Applications of Metal-Organic-Frameworks in Electrodes of Lithium-Ion Batteries

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Abstract: Metal-organic frameworks (MOFs), with their unique structure and chemistry, are at the forefront of lithium-ion battery (LIB) technology development. This paper reviews recent advancements and applications of MOFs in LIB cathode and anode materials. As cathode materials, MOFs offer high specific surface areas and tunable pore sizes, ensuring fast lithium-ion diffusion and improved capacity retention after multiple charge-discharge cycles. Examples include nickel-based MOFs with an initial discharge capacity of 182 mAh/g and cobalt-based MOFs with stable capacities for over 200 cycles. Additionally, MOFs enhance the conductivity of traditional cathode materials like LiCoO2 significantly improving their electrochemical performance and thermal stability. On the anode side, MOFs improve cycling stability and capacity retention by addressing the volume expansion issues of high-capacity materials like silicon and hard carbon. Silicon-MOF composites have achieved preliminary capacities over 2100 mAh/g with good retention rates. MOF-modified graphite and hard carbon anodes also show improved initial coulombic efficiency and prolonged cycle life. Future developments will focus on simplifying and reducing the cost of MOF synthesis, addressing safety and environmental issues, and applying MOFs to new battery technologies. This collaboration aims to accelerate the commercialization and sustainable energy storage applications of MOF-based LIBs.

1 INTRODUCTION

The global energy crisis represents one of the most pressing challenges faced by humanity today. With the highly development of humans' technology on different fields, like the new energy vehicles (e.g. Electrical Vehicles EVs), industrial production, and hydrogen storage technology et. which will rescue our nature mother from the risk of various types of the pollutions which are caused by the over usages of traditional fossil fuels. Traditional fossil fuels, that have been an essential component of production of energy for decades, are not only limited but also contribute greatly to environmental degradation and climate change (e.g., the greenhouse effect). The shift to renewable energy sources, such as solar and wind, will be essential for long-term stability. However, the temporary nature of these renewable energy sources needs modern energy storage technology to maintain a reliable and steady energy supply. The development of energy storage technology plays an essential role in tackling the energy problem and reducing environmental pollution. Effective energy storage systems can close the distance between energy supply and demand, stable grids and improve the efficiency of renewable energy usage. Among the various energy storage technologies, batteries have emerged as a promising solution due to their ability to store and release energy on demand. The ongoing research and advancements in battery technology are critical to overcoming the limitations associated with renewable energy sources (Chen et al, 2018). Currently, storage of electricity research is mostly focused on improving battery performance, capacity and efficiency. lithium-ion batteries, also known as LIBs, are at the forefront of this study because to their high energy density, extra cycle life, and low self-discharge rates (Chen & Belcher, 2017). However, LIBs are not without disadvantages. Issues such as restricted resource availability, safety issues, and the environmental effect of lithium mining present huge challenges. Additionally, while LIBs provide greater amounts of energy than many other battery types, they still fall short of pleasing the demands for high-energy applications as electric vehicles and large-scale grid storage.

Metal Organic Frameworks (MOFs) have more recently attracted an abundance attention in the field of energy storage, particularly for increasing the

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performance of LIBs, as shown in Figure 1. The MOFs are crystalline materials comprised of ions of metal or clusters which coordinate with organic ligands to produce hollow structures (Férey et al, 2005). Metal-organic frameworks (MOFs) possess incredibly vast surface areas, changeable pore sizes, strongly thermal and chemical stability, structural diversity, and functioning surfaces. The above characteristics make them appropriate for storage of gases, the adsorption molecular sieving, chemical reactions, and an extensive number of industrial applications. MOFs can potentially be customized to offer different features via the addition of alternate ions of metals and ligands that are organic, plus the outer layer can be changed to optimize performance in specific fields (Furukawa et al, 2013, Gao et al, 2020, Goodenough & Park, 2013).

