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Synthesis of lithium mangan dioxide (LiMn_2O_4) for lithium-ion battery cathode from various lithium sources

S Priyono¹, N R Ginting², S Humaidi², A Subhan¹ and B Prihandoko¹

¹Research Center for Physics – Indonesian Institute of Sciences Kawasan PUSPIPTEK Gedung 442 Serpong, Tangerang Selatan, Banten, Indonesia

²Department of Physics- Faculty of Mathematics and Natural Sciences-University of North Sumatera Jl. Bioteknologi I Kampus USU Medan, 20155, Indonesia

E-mail: slam013@lipi.go.id

Abstract. LiMn_2O_4 as a cathode material has been synthesized via solid state reaction. The synthesis has been done by varying lithium sources such as $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 while MnO_2 was used as Mn sources. All raw materials were mixed stoichiometrically to be the precursors of LiMn_2O_4 . The precursors were sintered using high temperature furnace at 800 °C for 4 hours in atmospheric condition to form final product. The final products were sieved to separate the finer and smoother particles from the coarse ones. The products were characterized by X-Ray Diffractometer (XRD) to identify phases and crystal structure. The peak wave number was also determined using Fourier Transform Infra Red (FTIR) to find functional group. LiMn_2O_4 sheets were prepared by mixing active material with polyvinylidene fluoride (PVdF) and acetylene black (AB) in mass ratio of 85:10:5 wt.% in N,N-Dimethylacetamide (DMAc) solvents to form slurry. The slurry was then coated onto Al foil with thickness of about 0.15 mm and dried in an oven. LiMn_2O_4 sheet was cut into circular discs and arranged with separator, metallic lithium, and electrolyte in a coin cell. Automatic battery cycler was used to measure electrochemical performance and specific capacity of the cell. XRD analysis showed that sample synthesized with Li_2CO_3 has higher crystallinity and more pristine than sample synthesized with $\text{LiOH}\cdot\text{H}_2\text{O}$. FTIR analysis revealed that both of samples have identical functional group but sample with Li_2CO_3 source tend to degrade. Cyclic voltammetry data gave information that sample with $\text{LiOH}\cdot\text{H}_2\text{O}$ source has better electrochemical performance. It showed double oxidation/reduction peaks more clearly but sample with Li_2CO_3 source has higher specific capacity (64.78 mAh/g) than sample with $\text{LiOH}\cdot\text{H}_2\text{O}$ (50 mAh/g).

1. Introduction

Increasing dependence on fossil fuels has negative impact on the environment, so alternative energy becomes very important. Alternative energy systems such as solar, wind, and air often require batteries to store the energy. Batteries are devices that convert chemical energy into electrical energy. At present, batteries have become a part of everyday life, for today's modern life batteries have become a necessity inherently in every human activity especially related to electronic devices.

Batteries are used in almost every aspect of modern life. Although the primary (non-rechargeable) battery has a great usability, the secondary battery (rechargeable) looks more popular. In the secondary battery, the reversible electrode reaction and cells can be recharged [1]. Among the types of secondary



batteries, lithium ion batteries have received special attention [2]. The main reason for using Li ion battery technology is lithium is the lightest and most electropositive metal, thus providing high energy density. Li-ion batteries show a stable life cycle (over 500 cycles); those can be made in various sizes and also require less maintenance when compared to other batteries [3].

Lithium-ion battery consist of four main parts: cathode, anode, electrolyte, and separator. Cathode has higher voltage than anode and plays a role as the place where oxidation process take place, while anode has low voltage and acts as a place where lithium ion inserted into this during charge process. So, cathode material will determine the capacity of a battery and we will focus on this material including how to synthesize and characterize for lithium ion battery.

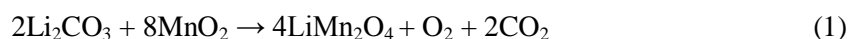
Some of the cathode materials in lithium ion batteries that have been synthesized are lithium manganese oxide (LiMn_2O_4), lithium cobalt oxide (LiCoO_2), and lithium ferro phosphate (LFP) [4] or mixed metal oxides which include cobalt (Co), nickel (Ni), aluminum (Al), and manganese oxides such as cobalt nickel aluminate (NCA) [5]. The cathode material used is lithium mangan oxide (LiMn_2O_4) which has theoretical specific capacity of 148 mAh/g with an electrical conductivity of about 10^{-6} S/cm, and higher voltage of about 3.9 Volt [6]. LiMn_2O_4 also has higher energy density than others because of high working voltage. LiMn_2O_4 has advantages over LiCoO_2 and Ni due to its abundant availability, cheap, environmentally friendly, and greater thermal stability [7]. Those are reasons why we will choose and synthesize LiMn_2O_4 for cathode material in lithium ion battery.

