Malays. J. Anal. Sci. Volume 29 Number 1 (2025): 899

MALAYSIAN JOURNAL OF ANALYTICAL SCIENCES

Journal homepage: https://mjas.analis.com.my/

Research Article

Comparison studies of MnCo and MnCoCr layered double hydroxide on polymer electrolyte's application

Fatin Nabihah Mukhtar, Nur Alyaa Kamal, Siti Nurul 'Afini Mohd Johari, Nur Alia Maisarah Saiful Bhari[4], and Nazrizawati Ahmad Tajuddin*

School of Chemistry and Environment, Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 UiTM Shah Alam, Selangor, Malaysia

*Corresponding author: nazriza@uitm.edu.my

Received: 1 August 2023; Revised: 7 December 2024; Accepted: 8 January 2025; Published: 20 February 2025

Abstract

Polymer electrolytes are electrolytic materials which can be found in batteries, fuel cells and other applications. In this study, $Mn_{3.0}Co_{1.0}$ and $Mn_{3.0}Co_{1.0}Cr_{1.0}$ layered double hydroxide (LDH) will be used as a filler in polymer electrolyte's application. The addition of a filler into polymer electrolytes can extensively be applied in commercial Li-ion batteries. LDH are lamellar compounds and have been prepared via alkali-free co-precipitation method. Synthesis of LDH using alkali could cause a major problem in the battery reactor such as corrosion and subsequently will affect the environment. Thus, alkali-free route is chosen to overcome the above-mentioned problems. The samples were characterized using TGA, PXRD, FTIR and FESEM to determine their thermal stability, crystallinity, chemical bonding and morphology. The samples were then used as a filler in polymer electrolyte films. Polyethylene oxide (PEO) was used as the host polymer and LDH samples as the filler. There were two systems conducted which are PEO and PEO with addition of fillers. The characterization was carried out on electrical conductivity by using EIS and as expected, the usage of the calcined $Mn_{3.0}Co_{1.0}$ LDH gave excellent performance compared to all other samples with 1.1276 x 10^{-8} S/m.

Keywords: alkali-free method, filler, polymer electrolyte, layered double hydroxide, EIS

Introduction

A broad class of materials with lengthy polymeric chains and high ion concentrations are referred as polymer electrolytes (PEs) [1]. Their applications in energy conversion and storage include as photoelectrochemical and electrochromic devices as well as electrochemical devices such as supercapacitors and solid-state batteries [2]. As mentioned by Zhou et al. (2019) [3], gel polymer electrolytes (GPEs), solid polymer electrolytes (SPEs) and composite polymer electrolytes (CPEs) are the three types of PEs that can be divided depending on their compositions. The liquid electrolyte is incorporated into GPEs created by the matrix of the swelling polymer host [4]. In SPEs, the desired polymer is combined with the electrolyte salt without the need of an organic solvent [4]. To improve ion conductivity and mechanical qualities, CPEs made of inorganic particles in SPE but with a high dielectric constant have been developed [5]. Wang et al. worked on polymer electrolyte's application employing MgAl LDH. Another name for LDH is anionic clays. Its general chemical formula is $[M^{2+}_{1-x} M^{3+}_{x} (OH_2)]^{x+} [A^{n-}_{x/n}]^{x-} \cdot mH_2O$, where x is the molar ratio of trivalent cation, A is the anion of choice with n valence, M^{2+} and M^{3+} are divalent and commonly trivalent metal cations, respectively [6]. M^{2+} and M^{3+} are situated within the brucite-like layers and the anions are sandwiched between the interlayer spacing of these layers [7]. LDH is a type of heterogeneous catalyst which has a wide variety of applications including water purification, catalysis, supercapacitors and biomedical applications [4]. LDH can be prepared by using a variety of methods such as co-precipitation method, mechanochemical method, sol-gel method, ion-exchange method, reconstruction method, oxide method, urea hydrolysis and hydrothermal treatment [8]. However, co-precipitation approach was chosen due to its simple technique of preparation, and recently, Tajuddin et al. (2018) has introduced the alkali-free method [8].

A technique known as the alkali-free method does not use an alkaline solution, which can contribute major negative effects towards the environment. An alkali-free method for synthesizing LDH is more preferred due to the availability of employing various metal group elements [9]. Therefore, the alkali-free method has been selected for this study to ensure environmental sustainability. Research has conducted a study that used NiCo LDH polyhedron as advanced anode for lithium-ion batteries [10]. The findings include a high specific capacity of 928.3 mAh/g at 100 mA/g, however alkali-free method was not used in the study. It was found that no other researchers have employed alkali-free method to prepare MnCo LDH and MnCoCr LDH in the usage of polymer electrolyte, thus due to this reason, MnCo/MnCoCr LDHs were chosen. In this work, alkali-free technique was used to synthesize MnCo LDH and MnCoCr LDH with molar ratios of 3:1 and 3:1:1, respectively. The characterizations before and after calcination of MnCo LDH and MnCoCr LDH samples such as thermal stability, crystallinity, chemical bonding and morphology were conducted via thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM), respectively. In addition, MnCo LDH and MnCoCr LDH were also distinguished in terms of their effectiveness as fillers in polymer electrolytes by using Electrochemical Impedance Spectroscopy (EIS).

LDH acts as a filler in polymer electrolyte's applications. According to Shaari and Kamarudin, fillers can be categorized into two categories: organic filler and inorganic filler. Examples of organic filler include carbon, natural polymers and synthetic polymers, meanwhile metals, silicate, aluminium oxide, zirconium dioxide, salts and hydroxide are some of the examples of inorganic fillers [12]. Each fillers have their unique dispersion strategy based on their categories [13]. As mentioned by Shaari and Kamarudin, [12] only the polymer's modulus can be improved by fillers, which also increases surface area and surface composition without altering or improving its mechanical strength. Other researchers have used a variety of LDH materials as fillers in polymer electrolyte, including MgAl LDH, NiCo LDH, NiAl LDH, and ZnAl LDH. To assess their effectiveness in the application of polymer electrolyte, MnCo LDH and MnCoCr LDH were utilised as fillers in this study. Polymer electrolyte films were produced by using the solution casting technique. Mn3.0Co1.0 LDH, Mn3.0Co1.0Cr1.0 LDH, and PEO were used as the polymer matrix, whereas MnCo LDH and MnCoCr LDH served as the filler. EIS instrument was utilised to characterize the effectiveness of MnCo LDH and MnCoCr LDH as fillers in polymer electrolyte application.