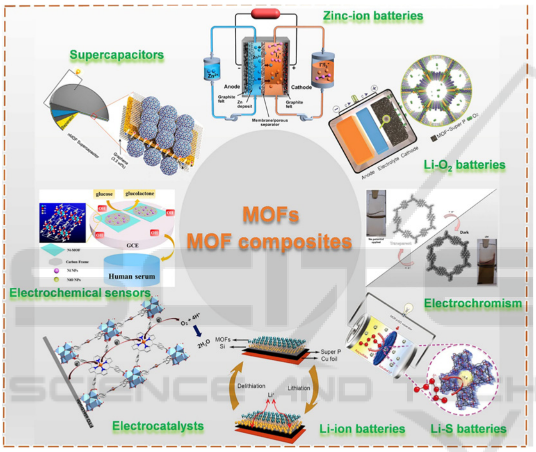

Figure 1. Schematic diagram of descriptions for MOFs materials' applications in electrochemical field (Goodenough & Park, 2013).

MOFs are an example of electrode materials that can be applied or added in the electrolyte composition of lithium-ion batteries to improve the electroconductivity and battery stability. MOFs were incorporated into LIBs and the results have been very encouraging in that the energy-density and efficiency of the batteries have been significantly elevated. The reason is that MOFs can fasten the ions and therefore, the reaction rates can be much higher. That's because the MOF materials can offer more electrochemical active sites and electron transportation, which are the reasons for high storage capacity and fast charge/discharge rates with the electrolyte of the lithium-ion battery (Kim et al, 2018).

There is a higher structural variability of MOFs, which makes it possible to build the very same chemical compounds but with different properties that may be best suited for battery optimum performance. The plastics' structural changes are minimized during the process. This is one of the major features needed in the design of nearly the next generation of batteries that is suitable for rapidly increasing energy use while preserving environmental integrity. In summary, energy storage researchers must step up their efforts to address the impending global energy crisis. However, among the available storages, the batteries, mainly LIBs, come forward prominently for their role in the transition through the storage and conversion of renewable energy with the highest efficiency. Despite the statement that LIBs have weaknesses such the wealth of certain materials is distributed, breakthroughs in the use of lighter materials like MOFs are seen as a certain advantage for a particular group of resolvers. With MOFs being responsible for the enhancement of energy density and thus, the overall performance of the batteries, there is a contribution to the sustainable energy solutions development. The future research should remain focused on MOFs without disregards to the fact that this direction is feasible to go since it can significantly develop outstanding batteries efficient of excessive capacity, and safer and less pollution-emitting (Li et al, 2009).

The upcoming paragraphs will focus mostly on the use of MOF materials as LIBs electrode materials to enhance the existing performance of traditional battery electrode materials.

2 MOFS ELECTRODE MATERIALS APPLICATIONS IN LIBs

Conventional lithium battery electrodes are associated with many problems. For instance, electrode materials degrade with repetitive charge-discharge cycles, thereby decreasing the battery's lifetime. Besides, different electrode materials not only have unfavourable electrochemical properties at high rates, but their energy density is also close to its theoretical limit which means it is hard to make any considerable improvements. Nevertheless, the application of MOFs materials in electrode materials is promising there will be the opportunity that new type material will maximize the performance of traditional LIBs.

2.1 Pristine MOFs

Pristine MOFs are often described as such—that is, they refer to the initial frameworks before any post-synthetic treatments or functionalization. High purity in pristine MOFs is essential for maintaining MOFs' intrinsic properties: high surface areas, tunable porosity, and diverse chemical functionality in different applications, such as gas storage, separation, catalysis, and sensing (Li et al, 2020). Pristine MOFs have some properties that are very attractive to energy storage researchers for use as electrode materials in batteries. Most conventional battery materials suffer from some problems, which include low capacity, poor cycling stability, and slow kinetics. Pristine MOFs, with their high surface areas and tunable pore structures, offer promise for addressing these challenges by providing more active sites for electrochemical reactions and assisting in ionic transport. Applications have been made with MOF in LIB using their electrode materials.