The simplest route to produce LiMn_2O_4 is via solid state reaction because it simply combines Li and Mn sources stoichiometrically and then sinters with appropriate temperature in atmospheric condition. There are two common raw materials that can be used as lithium sources: Li_2CO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$. Li_2CO_3 is conventional raw material which has high purity while $\text{LiOH}\cdot\text{H}_2\text{O}$ has low purity commonly used for paint. In this research cathode materials will be prepared with different source material of lithium such as $\text{LiOH}\cdot\text{H}_2\text{O}$ and Li_2CO_3 while MnO_2 is used as Mn sources. The goals of this research are to synthesize and characterize LiMn_2O_4 from different raw materials as well as to study the electrochemical performance of this material. This study is very important to substitute costly material like Li_2CO_3 with lower one like $\text{LiOH}\cdot\text{H}_2\text{O}$.

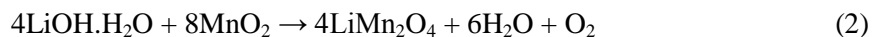
2. Experimental method

The synthesis process was done with two different sources of lithium. The first synthesis of LiMn_2O_4 used Li_2CO_3 and MnO_2 (sample A) while the second synthesis used $\text{LiOH}\cdot\text{H}_2\text{O}$ and MnO_2 (sample B). Synthesis on this research followed solid state reaction method, by mixing each of these materials based on the calculation of stoichiometry. The reaction can be explained by following formulas:

Sample A



Sample B



Raw materials were mixed and homogenized using mortar and pestle. Subsequently, the mixtures were sintered at 800 °C with high temperature furnace for 4 hours in air atmosphere. LiMn_2O_4 products were grinded and sieved to produce finer particle, which were then characterized by X-Ray diffraction (RIGAKU Japan) using Cu-K α as radiation source to know the phase and crystal structure. The angle used in diffraction measurement is 10 - 70°, with a scanning speed of 50 min⁻¹. Characterization using FTIR with iTR method was performed at wavenumber range of 400 - 4000 cm⁻¹ to know the existence of functional groups contained in the sample and to confirm the existence of phases.

Cathode sheets were made by mixing active materials (sample A and B) with binder (PVdF) and additive material (AB/acetylene black) in ratio 85:10:5 wt.% and diluted in N,N-DMac solution until slurry was obtained. After the slurry is formed, it was coated on Al foil with 0.15 um in thickness and then dried using an oven at 80 °C for 60 minutes.

In order to know the electrochemical performance, electrode sheet must be assembled into half-cell battery using coin cell in the glove box. Electrode sheets were cut into a circular shape with 14 mm in diameter and the separator was also cut with 18 mm in diameter. LiPF_6 solution was used as an

electrolyte. Battery performance test includes Cyclic Voltammetry (CV) and Charge/ Discharge (CD) performed with WBCS 3000, Automatic Battery Cycler Ver. 3.2. For performance test, two tests were conducted: cyclic voltammetry (CV) and charge discharge. For the CV test, the potential range is 3 V to 4.6 V with 0.01 mV/s while for the charge discharge test was done with a constant current of 0.05 mA (0.1 C) with a potential range of 3.3 V- 4.6 V.

3. Results and discussion

Figure 1 shows XRD pattern of LiMn_2O_4 samples prepared by solid state process. The ICDD (No 01-070-3120) card data of LiMn_2O_4 is also shown in the figure as the standard. It can be seen that both pattern have similarity with LiMn_2O_4 phase. Both samples were identified to have LiMn_2O_4 crystals. Sample A has purer phase and higher crystallinity with higher and sharper peaks than sample B. Sample B shows some impurities such as Li_2O and MnO_2 are existing denoted by triangle and star shape in the figure 1 respectively. The existence of these impurities can be caused by inhomogeneous precursors because $\text{LiOH}\cdot\text{H}_2\text{O}$ has different particle size. $\text{LiOH}\cdot\text{H}_2\text{O}$ is technical grade material with coarse grains so milling process must be done to homogenize the precursors.

