Effect of Natural Fe$_2$O$_3$ Doping on Performance of Lithium Phosphate Ceramic Glass as Secondary Battery Cathode

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ABSTRACT

Natural Fe$_2$O$_3$ doped lithium phosphate Ceramic-glass was made by glass route method at 900 °C with the composition of 5Li$_2$CO$_3$:15ZnO:x Fe$_2$O$_3$:(80 – x) P$_2$O$_5$ where x = 0; 0.5; 1.5 (in mol%). Thermal stability of sample was studied through determination of glass temperature $T_g$ and crystal temperature $T_c$. XRD pattern and LCR meter measurement were carried out to determine phase, structure and ionic conductivity of the ceramic-glass samples. LiFePO$_4$ was formed at 1.5% addition of Fe$_2$O$_3$. Ionic conductivity rises by the increasing Fe$_2$O$_3$ concentration. The highest electric conductivity is 8.42 x 10$^{-4}$ S/cm which was obtained at 1.5% addition of Fe$_2$O$_3$.

Keywords: battery cathode, ceramic-glass, conductivity, lithium phosphate

INTRODUCTION

The development of technology, especially in the field of portable electronics such as mobile phones, tablets, digital cameras, laptops, and others cannot be separated from the need for energy storage media. Batteries are one of the energy storage components and are an important part of various electronic devices. Research has been continuously developed to produce a more economical, environmentally friendly, stable and high capacity energy storage device. One of the best energy storage devices is the lithium-ion battery (Waluyo & Noerochiem, 2014).

The lithium battery has three main components namely cathode, anode, and electrolyte. The cathode material is one of the key points associated with battery performance, so intensive research is needed to focus on the cathode (Wungu, Kurniawan, Yuliarto, Kasai, & Iskandar, 2014). The first cathode material used in lithium batteries is LiCoO$_2$, then other cathode materials such as LiNiO$_2$, LiMn$_2$O$_4$, and LiFePO$_4$ appear. LiFePO$_4$ has recently been extensively studied as a cathode material for Li-ion batteries.

LiFePO$_4$ cathode material has an olivine-shaped structure with orthorhombic symmetry (Zhu, 2013). The olivine structure consists of FeO$_6$ in the form of octahedral and PO$_4$ in the form of tetrahedral. Lithium occupies an empty lattice close to FeO$_6$. FeO$_6$ and PO$_4$ stick reciprocally and form zig-zag skeleton. In both forms, oxygen sharing occurs. PO$_4$ performs edge-sharing with 1 FeO$_6$ and 2 LiO$_6$. This PO$_4$ structure causes the LiFePO$_4$ phase to remain stable during lithium ion release process (Nisa & Iskandar, 2013).

LiFePO$_4$ or lithium iron phosphate with olivine-like compound structure is one of the most widely used materials in Li-ion battery application research since it has some of the highlights including high theoretical capacity (170 mAh/g), stable, cheap and environmentally friendly. However, lacking performance levels of low electronic conductivity and ionic conductivity values about 10$^{-9}$ S/cm have limited the application (Striebel, Shim, Srinivasan, & Newman, 2005). High electric conductivity is an indicator that the material used meets the requirements as a battery material.

Several studies have been conducted to improve the electric conductivity of LiFePO$_4$, including carbon or metallic or metal oxide coating, ion doping, and particle size and morphology optimization (Zhang, Huo & Du, 2012). One of the new strategies is the manufacture of cathodes on secondary batteries in the form of glass ceramics by glass route method. According to Tatsumisago and Hayashi (2008), glass and glass-ceramics are
highly potential to be used as cathodes in lithium-ion batteries because of some of its advantages. On the other hand, natural ferrite proved able to increase stability factor (Widanarto, Sahar, Goshal, Arifin, Rohani & Effendi, 2013) and increase saturation magnetization and remanence magnetization (Widanarto, Jandra, Goshal, Effendi & Cahyanto, 2015). Furthermore, the natural ferrite was milled so that it is a nanomaterial. It is well known that nanometer-sized materials have special properties as well as in carbon nanotubes (Effendi, Yokoi and Kuroda, 2010). In this research, we will produce LiFePO₄ ceramic glass which is the target phase of lithium phosphate doped by natural Fe₂O₃ as a cathode on the secondary battery.

