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Synthesis and Evaluation of Pristine Co and Hybrid Ni-Co Metal-Organic Frameworks (MOFs) as Potential Electrodes for Electrochemical Energy Storage Applications

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Abstract: Hybrid metal-organic frameworks (MOFs) have many positive features like high porosity, surface area, and conductivity as compared to other materials. They have better potential than pristine ones due to the reason that hybrid materials have good faradic responses due to variable metal oxidation states. These all-favorable factors make hybrid MOFs more potential electrodes for energy storage. In this study, hybrid Ni-Co MOFs presented good specific capacitance of 745 F g^{-1} ($447 \text{ C g}^{-1} @ 1 \text{ A g}^{-1}$) in comparison with pristine Co MOFs of 109 F g^{-1} ($65.5 \text{ C g}^{-1} @ 1 \text{ A g}^{-1}$). Also, the hybrid MOFs showed superior electrical conductivity of 1353.3 S cm^{-1} as compared to pristine MOFs. The charge transfer resistance (R_{ct}) of hybrid MOFs was 2.271Ω pretty much greater than pristine MOF and other closely related studies. The best electrochemical performance was attributed to the synergic effect of Ni, Co, and organic ligand.

Keywords: MOF, energy storage, conductivity, porosity, dimethyl formamide

1. Introduction

Batteries use a closed system concept, in which the electrodes are the active masses which directly participate in the redox reactions and provide a medium for charge transfer at the same time. Capacitors, on the other hand, do not convert energy through oxidation/reduction reactions [1]. Lately, there is a focus on searching for new materials to enhance the characteristics of conventional energy storage devices to meet future requirements. In this regard, metal-organic frameworks (MOFs) have shown high potential. MOFs are materials which have high porosity then activated carbons (AC) [2] with a highly exposed surface area of $7,000 \text{ m}^2 \text{ g}^{-1}$ [3]. Two or more metal cations when combined, provide us with enhanced performance thus showing the formation of hybrid electrode material. Research has been conducted on both electrode materials, cathodes as well as anodes. They have good electrochemical performance like stability, catalytic activity, and adsorption properties due to variable oxidation states transition metals [4]. Few researchers like De Combarieu et al. [5] reported the preparation of a new hybrid cathode material using Iron MOF called MIL-53(Fe), i.e., $\text{Fe}^{3+}(\text{OH})_{0.8}\text{F}_{0.2}[\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2]$ and benzoquinone. Due to the redox properties of the benzoquinone molecules, electrochemical performance was enhanced. Han et al. [6] prepared a hybrid MOF of Ni and

Li. The performance of three MOFs was compared and results revealed that the hybridization of pristine MOFs is the main cause of their excellent performance. M-1,4,5,8-naphthalenetetracarboxylates (M = Li and/or Ni) MOFs were prepared by hydrothermal method, followed by heat treatment. This results in a charge capability of 1,084 mAh/g which dropped down to 482 mAh/g with the completion of 80 cycles. It was also observed that hybridization led to the fusion of good charge capacity and cyclic stability of Ni and Li-MOFs, respectively [6]. Similarly, Xu et al. [7] synthesized iron oxide electrode material with high porosity by using MOF precursor, MIL-88-Fe ($\text{Fe}_3\text{O}(\text{H}_2\text{O})_2\text{Cl}(\text{BDC})_3 \cdot n\text{H}_2\text{O}$). At a temperature of 0.2 °C, the oxide exhibited 911 mAh/g even at the 50th galvanostatic charge-discharge (GCD) cycle. At a slightly higher temperature of 10 °C, the capacity observed was 424 mAh/g [7]. In $\text{M}_3\text{II}(\text{CoIII}(\text{CN})_6)_2 \cdot n\text{H}_2\text{O}$, M = Co or Mn, had good potential to be used as an anode material. This study explored the open structure of Co MOFs with ion transportation, which exhibited a predominant high-power output with small voltage loss and a reversible capacity of 299.1 mAh/g. Between 20 to 2,000 mA g^{-1} current densities, MOF showed 34% of capacity retention [8]. Further studies include, Zn-Co-MOF@CuO composite presented a capacity of 308 C g^{-1} at 2 A g^{-1} maintained to 220 C g^{-1} , even at 20 A g^{-1} [9]. Ni/Zn bi-metallic CSN prepared through a hydrothermal approach showed 210 C g^{-1} at 0.5 A g^{-1} [10]. Among the different MOFs employed in these studies, Ni and Co-based materials have very good results owing to their small ionic radii (69 pm and 74.5 pm, respectively), which results in easy diffusion as compared to the other metals [11, 12]. Additionally, Zn, Ni, and Co have different oxidation states in comparison with K^+ , Li^+ , and Na^+ based materials so have superior electrochemical performance [13, 14]. So, this study relates to the electrochemical properties' evaluation of Co and hybrid Ni-Co MOFs. As per the obtained results, the hybrid Ni-Co MOFs showed a capacitance of 745 F g^{-1} pretty much greater than pristine Co MOF.

