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Synthesis of Lithium Mangan Oxide ($LiMn_2O_4$) Using Solution Method for Lithium Ion Battery Catodes Materials

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Abstract. Synthesis of Lithium Manganese Oxide ($LiMn_2O_4$) for Lithium Ion Battery Cathodes with Solution Method has been conducted. This experiment was carried out using the solution method. In this study, the synthesis was carried out by varying the calcination temperature. The raw materials used were Lithium Acetate ($C_2H_3O_2Li$), Manganese Acetate ($C_4H_6MnO_4.4H_2O$), Hydrochloric Acid (HCl), and Ethanol (C_2H_5OH) as solvents which were dissolved to become $LiMn_2O_4$ precursors. Synthesis was carried out at calcination temperatures of 600^{o}C, 700^{o}C and 800^{o}C, for 4 hours then pounded with a mortar until smooth. The characterization includes: The results of the STA test at 280^{o}C-380^{o}C showed a mass decrease of 11.9973% due to the release of mass of water vapor and decomposition of $C_4H_6MnO_4.4H_2O$ raw material. XRD analysis shows that the increase in peak temperature of the $LiMn_2O_4$ phase intensity is getting sharper, the peak showing the impurity Li_2O phase decreases. SEM analysis results show that the higher the calcination temperature, the larger the particle size is formed, because in the calcination process the densification process occurs.

Keyword: cathode material, solution method, Li-ion battery, lithium manganese oxide.

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1 Introduction

Batteries are used in almost every aspect of modern life. Everyday household items such as flashlights, TV remotes, and electric drills require batteries. Even away from home, we rely on batteries to power our MP3 players, cell phones, and laptops. People with pacemakers or other portable medical devices trust batteries very much. With increasing concerns about dependence on fossil fuels and their environmental impact, alternative energy has become a major concern. However, alternative energy systems such as solar, wind, and water often require efficient batteries to store their energy. Hybrid or pure-electric vehicles require high-performance

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batteries to compete with oil and gas engines. These devices drive the improvement of battery technology which is used in almost every aspect of modern life [1].

The battery is a device that converts chemical energy into electrical energy. Lithium batteries can be made as primary or secondary batteries. Both have different functions and characters. The primary battery has the ability to use only one time, one time discharge, while the secondary battery has the ability to charge / discharged repeatedly. In principle, this is due to the abundant availability of raw materials [2-3]. The electrochemical properties of $LiMn_2O_4$ are largely determined by crystal structure and oxide morphology [4-5]. $LiMn_2O_4$ has a spinel structure which has good structural stability during the charge-discharge process [6-7]. $LiMn_2O_4$ has a spinel structure with three dimensional intercalation capabilities. This causes the cathode material to be able to insert lithium ions in three directions. Lithium batteries are ion-based batteries with lithium ions as the spinel driving motor. $LiMn_2O_4$ shows a lack of resistance in the life cycle and an irreversible loss of capacity at high temperatures [8-9]. Insertion and extraction on $LiMn_2O_4$ spinel yields a mean voltage of 4 V. Spinel $LiMn_2O_4$ has advantages than Co and Ni material [10]. When a material is heated, the crystallization process will occur. Choosing the right temperature will determine the quality of the crystal structure formed and will affect the battery cell capacity. In this research, $LiMn_2O_4$ can be synthesized by solution method and calcination temperature variation will be studied.

2 Materials and Methods

Synthesis of $LiMn_2O_4$ powder using the solution method begins with weighing the raw materials, namely 2 g of $LiMn_2O_4$ powder, 0.7 g of $C_2H_3O_2Li$, 6.1 g of $C_4H_6MnO_4.4H_2O$, 10 mL of ethanol to dissolve sample A and 30 mL of ethanol to dissolve sample B, and 0.25 mL of HCl in solution of sample A and 2 mL of HCl in solution of sample B to maintain the pH and to make the solution not to coagulate.