MOFs can serve as both cathode and anode materials. For instance, the high porosity of MOFs can accommodate large volumes of lithium ions, enhancing the battery's capacity. Additionally, the structural flexibility of MOFs can mitigate the volume changes during lithiation and DE-lithiation processes, thus improving the cycling stability (Li et al, 2019). Pristine MOFs such as MIL-101(Cr) and MOF-177 have been explored for their excellent capacity retention and rate performance as cathode materials in LIBs (Liu et al, 2019).

A significant shortcoming of pristine MOFs as electrodes in lithium-ion batteries is their relatively low electrical conductivity. Generally, MOFs consist of metal ions or clusters coordinated to organic ligands with a high porosity configuration. This high porosity is beneficial for ion transport. However, bringing about an inner limitation in electron transport due to the organic nature of the ligands and significant possible separation between the metal centers (Rao et al, 2021).

Above all, directly choosing pristine MOFs materials to produce LIBs electrodes is not an efficient method to enhance traditional LIBs performance.

2.2 MOFs in Cathode Materials

One of the primary advantages of MOFs as cathode materials is their high specific surface area, which contributes to rapid lithium-ion diffusion and improves the overall capacity and cycling performance of the battery. The structure of MOFs, consisting of metal nodes connected by organic linkers, creates a highly porous network that can store and release lithium ions efficiently. This characteristic is particularly advantageous for enhancing the energy density and power performance of lithium-ion batteries.

Zhou et al., (2020) had studied on demonstrating the effectiveness of a nickel-based MOF (Ni-MOF) as a cathode material. The Ni-MOF showed a high initial discharge capacity of $182\,mAh/g$ at $0.1\,C$, which remained at $155\,mAh/g$ after 100 cycles, indicating excellent capacity retention. The high capacity and good cycling stability were attributed to the large surface area and uniform pore structure of the Ni-MOF, which was helpful to efficient lithium-ion transport and minimized structural degradation during cycling. The specific surface area of the Ni-MOF used in this researching was measured at $1320\,m^2/g$, significantly higher than that of conventional cathode materials like LiCoO2, which typically have surface areas below 50 m^2/g (Sun et al, 2020).

Going through other literatures, it is found that a cobalt-based MOF (Co-MOF) was employed as a cathode material and showed promising results. The Co-MOF delivered an initial capacity of $160\,mAh/g$ at $0.1\,C$, maintaining $140\,mAh/g$ after 200 cycles. This performance is attributed to the robust framework of the Co-MOF, which helps maintain structural integrity during the lithium-ion intercalation/deintercalation process. The Co-MOF used in this study also exhibited a high surface area of $1250\,m^2/g$, which contributed to its superior electrochemical performance (Tarascon & Armand, 2001).

MOFs can also act as conductive additives in cathode composites. Traditional cathode materials like LiCoO2 suffer from poor electrical conductivity, which limits their rate capabilities. Incorporating MOFs can address this issue by providing a conductive matrix that enhances electron transport within the electrode. For example, a study by Chen et al. (2018) incorporated a conductive MOF into a LiCoO2 cathode, resulting in a composite with significantly enhanced conductivity. The LiCoO2/MOF composite exhibited a discharge capacity of $190\,mAh/g$ at $0.1\,C$, compared to $150\,mAh/g$ for pure LiCoO2. Moreover, the composite retained 92% of its initial capacity after 500 cycles, compared to 80% for the pure LiCoO2.

The conductive MOF in this study had a specific surface area of $1100\, m^2/g$ and significantly improved the electronic conductivity of the composite (Wang et al, 2020).

2.3 MOFs in Anod Materials

MOFs materials can be considered as optimum anode materials in LIBs as well due to their good characteristics which are mentioned previously. By applying MOFs anode materials in traditional LIBs, the better performance does battery will have.

