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The Effect of Stirring Time in the Synthesis of NMC-721 using Oxalate Co-precipitation

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Abstract. Li-ion batteries have the benefit of having a high storage capacity, a long cycle life, and being less damaging than present battery materials as a support for transportation in the future. The state of the cathode's manufacture is crucial since it plays a significant role. This study focused on synthesizing Nickel Manganese Cobalt Oxide -721 precursor with oxalate Co-precipitation using time parameters of 30, 60, and 180 minutes. Next, a variation of lithium hydroxide was added to the precursor, then calcined at 800°C. Nickel Manganese Cobalt Oxide -721 cathode was characterized by X-Ray Diffraction and XRF precursor data. The cathode crystal structure of Nickel Manganese Cobalt Oxide -721 is included in the hexagon structure, according to the findings of the X-ray diffraction study. Nickel Manganese Cobalt Oxide -721 has been successfully synthesized and can be used in lithium-ion batteries. Among the stirring processes of 30 and 180 minutes, the 180-minute technique produced the best NMC-721.

INTRODUCTION

One or more electrochemical cells make up a battery, a device that transforms chemical energy into electrical energy. The lithium-ion battery is the one that is currently utilized the most. Since Sonny first made lithium-ion batteries available for purchase in 1991, they have grown to be the most widely used type of electrical energy [1]. Compared to other secondary batteries, lithium-ion batteries have a longer cycle life (500–1,000 cycles), a higher potential difference, a better energy density, and a higher specific capacity. Lithium-ion batteries have also been extensively utilized as a power source for portable electronic devices, even in electric cars [2]. Indonesia has not started making electric cars yet. The 1,500 tons/year cathode active ingredient factory is anticipated to accomplish the government's objective to produce electric automobiles while also constructing Indonesia's economic infrastructure [3]. The cathode active ingredient manufacturer discovered this strategy after determining that the main component of electric vehicle batteries is lithium nickel manganese cobalt oxide. Due to this battery's high specific energy, its power and capacity have increased [4].

Additionally, the factory is slated to be in Morowali, which is in Central Sulawesi. What will hence construct the factory for cathode active materials next to the Tesla battery factory? Considering that it is anticipated that this plant will assist in supplying raw materials to Tesla's battery factory. The cathode active ingredient factory will create an electric vehicle-applicable active ingredient product in the form of a powder. China is the direct source of the raw materials used to manufacture cathode active ingredient powder. Li_2CO_3 , NiSO_4 , MnSO_4 , CoSO_4 , NaHCO_3 , and Deionized Water were needed to make Li(NMC). The primary components used in the production of lithium-based Li(NMC) cathode active ingredients are these five raw materials.

Because of their outstanding qualities, lithium nickel manganese cobalt batteries are frequently used as electrochemical power sources. The structure can be altered to achieve a high specific capacity, for example, depending on the battery's intended function. High production efficiency and minimal costs [5, 6]. The International Energy Agency (IEA) predicts that the number of batteries used in electric vehicle stock worldwide (excluding two- and three-wheelers) will rise from about 8 million in 2019 to 50 million in 2025 and close to 140 million in 2030, representing an increase of about 30% annually on average [7]. Used LIB includes carcinogenic and mutagenic heavy metals including nickel (Ni) and cobalt (Co), as well as toxic organic electrolytes that are bad for both the environment and human health. Due to their relative scarcity and high price, Li and Co are more sought-after than other metals as essential raw materials for the synthesis of LIB cathode materials. In addition to wasting resources, improper disposal of toxic metals and other dangerous materials also harms the ecosystem. Used LIBs must be managed and recycled properly to ensure efficient use of this finite resource and environmental sustainability [8]. Given the complexity of LIB, numerous recycling plans are viable. There are three fundamental categories of processes: direct recycling, hydrometallurgy (leaching), and pyrometallurgy (smelting) (physical processes). After removing and disassembling the battery and separating the electrode material on the utilized LIB, these three fundamental procedures can be completed. Depending on variables including the availability of resources, their qualities, and their amount and worth as recoverable materials, process components can be integrated in a variety of ways [9].

