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Solvothermal Synthesis of Nickel-Based Metal-Organic Frameworks for Supercapacitor Application

Sadiya Nuhu[a], Abdussamad Mukhtar Mohammed[b], Mohammed Zaharaddeen Musa[a,c],
Halima Aliyu[a], Habu Abba[b], G. Mukhtar[d], Abdulrahim Ibrahim[e],
Nasar Mansir [a] and Mustapha Balarabe Idris[a,*]

[a] Materials Electrochemistry and Energy Storage Devices Laboratory,
Department of Chemistry,
Faculty of Physical Sciences,
Federal University Dutse,
Jigawa 7156,
Nigeria.

[b]Department of Chemistry,
Faculty of Science,
Yobe State University,
Damaturu,
Nigeria.

[c]Department of Physical and Chemical Sciences,
Faculty of Science,
Federal University of Health Sciences,
Ila-Orangun,
Osun State,
Nigeria.

[d] Department of Science Education,
Faculty of Education,
Bauchi State University,
Gadau,
Bauchi State,
Nigeria

[e] Department of Pure and Applied Chemistry,
Kaduna State University,
Nigeria.

Email: idris.mb@fud.edu.ng

**Author for Correspondence*

Abstract

In the field of energy storage and conversion, metal-organic frameworks (MOFs), have garnered a lot of attention because of their special qualities, which include their large surface area, regulated morphology, and adjustable pore size structures. MOFs with the combined properties of electric double-layer capacitance and pseudo capacitance have been investigated as supercapacitor electrode materials. It has been observed that the kind of coordinating ligand employed during synthesis has a major impact on both the textural and surface characteristics of MOF. In this study, we reported a synthesis of nickel-based metal-organic frameworks (Ni-MOF) by a simple solvothermal method. The microscopic studies revealed that the as-synthesized material exhibits a rod-like morphology with a high crystallinity as confirmed by microstructural and powdered X-ray diffraction analysis respectively. The electrochemical studies revealed that the as-prepared electrode materials exhibit a specific capacitance of 814.6 F g^{-1} at a current density of 6 A g^{-1} in a 1 M KOH aqueous electrolyte.

Keywords: Energy density, Renewable energy, Metal-organic frameworks, Supercapacitor, Solvothermal.

INTRODUCTION

Supercapacitors (SCs) are among the most promising electrochemical energy storage devices for intermittent renewable energy storage owing to their high-power density, long cycle life, low cost of maintenance, etc (Iwama *et al.*, 2017). SCs are divided into two categories: electric double-layer capacitors and pseudocapacitors, depending on how they store charge. While electric double-layer capacitors exhibit excellent rate capability and close to unlimited cycle life, pseudocapacitors deliver high energy density at the expense of low energy density and inferior cycling stability. The metal-organic frameworks (MOFs), also known as porous coordination organic polymers have been investigated as a promising electrode material for SCs due to their unique properties such as tunable pore size, variable structure, and high surface area compared with the other types of electrode materials like carbon-based materials, transition metal oxides and conducting polymers (Fracaroli et al., 2014). Due to their large surface area and variable oxidation states arising from the central metal ions, MOFs combine the characteristics of both pseudocapacitance and electric double-layer capacitance and thus exhibit superior specific capacitance (Ke *et al.*, 2015; Li et al., 2019). The major drawbacks of MOFs when utilised as electrode material for SC are low conductivity and structural collapse which results in sluggish kinetics towards the diffusion of electrolyte ions and poor cycling stability respectively, (Idris *et al.*, 2024; Yan *et al.*, 2016). Various strategies were adopted to overcome these drawbacks (Calbo *et al.*, Raza *et al.*, 2023). Regarding the morphology and electrical properties of MOFs, it has been established that the molecular length of organic linkers influences the pore size and surface area of MOFs (Chong *et al.*, 2023). For example, the proportion of BTC to PTA ligands was varied to create the Ni-based MOF layered structure by Zhang *et al.*, 2020. The material synthesized delivered a capacitance value of 920 F g^{-1} at a current density of 1 A g^{-1} after applying as an electrode for SCs (Zhang *et al.*, 2020). Another investigation carried out by Yang's teams involved the preparation of a layered structure Ni-MOF which exhibits a specific capacitance of 1127 F g^{-1} at a current density of 0.5 A g^{-1} (Yang *et al.*, 2014). Using trimesic acid as an organic ligand, Du's group developed a hierarchical porous Ni-MOF nanostructure, the results show the specific capacitance of 1057 F g^{-1} at 1 A g^{-1} current density (Du *et al.*, 2018). The ultrasonication method was used by Yan's group in synthesizing accordion-like Ni-MOF and the material delivered an excellent specific capacitance of 988 F g^{-1} at a current density of 1.4 A g^{-1} and good rate capability (Yan *et al.*, 2016). Meanwhile, a three-dimensional open structure Ni-MOF (Ni(II) [Ni_2(H0.67bdt)3] ·10.5H_2O]) was synthesized by Ouellette team (Ouellette *et al.*, 2011), using 1, 4-bis(1H - tetrazol -5 - yl)benzene(H_2bdt) as ligand, and the study have shown that the ligand

