Synthesis and Characterization of Nickel Metal-Organic Framework for Supercapacitor Electrodes

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Abstract. A supercapacitor is a device of energy storage that boasts high energy and power density, utilizing an electrostatic double-layer mechanism and pseudocapacitance reactions to store energy. Electrode materials, like nickel, have garnered attention because of their high theoretical capacitance, availability, simplicity in production or synthesis, and chemical durability. In spite of these benefits, obstacles like poor rate capability and limited cycling properties hinder its widespread application. Nickel Metal-Organic Framework (Ni-MOF) was produced through solvothermal synthesis at 150°C and applied as a supercapacitor electrode. MOF-based material is chosen as a supercapacitor electrode because of its oustanding surface area, numerous mesopores, abundant active sites, and good electrical conductivity, all contributing to improving the supercapacitor's specific capacitance. Ni-MOF was synthesized and analyzed using multiple analytical methods, like X-ray diffraction (XRD), scanning electron microscope (SEM), and Brunauer-Emmett-Teller (BET) study to verify the material's structure and morphology. The Ni-MOF based supercapacitor's electrochemical performance was evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). The test findings demonstrate the great potential of this material for high-power energy storage applications by demonstrating that the supercapacitor with Ni-MOF electrodes has a specific capacitance of 90.7 F g^{-1} at a current density of 0.5 A g^{-1}.

Keywords: *energy storage, supercapacitor, nickel metal-organic framework, solvothermal, specific capacitance.*

Received ________, Revised _________, Accepted for publication __________

1 Introduction

One of the fundamental or necessary necessities of people is energy, particularly electrical energy. Power plants generate electrical energy from various sources of energy. According to the 2007 Energy Law and the 2014 National Energy Policy, the utilization of renewable energy will be developed in the long term. The primary energy mix is expected to contain 23% new and renewable energy by 2025 and 31% by 2050. Future electricity development, particularly in the generation sector, will continue to shift towards new and renewable energy or power plants with environmentally friendly technology, in line with PLN and the government's efforts to transition to Net Zero Emission (NZE). Indonesia, via the Ministry of Energy and Mineral Resources' (ESDM) press release No. 359.Pers/04/SJI/2021, a target has been set to reduce emissions and reach net zero by 2060 or earlier. To reach this goal, Indonesia has established five key principles: enhancing the adoption of new and renewable energy (NRE), decreasing fossil fuels, promoting electric vehicles in the transportation sector, boosting electricity usage in homes and businesses, and implementing carbon capture and storage (CCS). To support the provision of renewable energy (RE), energy storage is vital in maintaining a steady and dependable energy supply over long periods. Energy storage is essential because some sources cannot be relied upon indefinitely. The electrical grid faces several challenges, such as voltage fluctuations, reverse power flow, frequency variations, and harmonics. These challenges arise from the uncertainty of renewable energy generation. Wind doesn't always blow to drive turbines, sunlight cannot be optimally utilized during cloudy weather or at night, and even hydropower plants sometimes face the threat of drought.

Previously, electrical energy storage relied solely on batteries and capacitors. Because of their large energy storage and very low output, batteries have been the most popular and extensively utilised choice (Abdel Maksoud et al., 2020). Capacitors are still the most appropriate option, nevertheless, when large power levels of energy are needed. Despite their advantages, batteries and capacitors fall short in terms of storing high energy density and providing sufficient power output required for the efficient operation of new and renewable energy systems. Currently, energy conversion and storage systems make extensive use of supercapacitors. A supercapacitor is an electrochemical energy storage device with high energy density and power density, long lifespan, and short charging and discharging times, giving supercapacitors greater potential than batteries (Sun et al., 2018). Supercapacitors utilize a larger electrode surface area, with thinner electrolyte solutions and dielectric materials, reducing the distance between electrodes. Supercapacitors are described as capacitors that offer large storage capacity, much greater than other capacitors, with low internal resistance. In addition to having high power density, 10 to 100 times greater, and excellent cycle life (>106 cycles), supercapacitors are lightweight and operate across a more comprehensive temperature range, from -40°C to 70°C (Abdel Maksoud et al., 2020). Moreover, the ease of packaging and low maintenance costs are key benefits that supercapacitors offer compared to other energy storage devices.

