

Article

Morphology and Particle Size of a Synthesized NMC 811 Cathode Precursor with Mixed Hydroxide Precipitate and Nickel Sulfate as Nickel Sources and Comparison of Their Electrochemical Performances in an NMC 811 Lithium-Ion Battery

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Abstract: Cathode precursors of lithium-NMC 811 were synthesized by the coprecipitation method using two different nickel sources, namely mixed nickel–cobalt hydroxide precipitate (MHP) and nickel sulfate. The characteristics of the synthesized precursors were compared with the characteristics of the commercial NMC 811 cathode precursor obtained from the international market. The XRD analyses identified that the diffraction peaks of the three precursor materials were in close agreement to that of $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, with the figure(s) of merit (FoM) of 0.81, 0.88, and 0.9, respectively, for the synthesized precursor that used MHP as the source of nickel (SM-LNMCO-811), nickel sulfate as the source of nickel (SX-LNMCO-811), and the commercial precursor (K-NMC-811). The elemental analysis of the synthesized precursors revealed the Ni:Mn:Co mol ratios of 0.8:0.08:0.12 and 0.76:0.11:0.13 for SM-LNMCO-811 and SX-LNMCO-811, respectively. The SEM analysis revealed that SX-LNMCO-811 and K-NMC-811 showed a similar particle morphology with a spherical shape; the SM-LNMCO-811 exhibited an irregular particle morphology. The particle size analysis showed that SM-LNMCO-811 had the largest average particle size (285.2 μm) while K-NMC-811 and SX-LNMCO-811 samples had almost the same average values (i.e., 18.28 and 17.16 μm , respectively). The results of the charge–discharge measurement of the fabricated battery cylindrical cells with SM-LNMCO-811, SX-LNMCO-811, and K-NMC-811 as cathode materials showed the best discharge value of the SX-LNMCO-811 sample at 178.93 mAh/g with an initial efficiency of 94.32%, which is in line with the electrochemical impedance measurement results that showed the largest ion conductivity and lithium ion diffusion coefficient value of the SX-LNMCO-811 sample that utilized the synthesized nickel sulfate as the source of the nickel.

Keywords: nickel; co-precipitation; synthesis; cathode precursor; charge–discharge

1. Introduction

The global initiative for reducing greenhouse gas emissions has transformed the utilization of fossil-fuel-based vehicles into electric vehicles (EV) in the transportation sector. Martins et al. (2021) reported that the growth of new electric vehicles and electric vehicles in use is exponential [1]. Lithium-ion batteries (LIBs) have been the technology of

choice for EVs due to their versatility in terms of energy density, self-discharge properties, thermal stability, and lifecycle [1–3]. The types of LIBs used in EVs are classified based on the compositions of their cathode materials; the most used ones are lithium manganese oxide (LMO), lithium iron phosphate (LFP), lithium cobalt aluminum oxide (NCA), and lithium nickel manganese cobalt oxide (NMC).

The performance of a Li-ion battery is highly dependent on the performance of the cathode or positive electrode. Lithium-ion batteries are also classified based on the type of material that makes up the cathode. The cathode material is a crucial factor that determines the capacities of battery cells, both charge and discharge capacities, and battery life. Cathode characteristics play an essential role in the electrochemical performance of battery cells because the process of conducting electric currents in the battery takes place through the intercalation–deintercalation mechanisms of lithium within the structure of the cathode material [4].

One of the cathode materials currently predicted to be the most utilized in Li-ion batteries is a lithium–nickel–manganese–cobalt oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$), popularly called NMC. Li-ion batteries of the NMC type are known to have high-energy densities, be safe, have long lives, and are relatively inexpensive [5]. The NMC offers a high specific energy density contributed by the presence of nickel and spinel structures from manganese. At the same time, cobalt prevents nickel from occupying the lithium sites, leading to a higher reversible capacity [3]. The NMC batteries have been manufactured in various Ni:Co:Mn molar ratios, namely 1:1:1, 5:2:3, 6:2:2, and 8:1:1 [3]. The higher mass proportion of nickel or the lower mass contribution of cobalt gives a lower battery cost due to the lower cost of the cathode raw materials. This type of LIB has been used by several prominent EV manufacturers, such as BMW, Chevy, and Nissan [1,6].

Various methods have been developed to prepare active materials for LIB cathodes, including co-precipitation, solid-state reaction, solvothermal, hydrothermal, emulsion-drying, combustion process, mechanochemical, spray pyrolysis, and sol–gel methods [7]. The co-precipitation method is one of the most widely used methods for preparing cathode precursor material of LIBs because of its simplicity, ease of scale-up, and ability to produce a homogeneous structure at the particle scale. The co-precipitation method is favorable in the battery industry because it can utilize various raw materials, such as sulfates, chlorides, organic anions, and nitrate salts. In addition, the process is simple and does not require sophisticated equipment [8,9].

This article discusses the characteristics and electrochemical performance of cathode precursor material of the NMC 8:1:1 synthesized by the co-precipitation method using mixed hydroxide precipitate (MHP) and nickel sulfate as nickel sources produced by extraction and refining of Indonesian nickel laterite ore. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was utilized in the co-precipitation stage as a chelating agent and ammonium hydroxide (NH_4OH) solution was used as a pH adjuster. For both synthesized cathode precursors, a commercial manganese sulfate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), cobalt sulfate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), and lithium carbonate (Li_2CO_3) were used as the sources of manganese, cobalt, and lithium, respectively. The analysis results of these synthesized precursors were compared with the characteristics of a commercial NMC 811 cathode precursor obtained from the international market. By utilizing these three types of cathode precursor materials, NMC 811 full and half cells of the 18650-type and coin type were prepared, and their electrochemical performances were tested. The objective of the study was to investigate the effect of raw material purity, especially nickel carrier, on the morphology, particle size, crystal structure, and figure of merit of the crystal in comparison to the standard material of the Li-NMC 811 cathode precursor ($\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$). Furthermore, the correlation between the morphology and particle size of the synthesized and commercial precursors with the electrochemical performance of the fabricated batteries using these cathode precursors was carefully analyzed.