There are several problems that need to be addressed in polymer electrolyte's application. First, the addition of alkali solution during the LDH synthesis process can extremely damage the battery reactor which gives corrosive effects. Since the process gives negative consequences on the products, thus it is no longer considered a green chemistry process. As a result, the alkali content needs to be reduced or removed by purification process. As it must be purified before use, it may be costly. To prevent the problems as mentioned above, an alkali-free approach will be developed in this research. In addition, utilising liquid electrolytes has significant drawbacks, including limited operating voltage, flammability and electrolyte leakage [4]. Polymer electrolytes can be used to replace the liquid electrolytes to alleviate the safety issues with Li-based batteries [3].

In addition, the unique characteristics of polymer electrolytes are low flammability, higher resistance to shock, vibration and mechanical deformation compared to liquid electrolytes, as well as better compatibility than inorganic solid electrolytes [3]. Therefore, polymer electrolytes were used in this study instead of liquid electrolytes. Besides, compared to LDH materials, employing other materials such as MnO_2 as a filler in polymer electrolyte's application would result in poor electrical conductivity values. As a proof, Yuhan Li et al. used MnO_2 act as a filler and the result obtained for the ionic conductivity was 1.95 x 10^{-5} Scm^{-1}. In contrast, the ionic conductivity obtained by other researchers that used LDH materials such as MgAl LDH as the filler was 2.7 x 10^{-4} Scm^{-1} [3]. Even though MnO_2 and MgAl LDH have the same dimensional filler, 2D and the same amount of filler used, 5% wt., the value of ionic conductivity of MgAl LDH is higher than that of MnO_2. Thus, LDH materials were developed in this study.

The advantages of fillers are to enhance ionic conductivity, mechanical strength and electrochemical stability. A continued study of LDH in polymer electrolytes results in the creation of new information and new applications for energy storage technologies. The efficiency of Li-ion batteries may be further increased with the addition of fillers to polymer electrolytes, therefore making them the most intriguing and researched possibilities for energy storage technologies. Consequently, it may be widely utilised in industrial Li-ion batteries and adjusted to the direction of future development of new chemical energy storage technology with huge capacity. This has the potential to financially benefit both the researchers and indirectly to the country. Polymer electrolytes offer many advantages and might have future benefits in energy storage technologies, thus, further continued research into this field is essential. Additionally, this study is correlated with Sustainable Development Goal (SDG) 7, with the aim to promote affordable and clean energy. Scientists are also creating innovative materials that are readily available on earth for the creation of sustainable energy sources, including batteries that has been mentioned by American Chemical Society (ACS). To provide peace and prosperity for society, environment and the world, this study can contribute to the achievement of the SDGs.

The aims of this project are to synthesize Mn: Co LDH 3: 1 and Mn: Co: Cr LDH 3: 1: 1 ratio via alkali-free co-precipitation method, to characterize MnCo LDH and MnCoCr LDH on thermal stability, crystallinity, chemical bonding and morphology of samples by using TGA, PXRD, FTIR and FESEM, respectively, and to compare the efficiency of MnCo LDH and MnCoCr LDH as fillers in polymer electrolyte's application.

Materials and Methods

Experiment

This study involved the synthesis of 3:1 MnCo LDH and 3:1:1 MnCoCr LDH via alkali-free co-precipitation method. These LDHs then underwent characterizations by using thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM). The fresh and calcined samples were used to prepare polymer electrolyte films via solution casting method. Polyethylene oxide (PEO), MnCo LDH and MnCoCr LDH were used as host polymer matrix, and filler, respectively. The instrument used to characterize the efficiency of MnCo LDH and MnCoCr LDH as the filler in polymer electrolyte's application was Electrochemical Impedance Spectroscopy (EIS).

LDH synthesis

The two types of LDH catalyst prepared in this work are MnCo LDH with 3:1 ratio and MnCoCr LDH with 3:1:1 ratio; both were prepared via alkali-free co-precipitation method.

The aqueous solutions of 1.5 M of MnCo and 1.5 M of MnCoCr were prepared by mixing to a molar ratio of Mn: Co 3: 1 and Mn: Co: Cr 3: 1: 1 with a final solution volume of 100 cm^3. Then, 100 cm^3 of 2 M $(NH_4)_2CO_3$ solution was added and acted as a buffer while stirring. To ensure the pH is constant at 8, an aqueous solution of ammonia was added dropwise into the mixture solution. Subsequently, the mixture solution was aged at 65°C overnight while stirring, then the resulting solid product was filtered and washed with deionized water from time to time until the range of pH was 7. Once the pH was 7, the precipitate was dried at 80°C. The product formed underwent calcination process at 415 °C for 5 hours. The ratios of Mn: Co 3: 1 and Mn: Co: Cr 3: 1: 1 were chosen because other research teams have used 4: 1 and 4: 1: 1 ratio. In addition, a comparison from both results can be made.

LDH physiochemical characterizations

The physiochemical properties of samples were characterized using thermogravimetric analysis (TGA), powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR) and field emission scanning electron microscopy (FESEM) as mentioned in the next section. The samples were examined by using SETARAM Setsys Evolution 18 (TG-DSC/DTA). Thermogravimetric analysis (TGA) was carried out under flowing nitrogen with sample heating to 800 °C at 10 °C/min^{-1} to evaluate the interlayer water and carbonate content of the samples. Powder X-ray diffraction (PXRD) spectroscopy was used to identify the crystalline structure of MnCo LDH and MnCoCr LDH materials by using PANalytical X'pert PRO model. It was operated at 40kV and 40mA using Cu K_α where the diffraction patterns were recorded with diffraction angle 2θ = 10°C to 80°C. Perkin Elmer (Model: Spectrum One) Fourier transform infrared spectrophotometer (FTIR) was used to provide the information on the chemical bonds of samples by producing an infrared adsorption spectrum. The spectrum was examined in the range of 4000 cm^{-1} to 600 cm^{-1} with a resolution of 4 cm^{-1}. Field emission scanning electron microscopy (FESEM) analysis was performed on Jeol JSM- 7600F Schottky with 3.0 kV accelerating voltage and a beam current at 1.0 mA to characterize and capture the microstructure images of MnCo LDH and MnCoCr LDH.

Preparation of polymer electrolyte films using solution casting technique

PEO system and PEO with the addition of MnCo/MnCoCr LDH are the two systems conducted. Both methods were adapted from a previously reported method [14]. To prepare polymer electrolyte films, the solution casting method was performed. Polyethylene oxide (PEO) acted as the polymer matrix, whereas MnCo LDH and MnCoCr LDH served as the filler. In this study, three fresh and calcined MnCo LDH and MnCoCr LDH with different compositions were prepared. **Table 1** and **Table 2** tabulated the composition of PEO of fresh and calcined MnCo LDH and MnCoCr LDH polymer electrolytes, respectively.