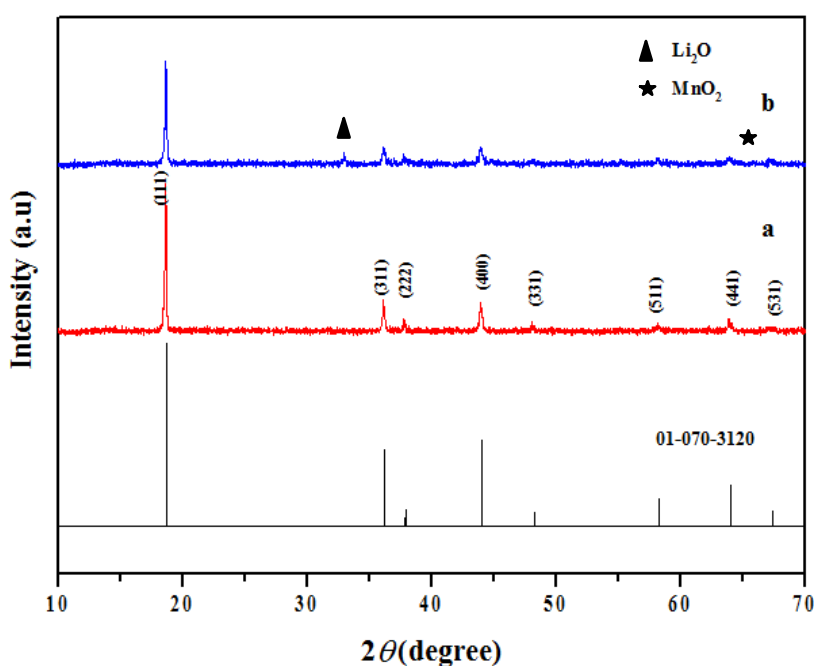


Figure 1. XRD pattern of LiMn_2O_4 synthesized with (a) Li_2CO_3 and (b) $\text{LiOH}\cdot\text{H}_2\text{O}$ as raw materials.

Infrared test has been done to study the metal-oxygen and metal-metal bond in the synthesized lithium manganate sample. Figure 2 shows IR spectrum of the synthesized LiMn_2O_4 sample. The vibrational frequencies at wavenumber 514.80 cm^{-1} and 526.73 cm^{-1} are associated with vibration of stretching group symmetry of Mn-O derived from element MnO_6 [8]. The Li-Mn vibration is located at the wavenumber of 310 cm^{-1} [9] so it does not appear at the spectrum. A peak below 1000 cm^{-1} indicates the frequency of metal-oxide vibration. The sample also shows an absorption band below 1000 cm^{-1} wavenumber [9]. In the infrared spectrum of LiMn_2O_4 also appears C=O group with vibration stretching at wave numbers 1630.42 cm^{-1} and 1630.47 cm^{-1} with low intensity which might come from CO_2 in air [10]. In the sample A peak at wave number of 1047.70 cm^{-1} is present, indicating the characteristic peak of CO-CO stretching C-O vibration [11]. This peak is not possessed by sample

B which was likely to have degraded to Li_2CO_3 . At wave number 3437.78 cm^{-1} and 3443.53 cm^{-1} there is an absorption band of the OH functional group of water molecules [12].

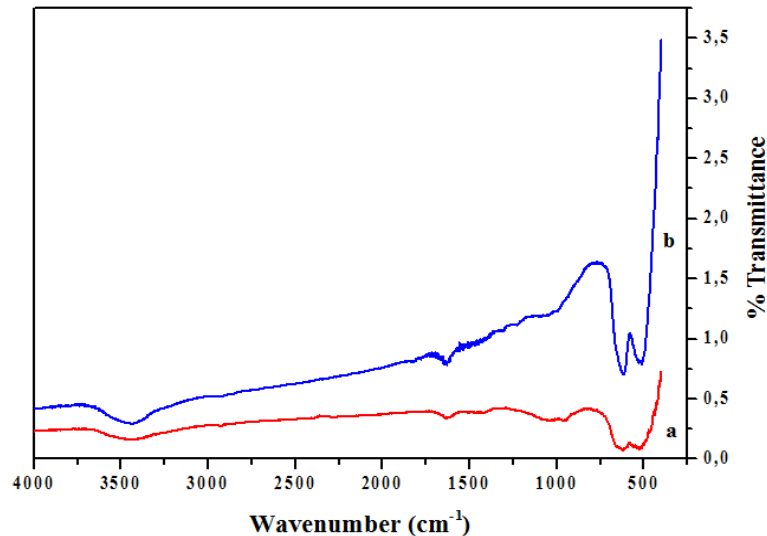


Figure 2. The FTIR spectra of LiMn_2O_4 which synthesized with (a) Li_2CO_3 and (b) $\text{LiOH}\cdot\text{H}_2\text{O}$.

Figure 3 shows double peaks of a pair reduction and oxidation peak for each sample. Reduction-oxidation peaks are related to insertion and de-insertion of lithium ion in LiMn_2O_4 . Every peak has two oxidation peak and two reduction peaks. The peaks in sample B is sharper and clearer than sample A, so sample B shows electrochemical process taking place faster than sample A. However, sample A has higher current peak than sample B which indicated that sample A has higher current response and gives higher ionic diffuse. Higher ionic diffuse will give higher specific capacity [13].

