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Electrochemical performance of LiMn$_2$O$_4$ with varying thickness of cathode sheet

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Abstract. Lithium-ion batteries are widely used as portable electrical energy storage devices because they have high energy densities and long life cycles. One of the cathode active materials used in the manufacture of Lithium-ion batteries is LiMn$_2$O$_4$ because of its easy and cheap manufacturing, has a long life cycle, high power applications, safe, and low toxicity of manganese basic materials. In this research, LiMn$_2$O$_4$ as cathode sheet has been made by doctor blade coating. This method was carried out by mixing LiMn$_2$O$_4$ with polyvinylidene fluoride (PVDF), Super P, and dimethylacetamide (DMAC) with weight ratio of 82.5 : 10 : 7.5, respectively, to obtain a well dispersed slurry. Slurry was superimposed on aluminum foil surface with various thickness of 200, 300 and 400 μm. Coin cell was assembled using electrodes, separator, lithium metal and electrolytes in the glove box. The cell battery was characterized by using cyclic voltammetry, charge discharge and electrochemical impedance spectroscopy in order to know the effect of active material thickness to cell battery performances. The results showed that active material with 400 μm in thickness had the best electrochemical performance due to a narrow and sharp reduction-oxidation peak pair, small polarization value of 0.0335 V as well as having charge and discharge capacities of 1.1249 mAh and 1.0914 mAh, respectively. Moreover, EIS result showed that 400 μm thickness of active material had highest conductivity value of $5.3922 \times 10^{-5}$ S cm$^{-1}$.

1. Introduction

Batteries are device that change chemical energy into electrical energy via electrochemical processes. There are two common types of batteries such as primary (non-rechargeable) battery and secondary battery (refill or rechargeable). The secondary battery allows a reversible electrochemical reaction in which electrical energy can convert back to chemical energy [1]. Among the types of secondary batteries, lithium ion batteries have received special attention because they have higher energy density, high capacity, slow self-discharge rate, low weight, high voltage, high specific energy and no memory effect [2, 3].

The lithium battery consists of four components: positive electrode (cathode), negative electrode (anode), electrolyte and separator. Separator is a porous membrane that serves to prevent the contact between the electrodes. The main function of the electrolyte is to facilitate the flow of Li ions to be regular and stable [4]. The electrolyte used in the battery is a mixture of lithium salts and organic
solvents. The anode receives the Li-ion during the charging cycle and transmits to the cathode during the lifecycle [5].

Lithium manganese oxide or LiMn$_2$O$_4$ is one of electrode materials that have good structural stability during the charge-discharge process. LiMn$_2$O$_4$ has a spinel structure with three-dimensional intercalation capability. This causes the cathode material to be inserted lithium ion in three directions. Lithium batteries are ion-based batteries with lithium ions as LiMn$_2$O$_4$ spinel drives show a lack of lifecycle resistance and irreversible loss of rapid capacity at elevated temperatures [6]. Lithium Manganese Oxide (LiMn$_2$O$_4$) is widely used as a cathode material for rechargeable lithium batteries. It is considered to have the potential for cathode material because of its abundant availability, environmentally friendly and affordable price, easy to manufacture, high specific theory capacity of 110 mAh/g, electrical conductivity of about $10^{-5}$ S/cm and large voltage range of 3.5-4.5 volt [7]. Another research reveals that LiMn$_2$O$_4$ synthesized with using Mn$_2$O$_4$ nano-crystal gives larger capacity than theoretical value 122.7 mAh g$^{-1}$ at 1 C rate [8].

The main challenge in the future deal with battery is how we get the highest capacity but it remain small in size [9]. There are so many factors affecting the capacity of the battery including the type of active material, the composition of the sheet and the thickness of active material involved in the electrochemical process [10]. Therefore, The increment thickness of active ingredients on the electrode per unit area is important in order to increase the capacity of the battery. However, addition of large amount a As a results, The optimization the amount of active material involved in the electrochemical reaction is required. Furthermore, the variations in the thickness of active materials in the manufacture of battery cells will be explained in this paper.

2. Experimental Methods

This research uses LiMn$_2$O$_4$ powder as an active material and it was synthesized from previous result containing more than 90 % desired phase. Slurry was prepared by mixing an active material, binder, and conductive carbon in ratio 82 : 10 : 7 to produce a cathode sheet. Polyvinylidene fluoride (PVDF) as a binder was solved in hot dimethylacetamide (DMAC) until homogeny, afterward acetylene black as a conductive agent was added dropwise during mixing followed by adding LiMn2O4 powder as an active materials to yield uniform slurry. The slurry was coated into aluminum foil with varying coating thickness of 200, 300, and 400 µm. The samples were represented by LMO 2, LMO 3 and LMO 4.

The sheet sample was cut into a circle with diameter of 16 mm and it was arranged with separator, electrolyte, metal Li and dropped by LiPF$_6$ in Ar filled glove box to develop a half cell. LiPF$_6$ acts as electrolyte and metallic Li as counter electrode. The electrochemical impedance spectroscopy (EIS) test is performed at a frequency of 0.1–20 kHz. The cyclic voltammetry (CV) test was performed at a voltage range of 2.7–4.5 V with a scan rate of 160 mV/s while the charge-discharge (CD) was performed at a voltage of 3.0–4.6 V with a speed of 0.1 C.

3. Results and Discussion

The chart of cyclic voltammetry (CV) indicates oxidation and reduction reactions. The presence of some oxidation—reduction buttons indicating a reversible reaction of a rechargeable sample that can be used to make a secondary battery. These oxidation and reduction pairs occur in the present manganese having oxidation numbers of +3 and +4 [12]. Each oxidation—reduction reaction has two oxidation peaks and two reduction peaks. The oxidation reaction is indicated at the upward-facing peak while the reduction reaction at the top facing downward.

