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Evaluation of Nickel Manganese Cobalt (NMC) 111 and Lithium Cobalt Oxide (LCO) products

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ABSTRACT: NMC 111 cathode material and the LCO cathode material have been carried out using the precipitation method. Based on the results of the pH test, the pH of NMC 111 and LCO were 7 and 8 respectively. Based on the Moisture Content test, the water content in NMC 111 was 5% - 15%, while the LCO cathode material had a moisture content of 0% - 15%. The water content is affected by the heating temperature when making the cathode material, when the heating temperature is higher, the less water will be produced. Based on the results of the FTIR characterization test and the SEM-EDX test on NMC 111, it was obtained that the particle size had a radius of about 30-40 µm with an irregular spherical shape and had an elemental ratio of NiMnCo close to 1:1:1. Whereas the results on LCO obtained a particle size that has a radius of about 2-5 µm with the shape of an irregular collection of gravel balls and contains the elements C, O, and Co. Based on the NMC 111 XRD test, peaks formed at 006, 012, 104, 015, 110, and 113. Meanwhile, at LCO, peaks formed at 006, 012, 104, 018, 110, and 113.

Keywords: $LiCoO_2$, NMC 111, cathode, high-voltage, Batteries, Energy Storage.

1. Introduction

A battery is a device that can convert the chemical energy contained in the active ingredients of the battery components into electrical energy through electrochemical reactions of reduction and oxidation reactions. Reduction reactions are reactions of adding electrons and decreasing oxidation numbers, while oxidation reactions are reactions of removing electrons and increasing oxidation numbers. Based on their use, batteries are divided into two types, namely primary batteries and secondary batteries. Primary batteries are batteries that can only be used for one-time use[1]. While the secondary battery is a battery that can be used repeatedly (rechargeable). The existence of this secondary battery can certainly save more costs because the energy can be renewed if it runs out. There are many types of rechargeable batteries, including lead-acid, alkaline, nickel-cadmium, nickel-hydrogen, nickel-metal hydride, nickel-zinc, lithium cobalt oxide, lithium-ion polymer, lithium-sulfur, vanadium redox, lithium nickel manganese cobalt. and sodium sulfur.[2]

One type of secondary battery that is widely used is lithium-ion. Lithium-ion batteries have a high energy and voltage density and have a long-life cycle. There are two types of active materials in a lithium-ion battery, namely the cathode and anode. The cathode is the material that has a lithium-ion source and most lithium-ion batteries are classified by the cathode material. The material commonly used as a cathode in lithium-ion batteries is lithium cobalt oxide ($LiCoO_2$), but the cobalt element contained in $LiCoO_2$ is a heavy metal that is harmful to the environment, has an expensive price, is reactive and unstable at high temperatures so it is prone to damage. explosion. $LiCoO_2$ cathode material has been widely used since the first commercialization of lithium-ion batteries in 1990. This material has a high operating voltage of 4.2V, but is toxic and has the potential to explode if used improperly[3].

Besides LCO, there is another cathode material, NMC (Nickel Manganese Cobalt). NMC was chosen as the cathode material for the battery because Nickel (Ni) provides high capacity but has poor thermal stability, Manganese (Mn) has good cycling and excellent safety levels, while Cobalt (Co) can increase electronic conductivity resulting in high capacity[4]. The combination of elements between nickel-manganese-cobalt can provide high-performance batteries. NMC has several advantages compared to other cathode materials such as high capacity, high heat, and current stability, and has a long-life cycle.[5]

Nickel Manganese Cobalt (NMC) 111 and Lithium Cobalt Oxide (LCO) cathode materials were tested using pH testing, Moisture content analysis, Fourier Transform Infra-Red (FTIR), X-Ray Diffraction (XRD), and Scanning Electron Microscope- Energy Dispersive X-Ray (SEM-EDX) so that the characteristics of the cathode material can be identified.

