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Adsorption of lithium in the manganese hydroxide precipitation processes

F Firdiyono¹, E Sulistiyono¹, L H Lalasari¹, M R Arwanda², and S Wahyuningsih²

¹Research Center of Metallurgy and Materials, Indonesian Institute of Sciences, Kawasan PUSPIPTEK Gedung 470, Tangerang Selatan, 15314, Indonesia
²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University, Surakarta

E-mail: f.firdiyono@yahoo.com

Abstract. Lithium Manganese is an important ingredient in the process of making lithium battery cathode materials. The purpose of this study was to observe the presence of lithium ions in the manganese hydroxide deposition process in mixing MnSO₄, LiCl, and NH₄OH. The expected result is that the adsorbed lithium ion reacts with manganese hydroxide and settles when sintered at high temperatures. In this experiment, the addition of MnSO₄ varied by 5, 10, 15, 20, 25 grams in 200 ml of LiCl solution with a concentration of 10 g / l and ammonia 25% by volume was added. The resulting solids were calcined at 800 °C for 24 hours. The results showed that the best adsorption of lithium ions on the addition of manganese sulfate was 15 g and 25 g. Characterization results obtained by solids have a 3.3% LiMn₂O₄ phase and 96.7% Li₂Mn₂O₄ at the addition of 15 g manganese sulfate. On the addition of 25 g of manganese sulfate, 36.6% of LiMn₂O₄ and 63.4% of Li₂Mn₂O₄ were obtained. The success of this study will make it easier for us to synthesize the manufacture of lithium battery cathode materials such as lithium manganese phosphate.

1. Introduction

Lithium is a natural product and one of the most needed materials in the present. This happened because of the rapid development of electronic equipment such as mobile phones, tablets, and portable computers, and electric cars in recent years. Industry analysts and lithium producers estimate that 28,000 tons of lithium are used throughout the year [1].

Brines are one of the most commonly used sources of lithium natural. Besides that, lithium can also be obtained by spodumene mineral, sea water, and geothermal fluid [2][3]. Among secondary battery types, lithium ion batteries have received special attention because they have a higher energy density, high capacity, slow self-discharge rate, low weight, high cell voltage, high specific energy and no effect memory [4]. The main reason for using Li-ion technology on these batteries is that lithium is the lightest metal and the most electropositive metal, thus providing a high energy density. Li-ion batteries show a stable life cycle (more than 500 cycles), can be made in various sizes and also require little maintenance [5].

Manganese is a reactive element that easily combines ions in water and air. Manganese was chosen because it is non-toxic, cheap and safe and has the ability to adsorb lithium ions which are realized in the form of Lithium Manganese Oxide (LMO) [6] or lithium manganese. It has the molecular formula of LiMn₂O₄ which is displayed in the spinel phase used in the cathode battery [7].
Lithium manganese can be used as cathode material in batteries that can be coupled with other materials such as lithium cobalt oxide (LiCoO₂), lithium nickel oxide (LiNiO₂) and lithium ferro phosphate (LFP). The advantage of LiMn₂O₄ material is a higher life cycle (500 cycles), thus facilitating the nature of rechargeable batteries. In addition, LiMn₂O₄ also has good structural stability during the charge-discharge process and is quite stable during intercalation. LiMn₂O₄ is a cathode material that is easily synthesized. It has good structural stability when compared to other types of cathode material [8].

In this research, we would investigate the lithium adsorption in a mixture of MnSO₄, LiCl, NH₄OH which was proven by identification using ICP-OES and XRD analysis. This analysis was used to ensure lithium adsorption during manganese hydroxide deposition.

2. Material and Methods

The research was conducted using materials such as manganese (II) sulfate, lithium chloride, and ammonia 25%. All materials have the type of pro analysis (PA) that were purchased from Merck Company. The research was conducted in four stages, namely preparation of MnSO₄ samples without lithium chloride, preparation of MnSO₄ samples with lithium chloride, calcination and characterization.

