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Study of the Synthesis NMC-622 Cathode Active Material with Oxalate Coprecipitation Method at Different Reaction Time

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Abstract. Renewable energy technology has a weakness namely intermittent which can be overcome by energy storage systems. Li-ion battery is one of the secondary batteries currently being developed which has promising performance to solve this problem. One of the most important components of a lithium battery is the cathode. In this study, $\text{LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$ (NMC-622) cathode was synthesized using the oxalate coprecipitation method. The control parameter namely the reaction time in this method affect the crystal structure and morphology of the product. Transition metal oxalate samples were prepared at different reaction times (40 and 60 minutes), then they were characterized using an X-Ray Diffraction (XRD) to observe the crystal structure and their composition formed. A Scanning Electron Microscopy (SEM) used to observe the surface morphology of the samples. XRD results of NMC-622 synthesized by a reaction time of 60 minutes showed the best results, based on the intensity ratio of peak (003) to peak (104) obtained, which was 1,238.

INTRODUCTION

A battery is a device that converts the chemical energy contained in the active material directly into electrical energy through an electrochemical redox (oxidation-reduction) reaction [1]. Secondary or rechargeable batteries are now replacing primary elements as they save resources and have a relatively small impact on the environment. The types of secondary batteries include Ni-Mh, Ni-Cd, Pb-acid, and the most prominent is Lithium ion (Li-ion). One of the advantages of Li-ion batteries is that they have a long lifecycle (500 to more than 1000 cycles), are good for use in various situations, especially in hot climates, and are higher efficiency than other rechargeable batteries [1,2]. In addition, Li-ion batteries still have many other advantages including high performance in the lithium ion transfer process, high energy density, no memory effect, small self-discharge possibility, can store large electrical capacity, and produce good cycle stability [3,4]. These advantages make Li-ion batteries very suitable to be used to overcome the intermittent in renewable energy technology as an energy storage system.

Li-ion batteries consist of several main parts, namely the negative electrode (anode), positive electrode (cathode), electrolyte and separator. The cathode is one of the most important parts of a Li-ion battery because the cathode is fully responsible for the lithium ion transfer process, both during the charging and discharging process [1]. $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ (NMC) is currently being widely developed due to its excellent performance. The composition of nickel, manganese, and cobalt in the NMC cathode synthesis can be adjusted according to what is needed. The function of

each NMC metal is that nickel (Ni) increases the current density and capacity of the cathode, manganese (Mn) can stabilize the crystal structure during the intercalation process of lithium ions and increase temperature stability, while cobalt (Co) can reduce the capacity lost during the process. cycles [5]. This research will focus on the active material of the NMC cathode with a composition of Ni:Mn:Co=6:2:2 (NMC-622) which has good thermal stability and high capacity [6].

There are several methods that can be used for the synthesis of NMC cathodes, namely hydrothermal, solid-state, sol-gel, coprecipitation, and others. Coprecipitation is a method based on the simultaneous deposition of more than one dissolved substance in order to form a homogeneous mixture with the help of a precipitate [7]. There are many control parameters in the coprecipitation synthesis that can affect the composition and morphology of the particles such as the pH value of the solution, temperature, stirring intensity, and reaction time which will play a role on the performance of the precursor as a cathode raw material.

The tap density and particle morphology of Ni(OH)₂ as a function of time in a continuous stirred-tank reactor using the hydroxide coprecipitation method were studied by Van Bommel et al. It was discovered that the tap density of particles gradually increased and then leveled off after 10 hours at 2 g/cm³. The SEM image of the particle morphology shows the gradual formation of spherical particles which become larger and finer as the reaction proceeds, this is used as an explanation for the tap density observations [8]. In a batch reactor, Dong et al. monitored the rate of coprecipitation of Ni and Mn oxalate in a solution with only one transition metal (TM) and a mixture of TM. Although TM has a wide range of solubility and precipitation rates, this report shows that under certain conditions and time scales, the resulting precipitate particles can have compositions that match the feed stoichiometry due to the synergistic interactions among nucleation and growth rates, and the best precipitate structure. [9]. This paper aims to synthesize the NMC-622 cathode by coprecipitation method with the parameter of reaction time. The product was then characterized by an XRD and SEM.

METHODOLOGY

Materials and tools

The materials used for the synthesis of the active material NMC-622 are NiSO₄·6H₂O, MnSO₄·H₂O, CoSO₄·6H₂O, H₂C₂O₄, NaOH, Li₂CO₃ industrial grade, NH₄OH analytical grade, and distilled water. The tools used are beaker glass, glass stirrer, spatula, measuring pipette, measuring cup, watch glass, thermometer, pH-meter, universal pH paper, analytical balance, magnetic stirrer, filter paper, glass funnel, oven, krusibel, furnace, and mortar.