2. Experimental Method

Nickel sulfate, manganese sulfate, and cobalt sulfate are dissolved in water at a concentration of 1 mol/liter in 50 liters of water. NaOH and oxalic acid are dissolved in water at a concentration of 1 mol/liter in 50 liters of water. Then both solutions were reacted in a batch reactor at 60oC for 3 hours. the solution was aged and washed with distilled water until the pH number reached 7. The precipitate was filtered and dried, and NMC 111 precursor was obtained. Lithium carbonate was added to the nmc 111 precursor, then sintered at 950˚C for 12 hours. The NMC 111 product material was sieved using a 200-mesh sieve.[6]

Cobalt sulfate is dissolved in water with a concentration of 1 mol/liter in 50 liters of water, then oxalic acid and NaOH are also dissolved in water with a concentration of 1 mol/liter in 50 liters of water. Then both solutions were reacted in a batch reactor at 60˚C for 3 hours. the solution was then aged and washed until the pH number reached 7. The precipitate was filtered and dried, and a cobalt oxalate precursor was obtained. Lithium carbonate is added to the cobalt oxalate precursor, then sintered at 950°C for 20 hours. The LCO product material was sieved using a 200-mesh sieve.[7]

The precursor and product of NMC 111 and LCO material was characterized using an X-ray diffractometer (MD-10 mini diffractometer) at a diffraction angle of $17<\theta<71°$ and CuK-α wavelength of 1.5418 Å), Fourier's transform infra-red (FTIR) spectroscopy (Shimadzu, Japan). The morphology of the cobalt phosphate and LiCoPO4 powders is investigated by scanning electron microscope (SEM JEOL Japan). [8]

3. Results and Discussion

3.1 pH Analysis

Table 3.1 pH Analysis Result

Time (hour)	pH	
	NMC 111	LCO
1	7	8
2	7	8
3	7	8

The cathode materials for NMC 111 and LCO were tested for pH number using a digital pH meter. Tests were carried out with variations of 1 hour, 2 hours, and 3 hours. The pH test aims to determine the pH of the NMC 111 and LCO solutions. Before the Ph test, NMC 111 and LCO were dissolved in 50 ml of distilled water and then stirred using a spoon, after dissolving the two materials were tested using a digital pH meter. The pH of the NMC 111 material with a variation of 1-3 hours was 7. Meanwhile, the pH of the LCO material was 8 with a variation of 1-3 hours.[9]

3.2 Moisture Content Analysis

Table 3.2 Moisture Content Analysis Result

Material	Porcelain Crucible Mass (gr)	Material Mass (gr)	Material Mass + Porcelain Crucible Mass Before Oven (gr)	Material Mass + Porcelain Crucible Mass After Oven (gr)	Material Mass After Oven (gr)	Water Content (%)
NMC 111	14,00	1	15,00	14,92	0,92	8
NMC 111	14,37	2	16,37	16,32	1,95	2,5
NMC 111	16,82	3	19,82	19,78	2,96	1,3
LCO	13,27	1	14,27	14,24	0,97	3
LCO	12,81	2	14,81	14,77	1,96	2
LCO	14,41	3	17,41	17,37	2,96	1,3

The results of the Moisture Content test obtained the water content contained in the NMC 111 and LCO materials. Materials were measured by weight before and after being placed in a vacuum oven for 3 hours with mass variations of NMC 111 and LCO 1-3 grams. From the results obtained, it can be seen that the mass after the vacuum oven is smaller than before being put into the oven, this indicates the presence of water content in the NMC 111 and LCO materials. Water content can be calculated by the following equation:

$$water\ content = \frac{initial\ mass - final\ mass}{initial\ mass} \times 100\%$$

From the calculation results, the NMC 111 cathode material has a water content of between 1% - 10%, while the LCO cathode material has a water content of 1% - 5%. The water content is affected by the heating temperature when making cathode materials, when the heating temperature is higher, less water will be produced.[10]

3.3 FTIR Analysis

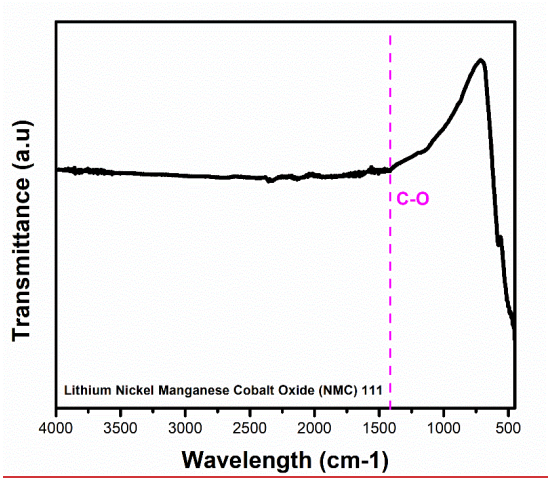


Figure 3.1 FTIR Analysis Result of NMC 111

Figure 3.1 shows a graph of the FTIR test results on the NMC 111 cathode material. From the FTIR test results, characteristic information was obtained indicating the presence of the C-O functional group at a wavelength of around 1400 cm-1. The presence of the C-O functional group is considered an impurity because the peak must indicate the oxide phase and not another phase, the appearance of the C-O group can result from excess Li sources during the sintering process.[11]