Table 1. Composition of PEO-fresh MnCo LDH and MnCoCr LDH polymer electrolytes

Sample Name	PEO (g)	PEO (wt.%)	MnCo/MnCoCr LDH (g)	MnCo/MnCoCr LDH (wt.%)
F1	1.0	99	0.01	1
F2	1.0	97	0.05	3
F3	1.0	95	0.09	5

F = Fresh sample

Table 2. Composition of PEO-calcined MnCo LDH and MnCoCr LDH polymer electrolytes

Sample Name	PEO (g)	PEO (wt.%)	MnCo/MnCoCr LDH (g)	MnCo/MnCoCr LDH (wt.%)
C1	1.0	99	0.01	1
C2	1.0	97	0.05	3
C3	1.0	95	0.09	5

C = Calcined sample

PEO system

1g of PEO was added into 50 mL of acetonitrile (ACN). The PEO was stirred into ACN by using a glass rod. Then, the solution was stirred overnight to get a homogeneous solution by using a heating mantle. The solution was casted into Teflon petri dishes and the sample was left to dry for 1-3 days to form film. All samples were prepared at room temperature and stored in a desiccator. The method was adapted from a previously reported method [14].

PEO and LDH system

1g of PEO was added into 50 mL of ACN. The PEO was stirred into ACN by using a glass rod. The different amounts of fresh MnCo/MnCoCr LDH samples which are 0.01g, 0.05g and 0.09g were added to the solution. The mixture solution was stirred overnight to get a homogeneous solution by using a heating mantle. Then, the solution was casted into Teflon petri dishes and the sample was left to dry for 1-3 days to form film. All samples were prepared at room temperature and stored in a desiccator. The steps were repeated by replacing fresh MnCo/MnCoCr LDH sample with calcined MnCo/MnCoCr LDH sample. The method was retrieved from a previously reported method [14].

Electrochemical studies of polymer electrolyte

All samples of each system were characterized to determine which system contributes electricity by using Electrochemical Impedance Spectroscopy (EIS). With the frequency used in the range of 50 Hz to 1 MHz, the conductivity measurements were performed by using HIOKI 3532-50 LCR HiTESTER. The area of specimen for all testing was 0.7855 cm^2, whereas the average thickness was in the range between 0.013 cm and 0.031 cm.

Results and Discussion

Layered Double Hydroxide (LDH)

MnCo and MnCoCr LDHs were successfully synthesized and characterized using five instruments which are TGA, PXRD, FTIR and FESEM. The discussion of each characterization is in the next sub-section.

The TGA/ DTG curves of MnCo LDH obtained are presented in **Figure 1**. The TGA/DTG thermograms of MnCo LDH show three weight loss stages. The first stage represents the process of interlayer removal water molecules or dehydration occurred around 25 ºC. It was followed by the second stage, dehydroxylation which is associated to the elimination of water from the LDH interlamellar domains [15] around 120 ºC and the last stages stage is the removal of the interlayer anion or decarboxylation and decarbonation processes in the range of 400 ºC to 450 ºC, where there is a point of the optimum temperature removing the interlayer carbonate from MnCo LDH.

The TGA/ DTG curves of MnCoCr LDH were displayed in **Figure 2**. The TGA/DTG thermograms of MnCoCr LDH also show three weight loss stages in the range of 125 – 425 ºC. The weight loss stages occurred at 125 ºC indicate the removal of water or dehydration. The second weight loss stage occurs around 225 ºC corresponds to dehydroxylation and there is a third weight loss observed about 425 ºC which corresponds to the weight loss of metal hydroxides to the corresponding metal oxides during thermal decomposition [16]. To conclude, fresh MnCo LDH and MnCoCr LDH underwent thermal decomposition at 415°C and 425°C, respectively which resulted in the destruction of the lamellar structure and the formation of metal oxides [17]. **Table 3** summarizes the decomposition temperature for the secondary and tertiary LDH.

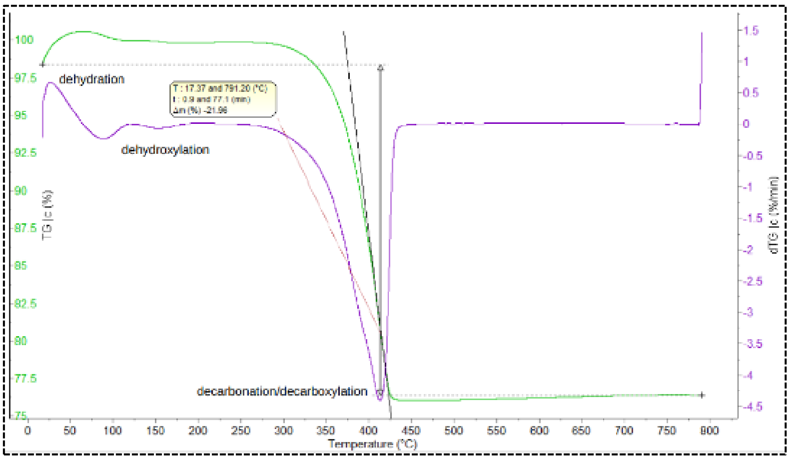

Figure 1. TGA profile of Fresh MnCo LDH

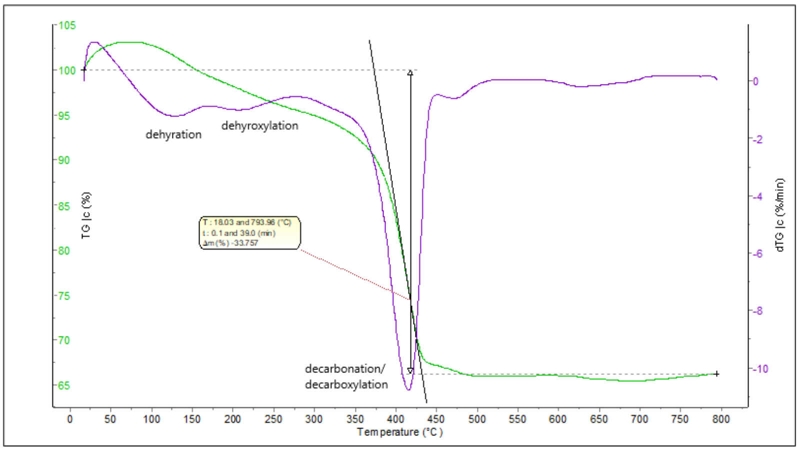

Figure 2. TGA profile of Fresh MnCoCr LDH

Table 3. The decomposition temperature of LDH measured by TGA

Materials	Decomposition (°C)	Weight Loss Stages	First Weight Loss (°C) (Dehydration)	Second Weight Loss (°C) (Dehydroxylation)	Third Weight Loss (°C) (Decarbonation/ Decarboxylation)
F-MnCo LDH	415	Three	25	120	415
F-MnCoCr LDH	425	Three	125	225	425

