Electrochemical studies on Ni, Co & Ni/Co-MOFs for high-performance hybrid supercapacitors

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Abstract
Metal-organic framework (MOF) of Ni-MOF, Co-MOF, and Ni/Co-MOF were synthesized by a facile hydrothermal method using Trimesic acid as structure directing linker. The physico-chemical properties of the synthesized MOFs were characterized by P-XRD (powder X-ray diffraction), FT-IR (fourier transform infrared spectroscopy), SEM-EDS (scanning electron microscopy/energy-dispersive X-ray spectroscopy), HR-TEM (high-resolution transmission electron microscope) and BET (Brunner Emmett Teller) surface area techniques. The supercapacitance performance of these MOFs were studied by electroanalytical techniques such as cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). Amongst the MOFs investigated, Ni/Co-MOF exhibited highest specific capacitance (Cₚ) of 2041 F g⁻¹ at a scan rate of 2 mV s⁻¹ and 980 F g⁻¹ at a current density of 2.5 A g⁻¹. Ni/Co-MOFs delivered a maximum energy density (ED) of 55.7 W h Kg⁻¹ at a corresponding power density (PD) of 1 K W kg⁻¹ and maximum PD of 9.8 K W kg⁻¹ at an ED of 41.6 W h Kg⁻¹. An outstanding supercapacitance performance with superior columbic efficiency of 98.4% and capacitive retention of 73% after 5000 cycles marks this material as potential candidate for supercapacitors (SCs). A comparative electrochemical study of these MOFs were made in three electrode system, further electrochemical performance was corelated with their physico-chemical properties.

1. Introduction

Due to an increasing energy consumption and rapid exhaustion of fossil fuel reserves, there is a vital demand for an efficient energy storage materials and devices. Thus, the development of high performance and competent energy storage devices (ESDs) has attracted significant attention in the present research scenario [1].

Supercapacitors are one of the ESDs with longer cycle life and fast charge–discharge rates in comparison with batteries. Hence, this device is considered to be used in a wide range of practical applications [2]. The efficiency of SCs primarily depends on the nature of electrode materials, their synthesis methods as well as their physicochemical properties [3]. SCs are classified into electrical double-layer capacitors (EDLCs) and pseudocapacitors (PCs) based on the charge storage mechanisms. The charge storage is due to charge accumulation process across an interface in EDLCs without any electrochemical reactions. On the other hand, in PCs charge storage is due to faradic redox reactions between electrode materials and electrolyte [4]. There are three broad categories of electrode materials used in SCs, which includes carbonaceous materials, metal transition oxides/sulfides/nitrides and conducting polymers [5, 6]. Carbon-based materials such as activated carbon, carbon black, carbon nanotubes, carbon nanospheres, mesoporous carbon, graphene, etc., are EDLCs materials. Transition metal oxides/sulfides [7] conductive polymers [8] are PCs materials which contribute mainly to pseudocapacitance. EDLCs exhibits higher cycle stability and lower Cs than PCs [5]. The electrode material with high surface area results in high charge storage by reducing hydroxyl ion (OH⁻) ion diffusion pathway [9]. The surface area of
Table 1. Comparison of electrochemical performance of present work with Ni-MOF, Co-MOF and Ni/Co-MOF reported in previous literature.

| Material | Discharge rate | System | Potential range (V) | Specific capacitance ($C_s$) | Capacitive retention (number of cycles) | References |
|----------|----------------|--------|---------------------|-----------------------------|----------------------------------------|------------|
| Ni-MOF   | 1 A g⁻¹        | 3 electrode | 0–0.4               | 1057 F g⁻¹                  | 70% (2500)                             | [20]       |
| Ni-MOF   | 1.4 A g⁻¹      | 2 electrode | 0–1.2               | 988 F g⁻¹                   | 96.5% (5000)                           | [21]       |
| Co-MOF   | 2 mA cm⁻²      | 3 electrode | 0–1.6               | 13.6 F cm⁻²                 | 69.7% (2000)                           | [22]       |
| Co-MOF   | 0.6 A g⁻¹      | 2 electrode | 0–0.5               | 206 F g⁻¹                   | 98.3% (1000)                           | [23]       |
| Ni/Co-MOF| 1 A g⁻¹        | 3 electrode | 0–0.48              | 758 F g⁻¹                   | 75% (5000)                             | [24]       |
| Ni/Co-MOF| 1 A g⁻¹        | 3 electrode | 0–0.4               | 1049 F g⁻¹                  | 97.4% (5000)                           | [25]       |
| Ni/Co-MOF| 2.5 A g⁻¹      | Three electrode | −0.1–0.55           | 980 F g⁻¹                   | 73% (3000)                             | Present work |

