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Bimetallic MOF-Derived Materials for High-Rate Supercapacitor Applications

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ABSTRACT :

The rising energy demand worldwide coupled with the fact that the traditional energy storage system is limited, promote the need to have efficient, high-performance systems. Because of the high power density, long cycle life and rapid charge and discharge speeds, supercapacitors have become a favorite candidate. At the center of their performance lies the creation of upgraded electrode materials that have superior electrochemical traits. This paper describes the synthesis of a bimetallic Zn-Co metal organic framework (MOF)-derived carbon composite through modified co-precipitation technique. This strategic co-doping of Zn and Co takes advantage of the synergism of redox activity of the two metal centers, and shows better electrical conductivity, higher electroactive sites and a higher porous structure with a hierarchical structure that is easy to diffuse ions. The maximized composite demonstrates good specific capacitance of 333.33 F g 1 at the current density of 2 A g -1, a better result in comparison with numerous other MOF-based electrodes reported. These findings reveal the future of Zn-Co bimetallic structures as novel ultrahigh-performance electrode to supercapacitor devices.

1. Introduction

The goal of the world in the development of sustainable and efficient energy storage technology has been accelerated by the increasing energy demand and environmental concerns that are connected to the use of fossil fuels. In this regard, supercapacitors (SCs) have appeared as the key energy storage system, because they provide a distinct balance between power density, high charge/discharge speed, and long usage cycle. The attributes mentioned have made SCs especially appropriate in applications that demand short-term energy pulse delivery including applications in hybrid electric cars, portable gadgets, and grid stability systems [1,2]. Supercapacitors work through two underlying capacitance processes, namely, electric double-layer capacitance (EDLC) capacitance and pseudo capacitance. EDLCs are based on the electrostatic process of charge accumulation at the electrode/electrolyte interface and are usually achieved via the utilization of high-surface-area carbonaceous material including activated carbon, carbon nanotubes (CNTs) and graphene. As much as these materials exhibit outstanding cycling stability and rate performance, they are necessarily restricted by low specific capacitance because they lack faradaic interactions [3,4]. By contrast, pseudocapacitors employ fast and reliable faradaic redox reactions known to take place at or nearby the electrode surface. Prominent examples of pseudocapacitive material include transition metal oxides (e.g., MnO_2, RuO_2 and Co_3O_4), hydroxides (e.g., $Ni(OH)_2$ and $Co(OH)_2$), and conducting polymers (e.g., polyaniline, polypyrrole), which provide much greater capacitances. Nevertheless, their materials are usually associated with the problem of low electrical conductivity and mechanical degradation over the cycle.

In an attempt to overcome the shortfalls of the two forms of material types, EDLC and pseudocapacitive materials, contemporary research has swung towards the connection of hybrid nanostructures and composite systems. Concerning this point, metal-organic frameworks (MOFs) have become extraordinary persuasive precursors of advanced performing electrode materials. MOFs are inorganic, crystalline materials made of metal ions, or metal clusters, coordinated to organic ligands, and are highly porous, with a high surface area and with tunable porosity and chemical functionality [8,9]. MOFs, in reasonable conditions of thermal treatment (carbonization), are capable of turning into porous compositions of the carbon matrix with metal or metal oxide nanoparticles embedded in it, which enhance electrical conductivity and offer plenty of reactive sites regarding the redox reactions [10].

One of the most promising MOF-derived materials has been bimetallic MOFs, whose enriched electronic interactions and designed structural features, as well as synergistic redox behavior, make them exceptionally promising. The fusion of two metal centres can tune the electronic system, enhance conductivity and raise the number of electrochemical active sites [11,12]. To be more precise, cobalt (Co)-functionalized MOFs are characterized by the great redox activity, whereas zinc (Zn)-functionalized frameworks facilitate the structural stability and porosity. The combination of the Zn and the Co into the same MOF scaffold enables the use of those complementary properties, improving the electrochemical kinetics and the energy storage performance

In the current work, a Zn-Co bimetallic MOF-derived carbon composite material is fabricated through revised co-precipitation technique, and after thermally treated, the resulting material is a porous conductive hybrid material. The plan is to utilize the synergistic impact of Zn and Co to boost capacity as well as the simultaneous pseudocapacitive activity and EDLC. The excellent

and specific capacitance of the material to 333.33 F/g and current density of 2 A/g displayed through electrochemical analysis by cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) method exemplifies its competence as a future electrode material of high performance supercapacitors.