**EXPERIMENTAL METHODS**

**Tools and materials**

Tools required in this research are 120 mesh sieve, Spatula, HEM (High Energy Milling) of Fisika Laboratoria P2F LIPI, Porcelain cup, Glass crucible, Furnace, Barnstead thermolyne 1300, Analytical Balance, Boeco BBL-31, pellet mold with a diameter of 0.9 cm, Origin software v. 8.0., XRD (X-Ray Diffraction) of P2F LIPI Serpong, DSC (Differential Scanning Calorimetry) of PSTBM-BATAN Serpong, Set of cyclic voltammetry equipment of P2F LIPI Serpong, and LCR (inductance (L), capacitance (C) and resistance (R)) meter of PSTBM-BATAN Serpong. Whereas the required materials are Natural Fe₂O₃ (milled an hour then heated to become Fe₂O₃), P₂O₅ (SIGMA, 99.9%) as glass base material, ZnO (Aldrich, 99.9%) as glass modifier and Li₂CO₃ (MERCK, 99%).

**Experimental Procedure**

Fabrication of Fe₃O₄ doped lithium phosphate ceramic glass was carried out by glass route method. The materials used are Fe₂O₃, Li₂CO₃, ZnO, and P₂O₅. Natural Fe₂O₃ iron sand has been milled an hour and then heated at 800 °C to become Fe₂O₃, as well as Li₂CO₃ (99%, MERCK) is used as a lithium converter to yield Li₂O, whereas ZnO as a glass modifier (99.9% Aldrich) and P₂O₅ (99.9% SIGMA) as a glass base material. The composition of the material is 5 Li₂CO₃: 15 ZnO: x Fe₂O₃: (80-x) P₂O₅, where x represents a concentration of 0; 0.5; and 1.5 mol%.

All the ingredients are weighed with a target of 10 g in each composition, then mixed in a glass crucible and stirred at room temperature to produce a homogeneous blend. Further, this homogenous mixture was melted at 900 °C for 90 minutes in the first electrical furnace. After that, the melt material was poured into a pre-heated mold in the second electrical furnace at one-third of the melting temperature (300 °C) and held for 3 hours until the sample solidified.

Production of ceramic glass cathode for was carried out by pulverizing the glass cathode sample, then it was taken 1.5 gram to be molded using pellet mold of 0.9 cm diameter and pressed using the hydraulic press at 1-ton pressure for 3 minutes. The pellet was then heated to a temperature between the glass (Tg) and the crystalline temperature (Tc) of the glass cathode sample, i.e., around 320 °C for 30 minutes. Further, the yielded ceramic glass cathode will be characterized its crystal structure by using XRD instrument, tested ionic conductivity by using LCR meter and analyzed its thermal properties by using DSC device.

**RESULT AND DISCUSSION**

**XRD characterization**

XRD patterns analysis of Fe₃O₄ doped lithium phosphate sample on the Fe₂O₃ concentration of 0; 0.5; and 1.5 (mol %) shows a different crystal phase. S-1 XRD pattern exhibits two phases that match to the ICDD (International Centre for Diffraction Data) database, i.e. 20: 23.11°; 41.85° and 44.50° which was identified as Li₂O; P₂O₅ (lithium oxide phosphide) according to ICDD number of 01-080-4545, and 20: 25.68°; 32.72°; 39.59°; 33.89° which was identified as Li₃C₀₃ (Lithium carbonate) according to ICDD number of 04-010-5115.

Natural Fe₂O₃ doping on lithium phosphate ceramic glass (S-2 and S-3 samples) is expected to form LiFePO₄ phase. On S-2 (0.5 % Fe₂O₃ doping) XRD pattern, it is emerged two phases, i.e. LiFeP₂O₇ (Lithium iron phosphate) at 20: 23.05°; 25.60°; 33.84°; 44.48° (ICDD number of 04-011-1388) and Fe₂O₃ hematite at 20: 33.22° (ICDD number of 00-001-105). In this S-2 sample, the LiFePO₄ phase has not obtained yet; however, its derivative, i.e., LiFeP₂O₇ appeared. Further, S-3 (1.5 % Fe₂O₃ doping) XRD pattern shows LiFePO₄ phase with orthorhombic crystal structure at the diffraction angle 20 of 29.73° according to ICDD database number 01-080-
Even though it is not a single phase due to appearing Fe phase at 2θ: 44.44º (ICDD number of 0000-006-0696), it indicates that glass route procedure synthesis LiFePO₄ glass ceramic successfully. The appearance of Fe phase may be due to the less homogeneous mixing process and incomplete combustion.

Figure 1. X-ray diffraction pattern of 0 % (S-1), 0.5 % (S-2) and 1.5 % (S-3) Fe₂O₃ doped lithium phosphate yielded from glass route method.