Electrode materials is also one of the key factors which affect their electrochemical performance. Hence, development of electrode materials with desirable porosity for SCs is an active field of research. In the recent years, unique materials like Metal-organic framework (MOF) are being explored as new low cost and efficient electrode materials for SCs [10]. MOF are the exceptional molecules with the combination of organic and inorganic moieties, typically arranged in a crystallized three-dimensional structure [10]. Various desirable properties of MOF have drawn tremendous attention towards a wide range of applications like storage or separation of gases, catalysis, magnetism, luminescence biomedicine, proton conduction, sensors, SCs etc. [11]. MOF are suitable for SCs as electrode materials because of their controllable pore sizes, metal ions with redox activity and high specific surface area [12–14]. The structure of MOF which include chemical structure and the geometries of the organic linkers is also an important parameter which affects their electrochemical performance [15]. The commonly used organic linkers with carboxylic acid functionality are benzene 1,4-dicarboxylic (terephthalic) acid, benzene 1, 3, 5-tricarboxylic acid (TMA, trimesic acid), and benzene 1, 2, 4, 5-tetra carboxylic acid. In this work, benzene 1, 3, 5-tricarboxylic acid (trimesic acid) was taken as organic linker [16]. Among the transition metals, Ni and Co have been selected in our study due to their abundance (ranked fifteenth and nineteenth in the Earth crust) [17], eco-friendly nature and low cost [18]. Ni-MOF as electrode materials for SCs exhibits high specific capacitance ($C_s$) with poor rate capabilities, whereas Co-MOF possesses low $C_s$ with excellent rate capabilities. An effective method to improve the rate capability of Ni-MOF is the introduction of Co metal ions into their MOF textures, which promotes electrochemical performance [17].

Electrochemical performance of various Ni-MOF, Co-MOF and Ni/Co-MOF based electrode materials are summarized in table 1. Numerous studies have confirmed that incorporation of Ni and Co metal ions into an organic framework is an efficient approach to improve their electrochemical performance in SCs. It was noticed that, the metal coordinated with organic ligand influences the morphological structure of MOF’s. For instance, the metal Ni would form a variety of hierarchical meso and microporous MOF’s structures such as flower, accordion and zigzag chain. On the other hand, Co-MOF were observed in layers and hexagon micro blocks depending on the synthesis conditions. Its noteworthy to mention that, the presence of Ni and Co metal ions together in MOF’s lead to various morphologies such as flower, symmetric geometry with cuboid rod microcrystals, wrinkled and crumpled nanosheets, dandelion like structures and hence influencing the electrochemical performance of SCs due to synergetic effect [9, 19]. It is worth mentioning that, the presence of Co metal ions in the Ni-MOF matrix improves cyclic stability reported in the literature that is presented in table 1. In the present work, Ni-MOF, Co-MOF and Ni/Co-MOF are hydrothermally synthesized and studied their supercapacitance behavior. The doping of Co metal ions into the Ni-MOF matrix results in increasing crystallinity of Ni/Co-MOF and operational potential window. Amongst the MOFs investigated, Ni/Co-MOF exhibited $C_s$ of 980 F g⁻¹ at a current density of 2.5 A g⁻¹. Ni/Co-MOFs delivered a maximum energy density (ED) of 55.7 Wh Kg⁻¹ at a corresponding power density (PD) of 1 K W Kg⁻¹ and maximum PD of 9.8 K W Kg⁻¹ at an ED of 41.6 Wh Kg⁻¹. An outstanding supercapacitance performance with superior cyclic efficiency of 98.4% and capacitive retention of 73% after 5000 cycles. Thus, Ni and Co-based MOF were studied as a novel promising electrode material for SCs.