The publications reporting the results of the characterization of nickel-based lithium batteries using the products of nickel ore extraction and refining as sources of nickel are very

limited. MHP is one of the intermediate products of limonite ore processing plants, which is the most produced and internationally traded, in addition to mixed sulfide precipitate (MSP). In this study, the results of the characterization of NMC 811 cathode precursors, which were synthesized by using MHP and nickel sulfate from the refining of Indonesian nickel laterite ore, are discussed. MHP was prepared by leaching the limonite ore in a sulfuric acid solution, which was then purified through two stages of iron and aluminum removal and nickel and cobalt precipitation. Furthermore, the MHP was purified into nickel sulfate by re-leaching of MHP in sulfuric acid solution at atmospheric pressure, followed by purification of the pregnant solution through a three-step solvent extraction process using Versatic-10 and Cyanex-272 and crystallization of the nickel sulfate from the purified solution. This study was in conjunction with the efforts of the refining industry development to treat nickel laterite ore in Indonesia for the EV battery markets. The results highlight the effect of the purity of raw materials on the characteristics of the obtained Ni-based cathode precursors and their electrochemical performance when used in the NMC 811 lithium-ion battery cells.

2. Materials and Methods

2.1. Cathode Precursor Synthesis and Battery Fabrication

The chemical composition of MHP and nickel sulfate used as the sources of nickel for the synthesized NMC cathode precursors are presented in Tables 1 and 2, respectively. The MHP was prepared by the precipitation of nickel and cobalt from a pregnant leach solution of Indonesian nickel laterite ore in sulfuric acid solution. Meanwhile, the nickel sulfate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) was prepared by further refining the MHP through the MHP re-leaching-three stage solvent extraction using Versatic 10 and Cyanex 272, followed by crystallization of the nickel sulfate. The detailed synthesis procedure of MHP and nickel sulfate is beyond the scope of this article. As the sources of lithium, cobalt, and manganese, lithium carbonate (Li_2CO_3), cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$), and manganese sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), respectively, from the market, were used. The raw materials for synthesizing the NMC 811 cathode precursor were prepared according to the specified stoichiometry of Li:Ni:Mn:Co. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) as a precipitating agent and ammonium hydroxide (NH_4OH) solution as a pH adjuster were added after MHP or nickel sulfate, cobalt sulfate, and manganese sulfate were homogeneously stirred with a magnetic stirrer. The mixture was stirred for 2 h after reaching a temperature of 60 °C under a stirring speed of 500 rpm. This procedure was conducted to precipitate Ni, Mn, and Co in the form of a mixed Ni–Mn–Co oxalate. The precipitate was separated from the solution by filtration using filter paper. The precipitate was then dried in an oven at 100 °C for 24 h. The products of the co-precipitation stage were labeled according to the sources of nickel in the initial raw materials, namely MHP and nickel sulfate. The precipitate prepared using MHP as the source of nickel was labeled by SM-NMC-811, while the one using synthesized nickel sulfate was labeled by SX-NMC-811. Both SM-NMC-811 and SX-NMC-811 samples were analyzed by X-ray diffraction (XRD), scanning electron microscope (SEM), and Fourier-transform infrared spectroscopy (FTIR) to determine their dominant phases and crystal structure, morphology, and chemical constituent.

The product from the co-precipitation process was then mixed with lithium carbonate (Li_2CO_3) in a solid state to form a mixture of an NMC oxalate and Li carbonate. The mixture of the NMC oxalate and Li carbonate was then calcined at a temperature of 600 °C for 6 h at a muffle furnace to form a Li–Ni–Mn–Co-carbonate by releasing CO_2 gas from the Ni–Mn–Co-oxalate constituent. The Li–Ni–Mn–Co-carbonate sample that used MHP as the initial source of nickel was labeled by SM-LNMC-811, while SX-LNMC-811 labeled the one that used nickel sulfate as the initial source of nickel. The SM-LNMC-811 and SX-LNMC-811 samples were characterized by FTIR, XRD, and SEM analyses. The calcination products of SM-LNMC-811 and SX-LNMC-811 were then sintered at a temperature of 800 °C for 12 h in a tube furnace with O_2 gas injection at 50 mL/min to convert the Li–MNC-carbonates to Li–MNC oxides. A schematic illustration of the precursor synthesis procedure is shown in

Figure 1. The products of the sintering processes were ground and sieved by a 200-mesh screen and then characterized by the FTIR, XRD, SEM, and particle size analyzer (PSA) analyses. The sintering product of the Li-NMC-oxide sample that used MHP as the initial source of nickel was labeled by SM-LNMCO-811, while the one that used nickel sulfate as the initial source of nickel was labeled by SX-LNMCO-811.

Table 1. The chemical composition of MHP used as the source of nickel for the synthesis of the NMC 811 cathode precursor.

Element	Content (%)
Ni	47.22
S	11.94
Mg	1.41
Mn	1.80
Co	1.12
Zn	0.72
Cl	0.26
Sb	0.20
Al	0.11
Pb	0.56
K	0.06
Cr	0.03
Fe	0.02
P	0.02
O & H	balance

Table 2. The chemical composition of the synthesized nickel sulfate used as the source of nickel for the synthesis of NMC 811 cathode precursors.

Element	Content	Unit
Ni	21.53	%
Co	132.65	ppm
Na	5379.1	ppm
Mg	226.52	ppm
Ca	123.93	ppm
Mn	18.23	ppm
Fe	205.19	ppm

The synthesized NMC 811 cathode precursor of SM-LNMCO-811 and SX-LNMCO-811 as well as the commercial NMC 811 cathode precursor were then prepared into slurries and coated on aluminum foil, which served as a current collector at the cathode. The cathode slurry was prepared with a mass ratio of the cathode precursor materials to polyvinylidene (PVDF) and acetylene black (AB) of 92:3:5. The PVDF and AB were used as binders. The ingredient was dissolved in N-methyl-2-pyrrolidone (NMP) solvent and mixed until it became homogeneous.

