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INFLUENCE COMPARISON OF PRECURSORS ON $LiFePO_4/C$ CATHODE STRUCTURE FOR LITHIUM ION BATTERIES

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ABSTRACT

Electricity is the most energy demanded in this era. Energy storage devices must be able to store long-term and portable. A lithium ion battery is a type of battery that has been occupied in a secondary battery market. Lithium iron phosphate / $LiFePO_4$ is a type of cathode material in ion lithium batteries that is very well known for its environmental friendliness and low prices. $LiFePO_4/C$ powder can be obtained from the solid state method. In this study the variables used were the types of precursors : iron sulfate ($FeSO_4$), iron oxalate (FeC_2O_4) and $FeSO_4$+charcoal. Synthesis of $LiFePO_4/C$ powder using Li:Fe:P at 1:1:1 %mol. Based on the XRD results, $LiFePO_4/C$ from $FeSO_4$+charcoal shows the $LiFePO_4/C$ peaks according to the JCPDS Card with slight impurities when compared to other precursors. XRD results of $LiFePO_4/C$ with precursors of $FeSO_4$ or FeC_2O_4 shows more impurities peaks. This $LiFePO_4/C$ cathode is paired with lithium metal anode, activated by a separator, $LiPF_6$ as electrolyte. Then this arrangement is assembled become a coin cell battery. Based on the electrochemical results, Initial discharge capacity of $LiFePO_4/C$ from the $FeSO_4$ precursor is 19.72 mAh/g, while $LiFePO_4/C$ with the FeC_2O_4 precursor can obtain initial discharge capacity of 17.99 mAh/g, and $LiFePO_4/C$ with $FeSO_4$+charcoal exhibit initial discharge capacity of 21.36 mAh/g. This means that the presence of charcoal helps glucose and nitrogen gas as reducing agents.

***Keywords**: Lithium Ion Battery; Lithium Iron Phosphate; Cathode; Solid state; Iron sulfate; Iron oxalate; Charcoal*

INTRODUCTION

In this era, electricity is the most increased energy need due to the demand for all economy sectors [1-2]. Electrical energy can be found everywhere but still a challenge due to it is not portable or can't be carried anywhere easily, while the amount of electricity need are always increasing. So, in this case we need an electrical energy storage device.

Battery is an such of device that is capable of storing electrical energy and can be applied to many electronic devices such as mobile phones, laptops, remote controls to electric cars. Batteries consist of 2 types: primary batteries or disposable batteries and secondary batteries or rechargeable batteries. Secondary batteries that have been circulating in the market are Lead acid, Nickel cadmium and Lithium ion. Lithium ion batteries have many advantages such as their environmental friendliness and relatively inexpensive so this really answers the needs of batteries for the future. In this decade, Lithium ion batteries have proven able to conquer consumers in the electric vehicle global market [3].

The Lithium ion battery arrangement consists of electrolyte, separator, anode and cathode. A battery with good performance is greatly influenced by the type of cathode. Cathodes that have been circulating in the market are $LiCoO_2$ [4], NCA [5][6] , $LiMn_2O_4$ [7] and $LiMPO_4$ [8]. Based on the cathode category, the highest environmental friendliness is $LiMPO_4$. $LiMPO_4$ is divided into several categories : $LiMnPO_4$, $LiCoPO_4$, $LiNiPO_4$ and $LiFePO_4$. $LiFePO_4$ battery is one of phosphate batteries that have trending topic due to their environmentally friendly [9] , The raw material is quite easy to obtained and $LiFePO_4$ does not produce impurities during the delithiation process [10].

$LiFePO_4$ cathode has advantages such as low cost, long cycle life (700-6500) [11], high thermal stability and does not contain explosive materials [9]. $LiFePO_4$ has a theoretical capacity of 170 mAh/g [12]. However, $LiFePO_4$ has shortcomings such as the low conductivity of 10^{-9}-10^{-10} S/cm and the low diffusion coefficient of 10^{-13}-10^{16}/s. The aims of addition the reducing agent to reduce / eliminate the possibility of oxidized iron. The reducing agent added are activated carbon [13], metal oxides [14] or the presence of dopants with supervalent metal ions [15]. The addition of carbon is intended to increase the value of battery conductivity due to carbon has a higher conductivity value of 1.25-2x10^3 S/cm [16].

