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Synthesis of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ Cathode Material Prepared Via Carbonate Co-Precipitation Method

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Abstract. The mixed transition metal of NiSO_4 , MnSO_4 , CoSO_4 has been co-precipitated with addition Na_2CO_3 to obtain precursor. This precursor was prepared via co-precipitation method with stirring times of 3 hours by using a magnetic stirrer. The precursor was filtrated and washed by a vacuum filter to reduce the sodium out of precursor, and then it was heated in oven to remove the H_2O from precursor. The precursor was mixed with LiOH . Finally, the precursor was calcinated at 800°C and cathode was characterized with XRD. The result of X-ray Diffraction test (XRD) showed that the cathode of $\text{Li Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ has crystallite size in the range of 7.63 – 31.46 nm.

INTRODUCTION

Advanced technology has been used in many things in human history. Most of these technologies require flexibility in battery application. Flexible objects that operate on electrical energy require an energy store to be able to run wirelessly. Therefore, energy storage is becoming an important aspect, especially during this millenniums. Batteries as an energy storage device have the ability to store electrical energy in the form of chemical energy, making it an ideal technology for wireless tools. Among the various types of batteries, lithium-ion batteries are preferred because of their rechargeability, high energy and power density, and safety. All lithium-ion batteries operate at relatively higher voltages than lead-acid and NiCd batteries. Electrodes, especially cathodes, are the main cause of large volumes. Lithium-ion battery cathodes have been under development since the latter half of the 20th century [1]. The first commercially successful cathode materials were layered LiCoO_2 or lithium cobalt oxide (LCO) with a specific energy density of 0.98 Wh/g and a specific volume density of 5.10 g/cm³ [2]. However, the capacity shown (140 mAh/g) is only half the theoretical value (280 mAh/g). Higher cobalt content also increases its harmfulness and tends to explode when the element Co^{4+} is formed. [3]

Rich nickel cathodes like LiNiO_2 , $\text{LiNi}_{0.8}\text{Mn}_{0.8}\text{Co}_{0.1}\text{O}_2$, are becoming an interesting topic due to their availability, high capacity, and excellent electrochemical performance and high conductivity due to Co and Mn doping, and it has a longer life than LiNiO_2 [4]. However, $\text{LiNi}_{0.8}\text{Mn}_{0.8}\text{Co}_{0.1}\text{O}_2$ have suffered the thermal runaway especially in Ni-

Rich Lithium ion batteries [5]. On the other hands, $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (NMC-442) has a solution. based on study from Ramesha *et al*, in 2020 showed that NMC-442 have highly ordered crystal structure, good thermal stability and lower cobalt content. [6]. Thus, in this experiment we will synthesis NMC-442 with carbonate co-precipitation method

The aim of this experiment is to synthesis NMC-442 via carbonate co-precipitation method with 3 hours stirring time and characterized with X-ray Diffraction. The carbonate co-precipitation was used because of its ability to improve the structural, discharge capacity of the battery and particle porosity. [8]

METHODOLOGY

The amount of 84.111 g of nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), 54.085 g of manganese sulphate hydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) and 42.093 g of cobalt sulphate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$) were used as transition metal sources for the synthesis 101.738 grams of sodium carbonate was used as a precipitant. A 2.0 M aqueous solution of NiSO_4 , MnSO_4 , CoSO_4 (Ni: Mn: Co = 4: 4: 2 molar ratio) and 2.0 M aqueous solution of Na_2CO_3 into a magnetic stirrer for 3 hours with a capacity of 1 L. The pH of the solution was maintained between 7 and 7.5 and was carefully controlled by the addition of carbonate solution. Stirring rates and temperatures of 300 rpm and 60 ° C maintained throughout the carbonate co-precipitation process. The recovered precursor was washed, filtered through 5 L of distilled water and then dried in oven at 100 ° C for 12 hours. The precursor was grounded with lithium hydroxide for 30 minutes and calcinated in furnace at 800° C for 15 hours. And lastly, the cathode from the furnace was characterized with X-Ray Diffraction



FIGURE 1. NMC 442 cathode result via carbonate co-precipitation method

RESULTS AND DISCUSSION

The obtained cathode of NMC-442 is shown in Figure 1. NMC-442 cathode XRD samples are prepared via carbonate co-precipitation method with a stirring time of 3 hours. There are four major peaks in the JCPDS chart 98-015-9849. These peaks match the reference at a specific degree 2θ of 18.660° , 36.724° , 44.446° , and 64.307° with miller index of (003), (101), (104), and (018) respectively [10].