2. Materials and methodology

2.1 Materials

Ethanol absolute was obtained from Sigma Aldrich with an assay of min. 99.8%, cobalt(II) nitrate hexahydrate purified from Merck with an assay of 99.0%. Nickel(II) nitrate hexahydrate from Daejung with an assay of 97%. N-dimethylformamide from Duksan with an assay of 99.5%. Terephthalic acid was obtained from Daejung with an assay of 97%.

2.2 Synthesis of pristine Co MOF and Ni-Co MOF powders

First, unary metal pristine Co MOFs were synthesized by a simple hydrothermal process. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.9 mmol) and benzene-1,4-dicarboxylic acid (1.5 mmol) (also known as BDC or terephthalic acid) were mixed in 52.5 ml of dimethylformamide (DMF) to form a solution by 30 min stirring. While stirring 1:1 ethanol/de-ionized (DI) water mix was prepared. 7.5 ml of this ethanol/DI water mix was added dropwise to the solution under constant stirring, after which it was left to stir for further 25 minutes. This stirred solution was then transferred to a 250 ml autoclave with Teflon lining. This autoclave was then transferred to an oven in which it was kept for 12 hours at 125 °C. The autoclave was then oven cooled followed by centrifugation and washing of unreacted material for 3 cycles with DI water and ethanol to prepare Co MOF. The prepared precipitates of Ni and Co MOFs were oven dried for 12 hours at 60 °C [15]. Using the same procedure, as depicted in Figure 1, Ni-Co hybrid MOF with different molar ratios were synthesized by varying the $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ratio to be 1:1 (1:1 Ni-Co MOF).