As much as 2 g sample were carried out in 2 different beakers. Each material is dissolved in a mixture of ethanol + HCl using a magnetic stirrer with a stirrer speed of 250 rpm, so that a solution of sample A ($C_2H_3O_2Li$ + HCl + ethanol) is formed and solution of sample B ($C_4H_6MnO_4.4H_2O$ + HCl + ethanol), after the solution of sample B is finished then it remains stirred for 1 hour. After that solution of sample A is mixed with solution of sample B while continuing to stir until a sol is formed, then the solution is stirred for 5 hours, then the solution is poured into a petri dish and put in an oven for 16 hours, after it is dry then crushed and put into the plastic sample, before the calcination process is carried out. The refined $LiMn_2O_4$ is then weighed with a digital scale, this aims to find out how much $LiMn_2O_4$ was lost during the calcination process and to determine the accuracy of the characterization results. Then the sample in the plastic sample is put into a crucible and calcined at a temperature of 600°C, 700°C, 800° C for 4 hours then pounded with a mortar until smooth. The synthesis process of

making $LiMn_2O_4$ cathode material using the solution method between $C_2H_3O_2Li$ powder and $2C_4H_6MnO_4.4H_2O$ according to the reaction:

$$C_2H_3O_2Li + 2C_4H_6MnO_4.4H_2O \rightarrow LiMn_2O_4 \quad (1)$$

The samples were then characterized by STA, XRD and SEM. In the anode powder manufacturing process, the active ingedients of LTO are mixed with Al_2O_3 and Carbon Super P. The three ingedients are mixed in the milling chamber. The milling chamber is inserted into the Planetary Ball Miller tool. The milling time is set for 2 hours at a speed of 20.00 Hz. The material that is finished is milled and crushed using a spatula until smooth. Then the sample was sintered at a temperature of 850ºC for 4 hours. After sintering, crush the sample using a pastel until smooth and even. A small sample was taken for characterization using XRD to determine the phase and crystal structure of LTO, SEM to determine the morphology of the sample, and CV to determine the electrochemical performance of LTO powder.

3 Result and Discussion

3.1 STA Analysis

$LiMn_2O_4$ powder was characterized thermally using a Simultaneous Thermal Analysis (STA) tool with the Linseis brand and the PT1600 type and the results of the data obtained were processed using Linseis Evaluation software to determine the sintering temperature of the $LiMn_2O_4$ powder.

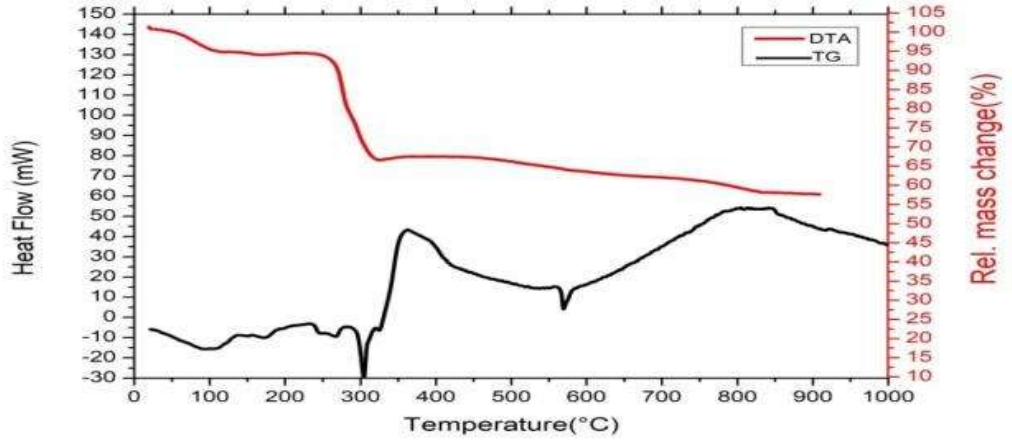


Figure 1. DTA-TG LTO of $LiMn_2O_4$

The results of the STA analysis (Figure 1) shows that DTA (differential thermal analysis) temperature range of 20°C-280°C in the form of a downward curved graph with a peak, at temperatures around 280°C which is the release of organic elements such as CO_2 and water vapor contained in the raw material and a phase occurs, in the temperature range 280°C-300°C which is an endothermic reaction (requiring heat) this peak is a decomposition process of $C_4H_6MnO_4.4H_2O$ due to its melting point, at a temperature of 300°C there is a melting of

Lithium Acetate ($C_2H_3O_2Li$), seen from material safety data that its melting point 80°C, in a temperature range of 400°C-800°C, there is a crystallization of LMO. In temperature of 570°C, it shows that the change in raw material has melted with a decrease in enthalpy of 34.43 J / g with the melting points of each raw material $C_2H_3O_2Li$: 283°C-285°C and $C_4H_6MnO_4.4H_2O$: 80°C. In addition, adjusted to the TG (Thermogravimetry) graph that in the temperature range 280°C-380°C there was a mass decrease of 11.9973% due to the release of mass of water vapor and the decomposition of $C_4H_6MnO_4.4H_2O$ raw material, in the next temperature range between 380°C-480°C there was a new phase formation, in the temperature range of 460°C-640°C, there was a mass decrease of 3.4191%, in the 640°C-1000°C temperature range there was a mass decrease of 6.5663%, and while the temperature range 480°C-900°C there was crystallization of $LiMn_2O_4$.

