

Effect of Natural Fe₂O₃ Doping on Performance of Lithium Phosphate Ceramic Glass as Secondary Battery Cathode

Mukhtar Effendi^{1,2*}, Dina Rahmawati³, Wahyu Tri Cahyanto¹, Wahyu Widanarto¹

¹Physics Department, Faculty of Mathematics and Natural Sciences, Jenderal Soedirman University, Purwokerto, Indonesia

²Research and Development Center of New and Renewable Energy, Jenderal Soedirman University, Purwokerto, Indonesia

³Physics Department, Faculty of Mathematics and Natural Sciences, Bandung Institute of Technology, Bandung, Indonesia

*email: mukhtar.effendi@unsoed.ac.id

Received December 01, 2016; Accepted August 09, 2017; Available online November 30, 2017

ABSTRACT

Natural Fe₂O₃ doped lithium phosphate Ceramic-glass was made by glass route method at 900 °C with the composition of 5Li₂CO₃:15ZnO:x Fe₂O₃:(80 - x) P₂O₅ 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. LiFePO₄ was formed at 1.5% addition of Fe₂O₃. Ionic conductivity rises by the increasing Fe₂O₃ concentration. The highest electric conductivity is 8,42 x 10⁻⁴ S/cm which was obtained at 1.5% addition of Fe₂O₃.

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, Yulianto, Kasai, & Iskandar, 2014). The first cathode material used in lithium batteries is LiCoO₂, then other cathode materials such as LiNiO₂, LiMn₂O₄, and LiFePO₄ appear. LiFePO₄ has recently been extensively studied as a cathode material for Li-ion batteries.

LiFePO₄ cathode material has an olivine-shaped structure with orthorhombic symmetry (Zhu, 2013). The olivine structure consists of FeO₆ in the form of octahedral and PO₄ in the form of tetrahedral. Lithium

occupies an empty lattice close to FeO₆. FeO₆ and PO₄ stick reciprocally and form zig-zag skeleton. In both forms, oxygen sharing occurs. PO₄ performs edge-sharing with 1 FeO₆ and 2 LiO₆. This PO₄ structure causes the LiFePO₄ phase to remain stable during lithium ion release process (Nisa & Iskandar, 2013).

LiFePO₄ 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 LiFePO₄, 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 LiFePO_4 ceramic glass which is the target phase of lithium phosphate doped by natural Fe_2O_3 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 voltimetry 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 Fe_3O_4 (milled an hour then heated to become Fe_2O_3), P_2O_5 (SIGMA, 99,9%) as glass base material, ZnO (Aldrich, 99,9%) as glass modifier and Li_2CO_3 (MERCK, 99%).

Experimental Procedure

Fabrication of Fe_2O_3 doped lithium phosphate ceramic glass was carried out by glass route method. The materials used are Fe_2O_3 , Li_2CO_3 , ZnO, and P_2O_5 . Natural Fe_3O_4 iron sand has been milled an hour and then heated at 800 °C to become Fe_2O_3 , as well as Li_2CO_3 (99%, MERCK) is used as a lithium converter to yield Li_2O , whereas ZnO as a glass modifier (99.9% Aldrich) and P_2O_5 (99.9% SIGMA) as a glass base material. The composition of the material is 5 Li_2CO_3 : 15 ZnO: x Fe_2O_3 : (80-x) P_2O_5 , 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 (T_g) and the crystalline temperature (T_c) 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 Fe_2O_3 doped lithium phosphate sample on the Fe_2O_3 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. 2 θ : 23.11°; 41.85° and 44.50° which was identified as $\text{LiO}_{0.75}\text{P}_{0.25}$ (lithium oxide phosphide) according to ICDD number of 01-080-4545, and 2 θ : 25.68°; 32.72°; 39.59°; 33.89° which was identified as Li_2CO_3 (Lithium carbonate) according to ICDD number of 04-010-5115.