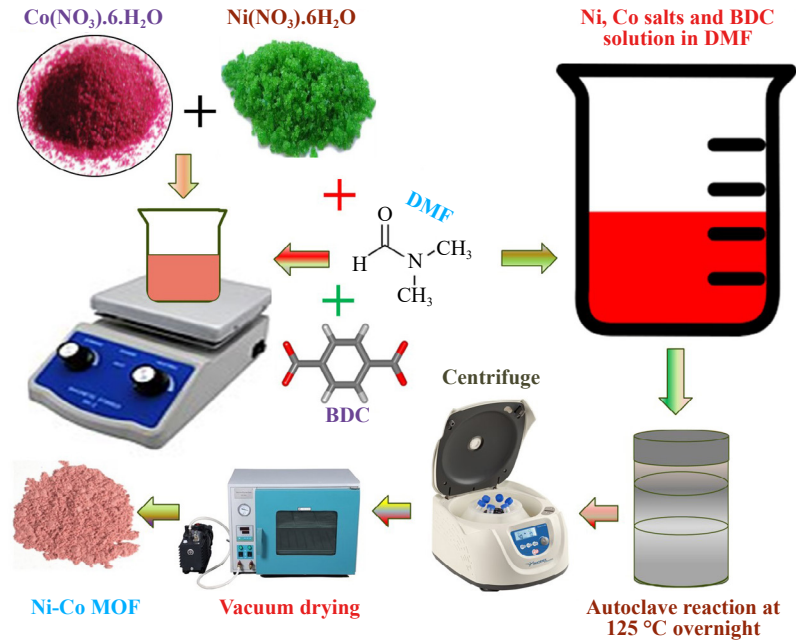


Figure 1. Experimental steps followed for the preparation of Co and Ni-Co MOFs

2.3 Synthesis of pristine Co MOF and Ni-Co MOF powders

Prepared compositions were evaluated electrochemically in a three-electrode assembly. The active materials (MOFs) were deposited on nickel foam (substrate) whereas, platinum and Hg/HgO were used as counter and reference electrodes respectively. A slurry consisting of Ni-Co MOF (1:1) was used as active material (8 mg), acetylene black (1 mg), and polyvinylidene fluoride (PVDF) solution (1 mg in 50 μL). After this, the slurry was deposited onto nickel foam ($1 \times 1 \text{ cm}^2$) followed by oven drying for 8 hours at 90 $^\circ\text{C}$. Electrochemical characterization was done using a potentiostat/galvanostat Reference 3000 by Gamry USA, in three electrode assemblies. The specific capacity/capacitance (F g^{-1}) was calculated using the following equations reported in the literature [16-18].

$$Q_s = \frac{1}{mv} \int_{V_i}^{V_f} I \times V dV \quad (1) [16]$$

$$C_s = \frac{\frac{1}{mv} \int_{V_i}^{V_f} I \times V dV}{\Delta V} \quad (2) [17]$$

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \quad (3) [18]$$

where Q_s and C_s are specific capacity/capacitance, I is the current density in A g^{-1} , m is active mass in grams (g), and Δt is the discharge time in seconds (s) and ΔV is the potential range in volts (V).

3. Results and discussion

3.1 Microstructural and electrochemical evaluation of pristine Co and Ni-Co MOF

Figures 2(a) and 2(b) explain the morphological analysis of hybrid Ni-Co MOF from SEM (Zeiss Evo 15). It is quite clear that Ni-Co MOF has an ideal small rectangular block-like structure as reported in the literature [19]. The

structural morphology indicates that there is a high surface area and efficient porous active sites for electrochemical reactions. These are very important parameters for an excellent electrochemical reaction to take place which results in increasing the specific capacity, capacitance, and electrical conductivity as explained in the preceding sections.