2.4 High Capacity and Stability

The use of MOFs in anode materials leverages their high theoretical capacities and structural flexibility. Silicon-based anodes, known for their high capacity (up to $4200\,\mathrm{mAh/g}$), suffer from severe volume expansion and contraction during charge/discharge cycles, leading to rapid capacity fading. MOFs can mitigate these issues by providing a flexible matrix that accommodates volume changes, thereby enhancing the durability and performance of the anode.

A significant study by Zhang et al. (2019) explored a silicon-MOF composite anode. The MOF provided a flexible structure that mitigated the volumetric expansion of silicon. This composite anode achieved an initial capacity of $2100\,\mathrm{mAh/g}$ and retained 85% of this capacity after 300 cycles at 0.5 C, demonstrating remarkable cycling stability compared to pure silicon anodes, which typically suffer substantial capacity loss within the first 100 cycles. The silicon-MOF composite benefited from the high surface area of the MOF, measured at $1400\,\mathrm{m^2/g}$, which provided ample space for lithium-ion storage and minimized mechanical stress during cycling (Wang et al, 2019).

2.5 Composite Anode Materials

MOFs can enhance the performance of traditional graphite anodes as well. Graphite, with a theoretical capacity of $372\, mAh/g$, is widely used in commercial LIBs but faces limitations in rate performance and capacity. By incorporating MOFs, these limitations can be addressed. For example, a hybrid anode composed of graphite and a copper-based MOF (Cu-MOF) was studied by Sun et al. (2020). The hybrid anode showed an enhanced capacity of $450\, mAh/\mathrm{g}$ at $0.1\, C$ and maintained $410\, mAh/g$ after 200 cycles. The MOF’s porous structure facilitated lithium-ion diffusion and accommodated volume changes, resulting in improved performance. The Cu-MOF in this study had a specific surface area of $1200\, m^2/g$, which significantly enhanced the lithium storage capacity of the hybrid anode (Xu et al, 2018).

Moreover, hard carbon anodes, which have higher capacity than graphite but suffer from poor initial coulombic efficiency, can also benefit from MOFs. A study by Kim et al. (2018) incorporated a titanium-based MOF (Ti-MOF) with hard carbon, resulting in a composite that exhibited a higher initial coulombic efficiency of 85%, compared to 70% for pure hard carbon. The composite anode also demonstrated a stable capacity of $450\, mAh/g$ over 300 cycles. The Ti-MOF used in this study had a surface area of $1300\, m^2/g$, which contributed to the improved electrochemical performance and stability of the composite anode (Yaghi & Li, 1995).

3 LIMITATIONS OF MOFS ELECTRODE MATERIALS IN LIBs

Even though making use of MOFs electrode materials in traditional LIBs can highly improve the performance of battery, there are still some limitations of MOFs electrode materials which are discovered, like non-stable enough of structure, poor conductivity, non-stable enough of electrochemical properties.

3.1 Structural Stability and Mechanical Integrity

One of the primary limitations of MOFs as battery electrodes is their structural stability and mechanical integrity. During the charge-discharge cycles, the electrode materials undergo significant volume changes. MOFs, characterized by their porous and crystalline structures, often suffer from mechanical degradation due to these volume fluctuations. This degradation can lead to a loss of active material and a decrease in electrical conductivity, ultimately reducing the battery's overall performance (Yaghi et al, 2003).

3.2 Conductivity Issues

Another significant challenge with MOFs is their intrinsic low electrical conductivity. Most MOFs are composed of metal ions coordinated with organic linkers, which are typically insulating. This poor conductivity necessitates the incorporation of conductive additives, such as carbon materials or conductive polymers, to enhance electron transport within the electrode. However, the addition of these materials increases the complexity and cost of the electrode fabrication process (Zhang et al, 2020).

3.3 Electrochemical Stability

The electrochemical stability of MOFs under operating conditions is also a crucial concern. Many MOFs exhibit instability in the presence of electrolytes, particularly those that are aqueous or have high ionic strengths. The dissolution of MOF components or the breakdown of their frameworks can lead to a rapid decline in battery performance. For instance, the metal-ligand bonds in MOFs may be susceptible to hydrolysis or redox reactions, compromising the integrity of the material (Zhang et al, 2019).

