Effect of composition of LiMn$_2$O$_4$ cathode sheet on the electrochemical performance of lithium ion battery

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Abstract. The effect of composition of LiMn$_2$O$_4$ sheet on the electrochemical performance of lithium ion battery has been studied. LiMn$_2$O$_4$ powder is synthesized by solid state reaction method using raw material such as LiOH.H$_2$O and MnO$_2$. Raw materials are stoichiometrically mixed and milled using planetary ball milling for 4 hours to become precursor. The precursor is sintered using a muffle furnace at 800 °C for 4 hours in a free air atmosphere. The sintered material is pulverized and sieved 200 mesh to form a fine LiMn$_2$O$_4$ powder. The material is analyzed by XRD to determine the phase and crystal structure. Powder is prepared for sheet by mixing with PVDF binder and carbon black additive in various ratio such as 85:10:5, 88:8:4 and 90:7:3. After becoming slurry, the slurry was coated onto Al foil with 300 µm in thickness and dried at 70 °C for an hour. The sheet is assembled into a half cell battery with Li metal as the counter electrode and LiPF$_6$ as liquid electrolyte. The battery cell is measured by using the automatic battery cycler WBCS 3000 to determine the electrochemical performance. The measurement showed that samples with composition 90% active material has highest capacity with 3.6 mAh but gives bad cycle.

1. Introduction
The consuming of energy in recent decade is currently increasing such as laptops, cellphones and other electronic goods. That problem is what the researchers talk about, the longer the energy decreases, while the time for renewal requires energy takes a long time[1]. The use of electronic goods must have sufficient energy storage capacity in accordance with needs. For example lithium ion batteries are media that can connect electrically electrochemical cells that can store and distribute electrical energy. Lithium ion batteries today continue to develop in the future as time goes by. Researchers continue to conduct research to create storage capacity that has considerable storage space [2]. The research was carried out on the side of the constituent materials such as cathodes, anodes and electrolytes.

Lithium manganese oxide (LiMn$_2$O$_4$) is a cathode material that has a host in three dimensions, so that the direction of the crystals that intersect between the grains is not much affected[3]. Lithium manganese oxide (LiMn$_2$O$_4$) with spinel structure is a promising cathode material for secondary lithium ion batteries[4]. This compound has several advantages that can be used as a substitute for Ni or Co oxide. The advantages of LiMn$_2$O$_4$ are cheap, abundant and easy preparation, non-toxic, good
thermal stability, high discharge potential (4 V vs. Li), 120 mAh / g capacity, high energy density, charge-discharge reaction fast, high coulombic efficiency and low self-discharge.

2. Experiments

In this study using the main material, LiOH.H₂O and MnO₂ powder, the synthesis in this study carried out with solid state reaction method, by mixing each of these materials based on stoichiometric calculations and chemical reaction equations:

\[ \text{LiOH.H}_2\text{O} + \text{MnO}_2 \rightarrow \text{LiMn}_2\text{O}_4 \]

Firstly, the raw material was weighed stoichiometrically and then mixed until it distributed well. LiMn₂O₄ precursors were sintered at 850°C for 4 hours with temperature 2°C / min under the atmosphere condition. The results of sintering were grounded and sieved to 200mesh into the final product of LiMn₂O₄ powder. Some samples of Al doping LiMn₂O₄ powder were made into slurry by mixing the activating agent, PVDF and acetylene black with ratio 85:10:5, 88:8:4 and 90:7:3 dissolved in DMAC solution while heated with hotplate at 80°C and stirred in 300 rpm. When the slurry was formed, then coated on Al foil with a thickness about 150 µm through the doctor blade method and put in the oven at 110°C for 1 hour. Al doping LiMn₂O₄ cathode sheet was cut into a square with a size 10 mm and arranged into half a cell battery in a coin cell with Li metal as a counter electrode, LiPF₆ electrolyte and separator.

The final product then will be carried out for XRD analysis by Smart Lab 3KW RIGAKU with a 2θ angle ranging from 10° to 70° to find out the crystal structure and the phase formed. Cell coin-shaped battery cells were tested for Cyclic Voltametry (CV) and Charge-Discharge (CD) with automatic battery cycler WBCS 3000. The CV was carried out at a voltage range of 3.0 - 4.5 V with a scan rate 30 μV / s. While the CD in the voltage range is about 3.3 - 4.4 V with a rate 0.1 C

3. Result and Discussion

3.1. Result of X-Ray Diffraction Analysis

In this study, crystal structure and lithium manganese oxide phase using X-ray diffraction analysis with NGAKU angle at 10°-70° was done. Analysis of crystal structure and phase in LiMn₂O₄ powder was carried out with solid state reaction method. From the XRD analysis for LiMn₂O₄ sample, the qualitative analysis can be founded in Fig. 1 and Fig. 2.