2.1. Preparation of MnSO₄ Samples without Lithium

The initial stage of the study was to weigh MnSO₄ in mass variations, namely 5, 10, 15, 20, and 25 grams. Each sample was dissolved with 200 ml of distilled water and added 25% by volume of ammonia according to its stoichiometric calculation. Then the sample is stirred for 1 hour and filtered. The residue obtained is then dried in an oven for 14 hours at a temperature of 100 °C. Furthermore, the drying residue in the form of Mn(OH)₂ without lithium was weighed.

2.2. Preparation of MnSO₄ Samples with Lithium

The experimental steps are the same as above but in this second experiment, each solution was added with LiCl with a concentration of 10 g/L. After stirring, filtering, and drying, the residues obtained were weighed as Mn(OH)₂ with lithium.

2.3. Calcination

Calcination was carried out on Mn(OH)₂ residues for 24 hours with a temperature of 800 °C [9].

2.4. Characterization

The sample analysis was carried out by using ICP – OES (Inductively Coupled Plasma - optical emission spectrophotometers) on the filtrate samples. The X-Ray Diffraction (XRD) analysis was carried out on residue samples.

3. Result and Discussion

3.1. Adsorption of Lithium Ions during the Manganese Hydroxide Precipitation Process

Preparation of LiMn₂O₄ samples could be carried out through the precipitation stage using inorganic precursors [9]. In this experiment, the mixture of lithium chloride and manganese hydroxide was carried out more intensely until precipitation of manganese oxide was obtained which acted as an adsorbent and was able to absorb lithium. The precipitated residues were then calcined to produce homogeneous LiMn₂O₄ crystals. The possible reactions were as follows:

Precipitation reaction:

\[ \text{MnSO}_4(s) + 2\text{NH}_4\text{OH}_{(aq)} \rightarrow \text{Mn(OH)}_2(s) + (\text{NH}_4)_2\text{SO}_4(aq) \]  (1)

Calcination reaction:

\[ \text{Mn(OH)}_2(s) \rightarrow \text{MnO}_2(s) + \text{H}_2\text{O(l)} \]  (2)
\[
\text{MnO}_2 (s) + \text{LiCl}_{(aq)} \rightarrow \text{Li}_x\text{Mn}_y\text{O}_z(s)
\] (3)

Samples of manganese oxide deposited with lithium had a different morphology than MnO$_2$ without lithium. The most prominent morphological difference was that the color of the MnO$_2$ sample with lithium looks darker than the sample without lithium. The results of the measurement of the weight of the MnO$_2$ sample without the addition of lithium and with the addition of lithium can be seen in Figure 1.

**Figure 1.** The change of precipitated residue mass by drying at a temperature of 100 °C in various condition: (a) The addition of LiCl; (b) Without the addition of LiCl.

Based on Figure 1 showed that the residual mass precipitated with LiCl (Fig. 1a) had a mass greater than the residual sample precipitated without the addition of LiCl (Fig. 1b). The difference between the two types of precipitated residues was ranging from 0.11 grams to 3.72 grams which indicated the presence of lithium adsorbed when the Mn(OH)$_2$ precipitation process formed MnO$_2$.

**Figure 2.** The change of precipitated residue mass by calcination at a temperature of 800 °C in various condition: (a) The addition of LiCl; (b) Without the addition of LiCl.

3.2. Characteristic of filtrates by ICP-OES analysis

Manganese sulfate and lithium chloride used are the main constituents in the synthesis of lithium manganese. By analyzing the amount of lithium contained in the filtrate compared to initial solution (LiCl solution with a concentration of 10 g/L), it can also be known that the lithium was adsorbed in the manganese hydroxide precipitation process. The amount of ability of each adsorbent in absorbing lithium can be seen in the chemical composition of the precipitated solids [2]. The following results of ICP analysis on 5 filtrates can be shown in Table 1.
Table 1. The chemical composition of initial solution and filtrates in variation MnSO$_4$ mass

| MnSO$_4$ Mass (gram) | Li content (ppm) |
|----------------------|------------------|
| Initial solution     | 12571            |
| 5                    | 9406             |
| 10                   | 8894             |
| 15                   | 8919             |
| 20                   | 8197             |
| 25                   | 7907             |

Table 1 shows the greater the MnSO$_4$ used, the smaller the lithium content remaining in filtrates. This means that the greater the MnSO4 used, the greater the lithium which will be adsorbed in the process of manganese hydroxide precipitation. Based on the data above, the amount of lithium adsorbed during manganese hydroxide precipitation can be seen in Figure 3.