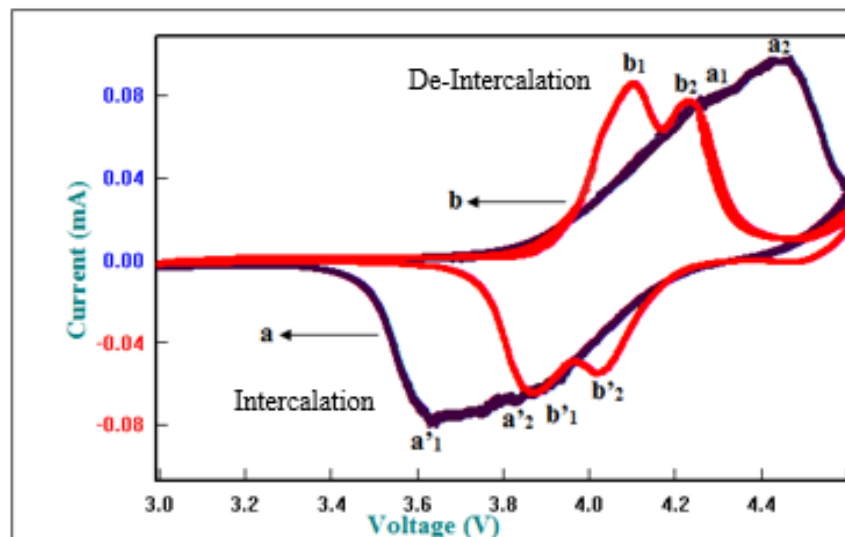


Figure 3. Cyclic Voltamogram of LiMn_2O_4 which synthesized with (a) Li_2CO_3 and (b) $\text{LiOH}\cdot\text{H}_2\text{O}$.

Figure 4 shows that specific capacity of LiMn_2O_4 synthesized with Li_2CO_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$. As stated in table 3, Sample A has higher specific capacity than sample B with 65 mAh/g and 51 mAh/g , respectively. Sample A having higher capacity can be caused by no existence of impurities phases in the sample, unlike with sample B which has other impurities such as Li_2O and MnO_2 . Both samples

show high coulombic efficiency indicating that both materials are good for battery but sample A can perform charge-discharge process with higher speed than sample B.

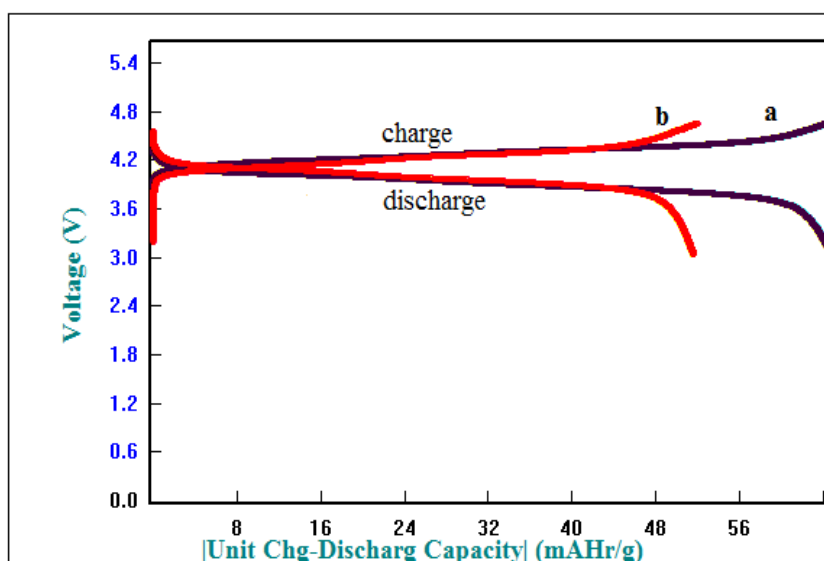


Figure 4. Charge-discharge of LiMn_2O_4 synthesized with (a) Li_2CO_3 and (b) $\text{LiOH}\cdot\text{H}_2\text{O}$.

Table 1. Specific Capacity and coulombic efficiency of LiMn_2O_4 .

| Sealant Compound | Voc (V) | Jsc (mA/cm^2) | FF | η (%) |
|------------------|---------|---------------------------------|------|------------|
| Hermetic A1 | 1.386 | 18.92 | 0.37 | 1.9 |
| Hermetic B1 | 1.427 | 26.38 | 0.38 | 2.9 |

4. Conclusion

LiMn_2O_4 had been successfully synthesized via solid state reaction with MnO_2 and $\text{Li}_2\text{CO}_3/\text{LiOH}\cdot\text{H}_2\text{O}$ as starting materials. Sample A has better purity and crystallinity than that of sample B. However, FTIR spectrum shows CO_2 bonding within sample A, which is expected from Li_2CO_3 as lithium sources. Cyclic voltammograms show that both samples give oxidation and reduction peak as an indication that the sample has reversibility characteristic. Charge-discharge testing shows that sample A has higher specific capacity (65 mAh/g) than that of sample B (54 mAh/g).

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