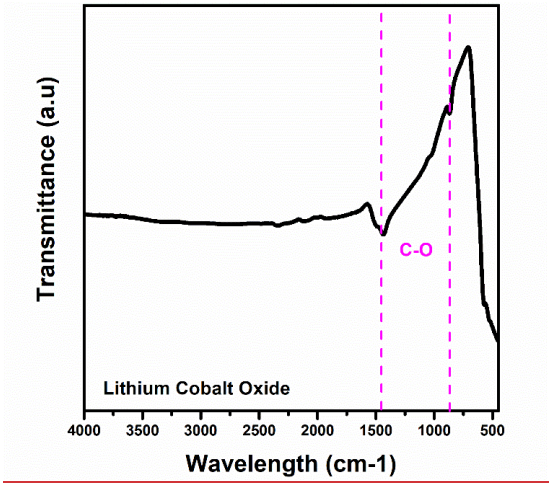


Figure 3.2 FTIR Analysis Result of LCO

Figure 3.2 shows a graph of the FTIR test results on the LCO cathode material. The results of the FTIR test obtained characteristic information indicating the presence of the C-O functional group at a wavelength of about 1400 cm-1 and 900 cm-1. The presence of the C-O functional group is considered an impurity because the peak must indicate the oxide phase and not another phase, the appearance of the C-O group can result from excess Li sources during the sintering process.[12]

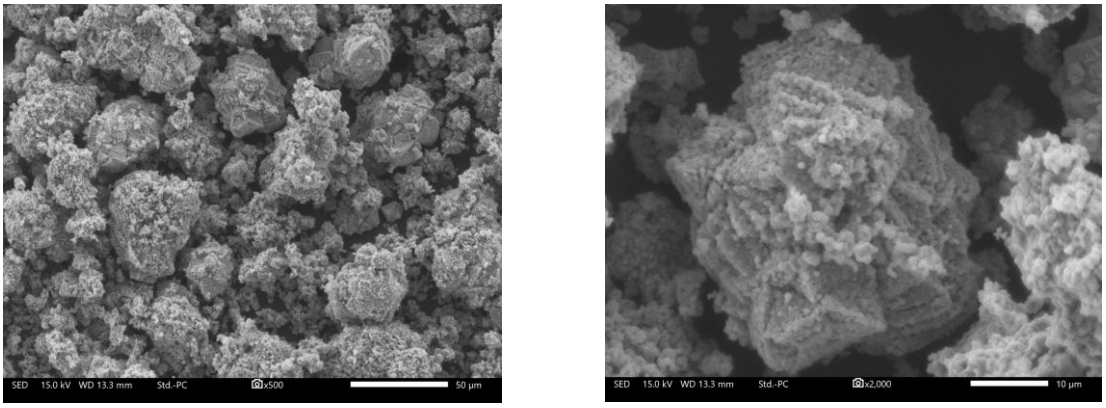
3.4 Scanning Electron Microscope – Energy Dispersive X-Ray

Table 3.3 Energy Dispersive X-Ray NMC 111 Analysis Result

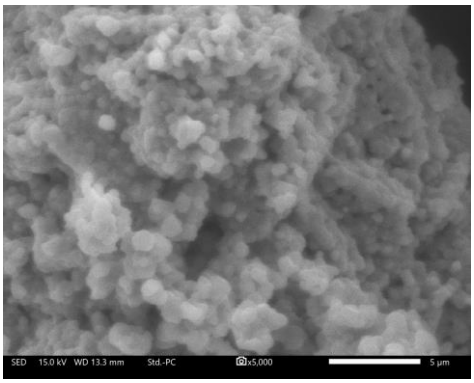
Element	Line	Mass%	Atom%
C	K	3.39±0.23	8.06±0.55
O	K	34.20±0.77	61.08±1.37
Mn	K	15.60±0.85	8.12±0.44
Co	K	24.14±1.37	11.71±0.67
Ni	K	22.67±1.47	11.04±0.72
Total		100.00	100.00
Spc_005		Fitting ratio 0.0516	

