

Synthesis of Nickel-based Metal-Organic Framework for use as electrodes in supercapacitors through microwave-assisted solvothermal synthesis

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Abstract

A nickel-based MOF was formed using NiCl_2 and trimesic acid ligands, in a 2:1 stoichiometric ratio, using the microwave-assisted solvothermal synthesis method. The reaction mixture was heated to 150°C , for durations ranging from 10 to 50 minutes. The highest yield was achieved after 40 minutes of irradiation, while after 50 minutes, the crystals were larger, and the reaction went to completion. In cyclic voltammetry, the specific capacitance of 6.77 F g^{-1} was achieved. Compared to conventional solvothermal synthesis, this method required lower energy usage.

1. Introduction

Capacitors are devices that store electrical energy through capacitance, using two electrical conductors separated by a dielectric (a polarizable electrical insulator). A current passing through a capacitor causes an electric field to develop across the dielectric, causing opposing charges to build up on both conductors. However, capacitors suffer from several limitations, such as their low cyclic stability and capacitance, which generally range from 1 picofarad to 1 millifarad. Unfortunately, they have low capacitance, stability and high cost (Yang, Xiong, Zheng, Qiu, & Wei, 2014). This forces some applications to use batteries, despite preferring the advantages of capacitors (e.g. fast charging and discharging). These applications include battery backup solutions and provision of energy in grid power surges. Batteries are also not ideal as they have slow charge and discharge rates, as batteries take 0.3-3 hours for charging and 1-5 hours for discharging, compared to supercapacitors which take only 0.3 - 30 seconds to fully charge and discharge (Kumar et al., 2017). Batteries also have low cyclic stability. Even batteries designed for cyclic stability, such as Tesla batteries, can only retain 93% of their capacity after 785 cycles (Teslanomics, 2017).

Supercapacitors are a class of capacitors that store 10 to 100 times more energy, yet tolerate far more charging cycles than regular capacitors. These characteristics are achieved in electrostatic double-layer capacitors (EDLCs), which take advantage of the double-layer

effect to store charge, and also in pseudocapacitors, which store and release charge through fast redox reactions (Zhang & Zhao, 2009). This allows supercapacitors to tolerate more charging cycles than regular capacitors, allowing them to replace batteries in areas that traditionally rely on batteries. Supercapacitors have charge-discharge speeds of seconds instead of hours, and higher cyclic stability, with minimal loss of capacitance after thousands of cycles (Jiao, et al., 2016), exceeding the capabilities of current battery technology. Much attention has been given to supercapacitors, due to their multitude of potential applications, such as in the fast charging and discharging of electric vehicles (Yoo, Sul, Park, & Jeong, 2008), as well as in grid storage for excess renewable energy (Miller & Simon, 2008).

Currently, most supercapacitors make use of carbon-based materials such as activated carbon, carbon nanotubes, and holey graphenes as their main active material. However, metal-organic frameworks (MOFs) are now under the spotlight. MOFs are a new class of materials with astoundingly high porosity, uniform cavities, good thermal stability, and high surface area (Hashemi et al., 2017), making them suitable for use in supercapacitors. They have higher surface areas than the aforementioned carbons, allowing greater double-layer effects (Sheberla, et al., 2016) in EDLCs. In pseudocapacitors. They also have the upper hand as they have unique pseudocapacitive redox centers that can be used as an electrode material (Yang, Xiong, Zheng, Qiu, & Wei, 2014). These characteristics make MOFs a better candidate in supercapacitor applications, than carbon-based solutions. In efforts to allow MOFs to be used in capacitors, investigations have been conducted to allow for adjustable pore size distribution, higher surface area, abundant active sites and excellent electrical conductivity (Zhao et al., 2018), through various MOF structures and their derivatives.

However, some challenges inhibit the widespread use of MOFs in supercapacitors. For example, their high porosity is coupled with abysmal electrical conductivity. These non-conductive MOFs cannot be used to store electrical charge and cannot be used directly in supercapacitors, and require heavy modification through methods such as doping with electrical conductive polymers or metal cations (Yue, et al., 2014) or changing the ligand (Xu, Guo, Yao, Fu, & Wang, 2016). However, some MOFs do demonstrate high conductivity. In 2014, Yang et al. synthesized a layered two-dimensional Ni-MOF

successfully, and used it in a supercapacitor electrode. The Ni-MOF demonstrated good rate capability, large capacitance and high cycling stability.