Figure 1 shows that all LMO samples had good electrochemical performance which was indicated by the presence of two oxidation peaks and two reduction peaks formed. However, the LMO 4 sample shows a narrower and sharper oxidation—reduction counterpart than the LMO 2 and LMO 3 samples. Therefore, the LMO 4 samples revealed rapid electrochemical reactions and caused the intercalation/de-intercalation process of lithium ions to take place at a faster rate. Peak on the LMO 4 sample showed a higher peak thus having a larger capacity than other samples. This is due to the amount of active material used is more. The results indicated that the more active material, the greater
of the current response because more mass of active materials involved in the oxidation—reduction process.

![Figure 1: Cyclic voltamogram of LiMn$_2$O$_4$ with different thickness](image)

According to table 1, the results showed that the LMO 4 sample has the greatest polarization voltage and the LMO 2 sample has the lowest polarization voltage. However, the large polarization voltage has detrimental effect because decrease the battery performance. This is because the thicker the layer of the active material, the greater the polarization voltage. There is a correlation between longer diffusion and migration paths for lithium ions with the ohmic and mass transport because all material as site for electron transport has inner resistivity. The thicker of electrode has more resistivity. The longer cable the more energy we use to move electron in the cable, thus ohmic polarization will be greater.

Figure 2 shows charge—discharge patterns from LiMn$_2$O$_4$ with different thickness and all samples were charged-discharged from voltage 3 V to 4.6 V. Each samples show two plateaus with voltage 3.9 V and 4.2 V indicating the working voltage of LiMn$_2$O$_4$. The charge—discharge pattern of LiMn$_2$O$_4$ presented stair-like curve indicating transition of Mn$^{3+}$/Mn$^{4+}$ [13]. The results also showed that the thicker of electrode, the higher of capacity because more active material contained in the sheet. Sample LMO 2 and LMO 3 exhibit a capacity of about 0.5 mAh and it effect stable curves until 6 cycles. However, sample LMO 4 has higher capacity of about 1 mAh, however, it generate unstable curve in cycle 6.

Electrodes of excellent EIS test results on the graph will form a semi-circle pattern (semi-circle) and a straight line. The semi-circle on the EIS relates to the magnitude of the electron resistance ($R_e$) and the charge transfer ($R_{ct}$) resistance. According to figure 3, it showed that the electrical conductivity of the samples are sufficient because all samples showed a semicircle and slightly diffuses lithium ions. The LMO 4 sample has the best electrical conductivity because it forms the smallest semicircle. It revealed that the high amount of active material caused improving the electrical conductivity.

| No | Sample | $V_{ak1}$ (V) | $V_{ak2}$ (V) | $V_{re1}$ (V) | $V_{re2}$ (V) | $V_{pol1}$ (V) | $V_{pol2}$ (V) | $I_{p1}$ (mA) | $I_{p2}$ (mA) | $P_1$ (vmA) | $P_2$ (vmA) |
|----|--------|--------------|--------------|--------------|--------------|--------------|--------------|------------|------------|-----------|-----------|
| 1  | LMO 2  | 4.09         | 4.2          | 3.94         | 4.09         | 0.15         | 0.11         | 0.1756     | 0.1853     | 0.7182    | 0.77826   |
| 2  | LMO 3  | 4.09         | 4.21         | 3.94         | 4.08         | 0.15         | 0.13         | 0.1656     | 0.1838     | 0.6773    | 0.7738    |
| 3  | LMO 4  | 4.11         | 4.21         | -            | 4.08         | 0.18         | 0.13         | 0.3674     | 0.3917     | 1.5100    | 1.6491    |
Figure 2. Charge-discharge chart of LiMn$_2$O$_4$ with different thickness (a) LMO 2, (b) LMO 3, and (c) LMO 4.

Figure 3. Electrochemical impedance spectra (EIS) of LiMn$_2$O$_4$ with different thickness.

Straight line indicates lithium ion diffusion or lithium intercalation and de-intercalation process. The presence of a straight line indicates the lithium ions can move easily from cathode through electrolyte and couple with electrons on anode. A more upright straight line signifies a faster diffusion process. The conductivity value can be known by the following equation:

$$\sigma = \frac{t}{R_{ct} \times A}$$

$R_{ct}$ is a charge-transfer resistance, $t$ is the sample thickness and $A$ is the surface area of the electrode.

Table 2. Electrochemical parameters calculated from EIS patterns
According to table 2, it showed that the lowest conductivity value is identified in LMO 3 sample with value of $1.1211 \times 10^{-5}$ Scm$^{-1}$ and the highest conductivity value is identified in LMO 4 sample with value of $5.3922 \times 10^{-5}$ Scm$^{-1}$. The increment of thickness in active material will enhance conductivity because of more carbon conductive contained in LMO 4 sheet.

4. Conclusions
LMO cathode sheets have been succesfully developed by mixing LiMn$_2$O$_4$, PVDF and Super P active material with 82.5 %: 10 %: 7.5 % weight ratio and prepared with various thickness of 200 µm, 300 µm, and 400 µm. The LMO sample with a thickness of 400 µm had the best electrochemical performance.According CV (Cyclic Voltammetry) test, it revealed that the LMO 4 sample had a high, narrowand sharp peak oxidation reaction, therefore, LMO 4 had the best electrochemical performance. According to CD test (Charge-Discharge), it revealed that the LMO 4 sample had the smallest polarization voltage, hence LMO 4 had better battery performance than LMO 2 and LMO 3. According EIS (electrochemical impedance spectroscopy) test, it showed that the LMO 4 sample had the best conductivity eventhough having slow ion-lithium diffusion.

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