Table 3.3 contains the results of the SEM-EDX test on NMC 111. The table provides information regarding the percentage of each element forming the cathode material and the percentage of the EDX test for NMC 111 cathode material. It can be seen in table 4.3 that NMC 111 has a ratio of Ni atomic composition MnCo was 11.04±0.72 : 8.12±0.44 : 11.71±0.67.[13] The ratio of these three atoms

is close to 1:1:1, this means that all atoms have an even distribution throughout the place[14]



(a) 500x (b) 1000x



(c) 5000x

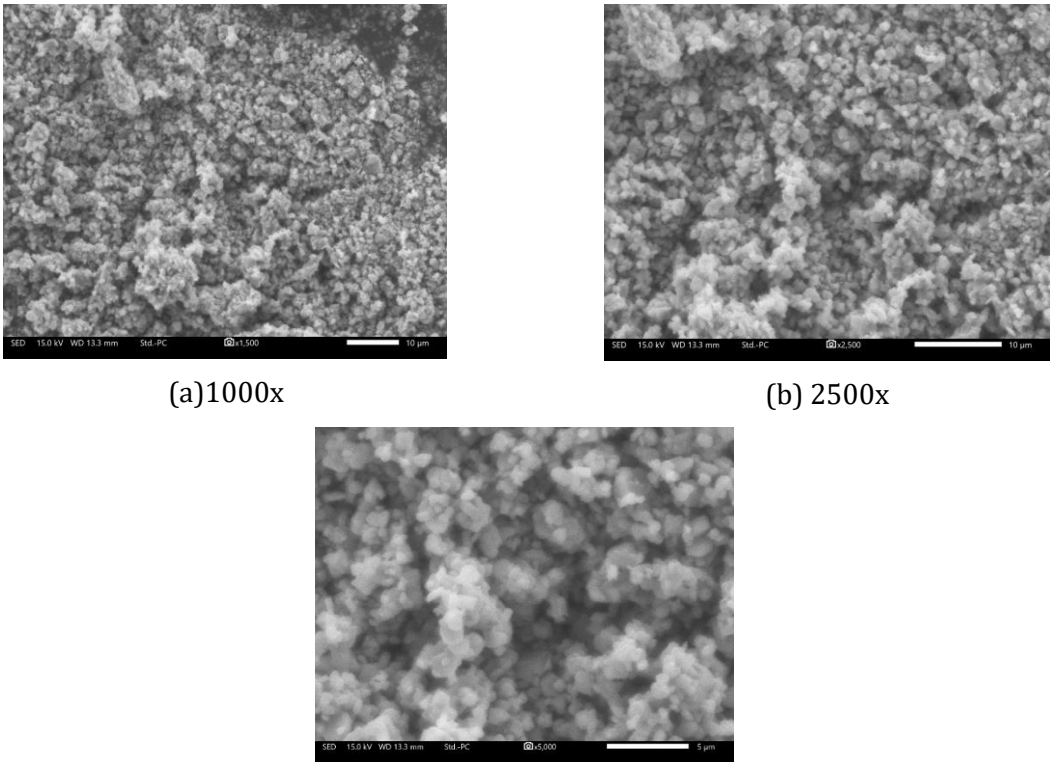
Figure 3.3 SEM Analysis Result of NMC 111

In the SEM test results, the particle size and also the morphology of the cathode material are tested[15]. Figure 3.3 C shows the results of the SEM test on NMC 111 which has an irregular shape of a collection of spherical grains. When enlarged it is known that it is composed of smaller spherical molecules. It is known that NMC 111 has a radius dimension of around 30-40 μm.[16]

Table 3.4 Energy Dispersive X-Ray LCO Analysis Result

Element	Line	Mass%	Atom%
C	K	3.47±0.22	8.04±0.52
O	K	36.56±0.76	63.62±1.32
Co	K	59.97±2.07	28.33±0.98
Total		100.00	100.00
Spc_004		Fitting ratio 0.0444	

Table 3.4 contains the results of the SEM-EDX test on LCO. The table provides information regarding the percentage of each element forming the cathode material, and the percentage of the LCO cathode material EDX test. It can be seen in table 4.4 that LCO has C, O, and Co elements. All transition elements have an even distribution throughout the place.