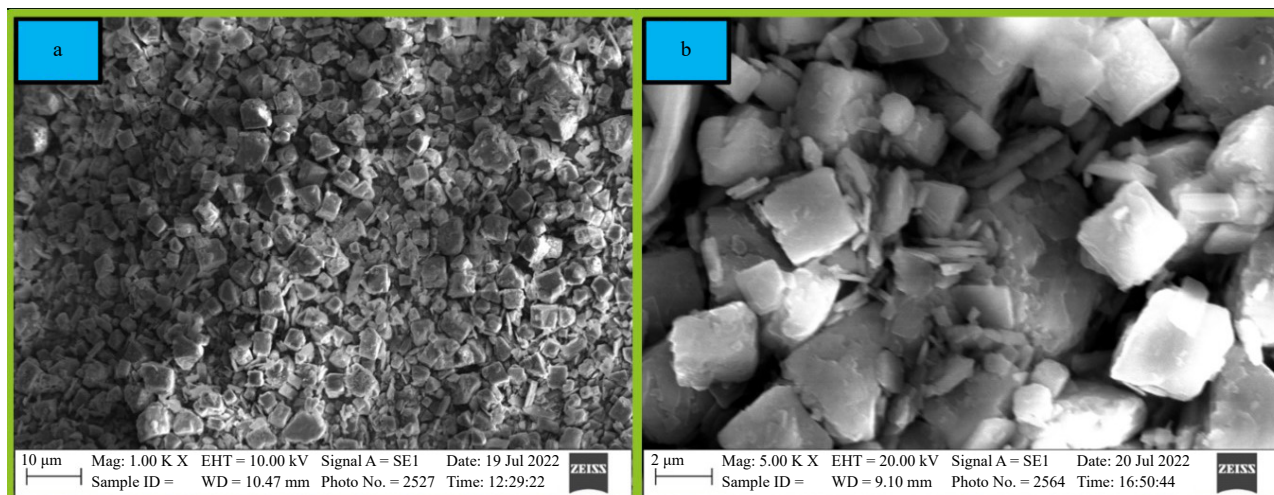


Figure 2. SEM image of Ni-CO hybrid MOF at (a) low and (b) high

Figures 3(a) and 3(b) represent the cyclic voltammetry (CV), and GCD curves in scan rate and current densities range of 5 to 100 mV s^{-1} and 1-10 A g^{-1} respectively. All plots showed visible reduction and oxidation peaks up to 30 mV s^{-1} which can be attributed to oxidation peaks of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Co}^{2+}/\text{Co}^{3+}$. As the scan rate increases above 30 mV s^{-1} , the reduction and oxidation peaks shift towards the negative and positive voltages, respectively, which was due to the inbuilt internal resistance of electrodes. Furthermore, according to Figure 3(c), the area enclosed by the 1:1 Ni-Co MOF CV plot is the greatest as compared to pristine Co MOF at the same scan rate of 10 mV s^{-1} indicating much better faradaic features [20]. According to Figures 3(d), 3(e) and 3(f), the GCD results concluded the best electrochemical behavior of 1:1 Ni-Co MOF as compared to the other candidates, based on the maximum discharge time. In Figure 3(f), the discharge time of hybrid MOF at 1 A g^{-1} is greater as compared to pristine Co MOF. The specific capacitance values calculated for pristine Co and hybrid Ni-Co MOFs were 109 F g^{-1} and 745.3 F g^{-1} @ 1 A g^{-1} respectively (Figure 4(a) and 4(b)). Thus, hybrid MOFs depict higher specific capacitance not only from pristine MOF but also higher for the values reported in the literature for Ni-Co MOF/ GO_2 (447.2 F g^{-1} @ 1 A g^{-1}) [21]. The values for R_s , R_{ct} resistances of pristine Co, and hybrid Ni-Co MOF were calculated from electrochemical impedance spectroscopy (EIS) model fitting and are given in Table 1 (Figure 4(c)). The R_{ct} value of pristine MOF is greater than hybrid MOF and also greater than literature-reported MOFs, e.g., calcined and decomposed $\text{MnO}_x/\text{NC}/\text{MnO}_2$ MOF derived composite showed R_s and R_{ct} values of 5.93 and 5.57 Ω respectively [22], pretty much greater than our reported results for hybrid Ni-Co MOF ($R_s = 1.459 \Omega$, $R_{ct} = 2.271 \Omega$) as evident from Table 1. The equivalent series resistance (ESR), electrical resistivity and conductivity have been calculated from the IR-drop method as determined by reported studies [16, 23] (Figures 4(d), 4(e) and 4(f)). The ESR and electrical resistivity of Co MOF are greater than that of hybrid Ni-Co MOF (Figures 4(d) and 4(e)). The electrical conductivity of hybrid MOF (1,353.3 S cm^{-1}) is pretty much greater than pristine Co MOF (800.3 S cm^{-1}) MOF (Figure 4(e)). The combined contribution of Ni and Co increases the redox reaction due to variable oxidation states. Its combination with the legend terephthalic acid creates the organic complex in which the metallic ions are entrapped. This increases the conductivity, surface area and many porous active sites for electrochemical reactions to take place. This combination produces very effective conductive paths for ionic intercalation so increases the oxidation and reduction reactions and increased the whole electrochemical performance of MOFs [24, 25].