Nickel Metal-Organic Framework (Ni-MOF) has attracted significant attention in energy storage systems because of its exceptional characteristics compared to other Metal-Organic Framework materials. MOFs possess highly porous structures, large pore volumes, high surface areas, adjustable geometric morphologies, flexible functionalities, a large number of active sites, strong electrochemical responses, and robust redox activity. These MOF properties have generated significant interest in developing supercapacitors to meet the demand for effective electrochemical energy storage (Nie et al., 2024). MOFs are a family of porous materials that can be one-, two-, or three- dimensional and are composed of metal ions and organic ligands joined by coordinating bonds. The most important bonding interactions in MOFs are coordinate bonds. Conversely, weaker forces such as hydrogen bonds, Van der Waals interactions, and metal-metal bonds contribute to structural flexibility and broaden the potential range of applications. MOFs, also referred to as porous coordination polymers (PCPs), are synthesized using cost-effective starting materials, such as metal salts from transition metals like Co, Fe, Cu, and Ni. These metals possess multiple coordination numbers, making them suitable for the design of various types of MOFs. Most nickel metals have been utilized to create MOFs as supercapacitor electrode materials due to they can offer active sites for redox behaviour, facilitating charge storage (Khokhar et al., 2022).

2 Materials and Method

The Study begins with material preparation, followed by the synthesis of Ni-MOF, nanoparticle characterization, and electrochemical testing to assess the performance of the Ni-MOF.

2.1 Materials

The materials used in this study were Nickel Nitrate Hexahydrate $Ni(NO_3)_2.6H_2O$, Terephthalic Acid (BDC), N,N Dimethylformamide (DMF), Ethanol, Deionized Water, and Aethylenglycol were purchased from Sigma-Aldrich.

2.2 Synthesis of Nickel Metal-Organic Framework (Ni-MOF)

The synthesis of Ni-MOF is carried out using the solvothermal method. Ni-MOF was produced using a Teflon-lined Autoclave after combining $Ni(NO_3)_2.6H_2O$

and BDC in a mixture of Aethylenglycol, DMF, Ethanol, and Deionized Water. The mixture was stirred at room temperature until homogeneous and fully dissolved before being placed in an oven at 150°C for 48 hours. The resulting product was a light green solid washed multiple times with Ethanol, then dehydrated at 60°C overnight.

2.3 Characterization of Nanoparticles

X-ray Diffraction (XRD) analysis was carried out for crystallographic phases identification of the MOF nanoparticles using a Rigaku Miniflex diffractometer, using Cu Kα radiation (λ = 0.15405 nm) on a 2θ scale of 3-90° with a scan rate of 5°/min. Scanning Electron Microscope (SEM) was performed to observe the surface structure of the sample using the Quanta 650 instrument. The scanning results are available in two formats: CBS, which is obtained from backscattered electron detector scanning, and ETD, which is obtained from secondary electron detector scanning. Nitrogen absorption-desorption isotherm was conducted in 77 K on BELSORP mini-X to obtain the Brunauer-Emmertt-Teller (BET) surface area.

2.4 Electrochemical Test

A dispersion was prepared by mixing 4 mg of Ni-MOF with distilled water, 2-propanol, and nafion, which was then deposited onto a 2x1 cm carbon sheet in a volume of 250 µl. Electrochemical tests, including Cyclic Voltammetry (CV) and Galvanostatic Charge-Discharge (GCD), were conducted using a CH Instrument workstation. The electrochemical properties of the Ni-MOF electrode were assessed using an Ag/AgCl electrode as the reference electrode and a Pt column as the counter electrode.

3 Result and Discussion

The morphology of Ni-MOF, as shown in Figure 1, was observed using a Scanning Electron Microscope (SEM), revealing a sheet-like structure with an approximate thickness of 0.137 µm.