Powder X-ray diffraction (PXRD) is one of the most effective techniques for qualitative and quantitative analysis of crystalline compounds. The sharp peaks indicate the crystalline nature of the LDHs as depicted in **Figure 3** and **Figure 4**. PXRD patterns verified the layered structure of fresh MnCo LDH and MnCoCr LDH as displayed in **Figure 3**. It shows that the sample arrangement is in ordered structure forming a crystal type shape where there are 7 significant peaks. The diffraction patterns are characteristic of the hexagonal unit cell and are observed with sharp and intense reflections at 2θ = 23°, 30°, 34°, 42°, 50°, 61° and 63° corresponding to the plane of (003), (006), (012), (015), (018), (110) and (113), respectively. These results revealed that the LDH samples have been effectively synthesized via an alkali-free co-precipitation method. **Table 4** shows the textural properties of d spacing and lattice parameter of LDH. The values of lattice parameters automatically can be obtained from PXRD data, and all corresponding parameters are tabulated in **Table 4**. In comparison with the findings of other studies, all values of lattice parameters correlated with the layered structure of hydrotalcite-like compounds [18]. The synthesized compounds do not exhibit any contaminants. As a result, PXRD analysis fully describes the formation of the LDH structure.

Figure 4 displays the PXRD pattern of MnCo LDH and MnCoCr LDH after calcination which shows sharp and intense peaks at (006), (101) and (102) reflections at $2\theta = 32^\circ$, 38° and 45°, corresponding to the mixed Mn-Co oxides [19]. Due to the destruction of the structure during calcination process, no layered structure peaks were seen in PXRD patterns in the calcined compounds hydrotalcite [20]. The result obtained nearly is aligned with [21] study of which the mixed oxide that appeared after calcination process exhibits reflections at $2\theta = 35^\circ$, 43° and 62°.

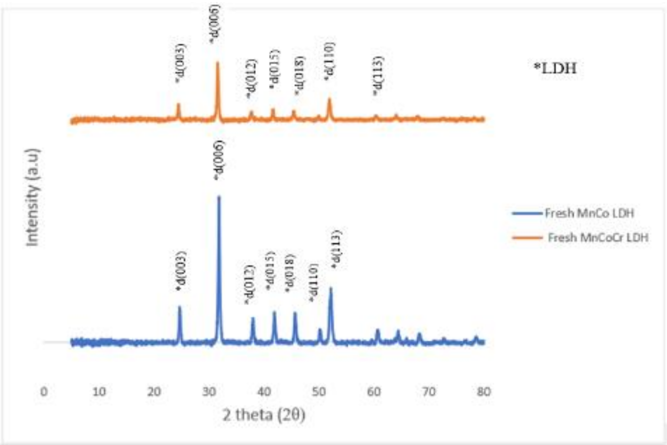

Figure 3. PXRD diffraction of fresh LDH

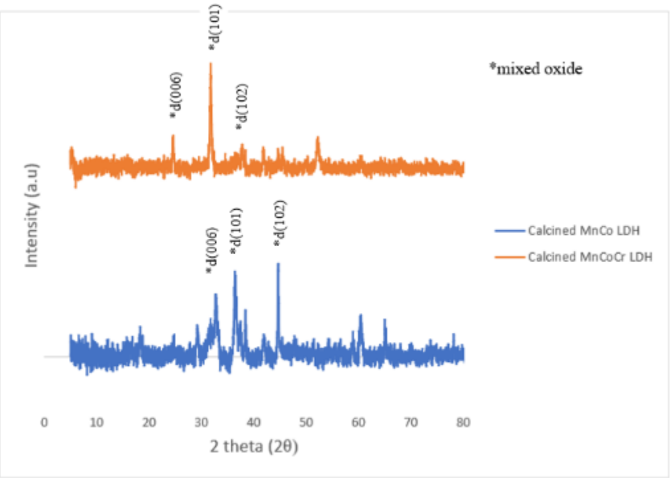

Figure 4. PXRD diffraction of calcined LDH

Table 4. The textural properties of d spacing and lattice parameter of LDH

Materials	d Spacing (A°)	Lattice Parameter (A°)	
		a	c
Fresh MnCo LDH	1.63	3.4	3.4
Fresh MnCoCr LDH	1.67	2.5	4.1
Calcined MnCo LDH	1.67	2.5	4.1
Calcined MnCoCr LDH	1.79	6.3	6.3

FTIR analysis was carried out on both fresh and calcined MnCo LDH and MnCoCr LDH. **Table 5** shows the summary of significant peaks presence in the samples. The strong and broad band at 3351.2 cm^{-1} (**Figure 5**), 3348.96 cm^{-1} (**Figure 7**) and 3343.51 cm^{-1} (**Figure 8**) are assigned to the stretching of O-H groups. The absorption band between 3300 – 3700 cm^{-1} with broad peak indicates the stretching of O-H groups that is present in the brucite-type sheets [18]. The same finding was also obtained by other researchers [18]. The weak band at 3306.4 cm^{-1} (**Figure 6**) in the calcined MnCo LDH sample is due to the vibration of physically adsorbed water and structural hydroxyl groups showing their loss throughout the calcination process [21]. The absorption bands at 1401.1 cm^{-1} (**Figure 5**), 1392.6 cm^{-1} (**Figure 6**), 1400.63 cm^{-1} (**Figure 7**) and 1404.01 cm^{-1} (**Figure 8**) indicate the C=O bending with a sharp peak. It is nearly aligned with the result from [8] at 1385 cm^{-1} which occurred in the vibration form of CO_3^{2-} in the interlayer of MgAl LDHs. The peaks appeared at 862.5 cm^{-1} (**Figure 5**), 864.3 cm^{-1} (**Figure 6**), 861.59 cm^{-1} (**Figure 7**) and 862.01 cm^{-1} (**Figure 8**), correspond to the Mn-O/Co-O stretching.