Figure 2. The ionic conductivity measurement results of lithium phosphate ceramic glass cathode. The line is the guide for the eyes. Black, Red and Blue lines are represent data of S-1 (0% Fe₂O₃), S-2 (0.5% Fe₂O₃) and S-3 (1.5% Fe₂O₃) sample, respectively.
lass cathode samples was carried out by using an LCR meter at a frequency range of 1 Hz-100 KHz with a reference voltage of 1.5 V. The following graph (Figure 2) represents the ionic conductivity measurement result.

These results show that there is a change in ionic conductivity value, which indicates the ion movement in the ceramic glass cathode sample during the measurement process. Each lithium phosphate ceramic glass cathode sample with a different concentration of Fe$_2$O$_3$ doping have the different ionic conductivity value. The increasing of Fe$_2$O$_3$ doping tents to the increasing of ionic conductivity. Further, from Fig.2, the minimum and maximum ionic conductivity values of each sample could be extracted and plotted (Figure 3).

The highest ionic conductivity value was obtained on the S-3 sample (1.5% Fe$_2$O$_3$ doping) that is $8.42 \times 10^{-5}$ S/cm, while the lowest value was attained on the S-1 (without Fe$_2$O$_3$ doping) sample that is $1.55 \times 10^{-5}$ S/cm. Compared to some previous studies related to the manufacture of battery cathode, which is about $10^{-5}$ S/cm (Striebel, Shim, Srinivasan, & Newman, 2005), these ionic conductivity values are much better.

**Cyclic voltammetry examination**

The cyclic voltammetry technique can provide the reduction/oxidation potential value of the electroactive materials. Oxidation and reduction reactions are essential concepts of chemical reactions occurring in electrochemistry. The existence of electrons that move from one atom to another or electron discharge (oxidation) and electron capture (reduction) means there are electrons flowing (Khopkar, 1990). The flow of electrons is an indication of the occurrence of electric current. The handover of electrons results in the charge changing of binding atoms or the involved chemical species. The charge changing is called oxidation and reduction events or known as redox reactions.

Examination using cyclic voltammetry method yielded a current-to-voltage curve of a potential which is known as a voltammogram curve (West, 1984). The cyclic voltammetry investigation was carried out for two cycles in the electric potential range from 0 to 4.0 V. The cyclic voltammetry examination results are showed in the following figure (Figure 4).

The three voltammogram curves in Figure 4 show that all three samples did not undergo a good redox reaction. All three samples only experienced an oxidation reactions, and the reduction reaction did not emerged. The oxidation reaction was characterized by a downward-facing peak. Oxidation peaks proceed when Li ions are released by the cathode and received by the anode (lithium metal), while the reduction peak appears when Li ions from the anode (lithium metal) are released and received by the cathode.

![Figure 3](image-url)  
**Figure 3.** Minimum (black point) and maximum (red point) ionic conductivity of correlates to mol % of Fe$_2$O$_3$ doping. The dotted line is the guide for the eyes.

**Ionic Conductivity Examination**

Measurement of the ionic conductivity of ceramic glass cathode samples was carried out by using an LCR meter at a frequency range of 1 Hz-100 KHz with a reference voltage of 1.5 V. The cyclic voltammetry technique can provide the reduction/oxidation potential value of the electroactive materials. Oxidation and reduction reactions are essential concepts of chemical reactions occurring in electrochemistry. The existence of electrons that move from one atom to another or electron discharge (oxidation) and electron capture (reduction) means there are electrons flowing (Khopkar, 1990). The flow of electrons is an indication of the occurrence of electric current. The handover of electrons results in the charge changing of binding atoms or the involved chemical species. The charge changing is called oxidation and reduction events or known as redox reactions.

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Oxidation reaction of S-1 sample occurs at a voltage of 4.0 V, whereas S-2 sample shows 2 peaks with the highest peak is identified as an oxidation peak occurring at a voltage of 2.8 V and S-3 oxidation peak occurs at a voltage of 2.9 V. In another hand, another cyclic voltammetry examination which was carried out by using lithium metal as anode and LiFePO₄ as cathode, yielded that oxidation reaction occurs at a voltage of 3.45 V while the reduction reaction occurs at a voltage of 3.15 V (Subhan, Rohman, Lestariningsih, & Purawiardi, 2014).

The cyclic voltammetry examination was carried out by involving other materials and arranged as battery cells (anode, cathode, electrolyte, and separator). Based on the above three voltammogram curves, all samples do not undergo a reduction reaction. These results proved that release of lithium ion from the lithium metal anode was not captured by the cathode, which may be caused by instability of the battery cell during the reduction reaction. Many factors influence this instability to include the hygroscopic characteristic of the lithium phosphate ceramic glass cathode as their constituent material, i.e., P₂O₅ which was characterized by sample getting wet when crushed in the slurry making process. The other possible factor is inappropriate electrolyte selection. In this case, the used electrolyte is lithium hexafluorophosphate (LiPF₆) in liquid phase caused the lithium phosphate glass ceramic cathode, where the reduction process occurs, becomes increasingly wet and unstable.