![Graph of Comparison XRD Analysis with Several Variations of Raw Material For LiOH, H₂O and MnO₂](image-url)
From Fig. 2. It can be seen that the phase formed is from LiO\(_2\) and MnO\(_2\) powder samples. Both samples were identified as having a crystalline structure of LiMn\(_2\)O\(_4\) with the highest peak at angle of 2\(\theta\) = 18.626\(^0\) with d spacing = 4.7599 Å. For raw materials LiOH.H\(_2\)O found several diffraction peaks which were not the peak of LiMn\(_2\)O\(_4\), founded at 2\(\theta\) = 36,100 with d spacing = 2,4863 Å were the phase of LiO\(_2\) while 2\(\theta\) = 37,916 with d spacing = 2,36952 Å were the MnO\(_2\) phase. This were in accordance with ICDD data with PDF-4 + 2015 RDB number. The LiMn\(_2\)O\(_4\) cathode active material had a low crystallinity. This was indicated by the peak intensity obtained in each diffraction pattern which is not very sharp and irregular.

3.2. Result of Charge-Discharge Test
Tests are carried out by equipment of WBCS 3000. It aims to determine the capacity of the LiMn\(_2\)O\(_4\) battery cathode. Charge-discharge measurements are done with a constant current of 0.05 mA (0.1 C) with a potential range of 3.2 V-4.59 V (Fig. 3).

In the capacity charge-discharge test, it obtained from LiMn\(_2\)O\(_4\) cathode for sample A was greater than the sample B and C. For sample A, charge-discharge capacity were 3.71 mAh\(^g\)\(^{-1}\) and 3.58 mAh\(^g\)\(^{-1}\), for sample B, the charge-discharge capacity were 2.4 mAh\(^g\)\(^{-1}\) and 2.3 mAh\(^g\)\(^{-1}\) while sample c, the charge-discharge capacity were 1.9 mAh\(^g\)\(^{-1}\) and 1.8 mAh\(^g\)\(^{-1}\). The capacity obtained at the time of test was far from the theoretical capacity about 148 mAh/g from the active material obtained due to the
impurities. This three samples had a very good efficiency above 90% based on the manual calculation of Coulomb efficiency.

Table 1. Data Analysis of Charge / Discharge For LiMn₂O₄

| Sample | Specific Capacity Charge (mAh/g) | Specific Capacity Discharge (mAh/g) | Coulombic Efficiency (%) |
|--------|----------------------------------|------------------------------------|--------------------------|
| A      | 3.71                             | 3.58                               | 96.49                    |
| B      | 2.4                              | 2.3                                | 95.83                    |
| C      | 1.9                              | 1.8                                | 94.73                    |

The results of charge and discharge analysis can be known large of the capacity for performance on lithium ion batteries. During the charge and discharger test the lithium ion battery reaction process will occur where when charging at the cathode, the lithium ion intercalates into the cathode host whereas, during the discharging process there will be de-intercalation of lithium ions which means the lithium ion exits the cathode host. To find out the capacity charge on a lithium ion battery use the coulomb efficiency formula (Table 1). Comparative analysis of the three samples that have been calculated based on the coulomb sample efficiency formula has a high capacity because the charge process has increased compared to discharge which causes number of lithium ions produced, move to the anode resulting in an increase in electric current generated at discharge compared to sample b and c.

3.3. Result of Cyclic Voltametry (CV) Test

Based on the results of cyclic voltammetry test by equipment WBCS3000, Automatic Battery Cycler Ver. 3.2., data obtained was in the form of a potential curve (V) to the current (A). This test was done with a scan rate 0.01 mV / s which has a potential range 2.8 V to 4.6 V. The result of CV test for three samples can be observed from the cyclic voltammetry graph in Fig.4.

![Cyclic Voltammetry of LiMn₂O₄ for samples A, B and C](image)

Fig.4. show the peak value of reduction (down) and oxidation (rising) in each sample. Reduction and oxidation peaks are related to insertion and de-insertion of lithium ions in LiMn₂O₄. The sample A had two oxidation peaks, A1 4.25 V and A2 4.18V while the A1 reduction peak was at 3.9V and A2 at 3.85V. While in the sample B, the oxidation value is the same as A1 and A2. The reduction sample values of B1 and B2 are equal to 4.04. Furthermore, the oxidation value for sample C was 4.45 and the reduction value was 3.78. During the cathodic scan, the reduction peak appeared at 3.9 V and 4.079 V with a working voltage 4.0V [5].
4. Conclusion
LiMn$_2$O$_4$ powder can be analyzed by using solid state reaction method. From X-Ray Diffraction analysis for LiMn$_2$O$_4$ cathode sheets, it consists of LiO$_2$, MnO$_2$ and LiMn$_2$O$_4$ materials. The results of the Cyclic Voltametry (CV) test showed that the formation process of the reduction and oxidation peaks was the characterization of the LiMn$_2$O$_4$ spinnel. Cyclic Voltametry (CV) curves in sample A and B have the same oxidation value but the high peak point of sample A is higher than B. The charge and discharge curves in sample A have a better current capacity value than the current capacity values of B and C. This three samples had a very good efficiency which is above 90% based on the manual calculation of Coulomb efficiency.

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