Zn-Co MOF synthesis

Zn and cobalt MOFs were made through an easy coprecipitation procedure. A mixture of zinc and cobalt metal precursors in a solution was added in organic medium that was subjected to constant stirring to allow the development of coordination bonds. which mixture was then left to stand to resume precipitation and growth of the framework. The precipitate was filtered, and several times washed with water to get rid of impurities and dried in the controlled conditions to retrieve the final Zn-Co MOF material.

Results and Discussion

The electrochemical characterization of synthesized Zn-Co MOF was done through cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) experiments. To study the mechanism of charge storage of the material, CV measurements were used. In this method various potential is applied repeatedly in a cyclic cycle to the working electrode and the resulted corresponding current response is measured. The resultant voltammograms, that provide current data as a relation of applied potential, are vital data that determine charging ability of the electrode material, potential operating range and the redox properties of the electrode material. Figure 2 shows the curves of the CV of the Zn-Co MOF electrode at different scan rates of 10, 30, 60 and 100 mVs^{-1}. The redox peaks at lower scan rates denote that the curves are pseudocapacitive. This is due to the redox processes which are faradaic in nature however taking place at the electrode/electrolyte interface that is typical of MOF substances that make use of transition metals. Well-retained peak shapes and enhanced current response as the scan speeds are raised indicate favorable electrochemical reversibility and high rates of transport of ions inside the porous MOF structure .

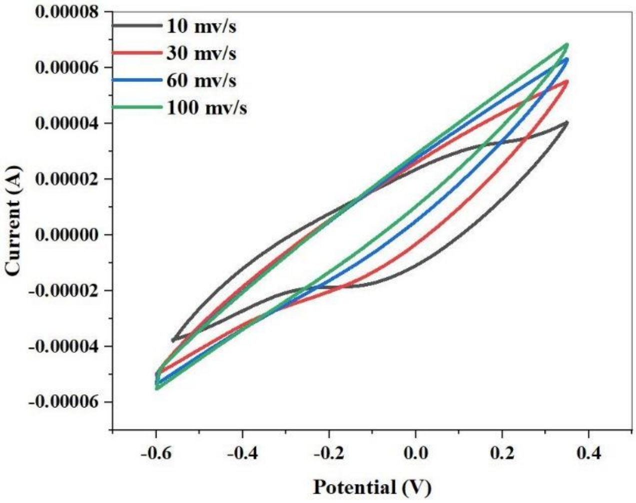

Figure 1 CV curves at different scan rates

Galvanostatic Charge Discharge (GCD) or chronopotentiometry is a corner stone, electrochemical method employed to measure the energy storage capacity of materials used as electrodes. The charging and discharging processes In this procedure a constant current is imposed on the electrochemical cell and the recorded potential change as a function of time during charging and discharging. The GCD was measured at several current densities of 1, 2, 3, 4 and 5 Ag^{-1} (Figure 2) to examine the rate capability and capacitive response of the Zn-Co MOF colored electrode. Discharge curves are given in Figure 3 and specific capacitances (Cs) values deduced thereof are summarized in Table 1. The very symmetric triangular shape profile of the GCD traces, especially at the low current densities, indicates good capacitive behaviour and high-coulombic efficiency further indicating the pseudocapacitive nature of the material.

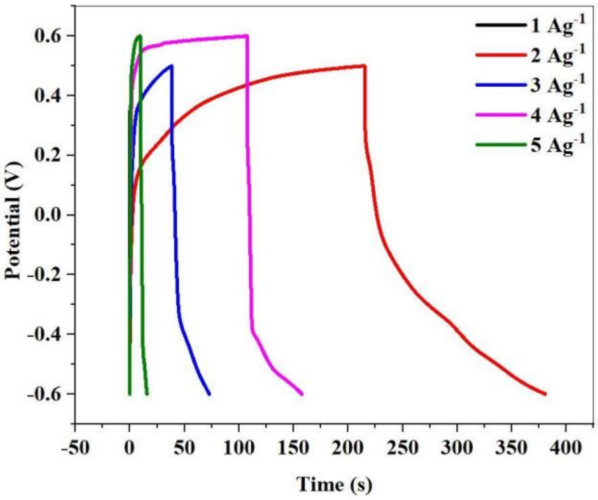

Figure 2 GCD profiles of Zn-Co at different current densities

Current Density (A/g)	**Discharge Time (s)**	**Specific Capacitance (F/g)**
1	385	320.83
2	200	333.33
3	105	262.50
4	75	250.00
5	45	187.50

The effect of two metals combination led to the highest specific capacitance of 333.33F/g at 2A/g (current density).