Secondly, the current synthesis methods for MOF is impractical for mass production due to its high energy and time requirements. The conventional method of MOF synthesis, known as conventional solvothermal synthesis, is done using conventional electric heating over long periods of time, taking up to several days under temperatures as high as 250°C (Morozan & Jaouen, 2012), creating high manufacturing costs. Therefore, alternative methods of synthesis have been developed. One such alternative is ultrasonic irradiation, where the precursor mixture is irradiated by ultrasonic waves (Li, et al., 2009). However, it is not universal and can only be used for specially designed MOFs (Jung, Yang, Kim, Kim, & Ahn, 2010). Another method is the electrochemical method, where a porous mesh is placed into an electrolyte consisting of the organic linker, the solvent, and water (Assche et al., 2012). Although this method requires less energy, it is even slower than conventional solvothermal synthesis, which could take up multiple days, because shorter times result in incomplete formation of the dense crystal layer.

On the other hand, MOFs can be synthesized using a more energy efficient method with a shorter duration, such as microwave-assisted solvothermal synthesis (Klinowski, Paz, Silva, & Rocha, 2011), where the precursor mixture is irradiated in microwave synthesizers. The MOF forms in less than an hour at temperatures as low as below 100°C (Choi, Kim, Jhung, Chang, & Chae, 2006), as the microwave radiation is directed at the reaction mixture, resulting crystal nucleation and growth to increase rapidly. It is a highly efficient process and results in significant energy savings, while maintaining crystal sizes and morphologies similar to that of conventionally synthesized MOFs. These reductions in energy and time requirements will enable MOFs to be synthesized at lower costs.

Choi et al. (2006) investigated the crystallinity and morphology of MOF-5 by varying the synthesis methods, with conventional heating (105°C for 24 h) being used for comparison. It was found that microwave irradiation forms MOF crystals after only 30 minutes of reaction, while conventional solvothermal synthesis required 24 hours. Yet, the surface area and CO₂ sorption capacity were not reduced, when compared with the conventional approach. Jhung et al. (2007) managed to prepare nanoporous Cr-MIL-101 as nano-sized crystals, which were

significantly smaller compared to the crystals formed by conventional solvothermal-related methods.

Hence, this study aims to adopt the method of microwave-assisted solvothermal synthesis for synthesis of Ni-MOF, due to its advantages in speed and simplicity, without compromising on quality. Thus, microwave-assisted solvothermal synthesis is one of the most promising new methods of MOF synthesis.

2. Objectives and Hypotheses

In this paper, a Ni-MOF was synthesized using microwave-assisted solvothermal synthesis. The MOF been used as the working electrode in a supercapacitor, as a pseudocapacitor. The optimum duration of microwave irradiation, was also determined.

It was hypothesized that Ni-MOFs can be synthesized through microwave-assisted solvothermal synthesis, with similar properties and capacitance to MOFs produced through conventional methods, with the highest yield being attained after 30 minutes of heating without reducing MOF quality (Choi, Son, Kim, & Ahn, 2008). For durations shorter than 30 minutes, the yield would be lower as some reactants remain unreacted; while for durations of over 30 minutes, crystal morphology would reduce the quality of the MOF.

3. Methods and Materials

3.1 Materials

Anhydrous dimethylformamide (DMF), hydrated nickel (II) chloride, potassium hydroxide, propan-2-ol, and trimesic acid (TMA) were purchased from Sigma-Aldrich. 95% ethanol was procured from GCE Chemicals. Polytetrafluoroethylene (PTFE) powder was bought from GoodFellow. Acetylene black powder was purchased from TIMCAL.

3.2 Methodology

3.2.1 Synthesis of Ni-MOF complex

0.134g of TMA was dissolved in 5mL of DMF using a volumetric flask. 5mL of 25mM NiCl₂ solution, also dissolved in DMF, was added dropwise into 2.5mL of the above TMA solution. This mixture was transferred into a vial and placed into the microwave synthesizer, which was set to 150°C. Irradiation time was varied between 10, 20, 30, 40, and 50 minutes for the samples, while the concentrations of reactants remained constant. After microwave

irradiation, the mixture was then centrifuged at 10°C at 3000 rpm for 15 minutes. The residual MOF powder was obtained.