2. Material and methods

The chemicals used in this work were Nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O), Cobalt nitrate hexahydrate (Co(NO₃)₂.6H₂O), Dimethylformamide (DMF), Trimesic acid, Potassium hydroxide (KOH), Polyvinyl difluoride (PVDVF), N-Methylpyrrolidone (NMP), Ethanol, and Isopropyl alcohol (IPA) of analytical grade obtained from a commercial source and were used without any further purification.
2.1. Synthesis of MOFs
Ni-MOF, Co-MOF and Ni/Co-MOF were synthesized using trimesic acid as organic linker and Ni, Co metal ions from their respective nitrate salts at room temperature. These MOFs were synthesized by a simple hydrothermal method to obtain uniform sized molecules of MOF’s [20]. The following procedure was adopted to synthesize individual as well as bimetallic MOF. Trimesic acid (0.0525 g, 0.25 mmol) and Ni (NO3)2.6H2O (0.4362 g, 1.5 mmol) were dissolved in 30 ml of N, N-dimethylformamide DMF with stirring at room temperature. The mole ratio of trimesic acid and Ni2+ was set to 1:6 [20]. After stirring for 30 min, the obtained light green solution was then transferred to a 100 ml Teflon-lined autoclave and heated to 170 °C for 16 h. After cooling to room temperature, the precipitate was centrifuged and washed with DMF and ethanol several times. Finally, the obtained product was dried in a vacuum oven at 80 °C for 24 h. Similarly, Co-MOF and Ni/Co-MOF were also prepared. Different coloured MOFs (Ni-MOF- light Green, Co-MOF- Purple, Ni/Co-MOF- light purple) were obtained depending on metal ions present in the system. The mole ratio of Ni and Co ions were taken 1:1 in the preparation of Ni/Co-MOF which exhibited maximum supercapacitance properties [18].

2.2. Material characterization
The crystallinity of the individual and bimetallic MOF’s was characterized by powder x-ray diffraction instrument Bruker, D8 ADVANCE ECO using Copper Kα radiation (λ = 0.154 nm). The Fourier transform infrared spectra were recorded on Shimadzu IRAfinity-1SWL instrument. The morphology and elemental mapping of individual and bimetallic MOF’s were examined by scanning electron microscopy/energy-dispersive x-ray spectroscopy (SEM-EDS: Zeiss ULTRA 55, Germany). High-Resolution Transmission Electron Microscope (HR-TEM) images of individual and bimetallic MOF’s were recorded on Jeol/JEM 2100 at an acceleration voltage of 200 kV. Brunner Emmett Teller (BET) surface areas of all the samples were acquired on Belsorp Max instrument. Initially the samples were degassed at 120 °C for 16 h and subjected to N2 adsorption desorption measurement.

2.3. Electrochemical studies
The comparison of electrochemical performance of Ni-MOF, Co-MOF and Ni/Co-MOF was carried out using the techniques such as cyclic voltammetry (CV), chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS) using CHI 660E electrochemical workstation with a three-electrode system in 1 M KOH electrolyte. The three-electrode system consisting of working electrode (Toray carbon paper coated with active material), a reference electrode (Saturated Calomel Electrode), and a counter electrode (platinum wire). The working electrodes were fabricated by mixing 85 wt% of active material with 10% of Ketjen black in mortar along with a binder (5 wt% of polyvinylidenedifluoride dissolved in 1-methyl-2-pyrrolidinone- NMP). The prepared slurry was coated on a pre-weighed current collector (Toray carbon sheet) of area 1 cm2. The electrodes were vacuum dried for 12 h and further active masses were calculated. The electrochemical performance of the materials were studied in three electrode system and compared their Cw, ED, PD and cycle stability.