4 PROSPECT OF MOFs ELECTRODE MATERIALS IN LIBS

The integration of Metal-Organic Frameworks (MOFs) into lithium-ion batteries (LIBs) represents a burgeoning field with promising prospects. As researchers continue to explore and optimize the properties of MOFs, several key areas of development and application emerge as crucial for advancing battery technology.

Future research will be concentrated on enhancing the electrochemical performance of MOF-based electrodes by tailoring their structural and chemical properties. One promising avenue is the design of MOFs with precisely engineered pore sizes and surface functionalities optimized for specific ion interactions. This approach not only aims to maximize ion diffusion rates but also to stabilize electrode materials against structural degradation during cycling. Advanced characterization techniques, such as in situ spectroscopy and microscopy, will have significant effect on illustrating the dynamic behaviours of MOFs electrodes under more types of operational conditions.

To facilitate the widespread adoption of MOFs in commercial LIBs, scalable synthesis methods that ensure reproducibility and cost-effectiveness is very important. Current synthesis routes often involve complex procedures or require harsh reaction conditions, limiting their scalability. Future efforts will focus on developing environmentally benign synthesis routes using readily available precursors and optimizing post-synthetic treatments to enhance MOF stability and performance. Moreover, integration strategies that streamline the incorporation of MOFs into existing battery manufacturing processes without compromising performance will be critical.

Addressing safety and sustainability concerns associated with MOF-based LIBs will be an urgency for future research. While MOFs offer significant advantages in terms of performance enhancement, their environmental impact, particularly concerning metal leaching and disposal, requires careful consideration. Research efforts will aim to develop MOFs using non-toxic metals and biodegradable organic linkers, as well as exploring recycling technologies to minimize waste. Furthermore, comprehensive studies on the long-term stability and safety of MOF-based electrodes under extreme conditions, including high temperatures and mechanical stress, will be essential to ensure the reliability of LIBs for diverse applications.

Beyond common LIBs, MOFs have the potential to completely revolutionize battery technologies such as sodium-ion cells (SIBs) and solid-state batteries (SST). SIBs, which utilize sodium ions instead of lithium ions, require electrode materials with mechanical characteristics similar to those chosen by LIBs. MOFs, with their configurable pore dimensions and varied chemical compositions, can possibly be adapted to accommodate greater sodium ions, increasing their possibilities in future-oriented energy storage devices. Similarly, the development of MOF-based solid electrolytes and separators provides the possibility of helping improve the safety and density of energy of solid-state batteries by providing stable ion transport pathways and effective barriers to dendrite formation.

Collaborative efforts between academia, industry, and government agencies will be crucial in advancing the development and commercialization of MOF-based battery technologies. Multidisciplinary research initiatives that combine materials science, chemistry, engineering, and computational modelling will accelerate the discovery of novel MOF materials and their integration into advanced energy storage systems. Furthermore, initiatives aimed at standardizing testing protocols and performance metrics for MOF-based electrodes will facilitate comparative studies and accelerate technology transfer from lab-scale demonstrations to commercial production.

5 CONCLUSION

The application of MOFs in lithium-ion batteries, particularly as cathode and anode materials, presents a promising avenue for enhancing battery performance. The high surface area, tunable pore size, and chemical versatility of MOFs contribute to improved capacity, cycling stability, and safety of lithium-ion batteries. Empirical data from recent studies underscore the potential of MOFs to revolutionize battery technology, offering significant improvements over traditional materials.

However, challenges related to cost, scalability, and integration into existing manufacturing processes remain. Future research should focus on addressing these challenges, developing more efficient synthesis methods, and ensuring the environmental sustainability of MOF materials. With continued advancements, MOFs hold the potential to play a pivotal role in the next generation of high-performance lithium-ion batteries.

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