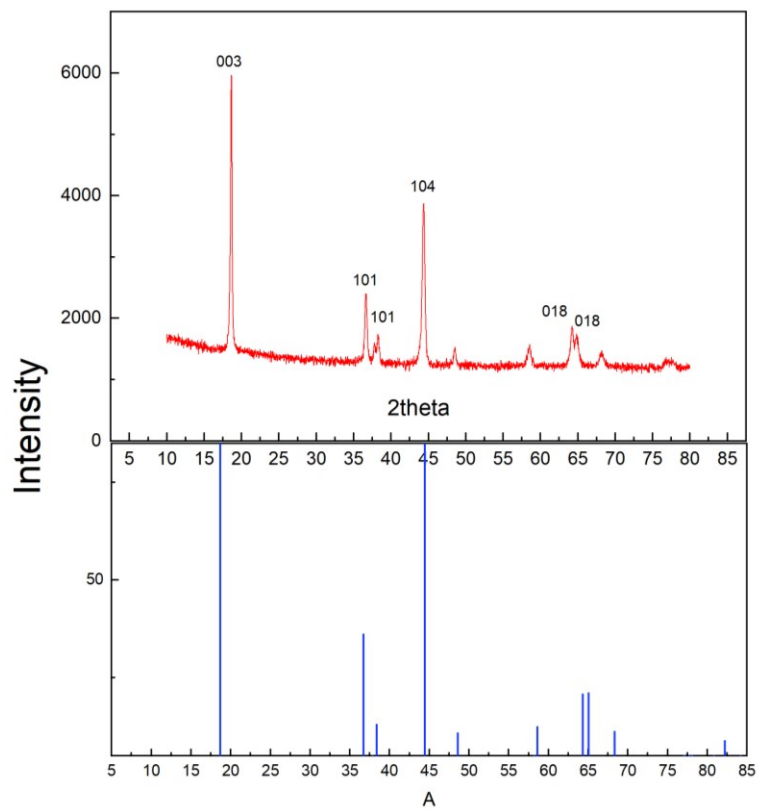


FIGURE 2. X-ray diffraction patterns of NMC 442 samples

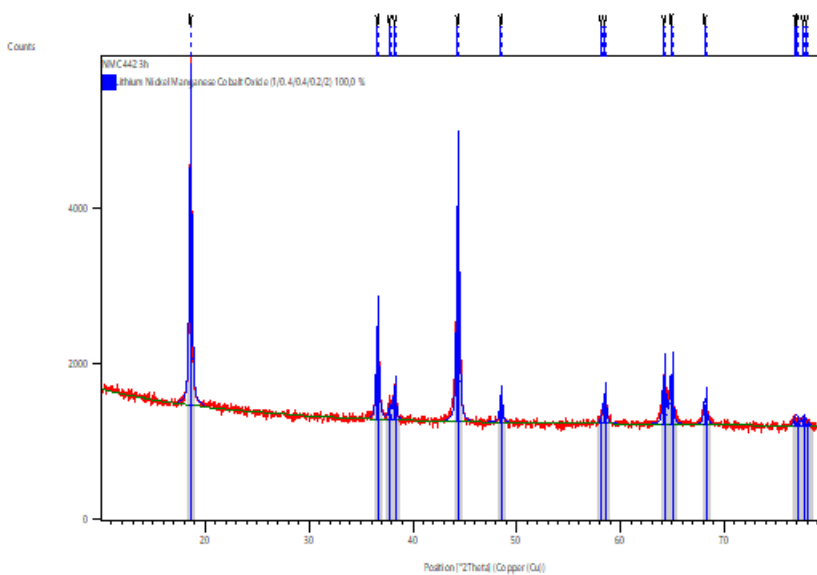


FIGURE 3. Rietveld refinement result of NMC 442 samples

The full width at half maximum (FWHM) based on the value of 2θ and the XRD characteristic can be used to determine the crystallite size (D_{XRD}) of using the Scherer's equation. the crystallite size of each sample on the selected diffractive plane was calculated and shown in table 1.

TABLE 1. Crystallite size of NMC 442 at many diffraction peaks

Diffraction Peaks	D _{XRD} (nm)	Peaks Height (°)
003	31,434	18,615
101	25,520	36,604
104	19,467	44,377
018	7,633	64,230

TABLE 2. Lattice Parameters of NMC-442

Formula	LiNi _{0.4} Mn _{0.4} Co _{0.2} O ₂
Space Group	R – 3m (Hexagonal)
Volume (Å ³)	101.92550
Density (g/cm ³)	4.7002
a (Å)	2.8720 (2)
b (Å)	2.8720 (2)
c (Å)	14.268 (2)
Alpha (°)	90
Beta (°)	90
Gamma (°)	120
R-expected (%)	2.69852
R _{wp} (%)	3.32335

Table 1 shows the crystallite size of the NMC-442 sample at many diffractive planes. D_{XRD} values range from 7.63 to 31.43 nm. Table 1 shows the crystallite size of each sample at various diffraction planes. As shown in figure 2, figure 3 and Table 1, the stirring time was long and the firing temperature is as high as 800 °C, so highly crystalline particles can be obtained. Table 2 shows the lattice parameters of NMC-442. Based on previous studies, highly crystalline materials mean that the diffusion coefficient of lithium ions is higher due to the wider intercalation pathways of the ions. This improves capacity and spread rate [11].

CONCLUSION

Based on the research, both carbonates of LiNi_{0.4}Mn_{0.4}Co_{0.2}O₂, (NMC-442) at a stirring rate of 3 hours coprecipitation process at 800 °C, produces four peaks with crystallite size values in the range 7.63 to 31.43 nm. Longer stirring times and higher temperatures produce larger crystallite size values.

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