(Fe-Co-Ni-Zn)-Based Metal–Organic Framework-Derived Electrocatalyst for Zinc–Air Batteries

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Zinc–air batteries (ZABs) have garnered significant interest as a viable substitute for lithium-ion batteries (LIBs), primarily due to their impressive energy density and low cost. However, the efficacy of zinc–air batteries is heavily dependent on electrocatalysts, which play a vital role in enhancing reaction efficiency and stability. This research highlights the crucial significance of electrocatalysts in zinc–air batteries and explores the rationale behind employing Fe-Co-Ni-Zn-based metal–organic framework (MOF)-derived hybrid materials as potential electrocatalysts. These MOF-derived electrocatalysts offer advantages such as abundancy, high catalytic activity, tunability, and structural stability. Various synthesis methods and characterization techniques are employed to optimize the properties of MOF-derived electrocatalysts. Such electrocatalysts exhibit excellent catalytic activity, stability, and selectivity, making them suitable for applications in ZABs. Furthermore, they demonstrate notable capabilities in the realm of ZABs, encompassing elevated energy density, efficacy, and prolonged longevity. It is imperative to continue extensively researching and developing this area to propel the advancement of ZAB technology forward and pave the way for its practical implementation across diverse fields.

Keywords: zinc–air batteries ; electrocatalysts ; metal–organic frameworks (MOFs) ; energy density ; energy storage and conversion

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1. Background on Zinc–Air Batteries

The energy demand has increased as a result of rapid urbanization and technological innovation. In order to combat human-caused global warming and keep up with the need for energy, it is becoming increasingly important to design an eco-friendly energy environment [1]. Li-based batteries, Zn-based batteries, Na-based batteries, and supercapacitors make up the most well-known green energy storage systems (ESS) [2][3]. Notably, Zn-based batteries have drawn a significant amount of interest because of their efficient electrochemical behavior, their affordability, and the abundance of Zn metal relative to lithium. However, their potential for long-term use is restricted due to their inadequate energy density of approximately 250 Wh kg^{-1} [4][5]. Recently, researchers have been devoted to the synthesis of metal–air batteries due to their exceptional energy density, which produces electricity via metal–oxygen redox reactions in the atmosphere [6]. Zinc–air batteries have a history that goes back to the early 1800s, when experiments began exploring the use of zinc and oxygen for generating electricity [7][8]. In the 1960s, researchers dedicated their efforts to improving zinc–air batteries, which are known for their high energy density and their ability to be recharged by replacing the zinc anode. These batteries found practical applications in hearing aids, military devices, and more. Recent advancements in materials science have led to the improved performance and durability of these batteries [9]. Scientists are actively addressing challenges such as anode corrosion and limited recharge ability to make zinc–air batteries suitable for widespread use [10]. Zinc–air batteries have promising properties that make them appealing for use in electric cars, renewable energy storage, and a variety of other applications. These features include their high energy density, cost-effectiveness, and environmental friendliness [9]. Ongoing research aims to unlock their full potential and enhance their overall performance.