The spectra show a peak in the range of 500 – 1000 cm^{-1} bands which refer to the metal oxygen metal bonding (M-O, O-M-O or M-O-M) in the lattice of LDH. The absorption peaks at 727.5 cm^{-1} (**Figure 5**) and 725.2 cm^{-1} (**Figure 6**) are attributed to the Mn – Co LDH bending, whereas the absorption peaks at 724.29 cm^{-1} (**Figure 7**) and 725.11 cm^{-1} (**Figure 8**) correspond to the Mn – Co – Cr LDH bending. The result correlates with [22] study, of which the stretching vibration of Mn-Co is at 690 cm^{-1}. Most values of absorption peaks which indicate the LDH bands are slightly different in all samples in the range between 724 – 861 cm^{-1}. The small peaks of the absorption bands at 1641.7 cm^{-1} (**Figure 5**), 1797.73 cm^{-1} (**Figure 7**) and 1801.69 cm^{-1} (**Figure 8**) correspond to the C=O stretching. The findings are nearly the same with [23] result, of which the C=O stretching occurred at 1730 cm^{-1}. All these bands have confirmed the formation of MnCo LDH and MnCoCr LDH structures.

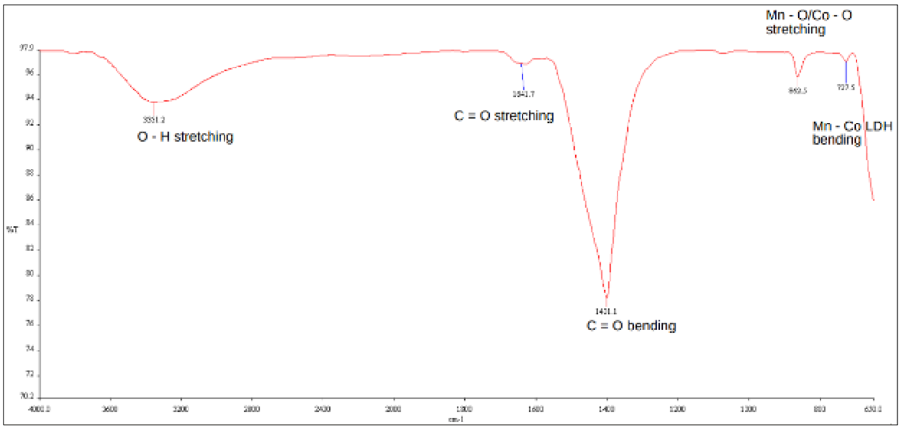

Figure 5. FTIR spectrum of fresh MnCo LDH

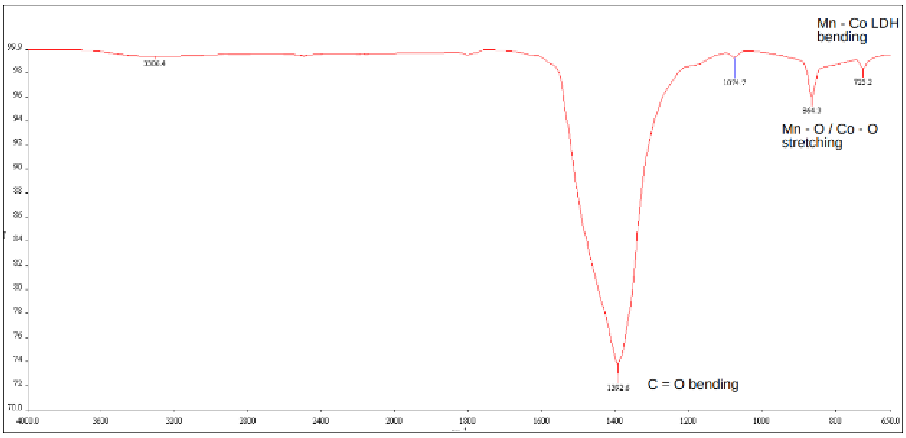

Figure 6. FTIR spectrum of calcined MnCo LDH

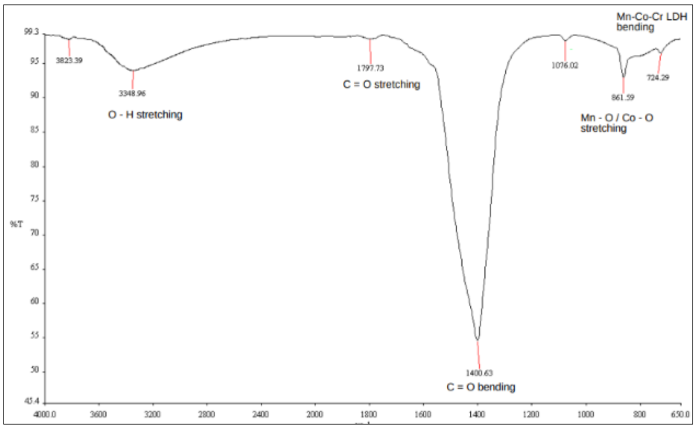

Figure 7. FTIR spectrum of fresh MnCoCr LDH

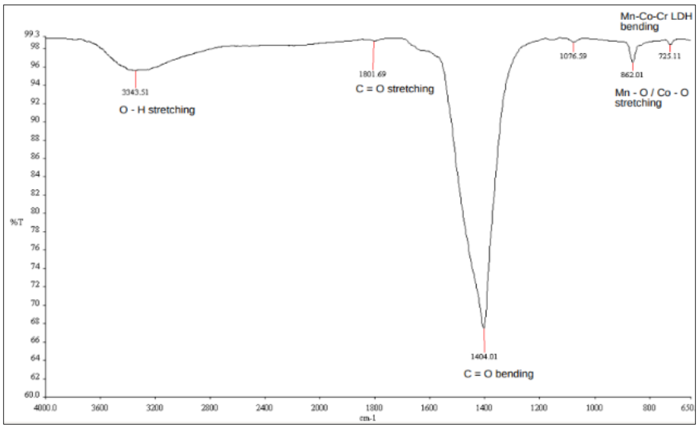

Figure 8. FTIR spectrum of calcined MnCoCr LDH

Table 5. The important IR absorption band present in the fresh and calcined MnCo LDH and MnCoCr LDH samples