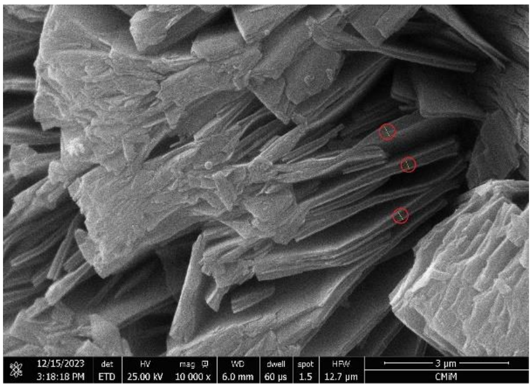

Figure 1 Morphology of Ni-MOF

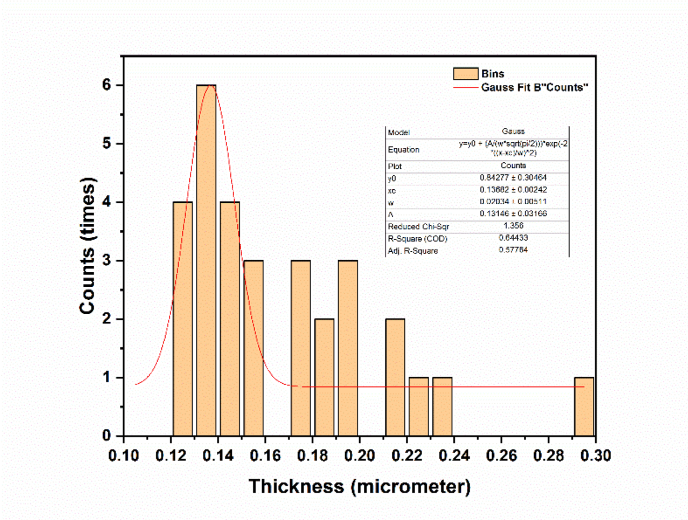

Figure 2 Thickness Size of Ni-MOF

Figure 3 presents the XRD diffraction pattern of Ni-MOF, where the results indicate a broadening peak within the 2θ range of 9-45°.

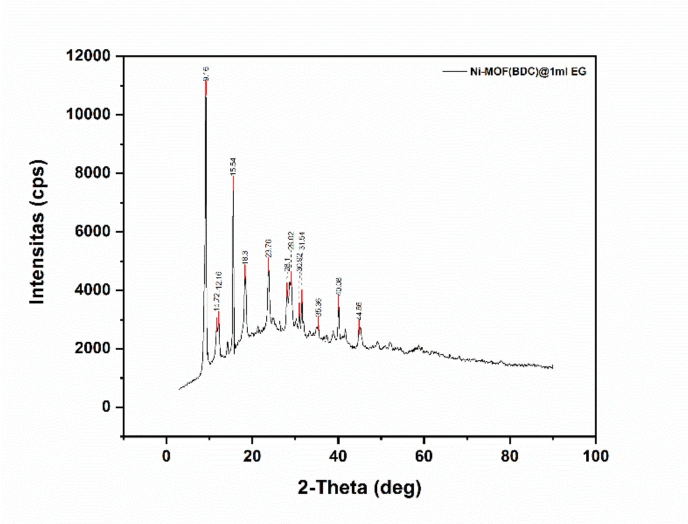

Figure 3 Crystallographic pattern of Ni-MOF

Using the Scherrer Equation Eq. (1), the average crystal size is 10.62 nm. When comparing the area under the crystalline peak with the total area, the result obtained is 61.43%, Ni-MOF is in the crystalline phase.

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

$$Crystallinity\ (\%) = \frac{Area\ of\ Crystalline\ Peaks}{Total\ Area} \times 100 \quad (2)$$

Table 1 Crystal Size

No	2-Theta (deg)	FWHM (deg)	Crystal Size (nm)
1	9.16	0.35195	22.645
2	11.72	0.54	14.789
3	12.16	0.56	14.266
4	15.54	0.29186	27.472
5	18.3	1.14864	7.005
6	23.76	1.88244	4.313
7	28.1	0.94	8.712
8	29.02	2.24	3.663
9	30.92	0.58	14.211
10	31.54	1.38	5.982
11	35.36	1.76	4.738
12	40.08	1.56	5.421
13	44.86	1.78	4.828

The Surface area was measured using the BET method. The particles were identified as mesoporous with a surface area of 9.3291 m^2 g^{-1}.