3. Results and discussion

3.1. Powder-X-ray diffraction (P-XRD)
The powder X-ray diffraction patterns of Ni-MOF, Co-MOF and Ni/Co-MOF are provided in figure 1. Ni and Co MOFs were found to be crystalline, on the other hand, Ni/Co-MOF was highly crystalline in comparison with Ni and Co MOFs as observed from XRD patterns. The XRD pattern of Ni-MOF exhibits diffraction peaks at 11.8°, 18.01°, 20.83°, 22.28°, 23.83°, and 33.48°, corresponding to (11–1), (150), (151), (220), (02–4) and (025) planes of Ni-MOF, respectively [26]. The diffraction pattern of the Co-MOF is in good agreement with the literature [27] and XRD pattern of Ni/Co-MOF exhibits evident diffraction peaks similarity with literature, probably have the layered topology crystal structure which is built by connected central metal ions with BDC ligands to form a 2D layered structure [9]. The two sharp peaks indicated at 2θ, 12.9° and 25.8° of Ni/Co-MOF correspond to d-spacing of 0.39 nm and 0.19 nm respectively.

3.2. Fourier transform infrared spectroscopy (FTIR)
The FT-IR spectra of Ni-MOF, Co-MOF and Ni/Co-MOF’s are shown in figure 2. FT-IR spectra verifies the presence of organic compounds and the formation of new functional groups in as-synthesized MOFs. FT-IR spectra of Ni-MOF, Co-MOF and Ni/Co-MOF, exhibits almost the same peak position except two extra peaks in spectra of Ni/Co-MOF. The broad bands at 3483 cm−1 and 2857 cm−1, which are found only in Ni/Co-MOF are attributed to the presence of hydroxyl groups and CH stretching vibration respectively [24]. Two strong bands at ~1629 and ~1286 cm−1 were assigned to the asymmetric and symmetric stretching modes of the coordinated (COO−) group respectively [28].
The peak at 1286 cm\(^{-1}\) is ascribed to the stretching vibration of C–O bond in the uncoordinated free carboxyl on the surface of the MOFs [29]. The band at 636 cm\(^{-1}\) was attributed to the stretching vibrations of para-aromatic CH groups and \(\delta\)-OH [28]. The separated bands between the asymmetric and symmetric stretching modes indicate that, \(\text{–COO}–\) of trimesic acid is coordinated to Ni\(^{2+}\) or Co\(^{2+}\) or Ni\(^{2+}\)/Co\(^{2+}\) via a bidentate ligand mode and the \((\text{BDC})^3\) metallic exhibits a polymeric structure [28]. This evidence can further confirm that the as-prepared samples are having MOF structure. The absorptions around 450 cm\(^{-1}\) can be ascribed to metal–oxygen–hydrogen bending vibration (Ni–OH or Co–OH or Ni–Co–OH in this system) [30].

3.3. Scanning electron microscopy (SEM)/Energy dispersive x-ray spectroscopy (EDS)

The SEM images of Ni-MOF, Co-MOF and Ni/Co-MOF are provided in figure 3. It can be clearly seen that the porous Ni-MOF exhibits flower-like structure in the range of 700 nm to 1.2 \(\mu\)m size (figure 3(a)). In Co-MOF, it is observed that the internal spinal structure of nanorods is more equally distributed in a scattered way than the aggregated state of Ni-MOF. The diameter of nanorod has appeared in the range of 15 to 25 nm (figure 3(b)). Ni/Co-MOF (figure 3(c)), showed nanolayered sheet morphology. Furthermore, EDS analysis was further

![Figure 1. XRD patterns of Ni-MOF, Co-MOF and Ni/Co-MOF.](image)

![Figure 2. FT-IR spectra of Ni-MOF, Co-MOF and Ni/Co-MOF.](image)
conducted to confirm the elemental composition of Ni-MOF, Co-MOF and Ni/Co-MOF. EDS analysis confirmed the presence of respective elements in all three MOFs.