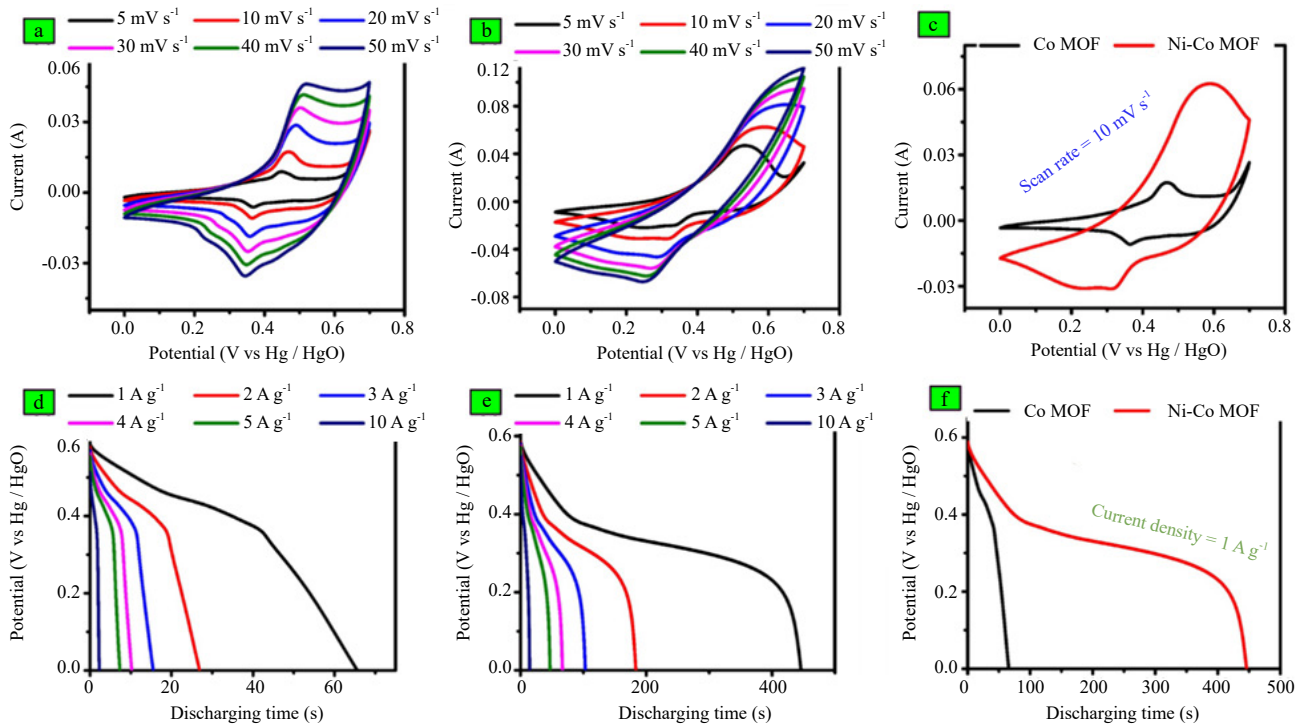


Figure 3. Electrochemical evaluation of pristine Co and hybrid Ni-Co MOFs: (a) CV of pristine Co, (b) hybrid Ni-Co MOFs, (c) CV comparison at 10 mV s^{-1} , (d) GCD of pristine Co, (e) hybrid Ni-Co MOFs, (f) GCD comparison at a current density of 1 A g^{-1}