Table 2 Result of BET Analysis

No	Spesification	Value
1	Surface Area	9.3291 m^2 g^{-1}
2	Average Pore Diameter	20.973 nm
3	Total Pore Volume	0.098 cm^3 g^{-1}

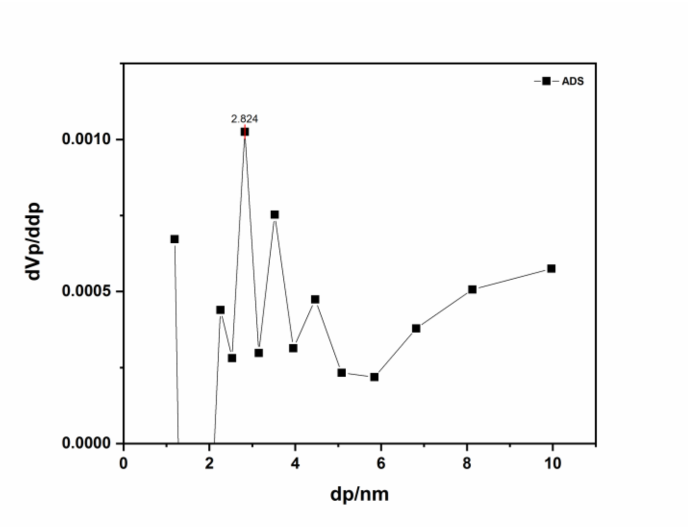

Figure 4 BJH-Plot of Ni-MOF

The electrochemical performance of the supercapacitor electrode were evaluated using two techniques: CV and GCD. The measurements were conducted in a 1 M KOH electrolyte. The CV test was performed over a voltage range from 0 to 0.5 V at different scan rates, ranging from 5 to 100 mV s^{-1}. Additionally, the electrochemical performance of Ni-MOF was evaluated using the GCD method at a constant current density of 0.5 A g^{-1}. Based on the GCD data, the specific capacitance of the supercapacitor electrode can be calculated using Stdanar Equation Eq (3).

$$C_{sp} = \frac{I \times \Delta t}{m \times \Delta V} \quad (3)$$

I is the discharge current (A g^{-1}), ΔV is the voltage window or discharge potential range (V), Δt is discharge time (s), and m is mass of the active electrode material (g).

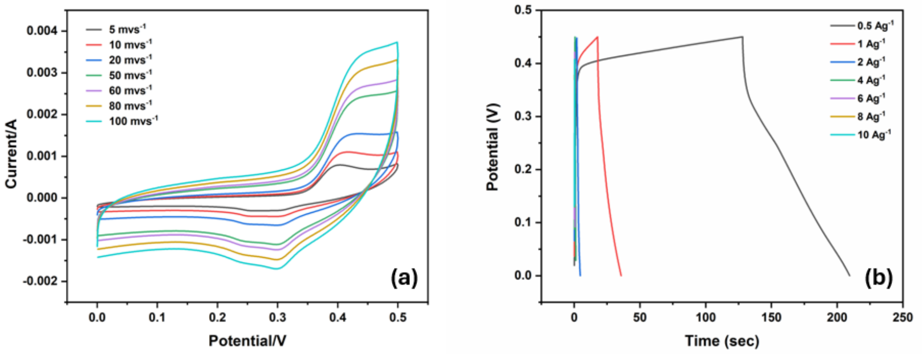

Figure 5 (a) CV Curve of Ni-MOF electrode at different scan rates (b) GCD profile of the Ni-MOF electrode at different current densities

Based on Figure 5b and Eq. (3), the specific capacitance value is 90.7 F g^{-1}.

4 Conclusion

The synthesis of Ni-MOF using the solvothermal method was successfully carried out, resulting in a specific surface area of 9.3291 m^2 g^{-1}, an average pore diameter of 20.973 nm, and the particles identified as mesoporous. The XRD results show that Ni-MOF is in its crystalline phase. In addition to demonstrating that the research material is nanomaterial, the performance test results indicate that Ni-MOF has a specific capacitance of 90.7 F g^{-1}. With these performance test results, the addition of a change agent is necessary to improve electrical conductivity, which is one of the weaknesses of MOF materials.

5 Nomenclature

K	=	Shape factor (usually taken as approximately 0.9)
λ	=	The wavelength of the X-ray used (Usually using 1.5406 Å)
β	=	Full width at half maximum (FWHM) of the peaks (in radians)
θ	=	Bragg angle (in radians)

Acknowledgement

This research was funded by PT PLN (Persero) and the Advanced Functional Materials Laboratory, ITB.

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