Precursor preparation

Ni_{0.6}Mn_{0.2}Co_{0.2}C₂H₄ (MC₂H₄) precursor was synthesized by the oxalate coprecipitation method. NiSO₄·6H₂O, MnSO₄·H₂O, and CoSO₄·6H₂O were dissolved in distilled water in molar ratio of Ni:Mn:Co = 6:2:2. Then to the 0.77 M aqueous solution of transition metal sulfate stirred with a magnetic stirrer added 2.2 M precipitate solution prepared by dissolving H₂C₂O₄ and NaOH in distilled water and appropriate amount of 25% NH₄OH as a chelating agent were also added to this mixture. The mixture was stirred at 60 °C and 300 rpm for (a) 40 and (b) 60 minutes. After reaction, the precipitate of the samples was filtered and washed several times to remove the residual ions (Na⁺, SO₄²⁻ or other ions). The precipitate of the samples was then dried at 120 °C for 2 hours. The precursors for 40 and 60 minutes reaction were then named NMC 622-1 and NMC 622-2, respectively.

Active material preparation

The obtained MC₂H₄ precursor and 3% excess Li₂CO₃ were mixed manually in zipped plastic. The mixture of the two samples was first calcined at 550 °C for 5 hours, and then heated at 900 °C for 12 hours in oxygen atmosphere to obtain LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ powders.

Sample preparation

The synthesized compounds were characterized by using X-Ray Diffraction (XRD) (PANalytical Empyrean with Cu K α radiation). The XRD used to analyze the phase composition and crystal structure of the samples. The morphological features were observed by using Scanning Electron Microscope (SEM) (JEOL JSM6510LA).

RESULTS AND DISCUSSION

XRD was used to characterize the crystal structure of the NMC-622 cathode active material. Figure 1 shows the XRD patterns of samples after refinement. All samples well-defined has α -NaFeO₂ hexagonal structure with a space group R-3m which is the general structure of a layered oxide cathode. The lattices (006/102) and (108/110) of the sample XRD patterns with reaction times of 40 and 60 minutes were both completely separated, indicating that the NMC-622 material has a hexagonal crystal structure and a good layer structure. The intensity ratio of $I_{(003)}/I_{(104)}$ is a parameter to determine the cation mixing in the lattice of the layered oxide, and a value higher than 1.2 indicates a lower degree of cation mixing. Cation mixing is a very undesirable condition because the positions of Ni²⁺ and Li⁺ will be swapped due to the similar size of Li⁺ (0.76Å) and Ni²⁺ (0.69Å) ions. The higher the ratio, the lower the rate of cation mixing and the more beneficial it is for lithium-ion transfer [10,11,12].

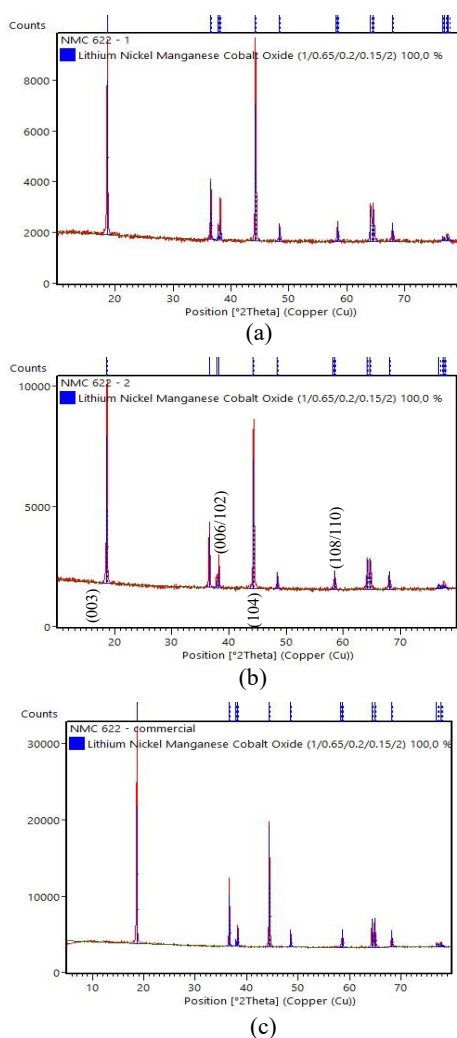


FIGURE 1. XRD Pattern of NMC-622 active aaterial prepared under different mixing time (a) 40 minutes; (b) 60 minutes; (c) the commercial NMC-622