3.3. Characteristic of precipitated residues

Characterization using XRD (X-Ray Diffraction) analysis was carried out on samples of residues calcined at a temperature of 800 °C. The results of the analysis were shown in Figure 4 and Figure 5.

The XRD analysis results in Figure 4 showed that lithium was successfully identified in the form of lithium manganese (IV) oxide (LiMn$_2$O$_4$) with a percentage reaching 3.3%. The lithium content identified in other forms was dominated by dilithium manganese oxide (Li$_2$Mn$_2$O$_4$) with a percentage of 96.7%. These results indicated that lithium manganese oxide was successfully formed in the Li$_2$Mn$_2$O$_4$ or LiMn$_2$O$_4$ phases. This result was also supported by the literature which stated that lithium can be adsorbed by manganese and will form a synthesis product of LiMn$_2$O$_4$ when calcined at temperatures of 800 °C [10]. The LiCl reagent which was a source of lithium was not fully effective in the formation of lithium manganese oxide when compared to using Li$_2$CO$_3$. The reaction of lithium manganese formation in this experiment was possible as follows:

LiCl$_{(aq)}$ + 2MnOOH$_{(s)}$ + $\frac{1}{2}$O$_2(g)$ $\rightarrow$ LiMn$_2$O$_4(s)$ + $\frac{1}{2}$H$_2$O$_{(l)}$ + HCl$_{(aq)}$.........................(4)

$\frac{3}{2}$LiCl$_{(aq)}$ + $\frac{1}{2}$LiMn$_2$O$_4(aq)$ + O$_2(g)$ $\rightarrow$ Li$_2$Mn$_2$O$_4(s)$ + $\frac{3}{2}$Cl$_{2(aq)}$..............................(5)
Figure 4. The XRD pattern of precipitated residues by using 15 grams of MnSO$_4$ with LiCl addition

Figure 5. The XRD pattern of precipitated residues by using 25 grams of MnSO$_4$ with LiCl addition

The phase of the formation of both types of lithium manganese products namely LiMn$_2$O$_4$ and Li$_2$Mn$_2$O$_4$ run systematically and gradually. The formation of the LiMn$_2$O$_4$ product occurred first at a temperature of 650 °C according to reaction (4) then proceed with the formation of the Li$_2$Mn$_2$O$_4$ product at a higher temperature of about 800 °C according to reaction (5) 9). Reactions (4) and (5) which are crystallization processes of LiMn$_2$O$_4$ and Li$_2$Mn$_2$O$_4$ which are controlled by diffusion of O$^2-$ ions in the samples.
The results of XRD analysis in Figure 5 showed that lithium in the dilithium manganese oxide phase (Li$_2$Mn$_2$O$_4$) is 63.4% and in the lithium manganese oxide (LiMnO$_4$) phase is 36.6%. The formation of LiMn$_2$O$_4$ and Li$_2$Mn$_2$O$_4$ products in a sample of 25 grams of MnSO$_4$ was also based on reactions (4) and (5) which were also affected by the presence of oxygen.

4. Conclusion
From the results of the experiment were obtained some conclusions, as follows: lithium can be adsorbed together with the manganese hydroxide precipitation process to form manganese oxide. The amount of lithium adsorbed was proportional to the reduction in lithium levels in MnSO$_4$, NH$_4$OH and LiCl solutions. The more mass of MnSO$_4$ used in the experiment indicates that more lithium was adsorbed in solution. Lithium adsorbed with MnO$_2$ formed lithium manganese oxide crystals with the dominant phase in the form of Li$_2$Mn$_2$O$_4$ and LiMnO$_4$ when dried at 100 °C and continued calcination at 800 °C.

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