Nickel Manganese Cobalt Oxide has a crystal structure similar to LCO and LNO [10]. In contrast to LCO, Nickel Manganese Cobalt Oxide has a larger specific capacity. The highest market share for batteries is anticipated to belong to nickel manganese cobalt oxide cathode materials [11, 12]. The NMC may be altered by varying the metal ratio because each metal contributes unique properties to the final product. The competition to develop high-quality Nickel Manganese Cobalt Oxide cathode materials with superior electrochemical performance is still going on. Numerous techniques, such as solid-state, hydrothermal, spray pyrolysis, sol-gel, and co-precipitation, have been employed to generate cathode materials [13]. Because it can produce Nickel Manganese Cobalt Oxide with good homogeneity and narrow particle distribution utilizing water-soluble raw ingredients that are simple to handle, this method is widely used to produce Nickel Manganese Cobalt Oxide [14]. This process needs a precipitation material in order to precipitate the substance. NaOH serves as a joint precipitating agent for hydroxide-based precipitation. The sensitivity of nucleation and particle growth in hydroxide-based co-precipitation, however, leads to low repeatability of particle morphology. Additionally, the homogenous mixture of Nickel Manganese Cobalt Oxide is produced because the Mn ion is extremely sensitive to oxidation. In order to complete the procedure, inert gas must be produced in large quantities. Larger particle sizes and lesser homogeneity from carbonate-based co-precipitation result in subpar electrochemical performance. Oxalate-based Co-precipitation can generate appropriate measurements of NMCs with good uniformity because of the reduced nature of the oxalate ion [15].

Oxalic acid was used as a precursor in the co-precipitation process by Nisa et al. to create Nickel Manganese Cobalt Oxide. The Oxalate Co-Precipitation method will be used in this study to create Nickel Manganese Cobalt Oxide -721 cathode due to more affordable and ecologically favorable than other precursors. The stirring time parameter was used in this study to determine the best Nickel Manganese Cobalt Oxide -721 cathode performance.

METHODOLOGY

Precursor and Cathode Preparation

The first step, known as co-precipitation, aims to precipitate the solution's oxalate, manganese sulfate, nickel sulfate, and cobalt sulfate. Distilled water was warmed up to 60 °C. NiSO₄·6H₂O, MnSO₄·H₂O, and CoSO₄·7H₂O of technical grade were dissolved in the preheated distilled water. To make the precipitating agent solution, technical grade oxalic acid, H₂C₂O₄·2H₂O, was dissolved in distilled water. Oxalic acid solution was combined with the transition metals solution, and the combination was stirred at 60 °C [16]. Technical grade 25%-NH₄OH was added to the mixed solution until the pH reached 6. NH₄OH had a role to form the crystals on nucleation formation [17]. During this technique, 2M MSO₄ and 0.75M precipitant solution were fully mixed on a hotplate while being stirred for about three hours. The ammonia and NaSO₄ side products of the sediments were eliminated by rinsing the resulting precipitate slurry with distilled water.

To remove any water that could have remained, the precursor was dried. The resulting residue was dried for three hours at 102°C in the oven. This operation gave dry powder precursor of Nickel Manganese Cobalt Oxide-721, which will now be produced by combining LiOH·H₂O powder. LiOH·H₂O needs to be added to the precursor in

order to make a cathode. The precursor and lithium were mixed in a mortar and pestle, and the resulting mixture was added to a crucible. Calcination was carried out at 800 °C for 12 hours. An active cathode material was the end result of this process.

Characterization of Active Cathode Materials

X-ray Fluorescence (XRF) and X-ray Diffraction (XRD) were used to characterize the materials (XRF). XRD was used to determine the phase, elemental makeup, and unit cell size of crystalline materials and microstructure [18, 19]. By employing the non-destructive analytical technique known as XRF, it is possible to determine the elemental makeup of materials. XRF analyzers may assess a piece's chemistry by detecting the fluorescence (or secondary) X-ray that a sample emits when the primary X-ray source activates it.

RESULTS AND DISCUSSION

The oxalate precipitation method is employed in this study along with a stirring time parameter. 30 minutes, 60 minutes, and 180 minutes were the study's time intervals. Three parts of the samples were used in the analysis. High score plus was used to process the data via X-Ray Diffraction (XRD). To comprehend the theory of x-ray diffraction in qualitative and quantitative analysis, the crystal system is first explained. The outcomes from the processed data are shown in **Table 1**.