Natural Fe_2O_3 doping on lithium phosphate ceramic glass (S-2 and S-3 samples) is expected to form LiFePO_4 phase. On S-2 (0.5 % Fe_2O_3 doping) XRD pattern, it is emerged two phases, i.e. LiFeP_3O_9 (Lithium iron phosphate) at 2 θ : 23.05°; 25.60°; 33.84°; 44.48° (ICDD number of 04-011-1388) and Fe_2O_3 hematite at 2 θ : 33.22° (ICDD number of 00-001-105). In this S-2 sample, the LiFePO_4 phase has not obtained yet; however, its derivative, i.e., LiFeP_3O_9 appeared. Further, S-3 (1.5 % Fe_2O_3 doping) XRD pattern shows LiFePO_4 phase with orthorhombic crystal structure at the diffraction angle 2 θ of 29.73° according to ICDD database number 01-080-

4082. Even though it is not a single phase due to appearing Fe phase at 2θ : 44.44° (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.

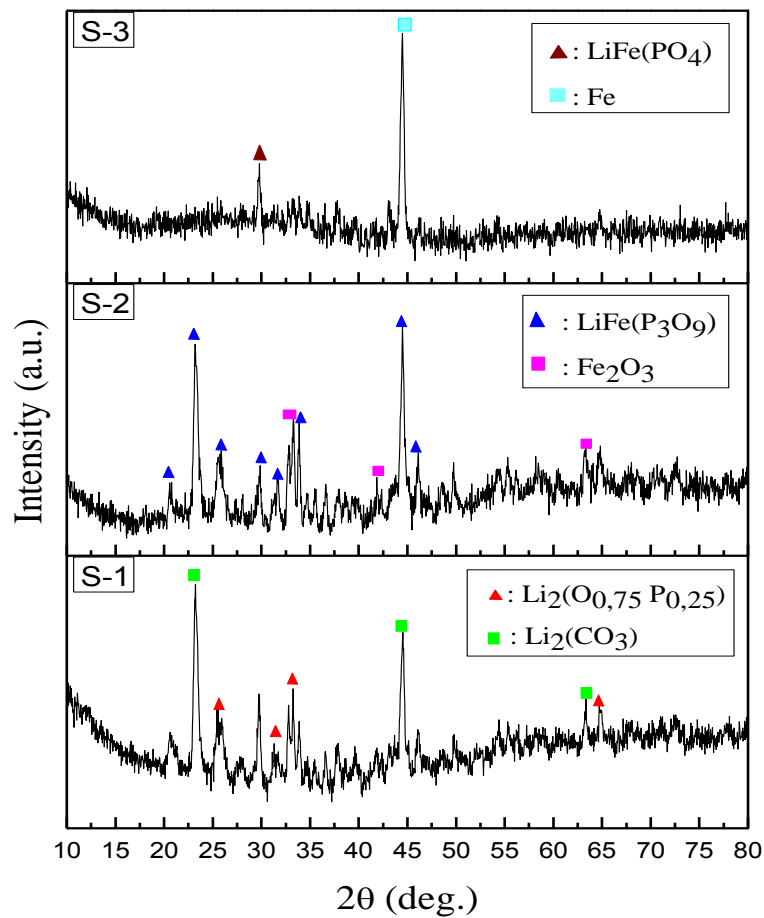


Figure 1. X-ray diffraction pattern of 0 % (S-1), 0.5 % (S-2) and 1.5 % (S-3) Fe₂O₃ doped lithium phosphate yielded from glass route method.

