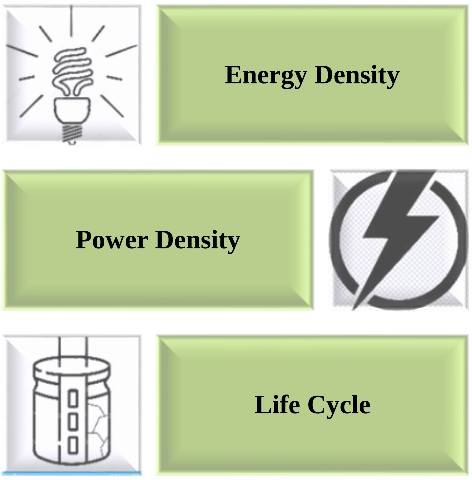

Fig. 2 - MOFs-derived supercapacitors outperform traditional materials in some properties

The versatility of metal-organic frameworks (MOFs) extends beyond their structural adaptability, encompassing a key environmental dimension. MOFs can be purposefully designed using sustainable and abundant metal and organic precursor materials. This strategic selection aligns with the burgeoning demand for green energy storage solutions, positioning MOF-based supercapacitors as highly attractive for applications where environmental sustainability is paramount. By utilizing readily available and eco-friendly metal sources alongside organic ligands derived from renewable feedstocks, MOFs embrace an inherently sustainable approach to material design. This commitment to environmental responsibility not only reduces dependence on scarce resources but also contributes to minimizing the overall environmental footprint associated with the synthesis of advanced energy storage materials. As the global focus intensifies on transitioning towards green technologies, MOF-based supercapacitors emerge as promising candidates that not only fulfill energy storage requirements but also resonate with the principles of sustainability, making them particularly appealing for applications where a commitment to environmentally conscious practices is a priority [22]–[24].

4. Future Perspectives

Metal-organic frameworks (MOFs) have emerged as frontrunners in the pursuit of innovative supercapacitor technologies, heralding exciting future perspectives that could revolutionize energy storage. As our collective focus shifts towards sustainable and high-performance solutions, MOFs offer a versatile platform with tunable properties, unlocking a myriad of possibilities for the future of supercapacitors. One key aspect of the future perspective lies in the tunability of MOFs. The ability to engineer their structures at a molecular level allows researchers to tailor properties such as porosity, surface area, and electrical conductivity. This inherent versatility positions MOFs as candidates for addressing current limitations in supercapacitors, enabling the design of materials optimized for enhanced energy storage, faster charge/discharge rates, and prolonged life cycle [19], [20].

The sustainability factor further elevates the appeal of MOFs in the context of future energy storage. MOFs can be crafted from sustainable and abundant precursor materials, aligning seamlessly with global initiatives for eco-friendly technologies. The environmental consciousness inherent in MOF-based supercapacitors not only addresses the pressing need for green energy solutions but also anticipates a future where energy storage technologies actively contribute to a more sustainable and resilient energy infrastructure. The integration of MOFs with emerging technologies and materials holds immense promise. Collaborations with conductive polymers, nanomaterials, or hybrid structures could yield synergistic effects, enhancing the overall performance of supercapacitors. This collaborative approach anticipates a future where MOFs serve as versatile building blocks in the development of advanced energy storage systems that surpass current benchmarks [22].

Moreover, the environmental sustainability embedded in MOFs, derived from abundant and eco-friendly precursors, positions them as catalysts for the green energy transition. The roadmap underscores the significance of this sustainability aspect, emphasizing that the future of energy storage must align with global efforts for a cleaner and greener future. MOF-based supercapacitors thus become not only technological marvels but also stewards of environmental responsibility. In near future, the direction extends into the uncharted territory of innovative synthesis techniques and the exploration of hybrid materials. By forging collaborations between MOFs and other conductive materials, researchers anticipate unlocking synergistic effects that enhance conductivity and stability. This roadmap charts a course towards materials that seamlessly integrate the strengths of MOFs with complementary materials, presenting a vision of hybrid supercapacitors that surpass current benchmarks [25, 26] [9], [25].

5. Conclusion

In conclusion, the future perspectives of MOF-based supercapacitors are characterized by their adaptability, sustainability, and collaborative potential. As research advances, the promise lies in harnessing the unique properties of MOFs to overcome existing challenges and to create energy storage solutions that align with the evolving landscape of sustainable and high-performance technologies. MOFs, with their molecular precision and environmental compatibility, are poised to play a pivotal role in shaping the future of supercapacitors. The journey ahead involves overcoming current limitations, harnessing the tunable properties of MOFs, and fostering collaborations to create hybrid materials. MOFs are poised to shape the future of supercapacitors, leading the way towards efficient, sustainable, and high-performance energy storage solutions.

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