3.2.2 Activation of Ni-MOF

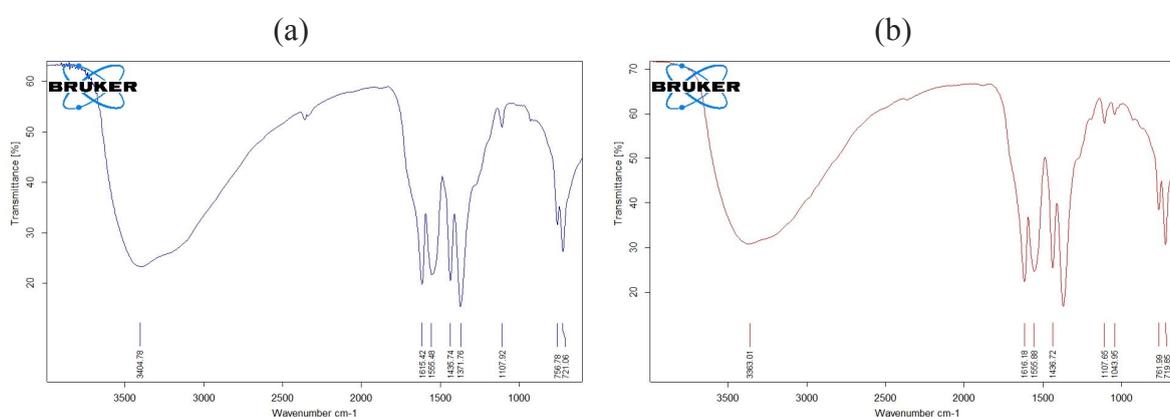
DMF was added until all of the MOF powder was soaked. The suspension was sonicated in a sonicator for 10 minutes, then centrifuged at 10°C at 3000 rpm for 15 minutes, and the residue is kept. This was repeated 2 more times. Ethanol was added until all of the MOF powder was soaked. The mixture was left in an orbital shaker overnight. Afterwards, the mixture was centrifuged at 10°C at 3000 rpm for 15 minutes, and the residue is kept. This was repeated 2 more times for solvent exchange, removing the DMF and replacing it with ethanol. The MOF powder was then dried in a vacuum oven for 6 hours at 70°C.

3.2.3 Assembly of Supercapacitor electrode

A homogeneous slurry of 70 wt% MOF powder, 20 wt% acetylene black, and 10 wt% PTFE binder were mixed in propan-2-ol and was then coated onto a piece of 1cm by 1cm stainless steel mesh and pressed at 6 tons per cm². The electrode was dried in an oven for 3 hours at 100°C, and then assembled in a three-electrode cell with the MOF electrode as the working electrode, AgCl as the reference electrode and platinum as the counter electrode. The electrolyte used was 6M KOH solution.

4. Results and Discussion

4.1 Fourier-Transform Infrared Spectroscopy



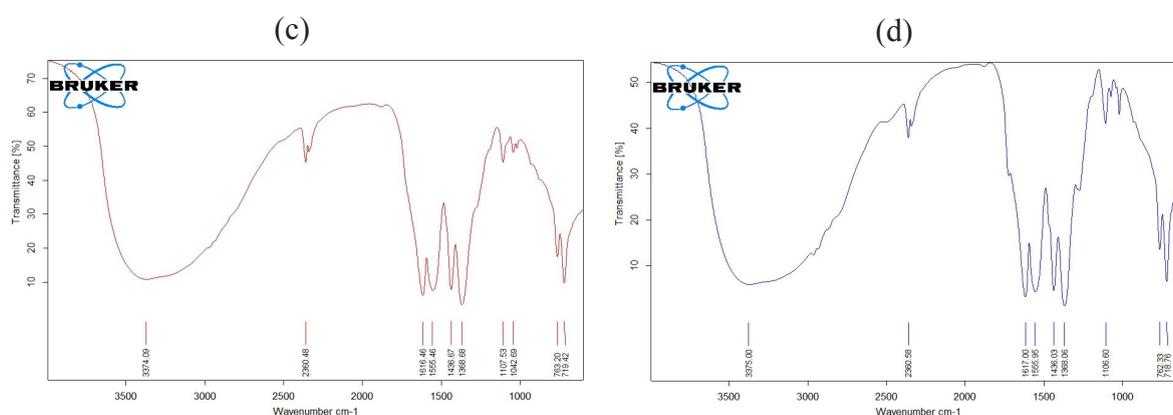
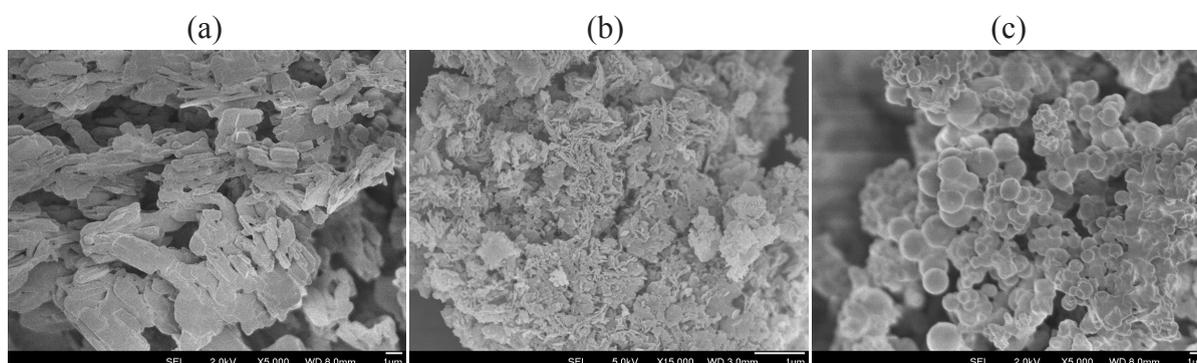