H_2bdt can participate in up to five different types of coordination modes with metal ions (Qiao et al., 2011; Zhang et al., 2016). We described in this work the synthesis of nickel-based metal-organic frameworks (Ni-MOF) using a straightforward solvothermal method. The prepared material exhibits a rod-like morphology with a high crystallinity as confirmed by microstructural and powdered X-ray diffraction analysis respectively. The electrochemical studies revealed that the as-prepared electrode materials exhibit a specific capacitance of 814.6 F g^{-1} at a current density of 6 A g^{-1} in a 1 M KOH aqueous electrolyte.

MATERIALS AND METHODS

Materials

Carbon black, double distilled water (DD-water), ethanol, iso-nicotinic acid ($C_6H_5NO_2$), N-methyl-2-pyrrolidine (NMP), sodium hydroxide (NaOH), polyvinylidene difluoride (PVdF), Whatman filter paper, and nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) were obtained from Sigma-Aldrich and utilised without undergoing additional purification.

Methods

Synthesis of Ni-based MOF

The synthesis of Ni-based MOF was carried out using a simple solvothermal method. Typically, 5.7 mmol of nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) and 2.4 mmol of iso-nicotinic acid ($C_6H_5NO_2$) which is equivalent to 7.3 and 26.1 % were added distinctly in 5 mL of NMP under vigorous stirring. Afterwards, 1 M solution of sodium hydroxide (NaOH) was added dropwise until a pH of 7 was achieved and the stirring was kept up at room temperature for 30 minutes. Subsequently, the mixture was put into a 50 mL Teflon-lined stainless-steel autoclave and heated for 18 hours at 180 °C. Subsequently, the Teflon-lined stainless-steel autoclave was removed then the solution was naturally allowed to cool to ambient temperature. The Ni-based MOF was recovered after a series of filtration and washing using distilled water and finally with ethanol. The produced samples were dried for six hours at 60 °C. The synthesized metal-organic frameworks containing nickel (Ni-MOF) synthesized at 180 °C, was named as Ni-MOF.

Physicochemical characterization of as-synthesized Ni-MOF

FTIR spectroscopy, energy dispersive X-ray spectroscopy (EDS), powder X-ray diffraction (PXRD), and scanning electron microscopy (SEM) were used to effectively characterise the synthesised Ni-based MOF nanomaterial.

Electrochemical characterization

As-prepared samples were electrochemically characterised using a three-electrode setup. In preparing the electrode, 70 wt % of the active material was grounded with 20 wt % of carbon black and 10 wt % of polyvinylidene fluoride. The mixture was made into a slurry by adding a few drops of NMP. The obtained slurry is coated onto stainless steel foil. The electrolyte was a 1 M KOH aqueous solution. Ag/AgCl and Pt foil were employed as reference and counter electrodes, respectively, while the active material-coated electrode functioned as the working electrode. Different scan speeds and current densities were used to record galvanostatic charge-discharge (GCD) and cyclic voltammograms (CVs), respectively.

