

The Effect of Lithium Excess on NMC-721 using Oxalate Co-precipitation

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ARTICLE INFO

Article history:

Received date 17 October 2022

Received in revised form 06 April 2023

Accepted 05 May 2023

Keywords:

Battery

Electric Vehicle

NMC

Cathode

Co-precipitation

ABSTRACT

Lithium Nickel Manganese Cobalt Oxide (Li-NMC) has been regarded as preferred cathode material for Lithium-ion battery (LIB), compared to other materials such as Lithium Cobalt Oxide (LCO) and Lithium Manganese Oxide (LMO). Ni-rich content displays severe cycling performance and needs to be addressed to improve its performance of electric vehicle. This research focused on synthesis NMC-721 precursors with the oxalate co-precipitation. Furthermore, a variation of lithium hydroxide with the excess of 3% and 5% were added into the precursors, then calcined at temperature 800 °C for 12 hours. The product of precursor was analyzed by X-Ray Fluorescence (XRF) and Particle Size Analysis (PSA) to analyze elemental composition and particle size, respectively. Meanwhile, the NMC-721 cathodes were characterized by an X-Ray Diffraction. The XRF data of precursor shows the ratio of transition metals at 7.5:1.5:1 identifying that more Ni content and less Mn content in the NMC-721, due to oxalate co-precipitation. The PSA shows that the average diameter of the precursor was 9.19 ± 0.31 (μm). The XRD result shows that the crystal structure of NMC-721 cathode belongs to hexagonal structure. It can be concluded that the NMC-721 were successfully synthesized and can be applied for lithium-ion battery.

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INTRODUCTION

Nowadays, Lithium-ion batteries (LIB) are becoming the main focus research in scope of energy source & storage, as it provides high energy density, extended life cycle, and lightweight. LIB consumption is forecasted to be increased which driven by raw materials demand in EV industry. Numerous industries have spurred technological advancements that have resulted in a vast range of diverse electronic gadgets being produced globally. The condition has forced the lithium-ion battery (LIB) consumption [1]. In addition to their great performance in the lithium-ion transfer process, high energy density, lack of memory effect, and low risk of self-discharge, lithium-ion batteries also have several other benefits. LIB technology is constantly improving to increase the specific capacity, lower pack prices, and enhance safety features [2].

The major performance enablers of batteries are advanced materials, such as cathodes which are also crucial in defining the cost structure, environmental impact, safety, and recyclability of battery cells. Lithium Nickel Manganese Cobalt Oxide (NMC) is one of the dominant battery materials because of their low price due to the less cobalt usage, high abundant, the stability of structure, high capacity due to high nickel content, heat stability from manganese, and long cycle life [2]. NMC-based cathodes, when compared to LiMO_2 ($M = \text{Ni, Mn, or Co}$) cathodes, also have the combined advantages of the three transition metals, with nickel being able to offer high specific capacities and Co and Mn being able to provide layered structures and improved structural integrity [3]. NMC-721 is much safer than NMC-811 because higher nickel content may lead to side reaction result and structural instability, which cause the capacity reduction [4].

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DOI: 10.59046/jbrev.v1i01.7

NMC-721 also has higher capacity than NMC-622 and NMC-532 [2].

NMC-721 cathodes can be synthesized through various methods. Due to inhomogeneous, poor purity, and low battery performance of self-ignition combustion (SIC), molten salt, sol-gel, solid state, and hydrothermal method, co-precipitation is better method to synthesize the NMC cathodes [5]. This research will conduct NMC-721 cathode synthesis by using Oxalate Co-Precipitation because it is cheaper and environmentally friendly than other's precursors. Nisa *et al.* have conducted NMC synthesis using oxalic acid as precursor and Co-precipitation methods, the NMC showed the most favorable features and performance, the discharged capacity reaches 153.60 mAh/g with a capacity retention of 70.9% after 100 cycles [6]. This method also gave good results on $\text{Li}_{1+x}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})_{1-x}\text{O}_2$ synthesis [7], NMC-811 synthesis [8], $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ synthesis [9], $\text{Li}_{0.05}\text{Ni}_{0.75}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ synthesis [10], and NMC-111 synthesis [11].

Besides choosing the optimum synthesis methods, the electrochemical performance of NMC is affected by the existence of high specific surface area, an inappropriate morphology, and irregular positioning of ions in the structure. The excess Li can improve this condition by creating a homogeneous intrusion network [12]. Refino *et al.* stated that adding a high aspect ratio of Si or other component on LIB might increase the capacity and have desirable character [13]. As a result, by adding 3% and 5% lithium content to the nickel precursor manganese cobalt, the research concentrated on the effects of lithium excesses (NMC-721). Based on the XRD diffractogram, lithium excesses in the nickel precursor manganese cobalt (NMC-721) were observed.