Materials	Characteristic Band	Wavenumber (cm^{-1}) (This Study)	Wavenumber (cm^{-1}) (Reference)	References
Fresh MnCo LDH	O – H stretching	3351.2	3450	[23]
	C = O stretching	1641.7	1730	[23]
	C = O bending	1401.1	1385	[8]
	Mn-O/Co-O stretching	862.5	860	[8]
	Mn – Co LDH bending	727.5	690	[22]
Fresh MnCoCr LDH	O – H stretching	3348.96	3450	[18]
	C = O stretching	1797.73	1730	[23]
	C = O bending	1400.63	1385	[8]
	Mn-O/Co-O stretching	861.59	860	[8]
	Mn-Co-Cr LDH bending	724.29	690	[22]
Calcined MnCo LDH	C = O bending	1392.6	1385	[8]
	Mn-O/Co-O stretching	864.3	860	[8]
	Mn-Co LDH bending	725.2	690	[22]
Calcined MnCoCr LDH	O – H stretching	3343.51	3450	[18]
	C = O stretching	1801.69	1730	[23]
	C = O bending	1404.01	1385	[8]
	Mn-O/Co-O stretching	862.01	860	[8]
	Mn-Co-Cr LDH bending	725.11	690	[22]

Field emission scanning electron microscopy (FESEM) is an analytical technique used to capture the surface morphology of materials. The figures display the microstructural images of fresh and calcined MnCo LDH and MnCoCr LDH samples which were characterized at 1k and 4k magnification. **Figure 9(a)** displays the structure of fresh MnCo LDH agglomerate together with big size in irregular shape, whereas the FESEM images of fresh MnCoCr LDH **(Figure 10(a))** shows that the structure does not stick or clump together and has better distribution. Both calcined samples also indicate the same results as the fresh samples as proven in **Figure 9(b)** and **Figure 10 (b)**. Studies from [24] and [25] observed the formation of ultrathin MnCo LDH nanosheets with smooth surfaces. Meanwhile, the formation of rough concave surface of MnCo LDH nano – needles was reported in another study [26]. In comparison with this study, both morphologies of samples are different from those of other studies. This might be due to the lack of expertise in the LDH synthesize technique.

Electrochemical studies

EIS measurement was performed to determine the conductivity of the prepared samples at a frequency range of 50 Hz to 100 kHz. **Table 6** tabulates and compares the thickness of sample, R_b and conductivity values of each sample of the PEO system, PEO and MnCo LDH system and PEO and MnCoCr LDH system. The sample thickness was measured by using thickness gauge, where the intersection point of the curve at the real part of the Cole - cole plot determines the value of R_b. Cole - cole plot is a graph on which Z' is the real part on X-axis against Z'' that is the imaginary part on Y-axis. The area of sample is constant, which is 0.7855 cm$_2$. The conductivity values were obtained from the calculation by applying the following formula and all corresponding parameters are tabulated in **Table 6**.

$$\mathit{conductivity} = \frac{t}{R_bA} \qquad \text{(Eq. 1)}$$

where t is the thickness of sample, R_b is the bulk resistance and A is the area of sample or electrode.

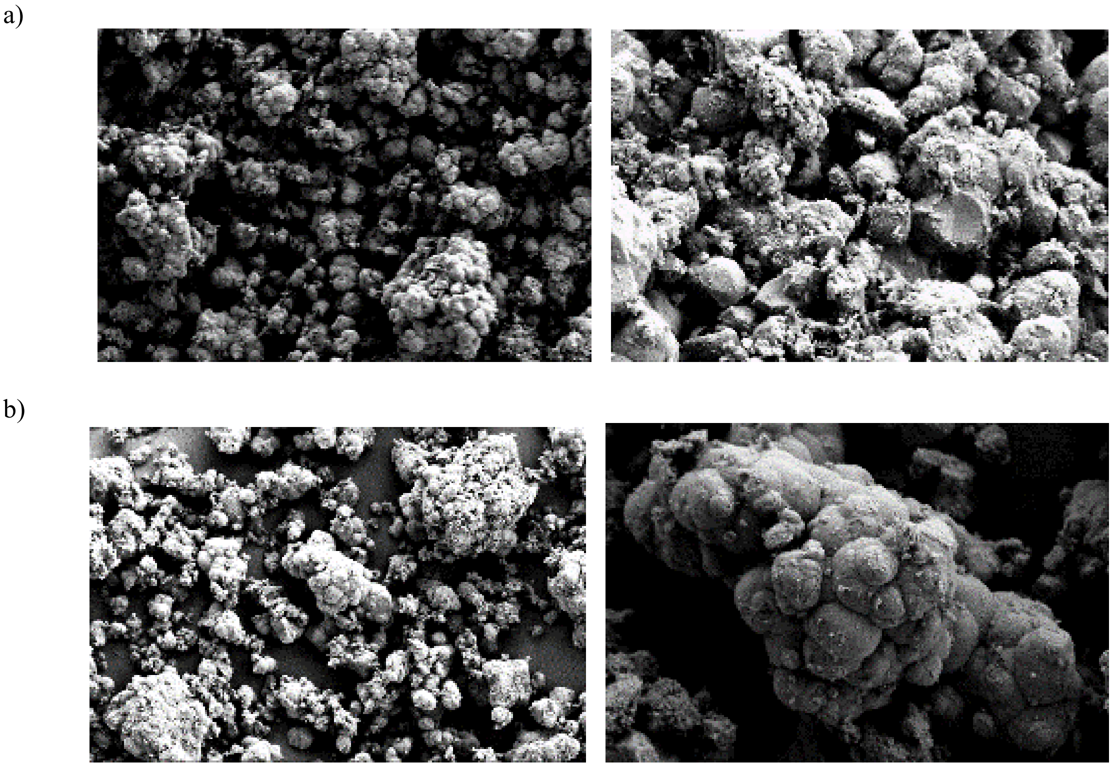

Figure 9. FESEM images at 1k (left) and 4k (right) magnification a) Fresh MnCo LDH, b) Calcined MnCo LDH