2. The Importance of Electrocatalysts in Zinc–Air Batteries

For zinc–air batteries to operate more effectively and efficiently, electrocatalysis is essential. There are numerous important reasons why electrocatalysts for zinc–air batteries are important. First, electrocatalysts speed up the conversion of oxygen molecules into hydroxide ions by facilitating the oxygen reduction process (ORR) at the cathode [9][11]. This enhancement in reaction efficiency leads to reduced energy losses during the ORR, thereby improving the overall battery performance. Bhardwaj et al. created a cubic $CaCu_3Ti_4O_{12}$ perovskite electrocatalyst and used it as the air electrode in a Zn–air battery, as perovskite-based composites have been proven to improve the catalytic activity [12][13]. The material demonstrated a high specific capacitance of 801 mAh g^{-1} and remarkable cycling efficiency during charge–discharge cycles, with a power density of 127 mW cm^{-2} [12]. Additionally, electrocatalysts lower the over potential required for electrochemical reactions by reducing the activation energy barrier. This results in improved energy efficiency and increased voltage output of the battery [11][14]. Quian et al. prepared web-like interconnected porous carbon through the pyrolysis of NaCl/ZIF-8 composite and used it as the electrocatalyst in a ZAB. The composite exhibited a 6.6% higher output power (55.0 mW vs. 51.6 mW) in comparison to Pt/C. Further, the battery's cycling life has been significantly enhanced and is now more than 140 h. This is 90 h more than Pt/C. The enhancement of performance can be attributed to excellent ORR activity and the stable discharge voltage of the composite [15]. To ensure the long-term functionality of zinc–air batteries that undergo repetitive charge and discharge cycles, electrocatalysts must exhibit excellent stability and durability [16]. A robust electrocatalyst can resist degradation and maintain its catalytic activity, thereby ensuring the prolonged performance and lifespan of the battery. Yang et al. created wrinkled MoS_2/Fe-N-C nanospheres that were used as an ORR/OER electrocatalyst for a wearable Zn-air battery. The device had a specific capacitance of 442 mAh g^{-1} and an outstanding power density of 78 mW cm^{-2}, with a cycle stability of 50 cycles at a current density of 5 mA cm^{-2}. Here, Fe-N_4 moieties combined with MoS_2 particles contribute to lowering the energy barrier of ORR and OER. Furthermore, the Fe-N-C shell protects the MoS_2 core from corrosion induced by alkaline electrolytes, which contributes to the device's long life [17]. Moreover, electrocatalysts facilitate the oxygen evolution reaction (OER) at the cathode, allowing the efficient rechargeability of rechargeable zinc–air batteries [18][19][20]. By accelerating the OER, electrocatalysts minimize energy losses during the charging process, enabling efficient and effective recharging. Effective electrocatalysts significantly enhance the power density, energy density, and overall performance of zinc–air batteries. They promote faster reaction kinetics, improve cell efficiency, and increase the specific capacity of the battery, making them particularly advantageous for high-energy-demand applications such as electric vehicles and grid energy storage [21]. Li et al. employed a low-cost green approach to develop a CoN/CoFe/NC bifunctional electrocatalyst. The composite demonstrated outstanding electrocatalytic characteristics, with a low potential of 1.609 V for OER and a half-life potential of 0.89 V for ORR. The enormous number of reactive sites produced by the two-phase interface formed by coupling two structures can be attributed to the material's exceptional OER and ORR performance. Furthermore, when employed as an air electrode in ZAB, the composite demonstrated an outstanding power density of 246 mW cm^{-2} and a constant voltage gap of 180 h [22]. Several studies have reported the capability of various MOF-based electrocatalysts to lower the overpotential and boost the stability, power density, and output voltage of the zinc–air battery [23][24][25][26]. In conclusion, electrocatalysts play a vital role in zinc–air batteries by enhancing reaction kinetics, reducing overpotential, ensuring stability, enabling rechargeability, and ultimately improving overall battery performance and efficiency. Continued research and development in electrocatalyst materials are crucial for further advancements in zinc–air battery technology.

3. Overview of Metal–Organic Frameworks (MOFs)

MOFs are crystalline materials made up of metal ions or clusters coordinated with organic ligands. They possess a porous structure with a large internal surface area, making them suitable for diverse applications. MOFs are synthesized through self-assembly, where metal ions or clusters bind with organic ligands to create extensive networks [27][28]. More than 20,000 MOF materials have reportedly been synthesized thus far, according to reports [29][30]. MOFs offer versatility at the molecular level, allowing researchers to design them with specific properties like pore size, surface chemistry, and thermal stability [27][31]. This adaptability enables customization for applications such as energy storage [32], separation [33], catalysis [34], and sensing [35]. The remarkable porosity of MOFs provides a substantial surface area for gas adsorption and storage, making them valuable for tasks like carbon capture and storage, as well as precise gas purification through selective separation [36]. In catalysis, MOFs act as platforms for organizing catalytically active sites, enhancing reaction efficiency by facilitating reactant accessibility. Their tunability also enables the incorporation of different metal species or clusters, leading to efficient and selective catalysts for specific chemical reactions. MOFs have further applications in drug delivery systems, utilizing their porous structure to encapsulate and deliver therapeutic agents with high loading capacities, controlled release kinetics, and targeted delivery [37]. Additionally, MOFs have been explored in sensing and detection, capitalizing on their selective adsorption capabilities to detect various analytes, including gases, volatile organic compounds, and heavy metal ions. By tailoring the MOF structure, their response to specific analytes can be customized, making them promising for sensor applications [38]. Overall, MOFs are a versatile and promising material class with wide-ranging applications in energy storage, gas storage, catalysis, drug delivery, and sensing. Continuous research and development in MOFs hold great potential for advancements and applications across industries [39][40].