Table 1 shows the ratio of $I_{(003)}/I_{(104)}$ and crystallite size calculation result for all samples. The intensity ratio of $I_{(003)}/I_{(104)}$ increased with increasing stirring time from 40 to 60 minutes, which means that the cation mixing decreases. Even so, the synthesized sample is still below the commercial NMC-622 which has the highest ratio. The crystallite size of the commercial sample is larger than the synthesized sample. Meanwhile, the crystallite size of the NMC-622 sample with a reaction time of 40 and 60 minutes is almost the same.

TABLE 1. Calculation result from XRD of the samples

Sample	Result	
	$I_{(003)}/I_{(104)}$	Crystallite size (nm)
NMC 622-1	0.96	62.16
NMC 622-2	1.23	62.63
The commercial NMC-622	1.71	83.24

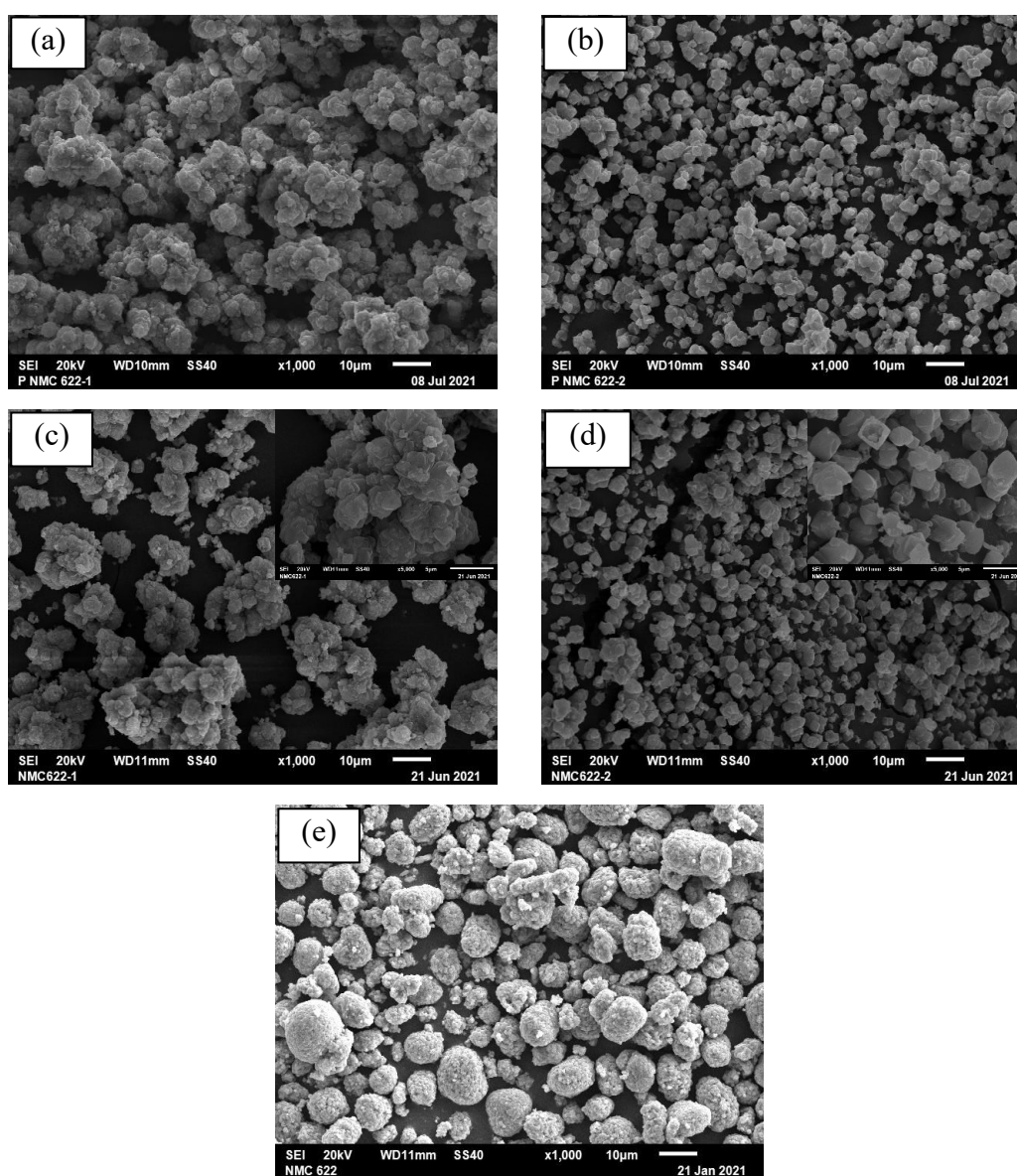


FIGURE 2. SEM images of MC_2H_4 precursor prepared under different mixing time (a) 40 minutes; (b) 60 minutes; NMC-622 active material prepared under different mixing time (c) 40 minutes; (d) 60 minutes; and (e) the commercial NMC-622