(a)1000x (b) 2500x

(c) 5000x

Figure 3.4 SEM Analysis Result of LCO

In the SEM test results, information is obtained about the particle size and also the morphology of the cathode material being tested. In Figure 3.4 it is known that the results of the SEM test on LCO which has the shape of an irregular collection of gravel balls. When enlarged it is known that it is composed of smaller molecules in the form of balls that are irregular in shape. It is known that the LCO has a radius dimension of about 2-5 μm.[17], [18]

3.5 X-Ray Diffraction Analysis

Analysis using X-Ray Diffraction produces a graph in the form of a diffractogram in the form of an arrangement of lines/peaks with different intensities and positions that are specific to the material being analyzed. Each crystalline phase has a characteristic diffractogram arrangement, this can be used for identification tests. By matching each peak that appears on the diffractogram at certain angle values of 2θ and d the results of the analysis with data from the Joint Committee Powder Diffraction Standard (JCPDS) can be used to determine the conformity of the crystal structure so that orientation information of the

crystal planes formed will be obtained. If all the orientations of the crystal planes are identified, it ensures that the crystal structure is compatible.[19]

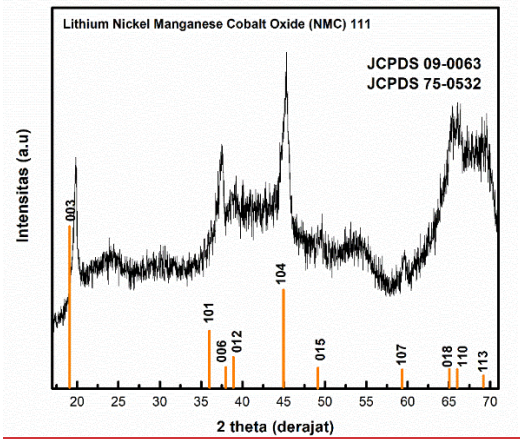


Figure 3.5 XRD Analysis Result of NMC 111

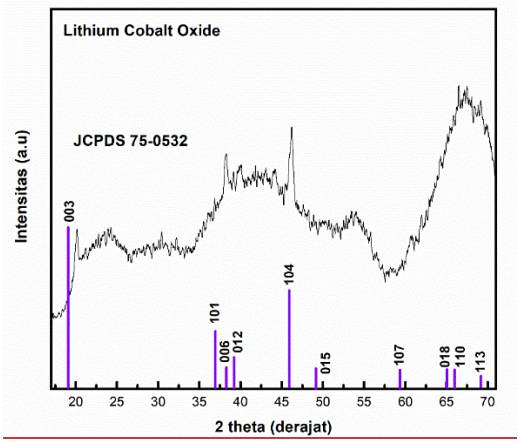


Figure 3.6 XRD Analysis Result of LCO

Figure 3.5 shows the results from the XRD test of the NMC 111 cathode material, namely several peaks have been formed according to JCPDS 09-0063 and 75-0532, at peaks 006, 012, 104, 015, 110, and 113, and some peaks have not yet been formed clearly. at peaks 003, 10, 107, and 018. Some of the peaks that have not yet formed can be caused because the peaks that appear are too small, this is because the material is still not homogeneous during the mixing process.[20]

Figure 3.6 shows the results from the XRD test of the LCO cathode material, namely most of the peaks have been formed according to JCPDS 75-0532, namely at peaks 006, 012, 104, 018, 110, and 113. Some peaks are still not formed at peaks 003, 101, 015, and 107. Some of the peaks that have not been formed can be caused because the peaks that appear are too small, this is because the material is still not homogeneous during the mixing process.[21]

4. Conclusion

NMC 111 cathode material and the LCO cathode material have been successfully carried out using the precipitation method. Quality Control on NMC 111 and LCO with several tests. Based on the results of the pH test, the pH of NMC 111 and LCO were 7 and 8 respectively. Based on the Moisture Content test, the water content in NMC 111 was 5% - 15%, while the LCO cathode material had a moisture content of 0% - 15%. The water content is affected by the heating temperature when making the cathode material, when the heating temperature is higher, the less water will be produced. Based on the results of the FTIR characterization test, it was found that the C-O functional group in NMC 111 and LCO was due to excess Lithium. Based on the results of the SEM-EDX test on NMC 111, it was obtained that the particle size had a radius of about 30-40 µm with an irregular spherical shape and had an elemental ratio of NiMnCo close to 1:1:1. Whereas the results of the SEM-EDX test on LCO obtained a particle size that has a radius of about 2-5 µm with the shape of an irregular collection of gravel balls and contains the elements C, O, and Co. Based on the NMC 111 XRD test, peaks formed at 006, 012, 104, 015, 110, and 113. Meanwhile, at LCO, peaks formed at 006, 012, 104, 018, 110, and 113.

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