$LiFePO_4$ has an olivine structure with FeO_6 octahedra, PO_4 tetrahedra and there is a 1-dimensional tunnel as a lithium ion diffusion channel.The electrode synthesis method has been widely developed in the world which are called solid state [17-18], carbothermal [19], mechanochemical [20], hydrothermal [21-13], sol-gel [22-23], solvothermal [24-25], electro-spinning [26-27], vapor desposition [28], microwave heating [29-30], freeze drying [31-32], spray pyrolysis [33-34] and coprecipitation [35-36]. The consideration of the method chosen is in terms of economic/low production cost and ease of processing. Solid state is a method that is able to answer these challenges due to it has been widely applied. In this study, $LiFePO_4$/C will be synthesized with variety of precursors namely iron sulfate ($FeSO_4$), iron oxalate (FeC_2O_4) and $FeSO_4$ + charcoal, so, we can find out the effect of different precursors.

METHODS

1. Material

$FeSO_4$, FeC_2O_4, Li_2CO_3, $NH_4H_2PO_4$ 99.99%, Glucose 99.99%, Acetylene black 99.99%, Poly vinil di fluoride 99.99%, N metyl pyrolidine 99.99%, Inert gas (Nitrogen), H_2O_2 50%, Aquadest, Aseton Lithium chip, Coin cell set, $LiPF_6$ (electrolite)

2. Methods

Solid state method [14-15] starts with mixed sources of iron, lithium carbonate and ammonium phosphate stoichiometrically. Then the mixture is grounded using a mortar until homogeneous. After that, the mixture was added glucose ($C_6H_{12}O_6$) as much as 30% by weight as a carbon source / reducing agent. Next, the precursors were put into the cruicible alumina and sintered into the furnace at 700°C for 10 hours under nitrogen (inert) gas flow. $LiFePO_4$/C powder was cooled to ambient temperature. Sample 1 ($FeSO_4$), sample 2

(FeC_2O_4) and sample 3 ($FeSO_4$ with the addition of charcoal to the top of the mixture/ not mixed with precursors).

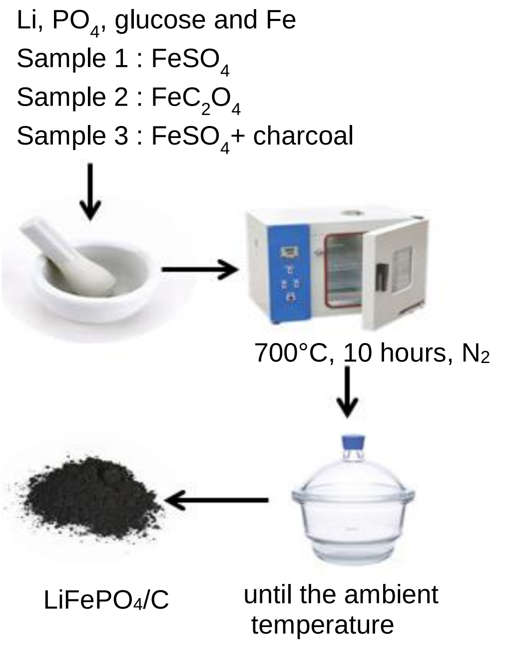

Figure 1. $LiFePO_4/C$ powder prepared through solid state method at 700°C for 10 hours under inert (nitrogen) gas flow.

3. Characterization

The obtained $LiFePO_4/C$ was characterized by electrochemical properties using coin cell batteries. First, the cathode paste was made by ratio of $LiFePO_4/C$: Acetylene Black: Polyvinylidene Fluoride (PVDF) at 80 : 10 : 10 % by weight. The mixture was dissolved into N-Methyl-2-pyrrolidone (NMP) until homogeneous. The paste was filtered using a 200 mesh filter. After that, the sheet was made using the Doctor blade method with a thickness of 200 nm (speed of 30 mm s^{-1}). The sheet was dried at 120 °C until the N-Methyl-2-pyrrolidone (NMP) content was evaporated and a dry $LiFePO_4/C$ layer was obtained. The sheet was pressed using a hot press machine.). The sheet was cut with a diameter of 19 mm and separator with a diameter of 20 mm. The coin cells were assemblied in a Glove box with full argon gas and containing H_2O maximal 1.0 ppm. The arrangement of coin-cell battery from bottom to top : positive cell - cathode sheet - separator - anode - spacer - spring and negative cell. The cell was filled with $LiFP_6$ electrolyte/each layer is added with electrolyte drop. The final step, the cell was pressed using crimping machine.

