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Review Article

Solidifying the future: Metal-organic frameworks in zinc battery development

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Highlights

- MOFs are crucial for overcoming obstacles in the commercialization of zinc batteries.
- Zinc batteries offer safety, high capacity, affordability, and sustainability.
- MOFs-based stabilization and solid-state electrolytes improve zinc battery stability.
- Our review covers zinc battery structures: pure metal, metal oxides, and porous carbon.
- Future advancements will use conductive MOFs to optimize zinc battery technologies.

Abstract

Zinc batteries offer distinct advantages owing to their notable safety profile, cost-effectiveness, and environmental friendliness. The zinc anode, in particular, stands out as a promising material for aqueous zinc batteries due to its array of benefits, including its lower potential, favorable cost, higher specific capacity, increased potential for hydrogen release, non-reactive properties, natural abundance, and ease of processing. However, the uncontrolled growth of zinc dendrites, electrolyte-induced damage, significant volume changes, and unstable interfaces have thus far impeded their commercial viability, posing obstacles to their further advancement. Recent efforts have focused on addressing these challenges through the utilization of structures derived from metals and their derivatives, resulting in significant progress regarding zinc anode issues. Strategies such as stabilization through metal-organic frameworks (MOFs) and their derivatives, solid-state electrolyte development, anode decoration, separator enhancement, and interface engineering have shown promise in stabilizing zinc anodes. The incorporation of these advancements could greatly benefit large-scale energy storage systems, capitalizing on zinc batteries' exceptional safety, high capacity, affordability, and sustainability. Moreover, the unique

properties of MOFs, including their ability to facilitate zinc ion transportation, large specific surface area, and highly porous topology, have garnered increased attention for their application in zinc ion batteries. This review aims to comprehensively explore the structural components of zinc batteries based on previous research contributions, encompassing pure metal structures, metal oxides, porous carbon materials, and their compounds. In particular, the review delves into the utilization of MOFs-based materials as interfaces for solid electrolytes, separators, three-dimensional zinc architectures, and solid-state electrolytes to enhance the cyclic stability of zinc anodes. Additionally, it examines the role of conductive MOFs across various categories of zinc-based batteries, highlighting their functionality, efficacy, and existing challenges. Finally, the review offers insights into the potential future advancements in this field, outlining the prospects for further harnessing the capabilities of conductive MOFs.

Introduction

The development of sustainable methods for storing and converting energy is of prime interest to researchers due to growing concerns about environmental pollution and the looming energy crisis. The escalating demand for energy, coupled with the necessity for renewable energy generation, underscores the importance of advanced electrochemical energy conversion and storage solutions. These solutions are crucial for developing sophisticated, reliable, and long-lasting energy storage systems (ESS) [1]. However, the diverse requirements of modern electrical developments indicate that it will be challenging to rely solely on a single type of device to meet all energy storage needs simultaneously. Metal-organic frameworks (MOFs) are perforated polymers created through the interaction of ligands with metal ions or their clusters [2]. Over the past decade, MOFs have demonstrated a broad range of potential applications, including energy storage, drug delivery, gas storage and separation, catalysis, and optical materials. Their use as multipurpose electrodes in energy storage has been particularly noteworthy [3]. The exceptional inherent qualities of MOFs, such as structural diversity, functionality, and adaptability, enhance ion conductivity and facilitate a more uniform metal deposition process on metal electrode surfaces. Recent advancements in MOFs have focused on developing materials that can withstand volume fluctuations and effectively prevent the growth of metal dendrites, thus improving the longevity and efficiency of energy storage devices [4].

The field of study dedicated to creating MOF-linked materials for enhanced storage devices is rapidly expanding and holds significant promise. Zinc (Zn), abundant in the Earth's crust, is widely recognized for its diverse applications in energy storage. With a redox potential of -0.763V relative to the standard hydrogen electrode (SHE), zinc offers high theoretical capacities of 5854mAh/cm^3 and 819mAh/g . Zinc's stable and eco-friendly supply chain further enhances its attractiveness for energy storage technologies. Recent advancements in the protection of Zn anodes and electrolytes have revitalized interest in zinc-based energy storage systems [5]. Among the various aqueous zinc-based electrochemical energy storage (EES) devices, zinc-air batteries (ZAB) and aqueous Zn-ion batteries (AZIB) show significant promise in meeting the demands for higher energy and power densities, respectively [6]. Before zinc-based systems can commercially challenge lithium-ion batteries (LIB), significant advancements in cathode materials are essential. It has been established that Zn anodes are compatible with aqueous-based electrolytes, making them suitable for various battery types, including Zn-air, nickel-zinc, and zinc-manganese batteries [7]. The sustainability, eco-friendliness, and performance of Zn-based batteries are drawing considerable interest in this research area. Alkaline zinc/manganese dioxide cells, a fundamental form of early batteries, have garnered scientific attention due to their numerous advantages, such as cost-effectiveness, ease of assembly, safety, a two-electron transfer mechanism, and the abundant presence of elemental Zn in the Earth's crust. These benefits have recently spurred significant interest in rechargeable ZIBs with moderate aqueous electrolytes ($\text{pH}\approx 7$). Metallic Zn is considered an excellent anode material for aqueous ZIBs [8].

Nonetheless, several critical challenges hinder the rapid development and practical implementation of these systems. Despite the progress made, issues related to the stability and performance of Zn anodes persist. MOFs and their derivatives have shown considerable promise in addressing these challenges. The numerous active sites, large surface areas, and flexible, uniform porous structures of MOFs contribute to the superior performance of electrolytes, porous carbon materials, and electrolytic compounds [9]. From a materials science and chemistry perspective, the active sites in MOFs, often composed of transition metals like Co, Fe, Ni, and Mn, serve as catalysts for the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). These metals facilitate the adsorption and reduction of oxygen molecules during discharge and their evolution during charging. Organic ligands enhance catalytic activity by providing additional coordination sites and stabilizing intermediates. Efficient ion and electron transport are essential for high-performance Zn-air batteries. Conductive additives like graphene or carbon nanotubes are often combined with MOFs to enhance electronic conductivity. Some MOFs are designed with intrinsic conductivity by using conductive metal nodes or creating pathways for electron delocalization through conjugated ligands. The high surface area and porous nature of MOFs facilitate the