The aluminum foil was coated by the cathode slurry of SM-LNMCO-811, SX-LNMCO-811, and K-NMC-811 with a thickness of 200 μm using a doctor blade coater. The coated aluminum foil was dried in a vacuum oven for 30 min at 150 $^{\circ}\text{C}$. Similar procedures were conducted on the reverse side of the aluminum foil with a coating thickness of 250 μm . The dry cathode sheet was pressed using a rotary pressing machine and then cut to obtain a sheet with a width of 5.6 cm. Each end of the cathode sheet was welded with aluminum using a welder machine and insulated to make it stronger. The next step was rolling the cathode with a graphite anode and a polypropylene separator. The anode sheet was welded to the battery cell sleeve, and the cover was threaded. The parts that were threaded were processed in the aging stage to compress the coils. After the aging stage, 5 mL of 1 M LiPF_6 electrolyte was filled into the sleeve, and the sleeve was closed and sealed.

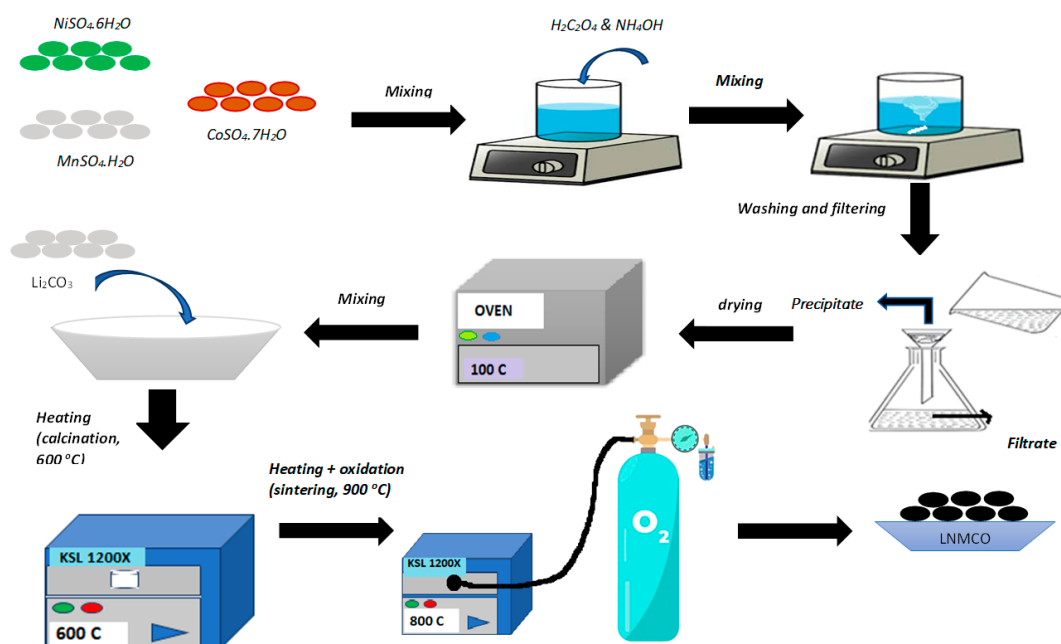


Figure 1. A schematic illustration of the NMC-811 cathode precursor synthesis.

2.2. Material Characterization

As mentioned, the characterizations of the synthesized materials were carried out using several devices. The FTIR analysis using Shimadzu serial no. A224158 type was conducted to identify compounds and functional groups formed in the synthesized materials after co-precipitation, calcination, and sintering stages. The XRD analysis using PANalytical X'Pert XRD, employing $\text{CuK } \alpha$ radiation and λ 1.54 Å, was performed to identify the structure and size of the crystals formed in the synthesized material precursors as well as the commercial precursor as a benchmark. The XRF analysis using PANalytical MiniPal 4 was carried out to determine the elemental constituent in the synthesized cathode precursor samples. Meanwhile, the analysis using a scanning electron microscope (SEM) (JEOL JCM-7000 type) was performed to determine the particle morphology of the synthesized and commercial precursors. Furthermore, the particle size analyzer (PSA) (Beckman Coulter) was used to determine the particle size of the synthesized NMC 811 cathode precursors after sintering and the particle size of the commercial precursor as a benchmark. The PSA results show the average particle size and the distribution of deciles of 10, 50, and 90 of the synthesized precursors and the commercial NMC 811 cathode precursor.

2.3. Electrochemical Performance Test of the Batteries

The charge–discharge performances and specific capacity of the fabricated Li-NMC-811 batteries with a variation of cathode material precursors at 1 and 100 cycles, and at various electrical charges, were measured using Battery System Test 8 (BST 8) from Neware 3000. The battery cell type used in the measurements of the charge–discharge using BTS 8 was a cylindrical full cell battery, 18650-type, and graphite/mesocarbon microbeads (MCMC) (MTI, America) as anodes. The parameters used in the measurements of the charge–discharge performances of the batteries are presented in Table 3. Electrochemical impedance spectroscopy (EIS) measurements using a potentiostat of EZstat Pro were also carried out to half-cells of the NMC-811 with a variation of cathode material precursors to determine the charge transfer resistance that was further used to determine the lithium ionic conductivity and diffusion coefficients of the lithium cation. The EIS measurements were performed at a DC bias of 4.3 V and a frequency range of 0.01–10,000 Hz. The analysis using Z-view software was performed to determine the electrical equivalent circuit that fits with the EIS measurement data.

Table 3. Parameters used in the measurements of the charge–discharge performances of the fabricated Li-NMC-811 batteries with a variation of cathode material precursors using Battery System Test 8 (BST 8), Neware 3000.

Parameter	Voltage	Electrical Charge
Constant current charge	4.25	1/20 C
Constant voltage charge	4.25	1/30 C
Constant current discharge	2.7	1/20 C

3. Results and Discussion

In this section, the results of the characterization of the synthesized cathode precursors using synthesized MHP and nickel sulfate as the initial sources of nickel as well as that of the commercial precursor are discussed. The results of the physical, structural, and morphological characterizations of the cathode precursors are then correlated with the electrochemical performances of the NMC 811 LIBs, which were prepared by using these three different cathode precursors.