3.4. High-resolution transmission electron microscopy (HR-TEM)

More details of the structural features of porous Ni-MOF, needle-like Co-MOF and layered Ni/Co-MOF were investigated by HR-TEM (figures 4(a)–(c)) and selected area electron diffraction (SAED) (figures 4(d)–(e)). Ultrathin nanosheets (figure 4(a)) with curled edges of Ni-MOF appears as sepal of flower with the thickness of approximately less than 5 nm and nano rods with high density was observed in Co-MOF (figure 4(b)). HR-TEM images (figure 4(c)) of Ni/Co-MOF confirms that overlapping nanoflakes of various sizes are present. The SAED patterns of Ni/Co-MOF clearly indicates the presence of high degree of crystallinity than Ni-MOF and Co-MOF.

3.5. Brunner Emmett Teller (BET) surface area analysis

The surface properties such as surface area, Pore size distribution (PSD) and pore diameter of the synthesized MOFs were examined by Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods. Figure 5 represents the N$_2$ adsorption desorption isotherms and PSD plots of Ni-MOF, Co-MOF and Ni/Co-MOF. Both Ni-MOF and Ni/Co-MOF exhibited typical type IV isotherm consisting of a hysteresis loop in a relative pressure range 0.4 to 0.9 indicating the mesoporous nature of MOFs. Furthermore, a vertical increase was observed in N$_2$ adsorption-desorption isotherms at low P/P$_o$ of Ni-MOF and Ni/Co-MOF. This indicates that a large number of micropores are present in both Ni-MOF and Ni/Co-MOF.

Table 2 gives the surface area, pore size distribution (PSD) and pore diameter of all the MOFs. Amongst the MOFs, Ni/Co-MOF exhibited high surface area of 126.6 m$^2$ g$^{-1}$ followed by Ni-MOF and Co-MOF. While the pore size remained nearly same. It is noteworthy that, the pore volume is more in case of Ni/Co-MOF and Ni-MOF in comparison to Co-MOF. From the PSD, it is noticed that the MOFs contains both micro and mesopores with maxima centred at 1.99, 2.47 and 2.29 nm for Ni-MOF, Co-MOF and Ni/Co-MOF respectively. Surface area and pore volume of Ni/Co-MOF is higher than Ni-MOF and Co-MOF is presumed to enhances electrochemical performance [9].
3.6. Electrochemical studies

The electrochemical studies of Ni-MOF, Co-MOF, and Ni/Co-MOF were initially examined by CV measurements in three electrode system using standard calomel electrode as reference and platinum wire as counter electrodes respectively at varied potential window ranging between $-0.2$ V to $0.7$ V in 1 M KOH solution. Initially, the stabilization of working electrodes were carried out by running 30 continuous CV cycles at a scan rate of $10$ mV s$^{-1}$. CV responses were recorded at different scan rates such as $2$, $5$, $10$, $20$, $30$, $40$, $50$, $60$, $70$, $80$, $90$ and $100$ mV s$^{-1}$ in the potential range $-0.1$ to $0.7$ V for Ni-MOF, $-0.2$ to $0.5$ V for Co-MOF and $-0.1$ to $0.6$ V for Ni/Co-MOF are provided in figures 6(a)–(c). The shape of the CV curves clearly indicates the presence of distinct redox peaks during the anodic and cathodic sweeps which contributes to the faradic pseudo capacitance.

The faradaic reaction occurring at the electrode-electrolyte interface arises due to Ni or Co or Ni/Co cations in the MOFs [25]. The current under CV curve increases with scan rate increase, indicating that voltammetric current is directly proportional to the scan rate, as expected for an ideal capacitive behaviour [31]. It is noticed that, with increase in scan rate anodic and cathodic peaks shift more towards positive and negative potential respectively. This was due to increasing internal diffusion resistance within the redox active material as scan rate was increased. Figure 6(d) represents a comparative CV plot of Ni-MOF, Co-MOF, and Ni/Co-MOF at a scan rate of $5$ mV s$^{-1}$, indicating much larger area for Ni/Co-MOFs than other MOFs. This suggests that, the larger amount of charges can be stored in the Ni/Co-MOF. The $C_s$ of Ni-MOF, Co-MOF, and Ni/Co-MOF for different scan rates were calculated using following equation [32].