RESULTS AND DISCUSSION

Physicochemical Characterization

The scanning electron microscopic (SEM) images of as-prepared Ni-MOF are shown in Fig. 1. The low magnification SEM images of Ni-MOF reveal the formation of aggregated plate-like microstructures (Fig. 1a and Fig. 1b). An interjoined and well-defined structures with rod-like morphology were seen in the high-magnification image of Ni-MOF (Fig. 1c).

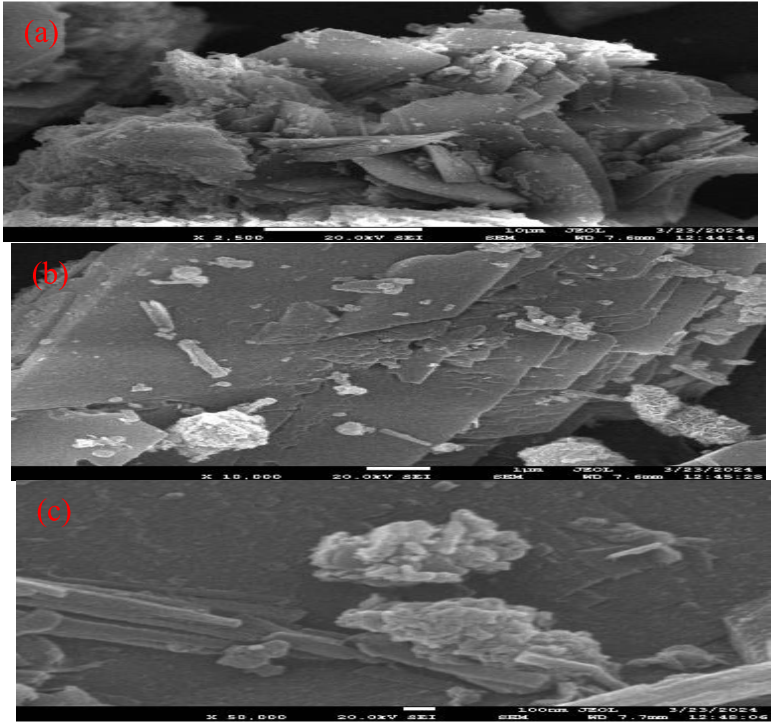

Fig. 1: SEM images of Ni-MOF recorded at (a,b) low magnification and (c) high magnification.

The Power X-ray Diffraction (PXRD) pattern of the prepared Ni-MOF is shown in Figure 2a and the peaks observed at 2θ of 8.2°, 10°, 12.5°, 25°, 17°, 23°, and 36° are indexed to Ni-based MOF (JCPDS No: 96-210-3422). The observed sharp and intense diffraction peaks indicate the formation of Ni-MOFs with a high degree of crystallinity which agrees well with the earlier reported literature (Manikandan et al., 2021; Zhang et al., 2020). The high purity of the sample is confirmed by the absence of additional peaks in the PXRD of Ni-MOF.