3.1. FTIR Analysis

The FTIR analysis was performed on the synthesized cathode materials after co-precipitation of M-oxalate, lithiation (mixing of the M-oxalate with lithium carbonate), and sintering stages. FTIR spectra of the synthesized NMC 811 cathode precursors after co-precipitation, lithiation, and sintering stages for those using MHP and nickel sulfate as the initial sources of nickel are presented in Figure 2a,b, respectively.

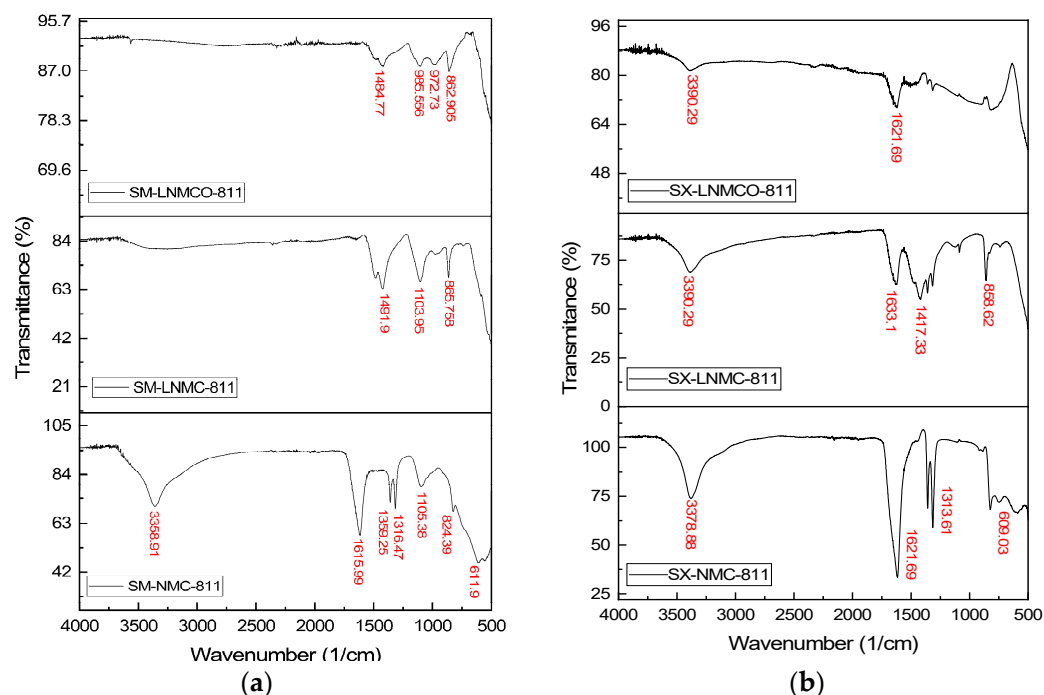
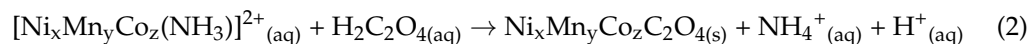
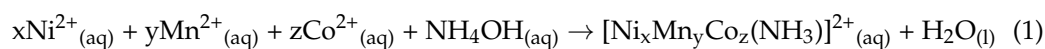


Figure 2. FTIR spectra of the synthesized NMC 811 cathode precursors after co-precipitation, lithiation, and sintering stages. (a) MHP as the source of Ni, (b) nickel sulfate as the source of Ni.

It was previously reported that the O-H bonding structure corresponded with the broad peaks at around 3300–3500/cm and 1600/cm. Meanwhile, the sharp peak located at about 1300/cm corresponded to the C-O bond [10–13]. The O-H and C-O bonds were identified on the FTIR spectra of both the SM-NMC-811 and SX-NMC-811 above-mentioned

wavenumber ranges, which indicated the co-precipitation of Ni-Mn-Co-oxalates that took place through the following reactions [10]:



Carbonate bonds began to be seen after the lithiation stage at wavenumber ranges of 800 to 880 cm^{-1} and 1410 to 1450 cm^{-1} . The dissociation of carbonate by releasing CO_2 gas after the sintering step is indicated by the attenuation of the C-O peak at about 1300/ cm .

3.2. XRD Analysis

The X-ray diffraction patterns of the synthesized NMC 811 cathode precursors that used MHP (SM-LNMCO-811) and nickel sulfate (SX-LNMCO-811) as sources of nickel, as well as that of the commercial precursor (K-NMC-811), are depicted in Figure 3. The XRD patterns of the three precursors show a relatively similar pattern with more noises exhibited by SM-LNMCO-811 and SX-LNMCO-81, which indicates more minor phases present in these materials. The XRD experimental data are compared to reference patterns of the Joint Committee on Powder Diffraction Standards (JCPDS) no. 96-152-0790 for $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ and the Figure of Merit (FoM) of measurement data with the reference was determined using Match! 3.14 software. The analysis identified that the diffraction peaks of the three precursor materials were in close agreement to that of $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The FoMs of the three precursors to $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ determined by Match! software are shown in Table 4. The FoM of the synthesized precursor that used nickel sulfate as the source of nickel (SX-LNMCO-811) and the commercial precursor (K-NMC-811) are both close to 1, which indicates their conformity to the reference material of $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. It was identified that the crystal structures of the precursor samples are hexagonal.