METHODOLOGY

Precursor and Cathode Preparation

Co-precipitation is the initial stage, which seeks to precipitate oxalate, manganese sulfate, nickel sulfate, and cobalt sulfate in the solution. Preheated distilled water was heated to 60 °C. In the preheated distilled water, technical grade $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ from Sumitomo, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved. Technical grade oxalic acid, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, was dissolved in distilled water to create the precipitating agent solution. The transition metals solution was then added to the oxalic acid solution, and the mixture was agitated at 60 °C. Until the pH reached 6, technical grade 25%-powder precursor NMC-721 was the result of this operation. To prepare an ideal NMC type's structure

it needs to be carried out on every single step on their process including to morphological changes during sintering. This process is needing an evolution at temperature around 300-1,080 °C for at least 5 hours [14].

The excess lithium was added by mixing $\text{LiOH} \cdot \text{H}_2\text{O}$ powder (6.3060 g and 6.4284 g for 3% and 5% excess Li, respectively) into the precursor NMC-721. To create a cathode, $\text{LiOH} \cdot \text{H}_2\text{O}$ must be included with the precursor. Using a mortar and pestle, the precursor and lithium were combined, and the resulting mixture was then added to a crucible. For 12 hours, calcination was done at 800 °C. This procedure produced an active cathode material as the product and the excess lithium was investigated by XRD.

Characterization of Active Cathode Materials

The materials were characterized by X-ray Fluorescence (XRF) (Bruker S2 PUMA), X-ray Diffraction (XRD) (PANalytical Empyrean), and Particle Size Analyzer (PSA) (HORIBA Partica LA-960). A crystalline material's phase identification, elemental composition, and unit cell size were both determined using XRD. The elemental composition of materials can be ascertained using the non-destructive analytical method known as XRF. By detecting the fluorescence (or secondary) X-ray that a sample emits when it is activated by a main X-ray source, XRF analyzers may determine the chemistry of a sample. Particle size analysis (PSA) is a generated experiment characterization of a size of particle. The angle of light scattering is inversely related to particle size when a laser beam is scattered by a collection of particles (i.e. the smaller the particle size, the larger the angle of light scattering) [15].

RESULTS AND DISCUSSION

Elemental Composition

To validate the NMC-721 sample results and identify contaminants, XRD and XRF analyses are needed. Table 1 shows the result of XRF data of precursor shows the ratio of transition metals at 7.5:1.5:1 identifying that more Ni content and less Mn content in the NMC-721.

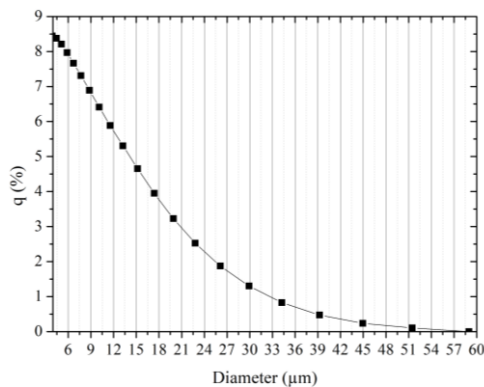
The ratio close to the ideal NMC, 7:2:1. Previous research which synthesized the NMC-811 through precipitation method also had a similar result. The NMC-811 precursor had a stoichiometry value below the desirable ratio. This could be caused by different solubility between nickel oxalate and manganese oxalate [16].

Table 1. XRF Analysis of NMC-721 Precursor

Element	Normalization
Ni	0.753
Mn	0.151
Co	0.097

Particle Size Distribution

The particle sized distribution for NMC-721 precursor sample without lithium excess was analyzed by Particle Size Analyzer. The particle sized distribution is shown in Figure 1 and in Table 2. The data show the decile data of D_{10} , D_{50} , D_{90} , and the average mean size is 9.19923 μm .

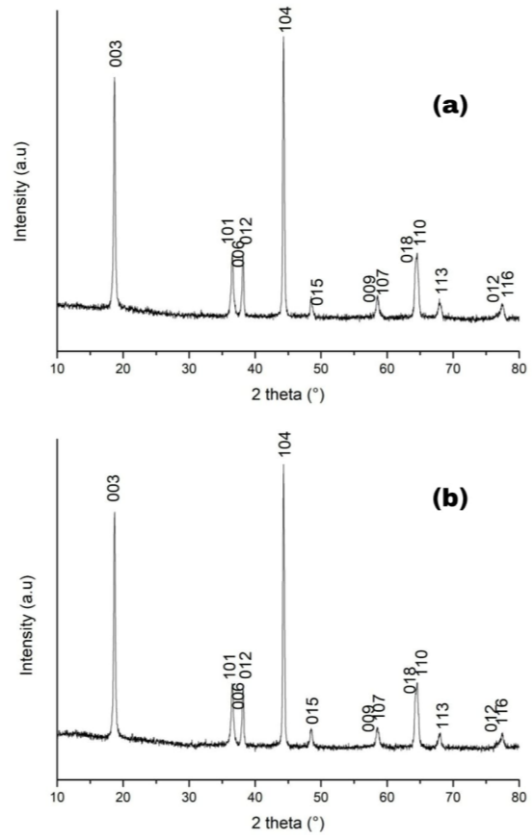
**Fig. 1.** PSA of Precursor NMC-721**Table 2.** Particle Size of NMC-721 Precursor