3.2 X-Ray Diffraction (XRD) Analysis

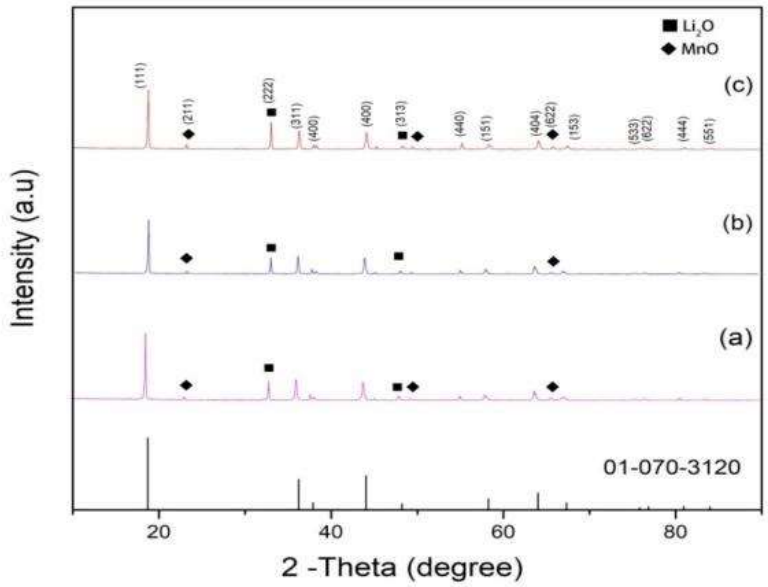


Figure 2. XRD Patterns of $LiMn_2O_4$ with calcination temperatures (a) 800°C, (b) 700°C, and (c) 600°C for 4 hours

Based on the results of the XRD analysis of $LiMn_2O_4$ powder, the resulting samples were sintered with calcination temperature variations of 600°C, 700°C and 800°C then XRD testing was carried out to identify the phase formed from each sample. The results of the XRD pattern of active material $LiMn_2O_4$ cathode in crystal field analysis can be seen in Figure 2. The crystal structure of the synthesized sample was characterized using Rigaku X-Ray Diffractometer with Cu Kα radiation operating at 40 kV and 30 mA. Diffraction data were collected every 4 s step with 0.010 with reference data with a measurement range at an angle of 10° - 90°. From the results of this test, it is obtained a curve that shows the intensity of the 2 angle, the XRD curve of the $LiMn_2O_4$ material with variations in calcination temperature can be seen in Figure 2. The test results with an angle of 2θ standard samples from ICDD data (International Center

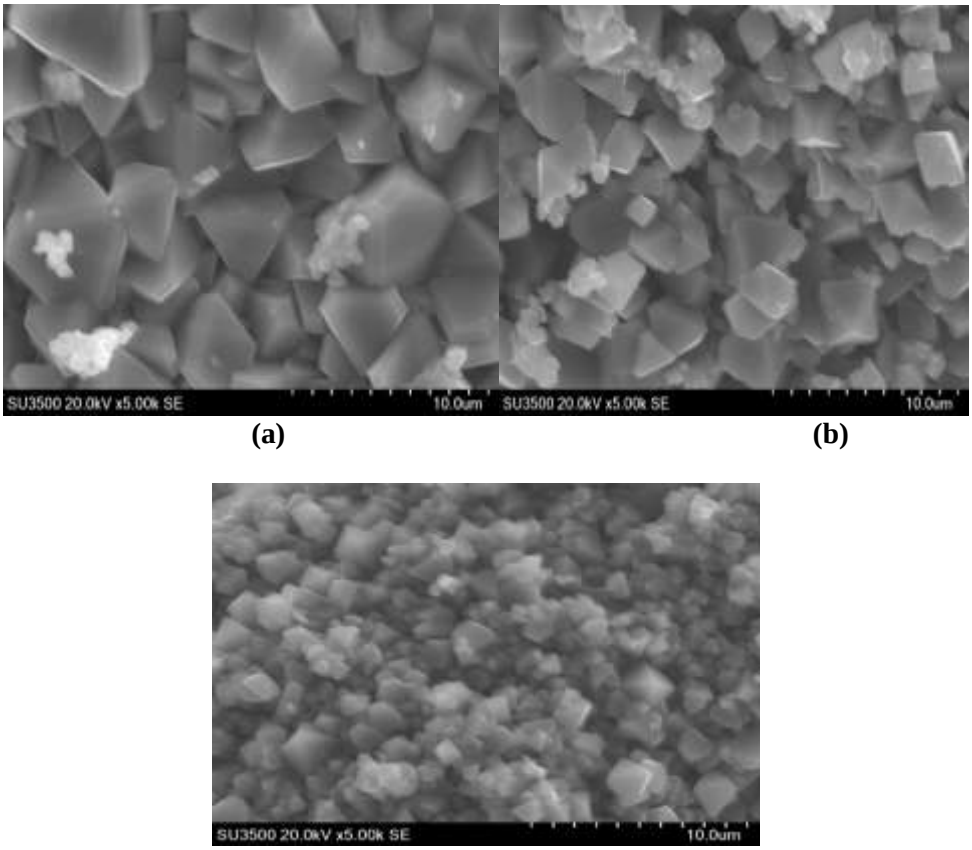
Diffraction Database) on PDF (Powder Diffraction File) with number 01-070-3120 which can be seen in Figure 2.