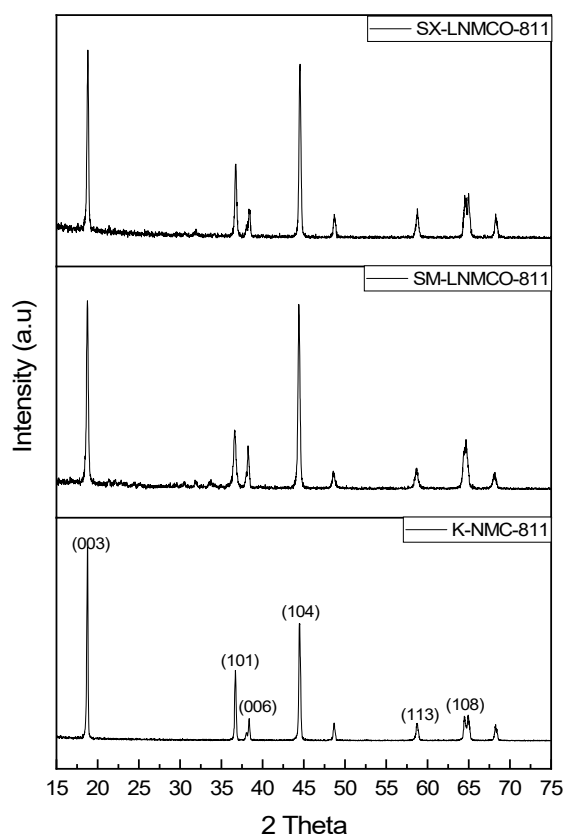


Figure 3. The X-ray diffraction patterns of SM-LNMCO-811, SX-LNMCO-811, and K-NMC-811.

Table 4. The FoM of the three precursors to $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$.

Precursor Sample	FoM (Figure(s) of Merit) to $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$
SM-LNMCO-811	0.81
SX-LNMCO-811	0.88
K-NMC-811	0.90

3.3. Elemental Analysis of the Precursor

As mentioned, the XRF analysis was utilized to determine the elemental constituent of the synthesized precursors (SM-LNMCO-811 and SX-LNMCO-811) and the commercial precursor (K-NMC-811). The elemental compositions of the synthesized and commercial precursors, which respect the contents of Ni, Mn, and Co (without taking oxygen into account) are presented in Table 5.

Table 5. Elemental compositions of Ni, Mn, and Co of the synthesized precursors (SM-LNMCO-811 and SX-LNMCO-811) and the commercial precursor (K-NMC-811) determined by XRF.

Sample	Ni (%)	Mn (%)	Co (%)
SM-LNMCO-811	71.01	6.85	10.30
SX-LNMCO-811	71.34	9.75	11.7
K-NMC-811	75.25	4.42	11.5

Based on the data of Ni, Mn, and Co percentages in the precursor samples, the mol ratios of these three elements were determined as shown in Table 6. It is apparent that the Ni:Mn:Co ratios are not exactly = 8:1:1 but are generally close to this desired ratio. A slight deviation from the designed stoichiometry was also reported by the previous researchers who analyzed the chemical composition of the NMC 811 commercial precursor [14]. On the other hand, it was also challenging to prepare the precursor with a stoichiometric ratio of metals, which exactly matched the expected composition in the laboratory.

Table 6. Comparison of Ni:Mn:Co elements contained in precursors K-NMC-811, SM-LNMCO-811, and SX-LNMCO-811.

Sample	Mol Ratio of Ni:Mn:Co		
	Ni	Mn	Co
SM-LNMCO-811	0.8	0.08	0.12
SX-LNMCO-811	0.76	0.11	0.13
K-NMC-811	0.82	0.05	0.13

3.4. Analysis of Morphology by SEM

The SEM analysis was carried out on the synthesized precursor samples after the sintering stage and the commercial NMC 811 cathode precursor to determine the morphology of the particle of the precursors. SEM micrographs of the precursors are depicted in Figure 4. As can be seen in Sections (a) and (c) in Figure 4, SX-LNMCO-811 and K-NMC-811 show a similar particle morphology with a spherical shape; the SM-LNMCO-811 exhibits an irregular particle morphology. The SEM micrograph of the SM-LNMCO-811 sample in Figure 4b demonstrates various shapes of secondary particles and poor aggregation of the primary particles to form a compact secondary particle, which is expected in association with the presence of impurities from MHP as the source of nickel. The low angle boundaries between the actual primary particles in a primary-like particle stimulate the development of nano-cracks, and this is exhibited by the morphology of the SM-LNMCO-811 sample. The spherical morphology of the SX-LNMCO-811 and K-NMC-811 samples agree with the one reported by Lin et al., 2016 [14].

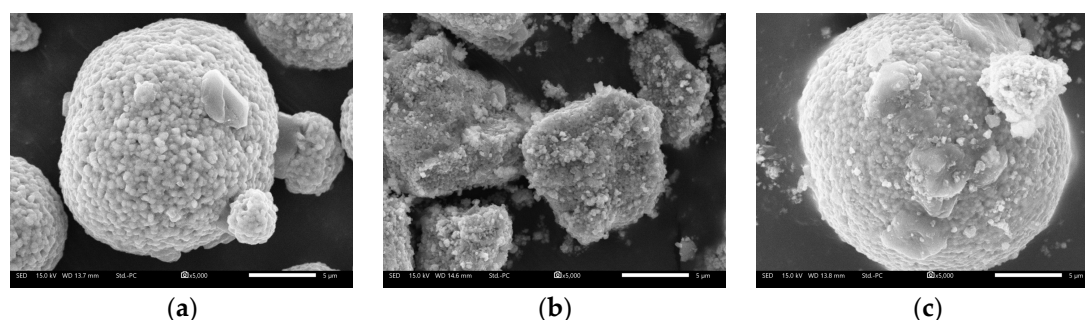


Figure 4. SEM micrographs of the precursors (a) K-NMC-811, (b) SM-LNMCO-811, and (c) SX-LNMCO-811.

3.5. PSA Analysis

The results of the particle size measurements of the precursors by PSA are presented in Table 7. The data show the decile data of D_{10} , D_{50} , D_{90} , and the average particle size of the precursors. D_{50} is also called the median particle diameter, where 50% of particles are larger than D_{50} and 50% are smaller. Meanwhile, D_{90} and D_{10} are the diameters of particles where 90% and 10% of the particles are smaller than these diameters, respectively.

Table 7. Results of particle size measurements of the precursors using PSA.