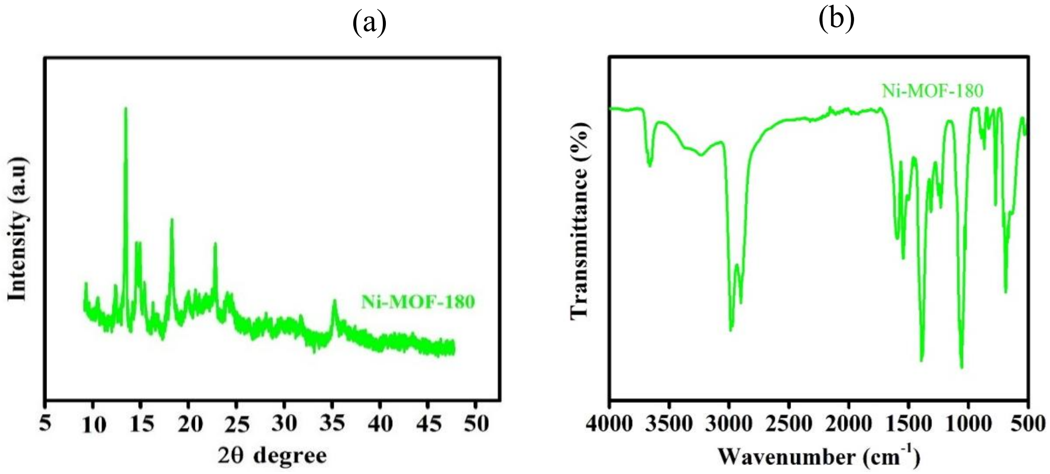

Fig. 2. (a) PXRD and FT-IR spectra of the prepared Ni-MOF.

Fig. 3b represents the FT-IR spectra of the prepared Ni-MOF. The band at 3675 cm^{-1} indicates the typical hydroxyl group (-OH) stretching vibration of the adsorbed water molecule, (Jiao et al., 2016). The absorption peak around 2978 cm^{-1} is attributed to C-H group stretching vibration, while 1921 cm^{-1} corresponds to the C-C stretching vibration in a ring. A bending vibration witnessed at 1591 cm^{-1} is ascribed to asymmetrical stretching vibration in the carboxylic group (-COO-). The peak at 1533 cm^{-1} is assigned to the bending stretching of C=C, whereas the peak at 1378 cm^{-1} corresponds to C-H stretching. An asymmetrical stretching of the metal hydroxyl bond (Ni-O-H) and stretching of the metal oxide (Ni-O) is witnessed at a wave number of 508 and 442 cm^{-1} respectively. The FT-IR results obtained in the presence study are in good agreement with the previous literature (Yang et al., 2014). The elemental analysis of the prepared Ni-MOF is investigated by using energy dispersive X-ray analysis and the result is presented in Fig. 3a. Only peaks corresponding to Ni, C and O were seen in the spectra of all Ni-MOFs which further confirm the purity of the samples. It can be seen that the elemental building blocks of Ni-MOF were uniformly distributed (Fig 3.3). The thermogravimetric curve of the as-prepared Ni-MOF is presented in Fig. 3b. The first weight loss observed in the range below 200°C, corresponds to the removal of adsorbed surface water molecules. The second weight loss witnessed in the range of 200-300°C is attributed to the removal of interstitial water molecules and unreacted ligands. While weight loss witnessed in the thermograms in the range of 400 °C to 600 °C is attributed to the breakdown of Ni-MOF into NiO (Yang et al., 2014).

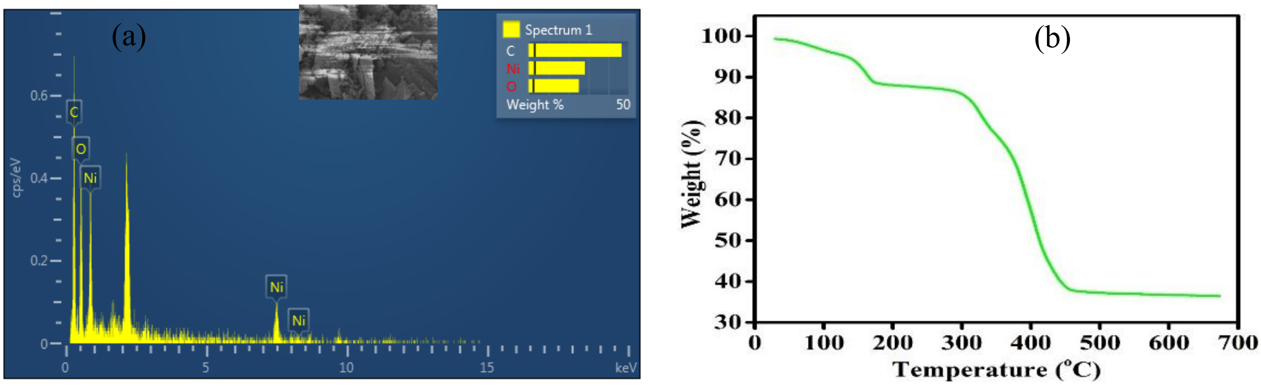

Fig. 3. (a) Energy dispersive X-ray spectra and (b) Thermogravimetric analysis curves of the prepared Ni-MOF.