4. Motivation for (Fe-Co-Ni-Zn)-Based MOFs-Derived Electrocatalysts

The motivation for employing electrocatalysts derived from Fe, Co, Ni, and Zn-based MOFs in zinc–air batteries can be attributed to several key factors. Firstly, Fe, Co, Ni, and Zn are abundant and widely available elements, making them cost-effective choices for electrocatalyst materials [41][42]. This utilization of abundant elements contributes to reducing the overall cost of the electrocatalyst, making it more economically feasible for large-scale production of zinc–air batteries. Moreover, materials derived from these MOFs exhibit high catalytic activity towards the ORR and OER occurring at the cathode and anode, respectively [43][44][45]. This enhanced catalytic activity facilitates the efficient and rapid conversion of oxygen molecules during discharge and recharge cycles, thereby improving the overall battery performance [46][47]. Tsai et al. developed a SAC (Fe, Ni, Zn)/NC bifunctional catalyst by anchoring a Fe-Ni-Zn triple single-atom catalyst (SAC) in an N-doped carbon structure. The material demonstrated excellent OER and ORR characteristics. Catalytic sites for OER and ORR reactions are provided by Fe-Nx, Zn-Nx, and Ni-Nx, and the synergetic combination of the three SAC in NC further enhances the catalytic activities. At 10 mA cm^{-2} current density, the composite displayed a half-wave potential of 0.88 V for ORR and a potential of 1.63 V for OER. A ZAB device with SAC (Fe-Ni-Zn)/NC as an air electrode demonstrated 809 mAh g^{-1} specific capacitance at 50 mA cm^{-2} and an outstanding power density of 300 mW cm^{-2}. It additionally achieved cyclic stability of 2150 cycles over 358.3 h at 10 mA cm^{-2} current density [48]. MOFs derived from Fe, Co, Ni, and Zn offer tunable properties as they can be synthesized with different compositions and structures [49]. This tunability allows researchers to optimize the electrocatalyst's performance by tailoring its structure, morphology, and composition to meet the specific requirements of zinc–air batteries, including activity, stability, and durability [50]. Additionally, MOFs derived from these metals often possess inherent structural stability, which is crucial for maintaining the electrocatalyst's integrity and functionality during prolonged battery operation [51][52]. For instance, Gui et al. reported that a (Fe-Co)-based MOF-derived hybrid catalyst enhanced the performance of a zinc–air battery, catalyzing ORR and OER, resulting in high peak power density and a longer charge–discharge cycle [53]. Their robust structures enable them to withstand the demanding electrochemical conditions experienced during charge–discharge cycles, ensuring the long-term performance and lifespan of the energy storage system [54]. Furthermore, combinations of Fe, Co, Ni, and Zn-based MOFs as electrocatalysts can exhibit synergistic effects, where the presence of different metal species enhances catalytic activity and stability beyond what individual metals can achieve alone. This synergistic effect contributes to the improved overall performance and efficiency of zinc–air batteries. Jin et al. performed in situ carbonization of metal ion-absorbed PANI precursors, resulting in a composite with alloy nanoparticles encapsulated graphitic layer which is uniformly distributed in a N-doped carbon framework. The electrocatalyst demonstrated remarkable stability in ORR and OER processes. Furthermore, the electrocatalyst was used as an air electrode for flexible ZABs, and the assembled ZAB displayed a long cycling life of 22 h with an elevated power density of 125 mW cm^{-2} [55]. By incorporating Fe, Co, Ni, and Zn-based MOF-derived electrocatalysts into zinc–air batteries, researchers strive to develop cost-effective, high-performance, and durable energy storage systems. These electrocatalysts possess favorable properties such as abundance, catalytic activity, tunability, structural stability, and potential synergistic effects, making them highly promising candidates for advancing zinc–air battery performance and enabling practical applications in various fields, including portable electronics, electric vehicles, and renewable energy storage. Ren et al. synthesized a (Fe-Co-Ni)-based carbon nanorod hybrid and studied its catalytic application in a zinc–air battery. They reported that the synergetic effect of the combination of different metal components facilitated the accessibility of the reactants, resulting in an ORR half-wave potential of 0.84 V and an OER potential of 1.54 V at 10 mA cm^{-2}. The zinc–air battery using the Fe-Co-Ni-based electrocatalyst exhibited a low voltage gap and longer durability [56]. Similarly, Li et al. reported a (Zn-Co-Fe)-tridoped-N-C nanocage as an efficient and stable electrocatalyst for the ORR in zinc–air batteries [57].

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