Figure 1. FTIR Results for samples that underwent (a) 10 minutes, (b) 20 minutes, (c) 30 minutes, and (d) 40 minutes of microwave irradiation

The samples were analysed with FT-IR Spectroscopy. The FT-IR graphs are similar between the samples, suggesting that products of similar structures were produced. In the graphs, the peak at 1110cm⁻¹ shows C-O stretching in benzene-1,3,5-tricarboxylate (BTC) (Zhu, et al., 2016); the peak at 1370cm⁻¹ shows C=C stretching of the BTC benzene ring (Sofi, Majid, & Mehraj, 2018); the peak at 1440cm⁻¹ shows symmetric vibration of the COO⁻ group; and the peak at 1560cm⁻¹ shows asymmetric vibration of COO⁻ group (Sanati & Andersson, 1993). These all points to the evidence that BTC is present. The absence of peaks between 1730cm⁻¹ to 1690cm⁻¹ shows that no protonated carboxyl groups remain, showing that H⁺ ions have been replaced by another cation, which is likely to be Ni²⁺ as no other cations were present.

4.2 Scanning Electron Microscopy (SEM)



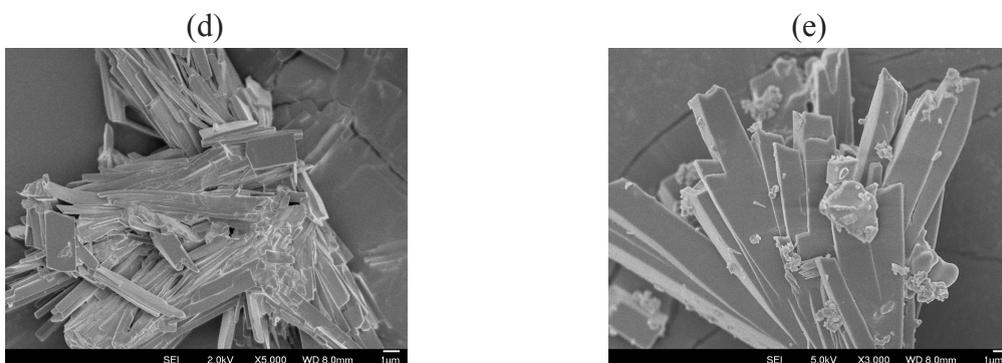


Figure 2. SEM images for samples that underwent (a) 10 minutes, (b) 20 minutes, (c) 30 minutes, (d) 40 minutes of irradiation, and (e) 50 minutes of irradiation

The samples were analysed using Scanning Electron Microscopy (SEM). Figures 2 (d) and (e) show smooth, rod-like crystals with a broad range of sizes, shapes and smoothness being formed, matching the findings by Zhang, et al. (2018), who synthesized a Ni-MOF using an alternative method, indicating that a Ni-MOF was successfully synthesized. Figures 2 (a), (b) and (c) did not exhibit the characteristics shown by Ni-MOF, showing that the reaction did not go to completion, resulting in varying forms and morphologies. The desired Ni-MOF structure was formed only after 40 minutes of irradiation, possibly showing that a certain threshold duration of irradiation was reached after this time. The increase in sizes of the crystals in the 50 minute sample compared to the 40 minute sample was attributed to a longer duration for the MOF to form.