4. Test

The obtained $LiFePO_4/C$ powder were tested using XRD diffraction to determine its crystallinity. Electrochemical properties were tested to determine the initial discharge capacity of the batteries.

RESULTS AND DISCUSSION

1. Reaction of $LiFePO_4$

There are two types of reactions in this battery : the litiation and delitiation that occurs in the process of charging and discharging Lithium ion batteries. During the charging process, lithium comes out of the $LiFePO_4$, while during the discharging process the lithium ion enters the $FePO_4$. The reactions during the charging and discharging process are below:

Charging :

$$LiFePO_4 \rightarrow Li_{1-x}FePO_4 + xLi + xe^- \quad (1)$$

Discharging :

$$Li_{1-x}FePO_4 + xLi + xe^- \rightarrow LiFePO_4 \quad (2)$$

2. XRD diffraction pattern

XRD test is used to determine the crystallinity of the material obtained whether it is in accordance with JCPDS Card $LiFePO_4/C$ or not and produce other impurities or not. The XRD pattern test use CuKα 2θ radiation in the range of 10-80 °. Diffraction test results can be seen in Figure 2 below :

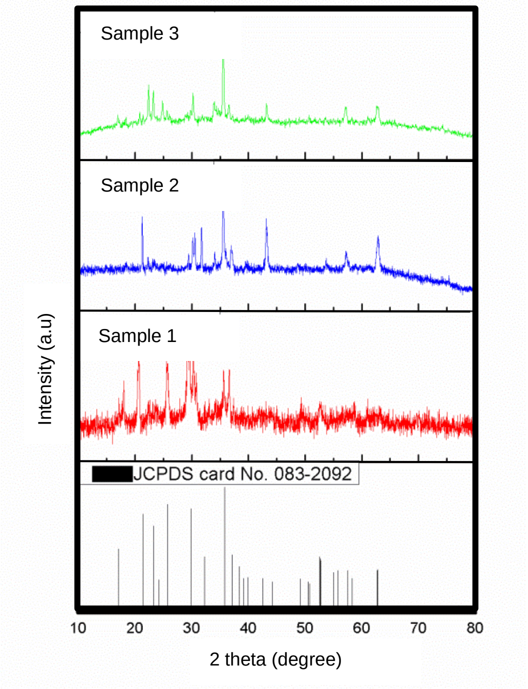

Figure 2. $LiFePO_4/C$ diffraction pattern with variable of precursor, sintered at 700°C for 10 hours under nitrogen (inert) gas flow

Figure 2 - sample 1 is the result of XRD $LiFePO_4/C$ particle test. This sample using iron sulfate/$FeSO_4$ as iron source and glucose as reducing agent. Iron sulfate, ammonium phosphate, lithium carbonate and glucose are grounded homogeneously. The mixture is put into the alumina cruicible and then heated into the furnace at 700°C for 10 hours under nitrogen (inert) gas flow. $FeSO_4$ was chosen due to the cheapest iron source compared to other iron sources such as iron nitrate ($FeNO_3$) [37] and iron chloride ($FeCl_3$) [38] which had been applied in the synthesis of $LiFePO_4$ previously. Glucose ($C_6H_{12}O_6$) not only as a conductivity enhancing agent but also as a reducing agent in previous research [39]. Based on the XRD results in sample 1, it can be seen that the main peaks of $LiFePO_4$ have been successfully formed in accordance with JCPDS Card 083-2092. However, there are still any impurity peaks which are at the peak of 18.5 ° 27.9 °, 31 ° 32 °, 33.3 ° and 34.5 °. Based on the appearance of product shows a black color on the inside but there are still red dots on the outside which means oxidation reaction still occurs due to the formation of Fe_2O_3 [40]. Oxidation reaction caused by the presence of oxygen content during the heating/sintering process in the furnace.