Sample Code	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	Average (μm)
SM-LNMCO-811	10.05	245.4	643.4	285.2
SX-LNMCO-811	5.345	12.94	38.36	17.16
K-NMC-811	2.159	15.74	38.85	18.28

The SM-LNMCO-811 sample, which used MHP as the source of nickel, has the largest average particle size, as well as D_{10} , D_{50} , and D_{90} . The K-NMC-811 and SX-LNMCO-811 samples have almost the same average values (i.e., 18.28 and 17.16 μm , respectively). These particle sizes of synthesized and commercial NMC-811 precursors are within the average size of the synthesized Li-NMC precursor reported by the previous investigators, namely spherical particles in the range of 15–20 μm [15]. The particle size of the cathode affects the intercalation and deintercalation processes during the charge–discharge processes, which determine the performance of the LIBs.

3.6. Charge–Discharge Analyses of the Batteries

The results of charge–discharge measurements of the fabricated batteries with SM-LNMCO-811, SX-LNMCO-811, and K-NMC-811 as cathode materials are presented in Figure 5. Figure 5a displays the charge–discharge profiles of the batteries with cathode precursor variations. Figure 5b presents the profiles of the specific discharge capacities (mAh/g) of the batteries for 100 testing cycles. Meanwhile, Figure 5c shows the profiles of the specific discharge capacities of the batteries under variations in the electrical charge (0.1 C, 0.3 C, 0.5 C, and 0.7 C).

The specific charge–discharge capacities of the batteries with cathode precursor variations (K-NMC-811, SM-LNMCO-811, and SX-LNMCO-811) and the initial efficiencies are summarized in Table 8. It can be seen that the best specific charge–discharge capacity was the battery cell whose nickel came from nickel sulfate (SX-LNMCO-811) followed by the battery with the commercial cathode precursor (K-NMC-811), and the battery with nickel source in the cathode precursor from MHP (SM-LNMCO-811). The initial efficiency of the battery cell whose nickel was from nickel sulfate was slightly higher than that of the battery with a commercial precursor material (K-NMC-811). Meanwhile, the battery whose nickel was from MHP demonstrated a significantly lower initial efficiency at a level of 37%. The Coulombic efficiency (CE) was monitored during the charge–discharge trial. SM-LNMCO-811, K-NMC-811, and SX-LNMCO-811 showed average CEs of 36.80%,

55.66%, and 58.31% after 100 cycles at 0.5 C, respectively. The specific discharge capacity of the battery cell with the SX-LNMCO-811 cathode precursor of 178.98 mAh/g is comparable with those of Li-NMC reported in the previous investigation results [16–21].

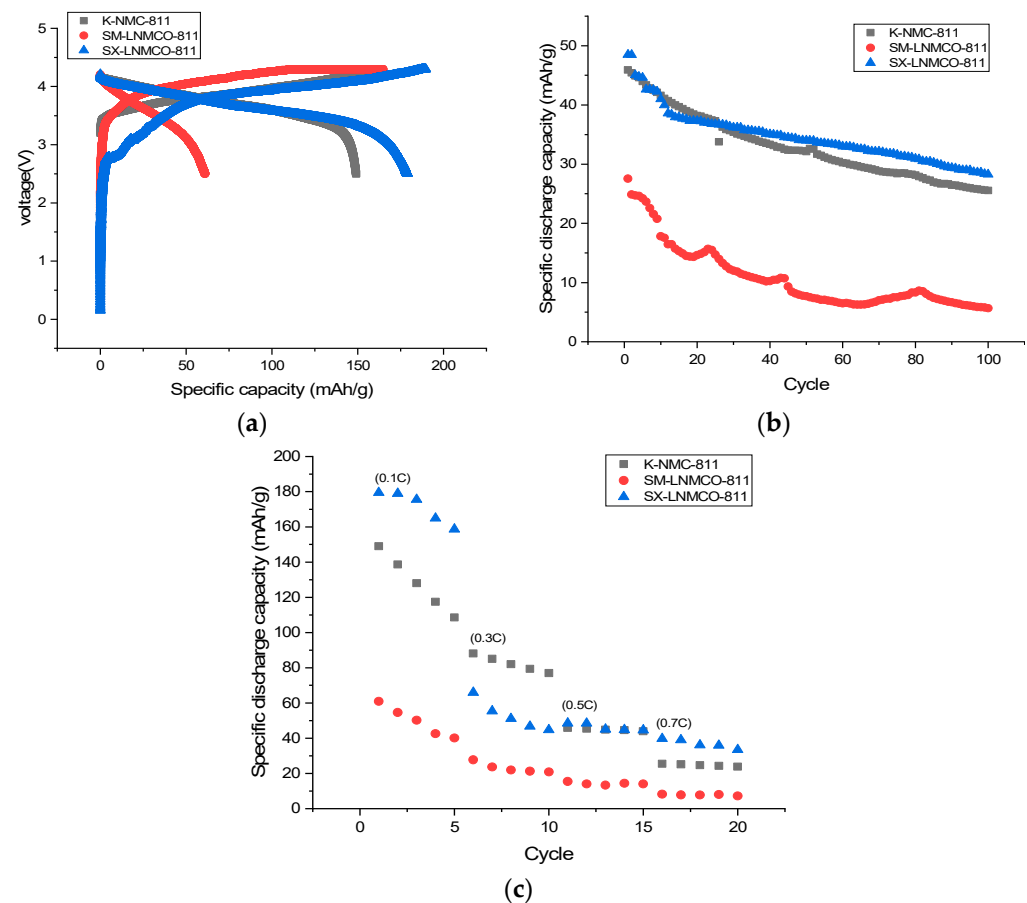


Figure 5. (a) Charge–discharge profiles of the batteries with cathode precursor variations, (b) profiles of specific discharge capacities (mAh/g) of the batteries for 100 testing cycles, (c) rate capability of material variation NMC-811.

Table 8. Results of the charge–discharge measurements of the fabricated batteries with SM-LNMCO-811, SX-LNMCO-811, and K-NMC-811 as cathode materials.