Electrochemical characterization

The CVs were recorded in 1 M KOH electrolyte at a potential window of 0 to 0.5 V as shown in Fig. 4a-b. A pair of well-defined redox peaks were seen in all the CV of the prepared sample which reveals the pseudocapacitive nature of the material. It has been well established that Ni-based MOF undergoes intercalation/deintercalation of OH^- ions during charge/discharge in 1 M KOH electrolyte (Manikandan *et al.*, 2021). The increase in the ease of the redox reaction might be ascribed to the increase in the facile transport of the electrolyte ions offered by abundant porous structures in Ni-MOF. The metal nickel ion inside the MOF framework promotes the Faradaic redox process, which occurs at the electrode/electrolyte contact. The oxidation peak and reduction peak, in particular, go towards more negative and positive potential, respectively, as the scan rate is increased (Fig. 4b). Besides the shift in both reduction and oxidation peaks, an increase in the integrated area of the CV curve is observed in the Ni-MOF electrode (Wang *et al.*, 2015; Wang *et al.*, 2016).

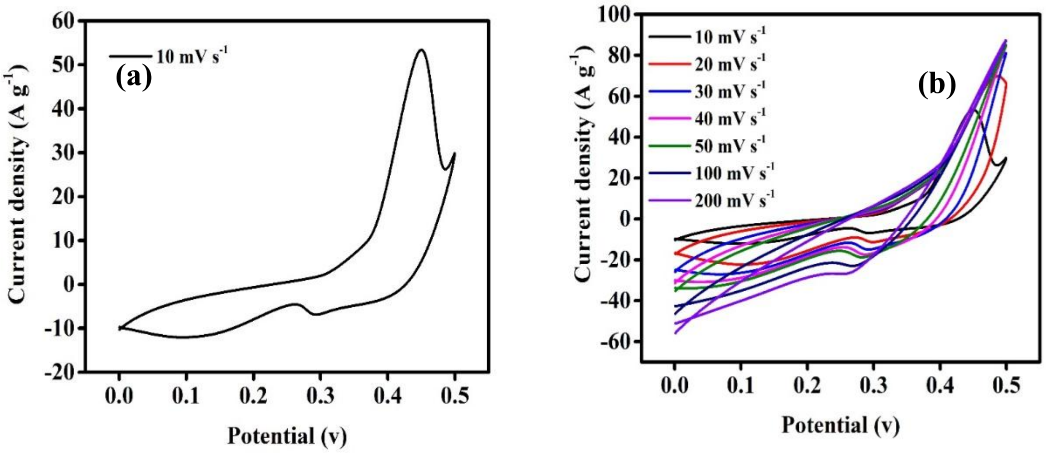

Fig. 4. CVs of the prepared Ni-MOF at a scan rate of 10 mVs^{-1} and (b) CVs recorded at various scan rates.

The galvanostatic charge-discharge (GCD) was carried out in 1M KOH electrolyte to further explore the pseudocapacitive properties of the prepared Ni-MOF electrodes and the results are presented in Fig. 5. The non-linear discharge curve further suggests that the capacitances of the as-prepared Ni-MOF are originated by the faradaic reactions which are consistent with the CV results (Fig. 5a). It is well observed that the Ni-MOF electrode demonstrates a longer discharge time at low current density (Fig. 5a).