Figure 2 - sample 2 is the result of XRD $LiFePO_4/C$ particle test using FeC_2O_4 as a source of iron with the solid state method. FeC_2O_4, ammonium phosphate, lithium carbonate and glucose are grounded homogeneously. The mixture is put into the alumina cruicible and then heated into the furnace at 700°C for 10 hours under nitrogen (inert) gas flow. Based on the XRD results - sample 2, it can be seen that some of the main peaks of $LiFePO_4$ have been successfully formed. However the main peaks at 17.75 ° and 25.90 ° did not form. In addition, impurity peaks are still formed, namely at the peak of 29.10 ° 30.50 °, 31.5 ° and 34.15 °. FeC_2O_4 was chosen due to iron source contains two carbon atoms which are intended as additional reduction agents apart from the presence of glucose and nitrogen (inert) gas. However, the content of four oxygen atoms becomes dangerous due to the formation of $LiFePO_4/C$ must be in an inert condition which means the oxygen content must be limited. Based on the results of sintering, Based on the appearance of product shows a black color on the inside but there are still red dots on the outside which means oxidation reaction still occurs due to the formation of Fe_2O_3 compounds [40]. Oxidation reaction

caused by the presence of oxygen content during the heating process in the furnace.

Figure 2 - sample 3 is the result of XRD $LiFePO_4/C$ particle test using $FeSO_4$ as a source of iron with the solid state method and the addition of charcoal. Iron sulfate, ammonium phosphate, lithium carbonate and glucose are grounded homogeneously. The mixture is put into the alumina cruicible then mixture top is covered with charcoal. The precursor is heated into the furnace at 700°C for 10 hours under nitrogen (inert) gas flow. Based on the XRD results, it can be seen that the main peaks of $LiFePO_4$ have been successfully formed. In addition, impurity peaks are still formed, namely at the peak of 23.10 ° 24.95 °, 28.55 ° and 34.3 °.

The presence of charcoal is intended as an additional reducing agent apart from the presence of nitrogen (inert) gas and glucose. The oxidation number in Charcoal or C will increased when charcoal is burned so that it automatically becomes a reducing agent. Based on the appearance of product shows a grayish black color which means it matches the color of $LiFePO_4$ in the commercial.

3. Electrotrochemistry

Electrochemical testing was carried out using a battery analyzer (Neware, China). The voltage applied at 2.5 - 4.2 volts using lithium metal as an anode. Based on the data obtained, sample 1 / $LiFePO_4/C$ from $FeSO_4$ obtained an initial discharge capacity of 19.72 mAh/g, while sample 2 / $LiFePO_4/C$ from FeC_2O_4 obtained an initial discharge capacity of 17.99 mAh/g, and sample 3 / $LiFePO_4/C$ from $FeSO_4$ + charcoal as a reducing agent obtained an initial discharge capacity of 25.63 mAh/g. However, all these capacities are still far from the theoretical capacity of 170 mAh / g [12]. Initial discharge capacity can be seen on the figure below :

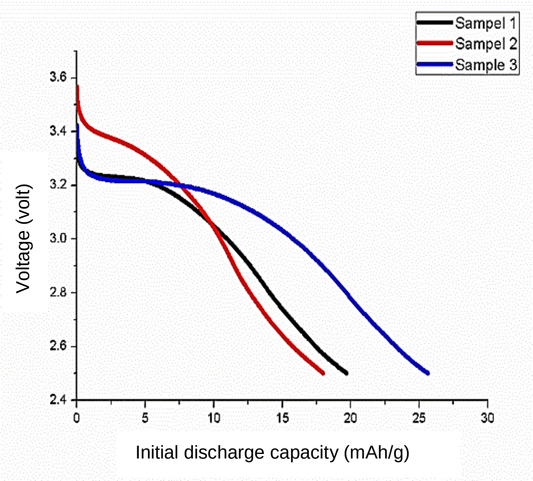

Figure 3. $LiFePO_4/C$ electrochemical test results with precursor variables.

CONCLUSION

Based on the data, we can conclude that $LiFePO_4/C$ can be synthesized by the solid state method. These $LiFePO_4/C$ particles use several types of precursor (iron source and carbon source), namely $FeSO_4$, FeC_2O_4 and $FeSO_4$+charcoal. Those three variables still exhibits impurity peaks, called Fe_2O_3. This is due to during heating process there is still any oxygen content which reacts with iron to produce Fe_2O_3. Sample 3 ($FeSO_4$ + charcoal) XRD pattern results is closest to JCPDS Card compared to other variables. The highest initial discharge capacity is shown in sample 3 which is 25.63 mAh/g.

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