The diffraction peaks that appear on XRD have the same thing as ICCD number 01-070-3120 for $LiMn_2O_4$ material. The full XRD analysis results can be seen in the attachment. Figure 2 shows the results of XRD processing with sinter temperature variations. The three samples were identified to have a $LiMn_2O_4$ crystal structure with the highest peak at an angle of $2\theta = 18.710°$ with a plane distance of d = 4.7387 Å. The data matches or matches the ICDD data with PDF number 01-070-3120. Based on Figure 2, it can be seen that the active material of the $LiMn_2O_4$ cathode has a low level of crystallinity, this is indicated by the level of peak intensity obtained at each diffraction pattern is not so sharp. In Figure 2 (a) is the XRD pattern of the $LiMn_2O_4$ sample calcined at 800°C, after matching with the database (ICDD- 01-070-3120) [11-12].

At a calcination temperature of 600°C, it is almost the same as the pattern formed almost the same as the XRD pattern in the 800°C sample. From this curve, the peak intensity of $LiMn_2O_4$ is formed and the intensity of the impurities decreases even very small, the impurities contained in this pattern are the Li_2O phase at the $2\theta = 48.07°$, this phase is a Li_2O phase which is quite stable at high temperatures. At a calcination temperature of 700°C the pattern formed is almost the same as the XRD pattern in the 800°C sample, it's just that the intensity of the peak of the phase is different, the peak intensity of the $LiMn_2O_4$ phase looks lower while the peak intensity of the Li_2O phase has increased. The Li_2O impurity phase of these two samples is the metastable Li_2O phase. In calcination temperature at 800°C indicates that the $LiMn_2O_4$ phase has been formed but there are impurities that were detected in the XRD spectrum. XRD measurements on $LiMn_2O_4$ material synthesized with $LiOH.H_2O$ showed that the $LiMn_2O_4$ phase had been formed but there were impurities detected in the XRD spectrum.

Meanwhile, with the synthesis of $LiOH.H_2O$, the peak of the $LiMn_2O_4$ phase is at an angle of 2θ 18.710°; 23.070°; 32.87°; 35.970°; 37.720°; 43.920°; 48.070°; 49.450°; 55.170°; 58.080°; 63.800°; 65.840°; 67.200°; 75.630°; 76.600°; 80.670°; 83.680°. In this research, obtained $LiMn_2O_4$ material with a pure phase at a calcination temperature of 600°C with a long calcination time of 20 hours. So that Li_2O impurities can be removed by increasing the temperature and the length of the calcination time [13]. From Figure 2, as a whole, it can be seen that the $LiMn_2O_4$ phase has been formed at a temperature range of 600°C - 800°C with a cubic crystal structure and Fd3m space group, but there is still impurity Li_2O which does not completely react. But along with the increase in temperature, the peak intensity indicates that the $LiMn_2O_4$ phase is getting sharper, while the peak showing the Li_2O phase the impurity decreases. The narrower and sharper peaks indicate that the crystal size formed from the $LiMn_2O_4$ phase is getting higher.