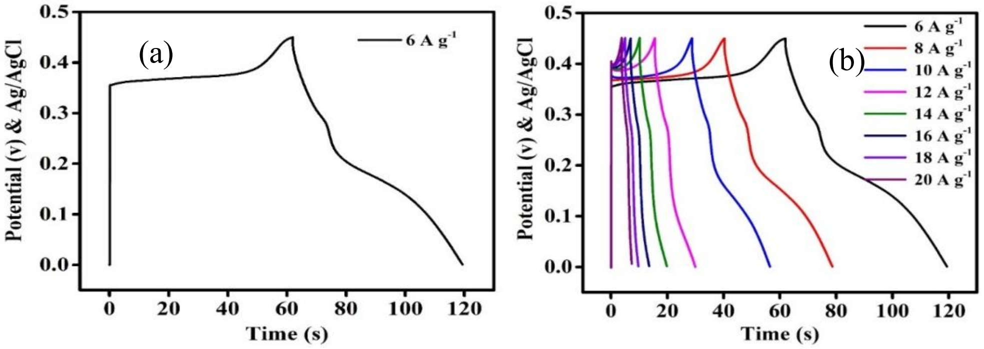

Fig. 5. (a) GCD of the prepared Ni-MOF at a current density of 6 A g^{-1} and (b) GCD recorded at various current densities.

The GCD curves were used to determine the specific capacitance values of the prepared Ni-MOF electrode (Fig. 5b), while the variation of specific capacitance as a function of current is presented in Fig. 6. It can be seen that the Ni-MOF electrode exhibits a specific capacitance of 814.6, 726.6, 675.3, 409.4, 319.5, 248.5, 199.1, and 164.7 F g^{-1} at a current density of 6, 8, 10, 12, 14, 16, 18 and 20 A g^{-1}, respectively. Furthermore, the electrode of Ni-MOF-180 could retain 21% of its initial specific capacitance when the current density is increased up to 20 A g^{-1} which reflects its moderate rate performance (Wang *et al.,* 2019; Zhou *et al.,* 2016).

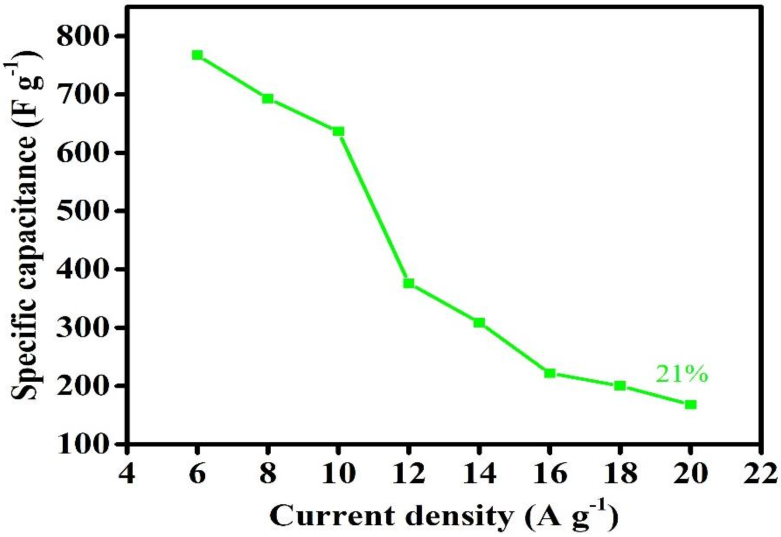

Fig. 6. Variation of specific capacitance as a function of current density for Ni-MOF electrode.

Conclusion

In summary, a Ni-MOF is successfully prepared by a simple solvothermal and the microscopic studies revealed that the as-synthesized material exhibits a rod-like morphology whereas the high degree of crystallinity of the sample is confirmed by X-ray diffraction analysis. The as-prepared electrode materials show a specific capacitance of 814.6 F g^{-1} at a current density of 6 A g^{-1} in a 1 M KOH aqueous electrolyte, according to the electrochemical studies. This material's smaller microsphere structure, which allows for greater interaction between the electrolyte and electrode for ion transport and access, is thought to be responsible for its good energy storage.

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