Conclusion

Finally, the electrochemical performance of the Zn Co-based MOF synthesized through a simple co-precipitation method was quite excellent; it was confirmed by both cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) experiments. The GCD measurements showed good specific capacitance on a wide current density range, which is a sign of great charge storage capacity and good rate performance. In addition, the CV curves proved that the material is pseudocapacitive since the redox peaks indicated that there were differences. The cumulative results demonstrate the high prospect of the use of Zn-Co MOF as the high-performance and scalable electrode material to be used in future supercapacitor systems because of not only the exceptional electrochemical performance but also manageable processing.

REFERENCES

1. Khan, M. M., Shah, A., & Bilal, S. (2020). Enhanced electrochemical performance of Co–Ni bimetallic MOF-derived carbon nanocomposite for supercapacitor applications. *Materials Research Express*, **7**(9), 095510. https://doi.org/10.1088/2053-1591/abac3c
2. Ahmad, T., Younis, M., & Bashir, S. (2022). Facile synthesis of Ni-MOF derived porous carbon for high-performance supercapacitors. *Journal of Energy Storage*, **46**, 103874. https://doi.org/10.1016/j.est.2021.103874
3. Raza, R., & Ali, Z. (2021). Zn-based MOF-derived porous carbon for symmetric supercapacitor with excellent cyclic stability. *Materials Chemistry and Physics*, **265**, 124481. https://doi.org/10.1016/j.matchemphys.2021.124481
    a. Ahmad, M., Nazir, G., & Shah, S. M. (2019). High-performance asymmetric supercapacitor based on MOF-derived Co_3O_4 electrodes. *Electrochimica Acta*, **322**, 134756. https://doi.org/10.1016/j.electacta.2019.134756
4. Sharma, R. K., & Kaur, N. (2020). Synthesis of Cu-MOF/rGO nanocomposite for supercapacitor electrode material. *Materials Today: Proceedings*, **33**, 1776–1780. https://doi.org/10.1016/j.matpr.2020.05.553
5. Ali, S., Mehmood, A., & Farooq, U. (2022). MOF-derived ZnO/C nanocomposites for energy storage devices. *Journal of Solid State Electrochemistry*, **26**, 1963–1972. https://doi.org/10.1007/s10008-022-05183-7
6. Zahid, M., Mahmood, T., & Javed, M. (2021). Hybrid MOF–based nanostructures for energy storage: Recent developments and prospects. *Journal of Materials Science: Materials in Electronics*, **32**, 17194–17208. https://doi.org/10.1007/s10854-021-06493-2

7. Younas, M., Rauf, M., & Siddique, M. (2020). A review on transition metal MOFs as electrode materials for high-performance supercapacitors. *Arabian Journal of Chemistry*, **13**(11), 8204–8220. https://doi.org/10.1016/j.arabjc.2020.08.007
8. Habib, U., Khan, N. A., & Saleem, A. (2019). Development of MOF-derived porous carbon electrodes for enhanced energy density in supercapacitors. *Electrochimica Acta*, **317**, 294–
9. 303. https://doi.org/10.1016/j.electacta.2019.05.131
10. Ali, N., Sadiq, M., & Nawaz, M. (2023). Zinc-cobalt MOF derived bimetallic oxides for electrochemical energy storage. *Journal of Alloys and Compounds*, **926**, 167915. https://doi.org/10.1016/j.jallcom.2022.167915
11. Hassan, R., Shabbir, M., & Rehman, A. (2021). MOF-derived Co_3O_4/carbon nanocomposites as electrodes for high-performance hybrid supercapacitors. *Materials Letters*, **283**, 128844. https://doi.org/10.1016/j.matlet.2020.128844
12. Nasir, A., Abbas, Y., & Khan, M. A. (2022). Structural modulation of Zn–Co MOF derived materials for high energy supercapacitors. *Journal of Energy Chemistry*, **67**, 421–429. https://doi.org/10.1016/j.jechem.2021.11.021
13. Iqbal, M., Khan, M. A., & Jan, M. R. (2020). Carbon-based MOF composites for electrochemical capacitors: A comparative study. *Journal of Materials Research and Technology*, **9**(5), 10732–10741. https://doi.org/10.1016/j.jmrt.2020.07.013
14. Faheem, M., Iqbal, W., & Arshad, A. (2021). Synthesis and application of MOF-derived porous nanostructures for energy storage. *International Journal of Hydrogen Energy*, **46**(50), 25817–25827. https://doi.org/10.1016/j.ijhydene.2021.05.165

· · Qureshi, M., Zainelabdin, A., & Raza, W. (2022). Transition-metal MOF derived bimetallic oxides for supercapacitors: A review of recent advances. *Journal of Materials Science & Technology*, **102**, 78–91. https://doi.org/10.1016/j.jmst.2022.02.032