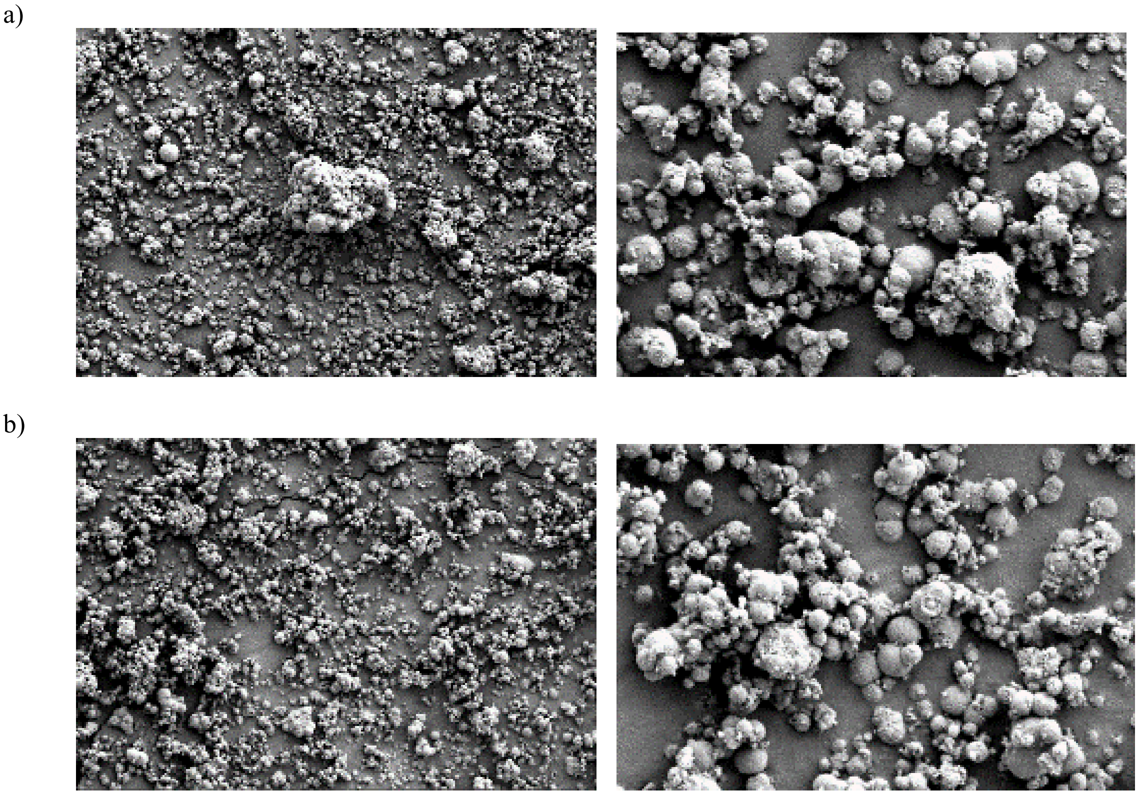

Figure 10. FESEM images at 1k (left) and 4k (right) magnification a) Fresh MnCoCr LDH, b) Calcined MnCoCr LDH

Table 6. Comparison between PEO system, PEO and MnCo LDH system and PEO and MnCoCr LDH system in terms of thickness of sample, R_b and conductivity values of each sample

Types of System	**Samples (g)**	**Thickness of Sample (cm)**	R_b **(ohm)**	**Conductivity (S/m)**
PEO system	PEO	0.02	3300000	7.7156×10^{-9}
PEO and MnCo LDH system	0.01 fresh MnCo LDH	0.018	3600000	6.3654×10^{-9}
	0.05 fresh MnCo LDH	0.014	3700000	4.8170×10^{-9}
	0.09 fresh MnCo LDH	0.027	3600000	9.5481×10^{-9}
	0.01 calcined MnCo LDH	0.017	3600000	6.0117×10^{-9}
	0.05g calcined MnCo LDH	0.031	3500000	1.1276×10^{-8}
	0.09g calcined MnCo LDH	0.02	3400000	7.4887×10^{-9}
PEO and MnCoCr LDH system	0.01g fresh MnCoCr LDH	0.013	3400000	4.8676×10^{-9}
	0.05g fresh MnCoCr LDH	0.014	3700000	4.8170×10^{-9}
	0.09g fresh MnCoCr LDH	0.017	3600000	6.0117×10^{-9}
	0.01g calcined MnCoCr LDH	0.023	3400000	8.6120×10^{-9}
	0.05g calcined MnCoCr LDH	0.021	3200000	8.3546×10^{-9}
	0.09g calcined MnCoCr LDH	0.018	3400000	6.7398×10^{-9}

From Table 4.4, it can be concluded that 0.05 g calcined MnCo LDH exhibits the most excellent electrochemical performance compared to other samples, which is 1.1276×10^{-8} S/m. The result can be confirmed by PXRD data obtained. It shows that the correlation between the lattice parameter is directly proportional to the d spacing as proven in the following formula:

$$\alpha = d\ x\ \sqrt{h^2 + k^2 + l^2} \qquad \text{(Eq. 2)}$$

where α is the lattice parameter, d is the d - spacing and h, k and l are miller indices of the lattice planes.

However, there is no correlation between the lattice parameter and the conductivity. To conclude, no correlation can be found in this study due to not enough data from Brunauer-Emmett-Teller (BET) surface area analysis.

From the results above, the 0.05g calcined MnCo LDH demonstrates superior electrochemical performance, boasting a conductivity of 1.1276 x 10^{-8} S/m due to the highest value of conductivity obtained among various samples.

Conclusion

The fresh and calcined MnCo LDH and MnCoCr LDH were successfully synthesized. All samples underwent physiochemical studies to determine their thermal stability, crystallinity, chemical bonding and morphology. To summarize, the calcination temperature of fresh MnCoCr LDH is higher compared to that of fresh MnCo LDH, which are 425 °C and 415 °C, respectively. The results from PXRD analyses of all samples show high crystallinity where all the peaks are sharp and narrow. All the peaks of LDH were identified which thus confirmed that the LDHs have been successfully synthesized. Besides, all LDH bending in the samples were found to be in the range of 861 cm^{-1} – 724 cm^{-1} in the FTIR spectra. Lastly, the microstructure images of each sample were also identified. Moreover, it has been found that 0.05 g calcined MnCo LDH exhibits the most excellent electrochemical performance compared to those of other samples, which is 1.1276 x 10^{-8} S/m. Therefore, the objectives of the study were met successfully.

Acknowledgement

The author expresses gratitude for the generous assistance provided by the University of Technology MARA (UiTM) in conducting this research. The study was made possible through a grant awarded to NAT under MyPair-STFC ISIS MUON NEUTRON SOURCE, UK (100-TNCPI/INT 16/6/2 (041/2024).