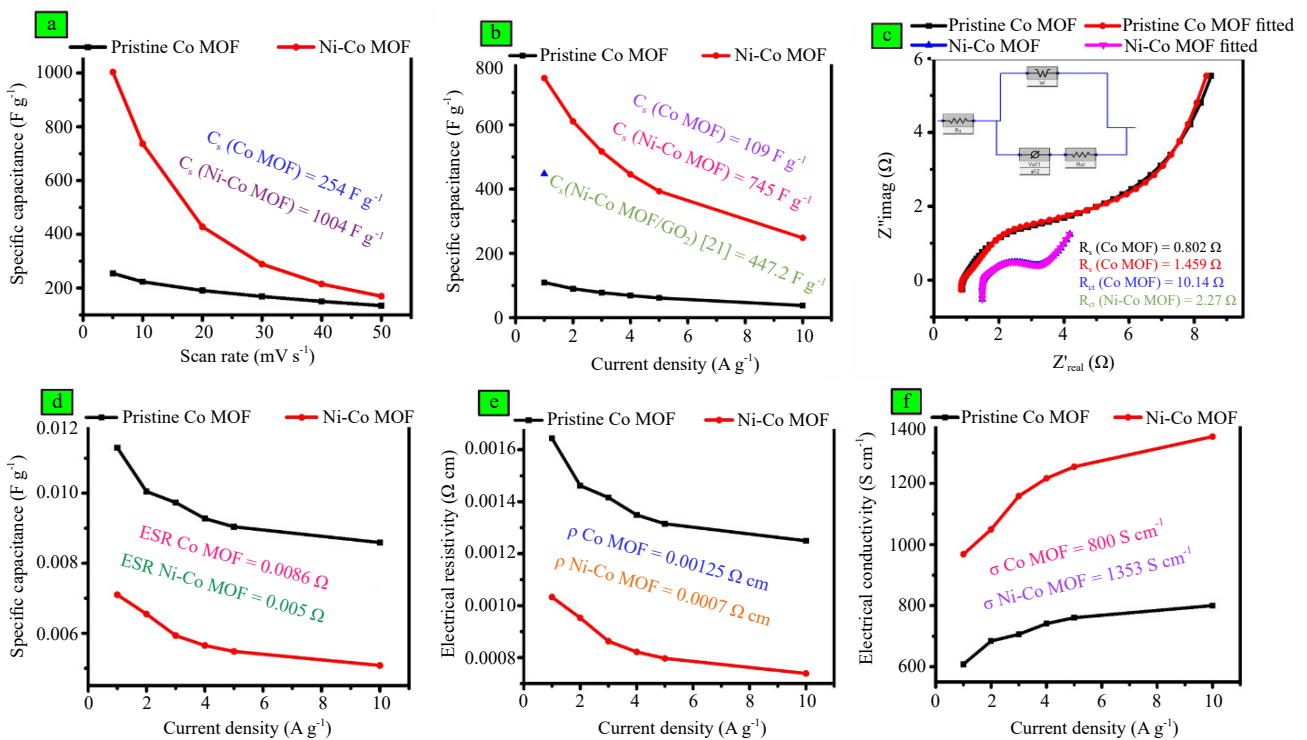


Figure 4. Comparison of electrochemical performance of pristine Co and hybrid Ni-Co MOFs: (a) specific capacitance of Co, (b) hybrid Ni-Co MOFs from CV and GCD, (c) EIS comparison of both compositions, (d) ESR, resistivity, (e) electrical conductivity of Co, (f) hybrid Ni-Co MOFs

Table 1. EIS model fitting data of both electrodes

Samples	R _s (ohms)	R _{ct} (ohms)	Warburg resistance, W (ohms)
Pristine Co MOF	0.802	10.14	0.048
Hybrid Ni-Co MOF	1.459	2.271	0.035

4. Conclusions

Hybrid MOFs have highly exposed surface area with a lot of active electrochemical reaction sites as compared to other materials which result in the increment of electrochemical reaction sites that increase the faradic reactions. Hybrid MOFs have good electrochemical performance as compared to pristine materials due to good oxidation-reduction characteristics because of variable valance transition metals (Ni, Co). In the present study, hybrid Ni-Co MOFs showed better capacitance of 745 F g⁻¹ (447 C g⁻¹ @ 1 A g⁻¹) than pristine Co MOF of 109 F g⁻¹ (65.5 C g⁻¹ @ 1 A g⁻¹), that may be attributed to the synergic effects of Ni, Co and organic ligand. Overall, obtained results show the hybrid Ni-Co MOFs as potential candidates to be used as electrode materials for energy storage devices applications.

Conflict of interest

There is no conflict of interest for this study.

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