TABLE 1. Results 30 minutes, 60 minutes, 180 minutes on Nickel Manganese Cobalt Oxide -721

Agreement Indices	S30	S60	S180
R_{ex}	2.55421	2.60278	2.60831
R_{wp}	3.57914	4.74157	3.19365
Goodness of Fit	1.96356	3.3187	1.49919
General Properties of Unit Cell			
a (Å)	2.88076	2.8893	2.87839
b (Å)	2.88076	2.8893	2.87839
c (Å)	14.2253	14.29367	14.21899
α (°)	90	90	90
β (°)	90	90	90
γ (°)	120	120	120
Volume (Å ³)	102.2369	103.383	102.0233
Assumed crystal system	Hexagonal	Hexagonal	Hexagonal
Crystal system	Trigonal (Hexagonal axes)	Trigonal (Hexagonal axes)	Trigonal (hexagonal axes)

The table above shows that the highest R_{ex} occurred at minute 180, with a value of 2.60831, and the lowest at minute 30, with a value of 2.55421. S30 has the greatest volume, which is 103,383 units. Next, S60 has the highest R_{wp} value, 4.74157, and the lowest R_{wp} value, 1.49919, at the 180th minute. The alpha, beta, and gamma angles for these three factors are identical. The findings of the goodness of fit between these three samples, S30, S60, and S180, which is at the 180th minute, are displayed in Table 1 and are equal to 1.49919. This number demonstrates that it has the best hexagonal structure of lithium Nickel Manganese Cobalt Oxide within 180 minutes. The difference in intensity occurs because the addition of the two different Lithium concentrations can affect the formation process of the precursor structure. In research, the distribution of ions will be erroneous the more lithium is added. A better layer arrangement is produced by a lower concentration of Li, as well as a lower concentration of Li^+/Ni^{2+} cation mixing [20]. Because the sintering temperature is lower, the R-value has demonstrated that it is not completely divided or split. Each step of the process, including morphological changes during sintering, must be completed in order to create the ideal sort of Nickel Manganese Cobalt Oxide structure [21].

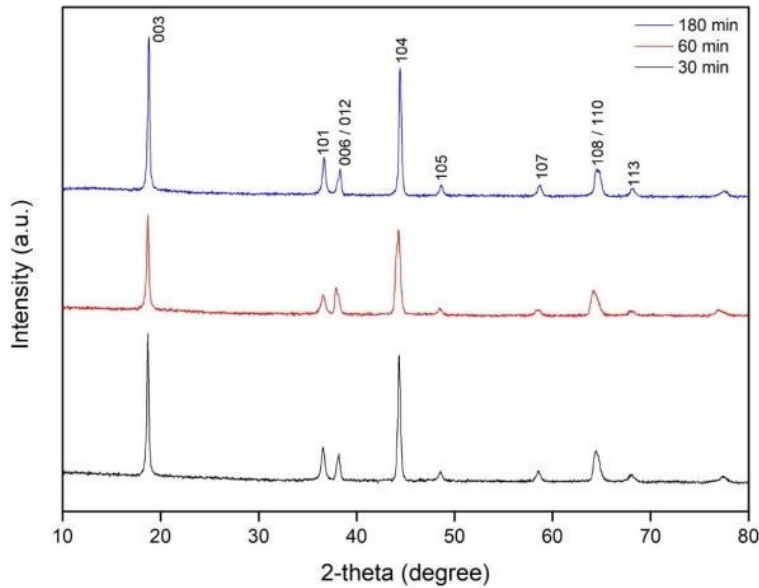


FIGURE 1. X-ray diffraction pattern for 30, 60, and 180 minutes stirring time of NMC-721

Figure 1 demonstrates that the XRD patterns of the two products of co-precipitation and excess Li obtained with stirring times of 30 minutes, 60 minutes, and 180 minutes exhibit a substantially similar pattern with higher noise than Nickel Manganese Cobalt Oxide -721 excess Li. The analysis identified that the double peaks at (006)/(102) and (018)/(110) correspond to a neatly structured layer [21, 10]. In addition, the clear separation of the double (101)/(012), (018)/(110), and hexagonal structure of the two powders shows a well-defined -NaFeO_2 layer structure having a space group R-3m (ICSD No.291468) without impurity peaks [22]. It is also similar to the commercial's Nickel Manganese Cobalt Oxide -721. Due to a reduction in the lattice volume, the diffraction peak shifts to a higher angle as the Li content rises. This higher angle corresponds to lower a- and c-axis lattice constants.