References

1. Bocharova, V., and Sokolov, A. P. (2020). Perspectives for polymer electrolytes: a view from fundamentals of ionic conductivity. *Macromolecules*, 53(11): 4141-4157.
2. Sharma, S., Pathak, D., Kumar, R., Sharma, V., Arora, N., Kaur, S., and Sharma, V. (2021). Nanocomposite polymer electrolytes for energy devices. In *Nano Tools and Devices for Enhanced Renewable Energy* (pp. 27-40). Elsevier.
3. Zhou, D., Shanmukaraj, D., Tkacheva, A., Armand, M., and Wang, G. (2019). Polymer electrolytes for lithium-based batteries: advances and prospects. *Chemistry*, 5(9): 2326-2352.
4. Chua, S., Fang, R., Sun, Z., Wu, M., Gu, Z., Wang, Y., ... and Wang, D. W. (2018). Hybrid solid polymer electrolytes with two-dimensional inorganic nanofillers. *Chemistry–A European Journal*, 24(69): 18180-18203.
5. Meng, N., Zhu, X., and Lian, F. (2022). Particles in composite polymer electrolyte for solid-state lithium batteries: A review. *Particuology*, 60: 14-36.
6. Qin, J., Shi, H., Lv, Q., He, M., Xu, Y., Chen, M., ... and Yu, J. (2023). Enhanced adsorption effect of defect ordering Mg/Al on layered double hydroxides nanosheets with highly efficient removal of Congo red. *Materials & Design*, 232: 112084.
7. Sadavar, S. V., Padalkar, N. S., Shinde, R. B., Kochuveedu, S. T., Patil, U. M., Patil, A. S., ... and Gunjakar, J. L. (2022). Mesoporous nanohybrids of 2–D Cobalt–Chromium layered double hydroxide and polyoxovanadate anions for high performance hybrid asymmetric supercapacitors. *Journal of Power Sources*, 524: 231065.
8. Tajuddin, N. A., Sokeri, E. F. B., Kamal, N. A., and Dib, M. (2023). Fluoride removal in drinking water using layered double hydroxide materials: preparation, characterization and the current perspective on IR4.0 technologies. *Journal of Environmental Chemical Engineering*, 11(3): 110305.
9. Mohd Agus, R. A., Deraman, S. K., and A Tajuddin, N. (2021). Synthesis and characterization of two-dimensional (2D) nanosheet zinc aluminum layered double hydroxide (Zn/Al LDH) via an alkali-free route. *Science Letters*, 15(1): 82-89.
10. Lu, Y., Du, Y., and Li, H. (2020). Template-sacrificing synthesis of Ni-Co layered double hydroxides polyhedron as advanced anode for lithium ions battery. *Frontiers in Chemistry*, 8: 581653.
11. Shaari, N., and Kamarudin, S. K. (2019). Recent advances in additive-enhanced polymer electrolyte membrane properties in fuel cell applications: An overview. *International Journal of Energy Research*, *43*(7): 2756-2794.
12. Li, J., Zhong, L., Li, J. X., Wu, H. F., Shao, W. W., Wang, P. Q., ... and Jing, M. X. (2023). Insights into the effects of different inorganic fillers on the electrochemical performances of polymer solid electrolytes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 671: 131704.
13. Ye, F., Liao, K., Ran, R., and Shao, Z. (2020). Recent advances in filler engineering of polymer electrolytes for solid-state Li-ion batteries: a review. *Energy & Fuels*, 34(8): 9189-9207.
14. Anuradha, K., and Arunkumar, A. (2023). Structural, conductivity and dielectric studies of pure and KCL doped polymer electrolyte films. *Materials Today: Proceedings*, 92: 1385-

1388.

15. Machrouhi, A., Khnifira, M., Boumya, W., Sadiq, M., Abdennouri, M., Elhalil, A., ... and Barka, N. (2023). Experimental and density functional theory studies of methyl orange adsorption on Ni-Al/LDH intercalated sodium dodecyl sulfate. *Chemical Physics Impact*, 6: 100214.
16. Chawla, M., Dubey, R., Singh, G., Sengupta, S. K., and Siril, P. F. (2017). Controlling the morphology of layered double hydroxides of Mn and Co and their exceptional catalytic activities. *Thermochimica Acta*, 654: 130-139.
17. Modrogan, C., Căprărescu, S., Dăncilă, A. M., Orbuleț, O. D., Vasile, E., and Purcar, V. (2020). Mixed oxide layered double hydroxide materials: Synthesis, characterization and efficient application for Mn^{2+} removal from synthetic wastewater. *Materials*, 13(18): 4089.
18. Cano, L. A., Barrera, D., Villarroel-Rocha, J., and Sapag, K. (2023). Influence of the synthesis method of layered double hydroxides on the textural properties and nitrate removal. *Catalysis Today*, 422: 114222.
19. Ibrahim, E. H., Tajuddin, N. A., and Hamzah, N. (2019). Synthesis and characterization of alkali free Mg-Al layered double hydroxide for transesterification of waste cooking oil to biodiesel: Effect of Mg-Al ratio. *International Journal Engineering Technology*, *7*: 154.
20. Zulkifli, M., Pungot, N. H., Tajuddin, N. A., Aluwi, M. F. F. M., Jumali, N. S., and Shaameri, Z. (2022). A short review on the influence of the preparation method on the physicochemical properties of Mg/Al hydrotalcite for glucose isomerization. *Malaysian Journal Analytical Sciences*, 26: 191-201.
21. Xu, W., Mertens, M., Kenis, T., Derveaux, E., Adriaensens, P., and Meynen, V. (2023). Can high temperature calcined Mg–Al layered double hydroxides (LDHs) fully rehydrate at room temperature in vapor or liquid condition?. *Materials Chemistry and Physics*, 295: 127113.
22. Naderi, L., and Shahrokhian, S. (2023). Metal-organic framework-assisted Co_3O_4/CuO@ CoMnP with core-shell nanostructured architecture on Cu fibers for fabrication of flexible wire-typed enzyme-free micro-sensors. *Chemical Engineering Journal*, 456: 141088.
23. Abdelrahman, A. A., Bendary, S. H., and Mahmoud, S. A. (2023). Synthesis and electrochemical properties of NiAl LDH@ RGO hierarchical nanocomposite as a potential counter electrode in dye sensitized solar cells. *Diamond and Related Materials*, 134: 109738.
24. Hsiao, Y. C., Liao, C. H., Hsu, C. S., Yougbaré, S., Lin, L. Y., and Wu, Y. F. (2023). Novel synthesis of manganese cobalt layered double hydroxide and sulfur-doped nickel cobalt layered double hydroxide composite as efficient active material of battery supercapacitor hybrids. *Journal of Energy Storage*, 57: 106171.
25. Kong, W., Li, J., Gong, J., Yu, Q., Chen, G., Chen, J., ... and Wang, W. (2023). Three-dimensional network structured $MnCo_2S_4$/$NiCo_2S_4$ electrode materials assembled with two-dimensional nanosheets as basic building units for asymmetric supercapacitor applications. *Journal of Alloys and Compounds*, 940: 168480.
26. Zhang, Y., Liu, S., Chen, Z., Zhang, Y., Zeng, T., Wan, Q., and Yang, N. (2023). Trimetallic layered double hydroxides with a hierarchical heterostructure for high-performance supercapcitors. *Journal of Energy Storage*, 61: 106700.