4.3 Energy-dispersive X-ray Spectroscopy (EDS)

Element	Mass %	Atom %
Carbon	35.49	59.25
Oxygen	20.54	25.74
Nickel	43.97	15.02

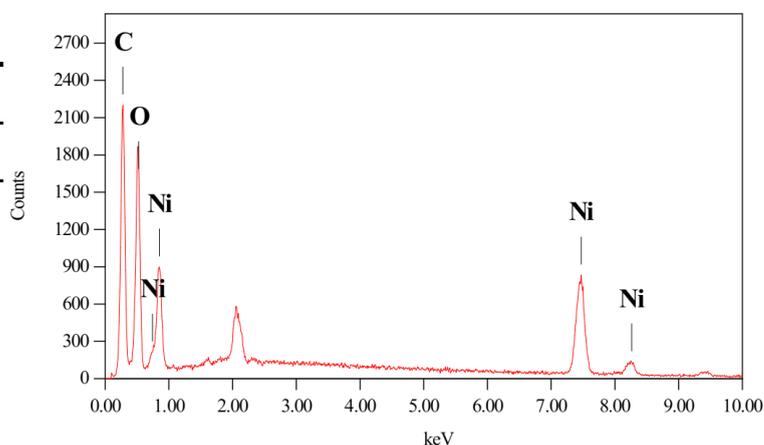


Fig. 3a. EDS results for 50 minute sample

Element	Mass %	Atom %
Carbon	42.71	58.90
Oxygen	32.99	34.15
Chlorine	0.54	0.25
Nickel	23.76	6.70

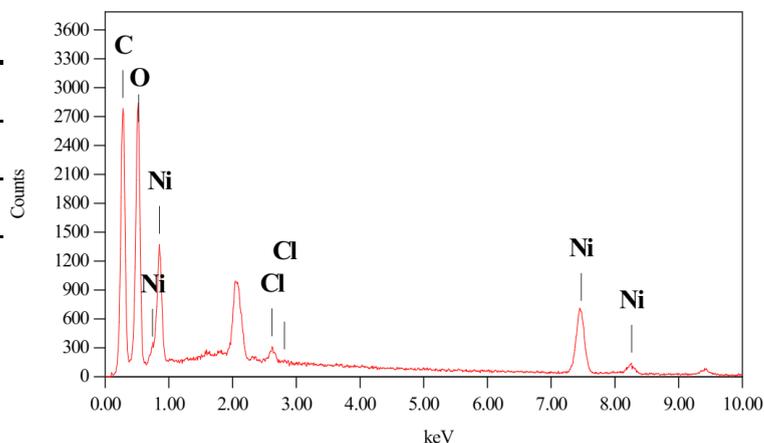


Fig. 3b. EDS results for 40 minute sample

With reference to Figure 3a, the 50 minute sample did not contain chlorine, while the other samples show the presence of chlorine, although all values were below 1%. This suggests that all reagents had reacted only after 50 minutes of irradiation, and the washing procedure was successful in removing the majority of the unreacted reactants, which corresponds to the extremely low percentage of chlorine present. The other EDS results can be viewed in [Appendix A1](#).

4.4 X-Ray Diffraction (XRD)

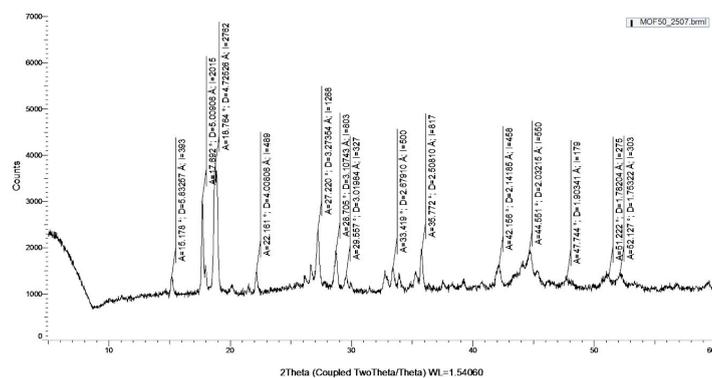


Fig. 4. XRD result for 50 minute sample

The XRD pattern of the sample obtained from microwave irradiation was well matched with that of as-prepared Ni-MOF by ball-milling method, as the peaks of the XRD graph match the characteristic peaks found by Zhang, et al. (2018), for peaks at 17.7° and 18.8° . The XRD intensity of the 1st peak at two theta of 17.7° increased with synthesis time from 10 to 50 minutes, indicating that structural stability of Ni-MOF increased simultaneously. The XRD intensity of the 2nd peak at two theta of 18.8° also increased with synthesis time, further

supporting that the quality of Ni-MOF increases with longer durations of microwave irradiation. The exact structure of the MOF could not be determined as simulation was not possible, due to lack of information. The other XRD results can be seen in [Appendix A2](#).