Figure 2 (a) and (b) shows the morphology of MC_2H_4 precursor. The sample prepared for 40 minutes has an irregular shape with rough surface, while at 60 minutes the morphology of the sample has a more regular size distribution and looks like a cube shape. Figure 2 (c) and (d) shows the morphology of NMC-622 active material calcined under the same condition. Cube particles with narrower size distribution were obtained from coprecipitation with 60 minutes of stirring time. While figure 2 (e) shows the commercial NMC-622 has a nearly uniform spherical particle shape. The regular shape of the particles allows the sample to have a high tap density, which corresponds to the volumetric capacity and energy density of practical Li-ion battery.

CONCLUSION

It is concluded that the reaction time carried out in the oxalate coprecipitation method affected the resulting NMC-622 cathode, indicated by changes in the two samples prepared for 40 and 60 minutes, which were shown by XRD and SEM results. However, the resulting synthesized samples were not as good as commercial ones, judging by the XRD results and the morphology of the samples, due to limited of reaction time. For improvement, it is necessary to perform a synthesis with more stirring time variables to determine the optimum time needed to produce the best product.

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REFERENCES

1. Thomas B. Reddy, "Linden's Handbook of Batteries, Fourth Edition", New York: McGraw-Hill, 2010.
2. Albright, G., Edie, J., Al-Hallaj, S. "A comparative of Lead Acid to Lithium-Ion in Stationary Storage Applications". AllCell Technologies LLC. March, 2012.
3. Gou, L., Hao, L., Shi, Y., Ma, S., Fan, X., Xu, L., "Onepot synthesis of a metal-organic framework as an anode for Li-ion batteries with improved capacity and cycling stability". *Journal of Solid-State Chemistry*, 210(1) 121-124. 2014.
4. Wu, F., Li, X., Wang, Z. and Guo, H., "Synthesis of chromium-doped lithium titanate microspheres as high-performance anode material for lithium-ion batteries". *Ceramics International*, 40(8):13195-13204. May, 2014.
5. Z. Tian, H. Yu, Z. Zhang, X. Xu, "Performance improvements of cobalt oxide cathodes for rechargeable lithium batteries", *ChemBioEng Rev* 5 111-118, 2018.
6. Noh, et al., "Comparison of the structural and electrochemical properties of layered $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ ($x = 1/3, 0.5, 0.6, 0.7, 0.8$ and 0.85) cathode material for lithium-ion batteries", *Journal of Power Sources*, pp. 121-130, 2013.
7. Patnaik, P., "Dean's Analytical Chemistry Handbook, Second Edition", New York: McGraw-Hill, 2004.
8. Van Bommel, A., and Dahn, J. R., "Analysis of the Growth Mechanism of Coprecipitated Spherical and Dense Nickel, Manganese, and Cobalt-Containing Hydroxides in the Presence of Aqueous Ammonia", *Chem. Mater*, vol. 21, no. 8, pp. 1500-1503, 2009.
9. Dong, H., & Koenig, G., "Compositional Control of Precipitate Precursors for Lithium-Ion Battery Active Materials: Role of Solution Equilibrium and Precipitation Rate", *Journal of Materials Chemistry A*, 2017.
10. M. Wang, Y.B. Chen, F. Wu, Y.F. Su, L. Chen, D.L. Wang, "Characterization of yttrium substituted $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ cathode material for lithium secondary cells", *Electrochimica Acta*, 55, 8815, 2010.
11. Y.M. Choi, S.I.P. yun, S.I. Moon, "Effects of cation mixing on the electrochemical lithium intercalation reaction into porous $\text{Li}_{1-y}\text{Ni}_y\text{Co}_y\text{O}_2$ electrodes", *Solid State Ionics*, 89, 43, 1996.
12. Kang, K., Ceder, G., "Factors That Affect Li Mobility in Layered Lithium Transition Metal Oxides", *Phys. Rev. B: Condens. Matter Mater. Phys*, 74, 94105, 2006.