$$C_s = \frac{1}{vW(V_a - V_c)} \times \int_{V_a}^{V_c} i \times Vdv$$

Where, $C_s$ is the specific capacitance in F g$^{-1}$, $V$ is the applied potential window ($V_a$ to $V_c$), $v$ is the scan rate in mV s$^{-1}$ and $W$ is the weight of the active material in g. The maximum $C_s$ obtained was 2041 F g$^{-1}$ for Ni/Co-MOF followed by Ni-MOF (1601 F g$^{-1}$) and Co-MOF (351 F g$^{-1}$) at a scan rate of $2$ mV s$^{-1}$. It is understood that, presence of both Ni and Co in MOFs has drastically improved the $C_s$ values up to 6 times as observed in pure Co-MOF. The lower $C_s$ of Co-MOF may be attributed to lower surface area available for the redox reactions. Herein, equal ratio of Ni:Co was taken as it contributes increased conductivity due to the relatively low activation energy for electron transfer between cations [18, 31]. It was noticed from figure 6(e) that, the $C_s$ values for all the materials
were found to be high at lower scan rates and eventually decreases with increase in scan rate. This is attributed to the fact that, at lower scan rates OH– ions get sufficient time to diffuse into micro and mesopores of MOFs electrodes contributing to higher pseudo capacitance and at higher scan rates, the duration of OH– ions diffusion is limited, resulting in a decreasing value of Cs\[^{33, 34}\]. However, it must be noted that, though Ni/Co MOFs exhibited highest Cs at low scan rates, the Cs decreased drastically with increase in scan rate. This may be due to greater shift in redox peak potential moving out of working potential. High surface area of Ni-MOF and Ni/Co-MOF leads large surface-to-volume ratio which favoured in supercapacitors, since it offers, a large contact area between electrode and electrolyte which reduces the OH– ion diffusion pathway\[^9, 35\].

To further investigate the electrochemical performance of Ni-MOF and Co-MOF, Chronopotentiometry (CP) was used at different current densities such as 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25 A g\(^{-1}\) and for Ni/Co-MOF, applied current densities are 2.5, 5, 7.5, 10, 12.5, 15, 17.5, 20, 25, 30 and 35 A g\(^{-1}\) in the various working potential range between \(-0.2 \text{ V to 0.55 V. Discharge curves of Ni-MOF, Co-MOF and Ni/Co-MOF at various}

![N\(_2\) adsorption desorption isotherms (inset: pore size distribution plot) of (a) Ni-MOF, (b) Co-MOF and (c) Ni/Co-MOF.](image)

**Table 2.** BET surface area (m\(^2\) g\(^{-1}\)), pore volume (cm\(^3\) g\(^{-1}\)) and mean pore diameter (nm) of Ni-MOF, Co-MOF and Ni/Co-MOF obtained using the N\(_2\) absorption-desorption isotherms.

| MOF      | BET surface area (m\(^2\) g\(^{-1}\)) | Pore volume (cm\(^3\) g\(^{-1}\)) | Mean pore diameter (nm) |
|----------|-------------------------------------|---------------------------------|-------------------------|
| Ni-MOF   | 104.35                              | 0.2034                          | 7.795                   |
| Co-MOF   | 11.40                               | 0.0179                          | 6.3084                  |
| Ni/Co-MOF| 126.67                              | 0.2463                          | 7.7785                  |
current densities in the potential range $-0.1$ to $0.45$ V for Ni-MOF, $-0.2$ to $0.5$ V for Co-MOF and $-0.1$ to $0.55$ V for Ni/Co-MOF are given in figure 7(a)–(c). Nonlinear nature of discharge curves from CP confirms that the pseudocapacitive behaviour of Ni-MOF, Co-MOF and Ni/Co-MOF, consistent with CV patterns. Based on Charge-discharge curves, $C_s$ was calculated for different current densities by using following formula [32].