4.5 Cyclic Voltammetry (CV)

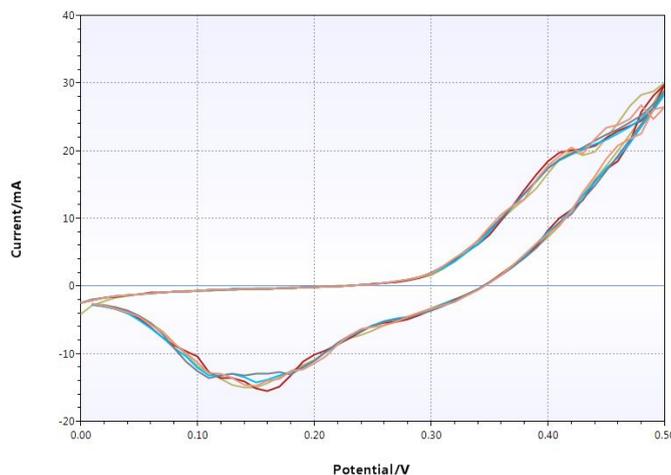


Fig. 5. CV graph of 40 minute MOF electrode

Cyclic voltammetry was conducted with a scan rate of 100mV s^{-1} , between 0.00V to 0.50V . A duck-shaped curve was obtained, indicative of the characteristics of redox reactions in pseudocapacitors with EDLC qualities which matches the findings of other papers (Yang et al., 2014) that displayed similar duck-shaped curves. This concludes that our Ni-MOF is capacitive and functions like a supercapacitor. Following the calculations in [Appendix A3](#), the specific capacitance of 6.67 F g^{-1} was derived.

4.6 Yield

Irradiation Duration/min	% Yield
10	20.8
20	42.8
30	43.4
40	62.3
50	44.0

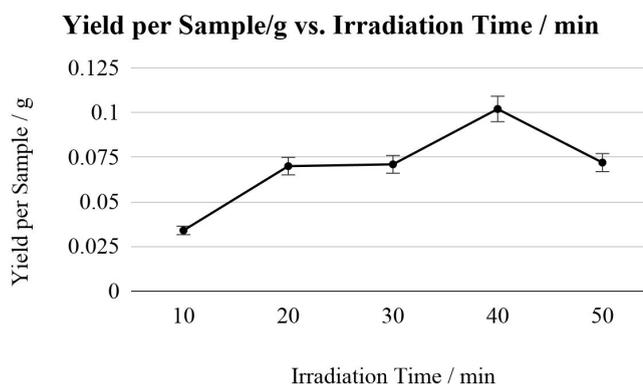


Fig. 6. Table and graph of yield against irradiation duration

The theoretical yield was calculated as the sum of the masses of NiCl₂ and TMA, under stoichiometric conditions. From 10 minutes to 40 minutes of irradiation, the yield was generally increasing at a non-constant rate, but at 50 minutes of irradiation, the trend is broken and the yield decreased unexpectedly. This suggests that the maximum yield is obtained after approximately 40 minutes of irradiation.

5. Conclusion

In this study, a Ni-MOF was successfully synthesized via microwave-assisted solvothermal synthesis. Through sonication, the presence of impurities was minimized in the final product, while still preserving a relatively efficient procedure. The optimal irradiation time for production of this MOF in industrial settings would be approximately 40 minutes, as it produces the highest yield, while the largest crystals formed after 50 minutes of irradiation. Finally, the capacitance of the electrode was low, possibly due to limitations in the experimental procedures, such as the MOF powder being non-adherent to the electrode, and the high electrical impedance of the stainless steel mesh as choice for electrode material, which has 40 times lower electrical conductivity than a copper mesh (Eddy Current Technology Incorporated, 2013).

5.1 Recognition of Potential Impact in Science, Society and/or Economics

This MOF can be used to produce supercapacitors, which have potential applications such as in hybrid cars, or in grid storage. Furthermore, the energy and time requirements for microwave synthesis are lower, effectively reducing the costs associated with traditional MOF production, which would thus lower the overall cost and increase the availability of MOFs to be used in supercapacitors. Alternatively, this MOF can be used in other areas, such as for gas adsorption applications or as a catalyst.

5.2 Recommendations for Further Work

The efficacy of alternative synthesis methods such as ultrasonic synthesis can be researched on in future studies. Less dangerous solvents and reagents should also be tested so as to minimise toxic waste production, such as ethanol as solvents. Other suitable materials for electrode synthesis can be investigated to find out the ideal combination to produce the electrode with the highest capacitance.