Cathode Precursor Variation	Specific Capacity Charge (mAh/g)	Specific Capacity Discharge (mAh/g)	Initial Efficiency (%)
SM-LNMCO-811	164.75	60.97	37
SX-LNMCO-811	189.71	178.93	94.32
K-NMC-811	158.28	149.05	94.17

The results of the charge–discharge measurements that show the performances of the battery cells are associated with two quite distinctive characteristics obtained from the analysis of the cathode precursors that used relatively pure synthesized nickel sulfate and relatively dirty MHP (as a source of nickel) as well as the commercial precursor. The two characteristics were morphology and particle size (i.e., secondary particle). The battery cell with the cathode precursor that used nickel sulfate as a nickel source and the commercial precursors showed particle morphology that tended to be spherical, while the battery cell with cathode precursors that used MHP as a nickel source had particle morphology that tended to be irregular. The cathode material with spherical particles provided more sites for lithium intercalation in comparison to the one with irregular particle morphology. The irregular shape of the particle of SM-NMC-811 led to a coarser secondary particle due to

ineffective primary particle aggregation. As can be seen in Table 7, the SM-LNMCO-811 had a much coarser average particle size than SX-LNMCO-811 and K-NMC-811. The particle sizes of the cathode materials played a decisive role in determining the electrochemical performance of the lithium-ion batteries, especially on the charge–discharge capacity, desired rate capacity, and cyclic stability [22]. Irregular particle morphology and a coarser particle size of the SM-LNMCO-811 contributed to the lower charge–discharge capacity of the battery cell and the capacity retention after 100 cycles.

The low efficiency of the battery cell with a cathode that used MHP as the source of nickel was associated with the presence of impurities. The presence of impurities induces side reactions that could form a passivation layer, which disrupts the reversibility of the Li^+ diffusion process and charge transfer. These side reactions (due to the presence of impurities) were indicated by an unstable specific discharge capacity of the battery cell with SM-LNMCO-811 at cycles 20, 40, and 80, as can be seen in Figure 5b.

3.7. EIS Measurements Results

Measurements of electrochemical impedance spectroscopy (EIS) were carried out to determine the impedances of the bulk and the cathode interface, charge transfer resistance, and the conductivity of the Li^+ ions intercalating during the discharge process of the batteries. The results of the measurements were impedances that changed with frequency under a given AC current. Figure 6 shows the Nyquist plots of the one-cycle measurement of the battery half-cell with SX-LNMCO and K-NMC-811. The EIS measurement data were processed with Z-view software to determine the electrical equivalent circuit (EEC) model that best fit the experimental data. The electrical equivalent circuit model that best fits the experimental data and the results of the fitting of the experimental data of SX-LNMCO-811 with the EEC model are illustrated in Figure 7a,b, respectively. The EEC in Figure 7a was suggested by the previous authors for the Nyquist pattern, which forms a semicircle and a straight-line pattern [23,24]. By using this EEC, the values of bulk resistance (R_b), charge transfer resistance (R_{ct}), capacitance (C), and Warburg impedance of the cells were then determined. The Nyquist curve of the battery cell with SM-LNMCO-811 (which uses MHP as the source of Ni) exhibited much noise and was not fit with the proposed model. Therefore, the data of R_{ct} , ionic conductivity, and Li^+ diffusivity for this sample cannot accurately be determined and the Nyquist curve of this battery cell is not presented in this paper.

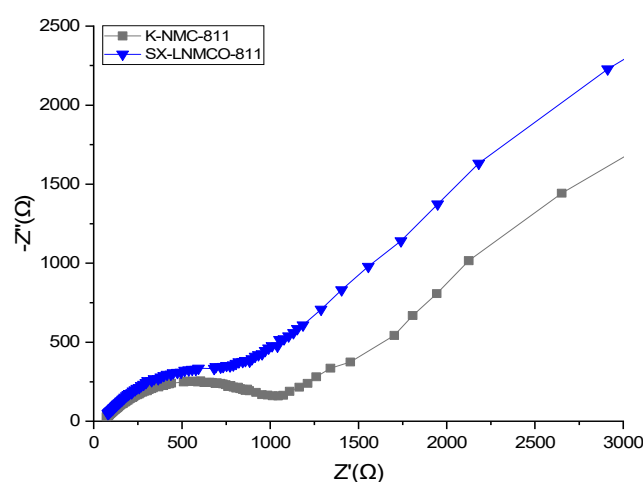


Figure 6. Nyquist plots of the one-cycle measurement of the batteries with cathode precursor variations.

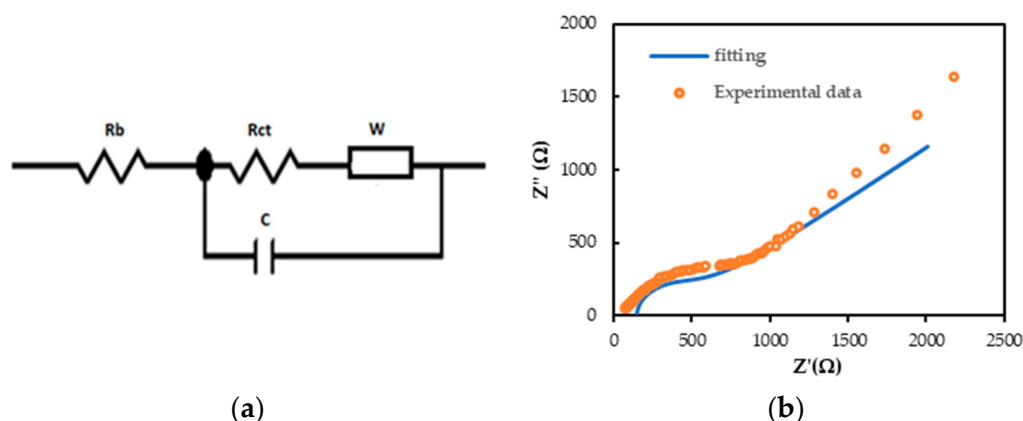


Figure 7. (a) The electrical equivalent circuit model that best fits the experimental data; (b) fitting of the experimental data of SX-LMNCO-811 with the EEC model.