**Charge-discharge examination**

Charge-discharge examination provides an information of material whether the material is active or passive, and an ability information of material to store energy. Charge-discharge examination results describe the electrode resistance in the process of charge and discharge. One cycle of charge-discharge step is equal to one charge process (an oxidation reaction, which releases lithium ion and electrons to the anode) and one discharge (the reduction reaction occurs, in which lithium ion and electrons enter the cathode). In this case, the charge-discharge examination was conducted with the voltage range of 2.20 – 3.65 V, and the results are shown in the following figure (Figure 5).
Figure 5. The charge-discharge curves of S-1 (0% Fe$_2$O$_3$) (a), S-2 (0.5% Fe$_2$O$_3$) (b) and S-3 (1.5% Fe$_2$O$_3$) (c).

The charge-discharge curves (Figure 5) describe that the ceramic glass cathodes base on lithium phosphate material doped by Fe$_2$O$_3$ at a concentration of 0; 0.5; 1.5 mol% are capable of performing a charge-discharge process such as the common battery cathode. It means that the current ceramic glass cathodes are already qualified to be applied as a secondary battery. From the charge-discharge investigation, it is known that the work voltage value of S-1, S-2 and S-3 are 3.128 V, 1.500 V, and 3.206 V, respectively. Further, the charge-discharge time of the samples can be pointed out. Charge and discharge durations of sample S-1 are 12 minutes and 17-23 minutes, respectively. Charge time of sample S-2 is 15-32 minutes without discharge. It could be caused by the damage of the test cell due to the testing process which was carried out repeatedly. The S-2 sample can only receive electric current without using it. Whereas the charge and discharge time of S-3 sample are 24-32 and 14-12 minutes, respectively. All three samples show the non-maximal charge and discharge time which is caused by the performance of the one-time charging and discharging processes are required almost the same time duration. Good batteries show faster charging times and longer discharging times. The charge-discharge data or the battery capacity values are displayed in the following table (Table 1).
Table 1. The battery capacity value of sample S-1 (0% Fe₂O₃), S-2 (0.5 % Fe₂O₃) and S-3 (1.5 % Fe₂O₃).

<table>
<thead>
<tr>
<th>Sampel</th>
<th>Vocp (V)</th>
<th>Current (µA)</th>
<th>Charge time (minutes)</th>
<th>Discharge time (minutes)</th>
<th>Capacity (µAhr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>3.128</td>
<td>100</td>
<td>12</td>
<td>17 – 13</td>
<td>38.5</td>
</tr>
<tr>
<td>S-2</td>
<td>1.500</td>
<td>50</td>
<td>15 – 32</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S-3</td>
<td>3.206</td>
<td>100</td>
<td>24 – 32</td>
<td>14 – 12</td>
<td>32.0</td>
</tr>
</tbody>
</table>

Based on the charge-discharge examination, the highest battery capacity value, i.e., 38.5 µAhr was found on S-1 sample with 0% Fe₂O₃ doping. Further, 1.5% Fe₂O₃ doping (S-3 sample) yielded the battery capacity value of 32 µAhr. More, the S-2 sample was damaged in the charge-discharge examination process so the battery capacity value of S-2 sample can not be specified. These battery capacity values are very small when compared to the theoretical value on the LiFePO₄ cathode which is about 170 mAHr. It can be concluded that the ceramic glass cathode of lithium phosphate with Fe₂O₃ doping succeeded in showing properties as a secondary battery because it is capable of producing charge and discharge processes, but this lithium phosphate glass ceramic cathode has not succeeded yet in showing a good capacity value.

CONCLUSION

Lithium phosphate ceramic glass cathode has been successfully produced by using glass route method with the percentage of material composition of 5 Li₃CO₃ : x Fe₂O₃ : 15 ZnO : (80-x) P₂O₅ where x = 0;0,5; 1,5 mol%. The orthorhombic crystal structure arose on the LiFePO₄ phase in the 1.5 mol% Fe₂O₃ doped sample. Fe₂O₃ doping increases the ionic conductivity of the lithium phosphate ceramic glass cathode. The minimum value of ionic conductivity is 1,55 x 10⁻⁴ S/cm of S-1 sample, that is cathode sample without Fe₂O₃. Whereas the maximum ionic conductivity value is 8,42 x 10⁻⁴ S/cm, which is achieved by S-3 sample, that is 1.5 mol% Fe₂O₃ doped sample.

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