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Appendix

A1. Additional Results for Energy-dispersive X-ray Spectroscopy

Element	Mass %	Atom %
Carbon	36.51	49.67
Oxygen	43.97	44.90
Nickel	19.52	5.43

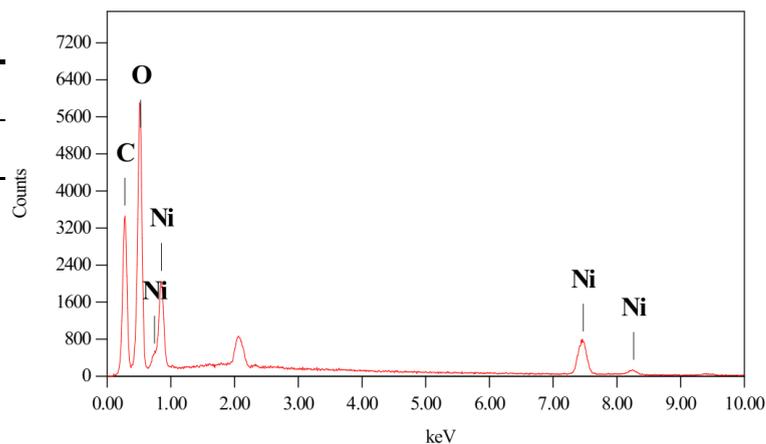


Fig. 3c. EDS results for 10 minute sample

Element	Mass %	Atom %
Carbon	37.06	50.33
Oxygen	43.33	44.18
Chlorine	0.19	0.09
Nickel	19.43	5.40

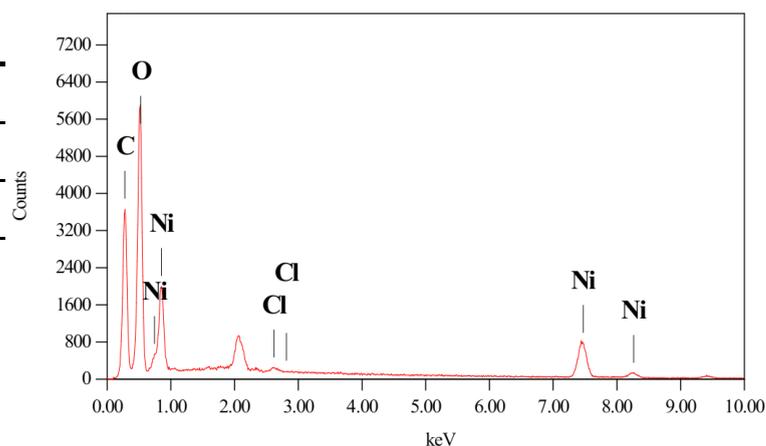


Fig. 3d. EDS results for 20 minute sample

Element	Mass %	Atom %
Carbon	47.31	61.01
Oxygen	35.41	34.29
Chlorine	0.79	0.34
Nickel	16.49	4.35