The circuit model in Figure 7a is a simplified Randles' cell in which infinite linear diffusion affects the electrochemical system, which is indicated by the formation of the Warburg impedance in the Nyquist curve. The Warburg impedance describes the impedance created by the lithium-ion diffusion process. It can be seen that the Nyquist curve in Figure 6 forms a semicircle and a straight-line pattern. The semicircle pattern is associated with the electrolyte resistance (R_b) under certain conditions between the electrolyte and the surface of the active material, the charge transfer resistance (R_{ct}), and the capacitance of the double layer at the interface of the electrode–electrolyte. Meanwhile, the straight-line pattern represents the diffusion process of lithium ions into the bulk of the electrode material (commonly defined as the Warburg diffusion). The value of R_{ct} is related to the kinetics of electrochemical reactions, which represent the Faraday charge transfer resistance, which is affected by the characteristics of the cathode materials and the coating used. The data of R_{ct} obtained by the EIS measurement and Z-view fitting of the data to the EEC in Figure 6 and the result of ionic conductivity calculation for the batteries with SX-LNMCO-811 and K-NMC-811 are presented in Table 9. It can be seen that the battery cell that uses the synthesized cathode precursor has better ionic conductivity than the commercial precursor and this measurement result is in accordance with the electrochemical performance of the samples obtained from the charge–discharge measurements. The ionic conductivity is calculated by the following equation [25]:

$$\sigma = \frac{l}{Ra} \quad (3)$$

in which σ is ionic conductivity (Siemens/cm), l is the thickness of the cathode, R is the charge-transfer resistance (the value of R_{ct} in Table 9), and a is the surface area of the cathode (cm^2). The ionic conductivity of the synthesized and commercial precursors obtained in this investigation is in the range of the ionic conductivity of Li-NMC reported by the previous investigator [25]. Furthermore, the diffusion ions of Li^+ for these cathode precursors were calculated by the following equation:

$$D_{Li}^+ = \frac{R^2 T^2}{2n^4 A^2 F^4 \sigma^2 C^2} \quad (4)$$

where C is the concentration of Li^+ in the active materials, F is the Faraday constant (96,500 C/mol), A is the surface area of the cathode (cm^2), T is the absolute temperature (K), n is the amount of the electrons participating in the charge transfer reaction (1), R is the ideal gas constant (8.314 J/K/mole), and σ is the Warburg coefficient (obtained from Z-view fitting). The data of the diffusion coefficient of Li^+ obtained by the calculation using Equation (5) for the battery cells with SX-LMNCO-811 and K-NMC-811 are presented in Table 10. As the data of ionic conductivity, the synthesized precursor has a higher Li^+

diffusion coefficient than that of the commercial precursor, which is associated with a faster movement of the Li^+ through the cathode layer. The value of the Li^+ diffusion coefficients obtained for the synthesized precursor is in the range of the value of the Li-NMC 811 cell, which is in the order of $10^{-9} \text{ cm}^2/\text{s}$ [26]. The results of the electrochemical performances of the cell with the synthesized precursor using nickel sulfate from MHP refining (SX-LNMCO-811) indicate that the purification process of MHP through re-leaching and the three-stage solvent extraction using Versatic 10 and Cyanex 272 can be adapted to prepare raw material for battery-grade nickel sulfate.

Table 9. The data of R_{ct} and ionic conductivity of the cells with SX-LNMCO-811 and K-NMC-811 cathode precursors.

Sample	R_{ct}	Ionic Conductivity (S/cm)
SX-LNMCO-811	826.066	1.20×10^{-7}
K-NMC-811	952.59	1.04×10^{-7}

Table 10. Calculation of the lithium-ion diffusion coefficients in SX-LNMCO-811 and K-NMC-811 samples.

Sample	$D_{\text{Li}^+} (\text{cm}^2/\text{s})$
SX-LNMCO-811	4.22×10^{-9}
K-NMC-811	1.57×10^{-9}

4. Conclusions

Cathode precursors of lithium-NMC 811 were successfully synthesized by the co-precipitation method using two different nickel sources, namely MHP and nickel sulfate. The XRD analyses identified that the diffraction peaks of the three precursor materials are in close agreement to that of $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$, with figure(s) of merit of 0.81, 0.88, and 0.9, respectively, for the synthesized precursor that used MHP as the source of nickel (SM-LNMCO-811), nickel sulfate as the source of nickel (SX-LNMCO-811), and the commercial precursor (K-NMC-811). The SEM analysis revealed that SX-LNMCO-811 and K-NMC-811 showed a similar particle morphology with a spherical shape; the SM-LNMCO-811 exhibited an irregular particle morphology. The SEM micrograph of the SM-LNMCO-811 sample that used MHP demonstrated various shapes of secondary particles and poor aggregation of the primary particles to form a compact secondary particle. The particle size analysis showed that SM-LNMCO-811 had the largest average particle size (285.2 μm); K-NMC-811 and SX-LNMCO-811 samples had nearly the same average values of 18.28 and 17.16 μm , respectively. The results of the charge–discharge measurement of the fabricated battery cylindrical cells with SM-LNMCO-811, SX-LNMCO-811, and K-NMC-811 as cathode materials demonstrate the best discharge value of the SX-LNMCO-811 sample at 178.93 mAh/g with an initial efficiency of 94.32%, which is in line with the electrochemical impedance measurement results that show the largest ion conductivity and lithium ion diffusion coefficient value of the SX-LNMCO-811 sample that utilizes the synthesized nickel sulfate as the source of nickel. The ionic conductivity of the SX-LNMCO-811 was $1.20 \times 10^{-7} \text{ S/cm}$, which was slightly higher than that of the commercial precursor ($1.04 \times 10^{-7} \text{ S/cm}$). The value of the Li^+ diffusion coefficients obtained for the SX-LNMCO-811 of 4.22×10^{-9} was in the range of the value for Li-NMC 811 reported by the previous investigators. The investigation results show that the refining of the intermediate product of nickel ore processing is a key factor in producing nickel-based batteries with good electrochemical performances.

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