Test	D_{10}	D_{50}	D_{90}	Mean Size
1	3.4470	6.6224	18.0216	9.016
2	3.9638	7.3450	18.0444	9.5098
3	3.4993	6.8414	17.7918	9.0719
Avg.	3.6367	6.9363	17.9526	9.1992

D_{10} and D_{90} are the diameters of particles where 10% and 90% of the particles are smaller than these diameters, respectively. Meanwhile, D_{50} is the median particles diameter, where 50% of particles are larger than D_{50} and 50% are smaller. The particle size of the cathode affects the intercalation and deintercalation processes during the charge-discharge processes, which determine the performance of the batteries [10].

Crystal Structure of Synthesized NMC

Figure 2 shows the entire diffraction pattern of NMC-721 with Li excesses 3% and 5%, respectively. The XRD patterns of the two co-precipitation and Li excesses products show a relatively similar pattern with more noises exhibited by 5% of the Li excesses' NMC-721. Wijareni *et al.* [10] said that the more noises shows at the pattern, the more minor phases present in the NMC-721.

**Fig. 2.** X-ray diffractometer patterns for the 3% excess Li (a) and 5% excess Li (b) on NMC-721

The analysis identified that the obvious separations of the (101)/(012), (018)/(110) doublets and hexagonal structure of both powders exhibited a well-defined layer structure of α -NaFeO having the R-3m space group (I.C.S.D. No.291468) with no impurity peaks [12]. This is also similar with the NMC-721 in the commercial. When the Li content increased, the diffraction peaks shifted to higher angles, corresponding to lower a- and c- axis lattice constants, due to a decrease in the lattice volume[17].

Table 3. shows the general properties of unit cell for the 3% and 5% lithium excess. Both 3% and 5% lithium excess have the hexagonal structure. The different intensity happened because the addition of both different concentration of Lithium can affect the formed process of precursor structure [14]. A smaller concentration of Li results in a better layered ordering and smaller concentration of $\text{Li}^+/\text{Ni}^{2+}$ cation mixing [18]. The R's value has shown that is not fully cleaved or splitted [17].

Table 3. General properties of unit cells

Properties	NMC-721 + 3% Li-excess	NMC-721 + 5% Li-excess
Crystal lattice a. (Å)	2.88158	2.88214
Crystal lattice b. (Å)	2.88158	2.88214
Crystal lattice c. (Å)	14.21451	14.2154
α (°)	90	90
β (°)	90	90
γ (°)	120	120
Volume (Å ³)	102.2173	102.2631
Assumed crystal system	Hexagonal	Hexagonal
Crystal system	Trigonal (hexagonal axes)	Trigonal (hexagonal axes)

Table 4 shows the parameters for layer cathode materials from the NMC-721 powders with 3% and 5% of Li-excesses which calculated from XRD pattern. The $I_{(003)}/I_{(104)}$ ratio is considered as an evaluation of the cation mixing degree [19].

Table 4. Parameter for layer cathode materials NMC-721 with 3% and 5% Li-excesses

Parameter	NMC- 721 + 3% Li- excess	NMC- 721 + 5% Li- excess	Ideal Value
$I_{(003)}/I_{(104)}$	0.9577	0.9570	>1.2 (desirable cation mixing)
c/a	4.9329	4.9323	>4.899 (ideal)

Based on the $I_{(003)}/I_{(104)}$ parameters, there's difference of 0.0007 between the 3% and 5% Li-excesses. This because of the differences of the concentration of the Li-excess. Both concentrations are below the ideal value (>1.2). It means the 3% and 5% of Li-excess do not have desirable cation mixing [17]. The condition caused by the Ni^{2+} ions increasing of discharge capacity in Li layer. This factor is certainly detrimental to the electrochemical performance [19]. The intensity ratio R could not be determined because the peak of (006)/(012) has not been separated yet. If the R value is lower, it makes hexagonal ordering [20].

The value of c/a corresponds to the stability of a layered structure as shown in the Table 4. There is no big difference between both powders. The value of 3% is a little higher than the 5% Li-excess, indicating a better layered structure after the addition of 3% Li. The factor is beneficial to enhance the electrochemical performance of the cathode

material [19]. The c/a value of both powders are higher than the ideal, but less than 4.96, it means the powders had partial cation mixing [21].

CONCLUSION

From this research it may be stated that author's has success to synthesis NMC-721 through the Co-precipitation method and validated by XRF, XRD, and PSA analysis results. Based on the XRD result the 3% of Li excess gave a better layered structure and partial cation mixing.

ACKNOWLEDGMENT

This work is fully financially supported by the National Battery Research Institute (NBRI) in fiscal year 2022.

AUTHOR CONTRIBUTION

E. Kartini and R. D. Nanda conceived of the presented idea. S. A. Kristianto and M. Fakhruddin developed the theory and performed the computations. All authors read and approved the final version of the paper.

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