The lithiated product from the co-precipitation process is then utilised and heated. The material that has been created is then determined from the end product in the cathode material. Figure 1 illustrates the results of the first test, which was X-ray diffraction similar to the prior characterization. The X-ray Diffractometer (XRD) pattern of LCO, Nickel Manganese Cobalt Oxide, and LN samples prepared after heat treatment showed a hexagonal structure, such as -NaFeO_2 layered (space group): R3 m). In instances with high Co and Mn content, which usually form layered structures at high temperatures, who can predict that the formation of layer-structured materials is not completed due to sub-optimal sintering temperatures? Who can foresee that the production of layer-structured materials is incomplete due to sub-optimal sintering temperatures in cases with high Co and Mn content, which typically produce layered structures at high temperatures? What increased the amount of Li in the source to make up for the Li that was lost during the high-temperature litigation (at 800 C)?

On the other hand, the appearance of Ni-rich cathode materials, especially those based on Ni, is optimal at lower temperatures. Therefore, at 800 C, the appearance of rock salt NiO is perfect, which inhibits the litigation process, and predicts that the litigation process is not successful. This phenomenon causes the construction of the Li_2CO_3 phase in the sample. Meanwhile, LMO shows a cubic spinel structure with space group Fd3m (lattice parameter $a = b = c$) [23].

TABLE 2. Parameters for Nickel Manganese Cobalt Oxide -721 material cathode coating with the time of 30,60 and 180 minutes.

Parameter	S30	S60	S180	Idea Value
$I_{(003)}/I_{(004)}$	1.134	1.334	1.202	>1.2 (desirable cation mixing) Cannot be calculated because the sample peaks (006)/(012) have not separated
$R = [I_{(012)} + I_{(006)}/I_{(101)}]$	N/A	N/A	N/A	Lower -> better
c/a	4.9380	4.9460	4.9399	<4.96 = partial cation mixing >4.899 = ideal

We can assess cleanly ordered and layered materials using the lattice characteristics and R values shown in Table 2. The least squares regression technique was used to get the lattice parameters for each sample. The material has crystallized, according to the lattice parameter's c/a value. C/A should weigh more than 4.899 [24]. Both Nickel Manganese Cobalt Oxide and LNO samples have values above the excellent c/a ratio, which means that the models have a well-ordered layered structure. The intensity of specific peaks in XRD indicates the degree of antisite interference of Ni^{2+} and Li^+ . Calculating the intensity ratio (IR) can reveal the presence of cation admixture, which is common in layered transition metal oxide cathode materials.

IR uses peaks (003) and (104); the results are listed in Table 2. Table 2 shows what cannot calculate the R- value for these three parameters because the splitting still needs to be done. This factor is undoubtedly detrimental to the electrochemical performance [23]. The greater significance of the c lattice parameter for the layered structure is typically blamed for the improved electrochemical performance. Because Li^+ and Ni^{2+} have identical atomic radii, Ni atoms can fill the Li layer. This causes disordered phase development to begin, which lowers the strength of the 003-diffraction peak associated with the layered structure (or even the complete loss of 003). The peak for the formation of the MO-type phase, for example, NiO). In this way, the ratio $I[003]/I[104]$ can serve as a qualitative indicator for ion exchange in oxide-layered structures. The fact that the precursor solution type had no effect on the crystallinity regardless of the nickel content and that the effect was restricted to the surface of the Nickel Manganese Cobalt Oxide particles further suggests that the precursor solution type had little influence on the lattice parameters. The intensity ratio R could not be determined because the peaks (006)/(012) have yet to be separated. If the R -value is lower, the quality of the crystal structure is higher. The value of c/a corresponds to the stability of the layered system, as shown in Table 2. There is no significant difference between the three parameters. The time value of 60 minutes is a little bit higher than that of 30 minutes and 180 minutes, indicating a more complex layering. This element contributes to cathode materials enhanced electrochemical performance [23]. The two powders' c/a values are greater than the optimum value but less than 4.96, indicating partial cation mixing in the powder.

CONCLUSION

The synthesized of NMC-721 has been successfully conducted. The best stirring time is 180 minutes by oxalate co-precipitation and the crystal structure is an agreement with the NMC commercial product.

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