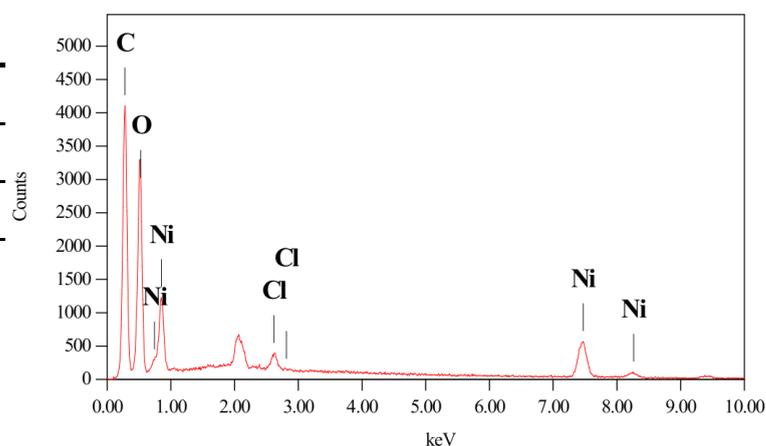


Fig. 3e. EDS results for 30 minute sample

A2. Additional Results for X-Ray Diffraction

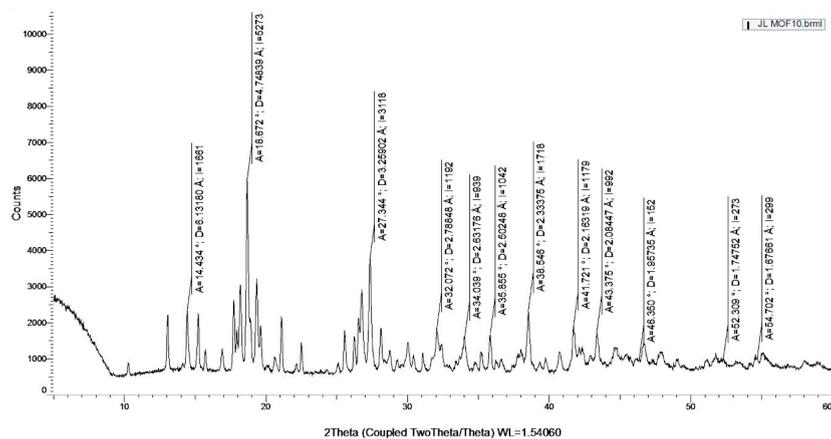


Fig. 4b. XRD result for 10 minute sample

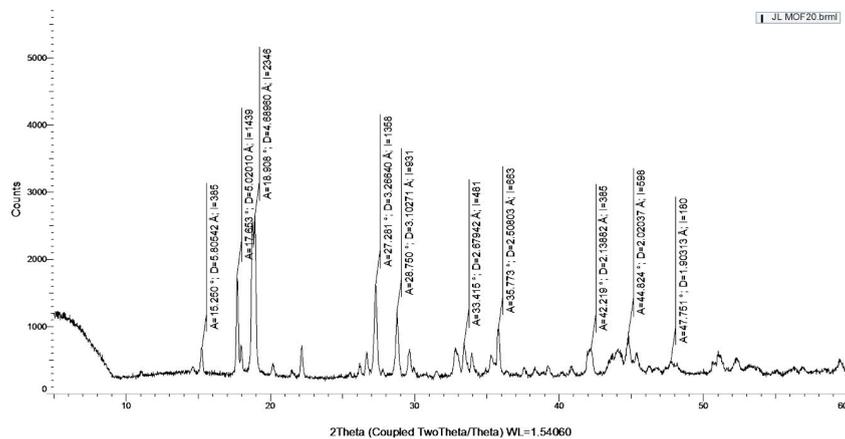


Fig. 4c. XRD result for 20 minute sample

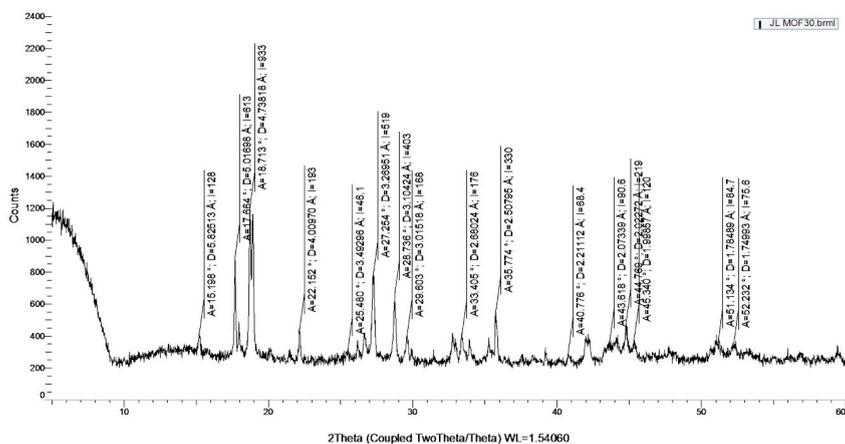


Fig. 4d. XRD result for 30 minute sample

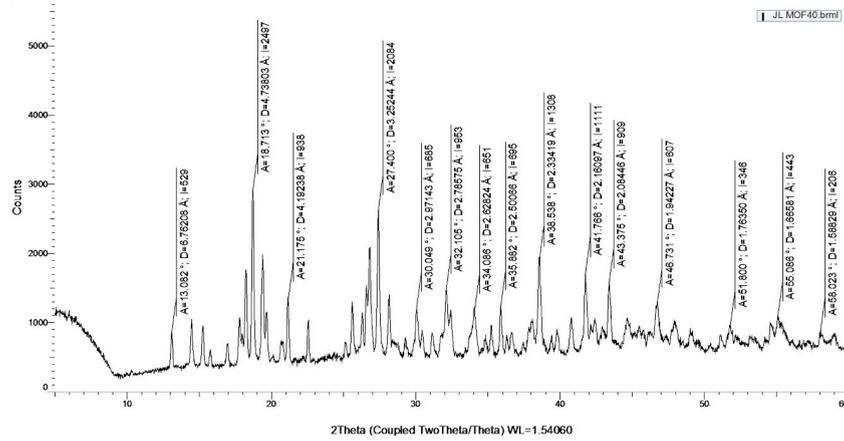


Fig. 4e. XRD result for 40 minute sample

A3. Calculation of Capacitance from Cyclic Voltammetry

$$C_{\text{specific}} = \frac{\int_{V_1}^{V_2} i(E) dE}{2 \left(\frac{dV}{dt} \right) (V_2 - V_1) (m_{\text{active material}})}$$

Where

- V_1 is the lower voltage bound
- V_2 is the higher voltage bound
- $\frac{dV}{dt}$ is the scan rate
- $m_{\text{active material}}$ is the mass of MOF on the electrode
- $i(E) dE$ is a given name for integrating the CV graph
- the integral refers to the area under the CV graph