$$C_s = \frac{I \times t_d}{W \times \Delta V}$$

Where, $C_s$ is the specific capacitance in F g$^{-1}$, $I$ is the applied current density in A, $t_d$ is the discharge time in s, $W$ is the weight of the active material in g and $\Delta V$ is the electrochemical potential window in V. From $C_s$,
calculations it is clear that, the $C_s$ achieved from Ni/Co-MOF (980 F g$^{-1}$) is larger than that of Co-MOF (125 F g$^{-1}$) and Ni-MOF (716 F g$^{-1}$). Higher $C_s$ of Ni/Co-MOF was originated from higher redox activities present in Ni/Co-MOF than in Ni-MOF and Co-MOF. With the increase in current density, the $C_s$ of Ni-MOF, Co-MOF and Ni/Co-MOF was decreased due to lower diffusion rates of OH$^-$ ions into the electrodes [36]. Furthermore, With the increase in current density, the $C_s$ of Ni/Co-MOF found to be 538 F g$^{-1}$ even at 25 A g$^{-1}$. This results clearly concludes Ni/Co MOF has good $C_s$ retention at higher current densities than Ni-MOF and Co-MOF. Void spaces formed from the intersections of these flake-like structures can offer a highly stable architecture that may be beneficial for the antidegradation and anti-collapse of the hierarchical structure when subjected to high cycle rates [19].

The important parameters determining the electrochemical performance of a SC device are the cycle stability, columbic efficiency, ED and PD. Herein, cycle stability analysis of Ni-MOF, Co-MOF and Ni/Co-MOF
were studied up to 10000 cycles. Ni-MOF exhibits less capacitance retention even with achieving higher $C_s$ than Co-MOF, wherein Co-MOF exhibits good cycle stability with capacitance retention nearly 100% after 5000 charge discharge cycles. The presence of Ni and Co metal ions in MOF achieves highest $C_s$ with moderate capacitance retention of 73% after 5000 charge discharge cycles. The columbic efficiencies of Ni-MOF, Co-MOF and Ni/Co-MOF were calculated by using following equation [32].

$$\eta = \frac{t_d}{t_c} \times 100$$

Where, $\eta$ is the Columbic efficiency in %, $t_c$ and $t_d$ are charging and discharging time in s. The plot of columbic efficiency against cycles are provided in figure 8(b). The columbic efficiency was retained till 98.4% after 5000 charge-discharge cycles. The observed high specific capacity, cyclic stability and Columbic efficiency are mainly due to the superior morphology of Ni/Co-MOF. Vijayakumar S et al observed that the thin layered nanosheets of Ni/Co-MOF has high surface to volume ratio that provides a large number of active sites for ion transfer [36]. ED and PD are two main critical parameters which evaluate the practical performance of supercapacitors. ED and PD are calculated by CP measurements using following equations [32].

$$ED = \frac{1}{2} \times C_s \times \Delta V^2 \times \frac{1}{3.6}$$

$$PD = \frac{ED}{t_d} \times 3600$$

Where, $ED$ is the energy density in W h Kg$^{-1}$, PD is the power density in W Kg$^{-1}$, $C_s$ is the specific capacitance in F g$^{-1}$, $\Delta V$ is the working potential range in volts and $t_d$ is the discharge time in s. The Ragone plot of Ni-MOF, Co-MOF and Ni/Co-MOF are given in figure 8(c). It’s remarkable that, higher ED of 55.7 W h Kg$^{-1}$ was achieved for Ni/Co-MOF due to higher specific surface area, pore size, additional redox reaction and electrical conductivity of Ni/Co-MOF than individual MOFs. The Ni/Co-MOF also offered a high PD of 9.8 KW Kg$^{-1}$ at an ED of 41.6 W h Kg$^{-1}$. Ni/Co-MOF exhibited high discharge time, $C_s$, ED and PD than individual MOFs.