3.3 Scanning Electron Microscope (SEM) Analysis



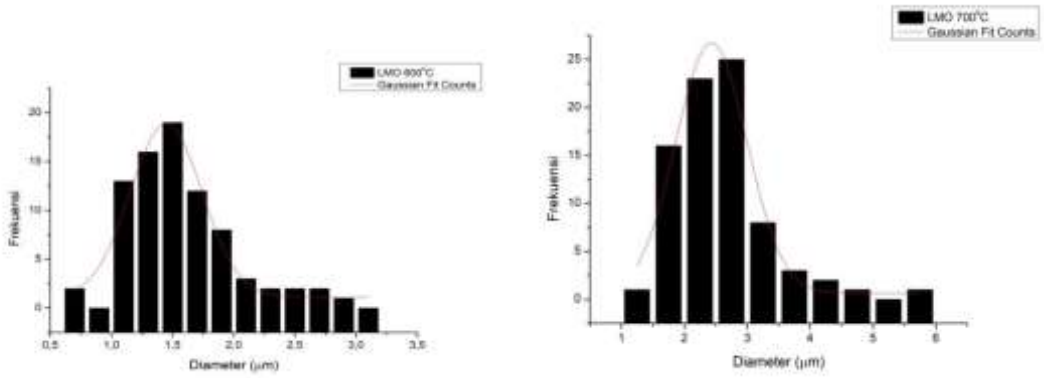
(a) **(b)**

(c)

Figure 3. Morphology samples of $LiMn_2O_4$ with calcination temperatures (a) 600°C, (b) 700°C, and (c) 800°C

The results of the morphological characterization of the sample using SEM (Scanning Electron Microscope) with a magnification of 5 k SE can be seen in Figure 3. Morphologically, the surface of $LiMn_2O_4$ samples at 600°C has a rough texture, while the 700°C sample begins to form a smoother surface and in the 800°C sample. the texture formed is smoother than the other two samples. All samples consist of small and large particles that form agglomerations with various particle shapes such as round, rectangular, square and irregular shapes. But in the 800^{o}C sample began to form gain boundaries on large particles, so that they appear to be in the form of smaller and finer particles. In calcination temperatures at 800°C sample there are also small particles that have a more uniform shape and gather to form one large material (bulk material).

To determine the particle size of the $LiMn_2O_4$ powder material in data processing used Image-J software using images obtained from SEM test results with a magnification of 5k SE. Data taken 80 times with large, medium and small particle sizes, the processing results are displayed in a graph in the form of a histogram in Figure 4.



(a) **(b)**

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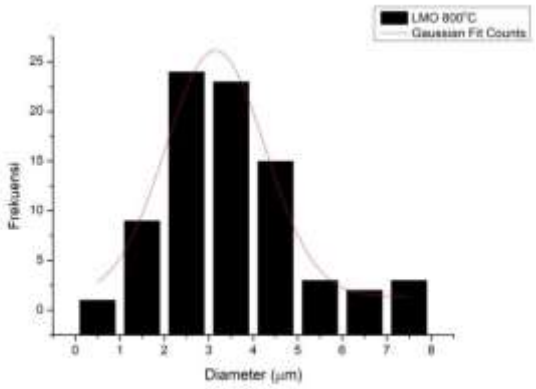

(c)

Figure 4. Histogram Particle Distribution of $LiMn_2O_4$ with calcination temperature variations (a) 600°C, (b) 700°C, and (c) 800°C

Figure 4 shows that particles have a size with micro order (μ), particles with a size below 125 μm increase with increasing calcination temperatures. The smallest average particle size was owned by the sample with a calcination temperature of 600°C of 1.74 μm, while the largest average particle size was obtained in a sample with a calcination temperature of 800°C of 4.77 μm. So it can be compared that the higher the calcination temperature, the larger the particle size formed. This happens because in the calcination process the densification (compaction) of the particles occurs, but in this study the holding time is only 4 hours so that there is no gain growth, therefore when the temperature is higher the size of the particles that are formed the bigger.

4 Conclusion

Synthesis of $LiMn_2O_4$ with calcination temperature variations of 400°C- 800°C is succesfully conducted by using solution method. DTA results that in temperature range 280°C-380°C decreased mass by 11.9973%, whereas in the temperature range between 380°C-480°C, there was a new phase formation, then in the temperature range 480°C-900°C occurred crystallization

of $LiMn_2O_4$. The XRD analysis results showed that the peak cathode intensity of the $LiMn_2O_4$ single phase was lower, while the peak intensity of the Li_2O phase increased. $LiMn_2O_4$ phase change has been formed at a temperature range of 600°C-800°C with a cubic crystal structure and space goup Fd3m. The narrower and sharper peaks indicate that the crystal size formed from the $LiMn_2O_4$ phase is getting higher. The calcination temperature in $LiMn_2O_4$ material characteristics, the particles size had below 125 μm increased as the calcination temperature increased.

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