Figure 8. (a) Life cycle test of Ni-MOF, Co-MOF and Ni/Co-MOF (b) Plot of capacitance retention and columbic efficiency of Ni/Co MOFs at current density 15 A/g. (c) Ragone plot obtained for Ni-MOF, Co-MOF and Ni/Co-MOF.
Electrochemical impedance spectroscopy (EIS) analysis was carried out to understand frequency dependency on supercapacitive performance and resistance offered by Ni-MOF, Co-MOF and Ni/Co-MOF in a frequency range of $10^{-2}$ to $10^5$ Hz at bias potential. Nyquist plots ($Z''$ imaginary versus $Z'$ real axis) of Ni-MOF, Co-MOF and Ni/Co-MOF was shown in figure 9(a). Nyquist plots consist of three regions i.e., intercept on the real $Z'$ axis at high frequency region, semicircle and straight line at low-frequency region. However, the intercept on the real axis at high frequency region is generally due to electrolyte resistance which arises due to combined resistance (solution resistance ($R_s$)) of ionic, electronic, intrinsic, diffusive and contact resistance between electrode and current collector [32]. It was noticed that, lower $R_s$ (1.85 $\Omega$) was observed in Ni/Co-MOF than individual MOFs. The diameter of the semicircle at low to high frequency region was owing to charge transfer resistance ($R_{ct}$) due to pseudocapacitive reactions and EDLCs. Higher $R_{ct}$ was found in Ni/Co-MOF than other MOFs, due to its higher polarization effect and charge transfer mechanisms. Nearly Straight line at the low-frequency region refers to superior capacitive performance of electrode without ion diffusion limitation [36].

Nyquist plot of Ni/Co-MOF clearly indicating a nearly vertical line, represents good capacitive nature compare to individual MOFs [37]. The inset shows impedance plot, further resistive and capacitive elements analysed using the ZSimpWin 3.21 software based on the well fitted electrical equivalent circuit $R_{ct}$($R_s$)(CdlRct)(CpRect)W.

The electrical equivalent circuit involves solution resistance ($R_s$), charge transfer resistance ($R_{ct}$), electron transfer resistance ($R_{ct}$), double layer capacitance (Cdl) and pseudocapacitance (Cp) [32]. The $C_s$ was calculated from EIS data using following equation [32].

$$C_s = \frac{1}{(2\pi f Z'')}$$

Where, $C_s$ is the specific capacitance in F g$^{-1}$, $f$ is the frequency in Hz and $Z'$ is the imaginary axis. The Ni-MOF, Co-MOF and Ni/Co-MOF exhibited $C_s$ of 395, 304 and 512 F g$^{-1}$ respectively (figure 9(b)). The dependency of
phase angle on frequency was exhibited in Bode plot of Ni-MOF, Co-MOF and Ni/Co-MOF was given in figure 9(c). The phase angle of ideal capacitor was $-90^\circ$, however in Ni/Co-MOF and Ni-MOF it was observed $-74.5^\circ$ and $-75.5^\circ$ nearly $-90^\circ$, whereas in Co-MOF phase angle was observed around $51^\circ$. The higher phase angle represents superior ideal capacitive nature of Ni-MOF and Ni/Co-MOF compare to Co-MOF. The electrochemical performance of the materials were also confirmed by comparing the electrochemical impedance spectroscopy (EIS) data of Ni/Co-MOF before and after testing for 10,000 cycles [38]. The solution and charge transfer resistances becomes less even after 10,000 cycles in the case of Ni/Co-MOF indicating that, the material has high stability with respect to its structure and morphology.

4. Conclusion

In summary, Ni-MOF, Co-MOF and Ni/Co-MOF were prepared by a facile hydrothermal process. The structural properties of hierarchical Ni/Co-MOF were confirmed from structural characterization. The electrochemical evaluation confirms that highly crystalline Ni/Co-MOF in 1 M KOH exhibits superior electrochemical performance with outstanding C$_e$ of 2041 F g$^{-1}$ at 2 mV s$^{-1}$ from CV and 980 F g$^{-1}$ at 2.5 A g$^{-1}$ from CP. The ED and PD for Ni/Co-MOF were determined as 55.7 W h Kg$^{-1}$ & 1 K W kg$^{-1}$ at a current density of 2.5 A g$^{-1}$. The Ni/Co-MOF also offered a high PD of 9.8 K W kg$^{-1}$ at an ED of 41.6 W h Kg$^{-1}$. Ni/Co-MOF also exhibited excellent columbic efficiency of 98.4% and 73% of capacitive retention after 5000 cycles. The superior electrochemical performance of highly crystalline Ni/Co-MOF than individual MOFs makes this material as one of the promising electrode materials for supercapacitors.

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