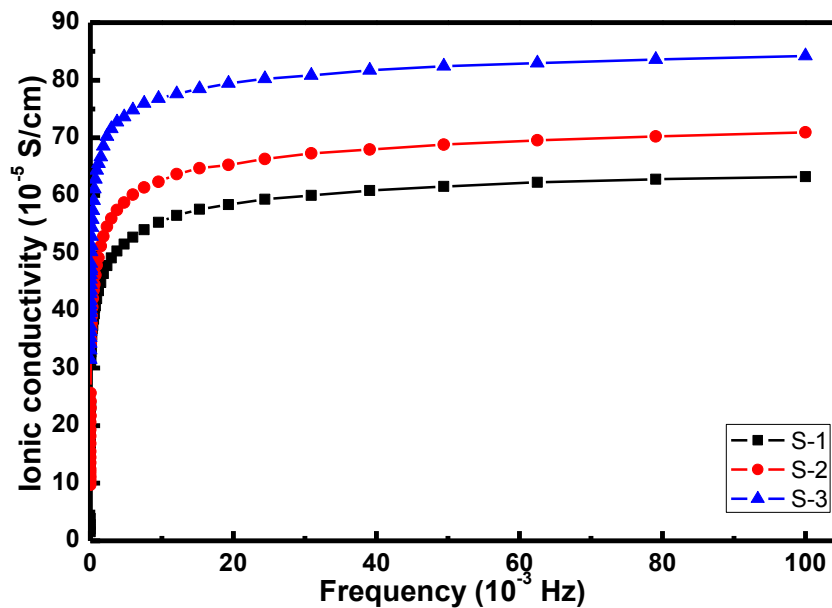


Figure 2. The ionic conductivity measurement results of lithium phosphate ceramic glass cathode. The line is the guide for the eyes. Black, Red and Blue lines are represent data of S-1 (0% Fe₂O₃), S-2 (0.5% Fe₂O₃) and S-3 (1.5% Fe₂O₃) sample, respectively.

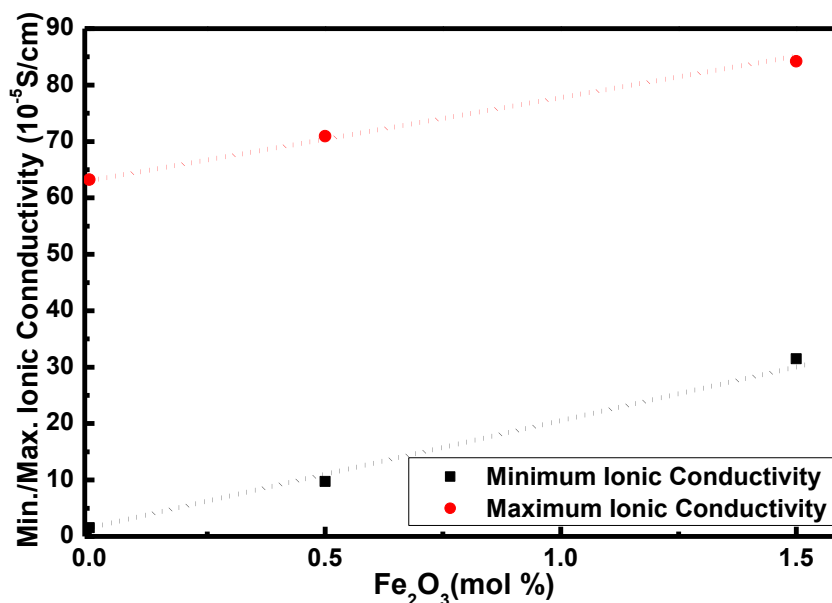


Figure 3. Minimum (black point) and maximum (red point) ionic conductivity of correlates to mol % of Fe₂O₃ doping. The dotted line is the guide for the eyes.

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 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 Fe₂O₃ doping have the different ionic conductivity value. The increasing of Fe₂O₃ 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% Fe₂O₃ doping) that is 8.42×10^{-4} S/cm, while the lowest value was attained on the S-1 (without Fe₂O₃ doping) sample that is 1.55×10^{-5} S/cm. Compared to some previous studies related to the manufacture of battery cathode, which is about 10^{-9} 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.

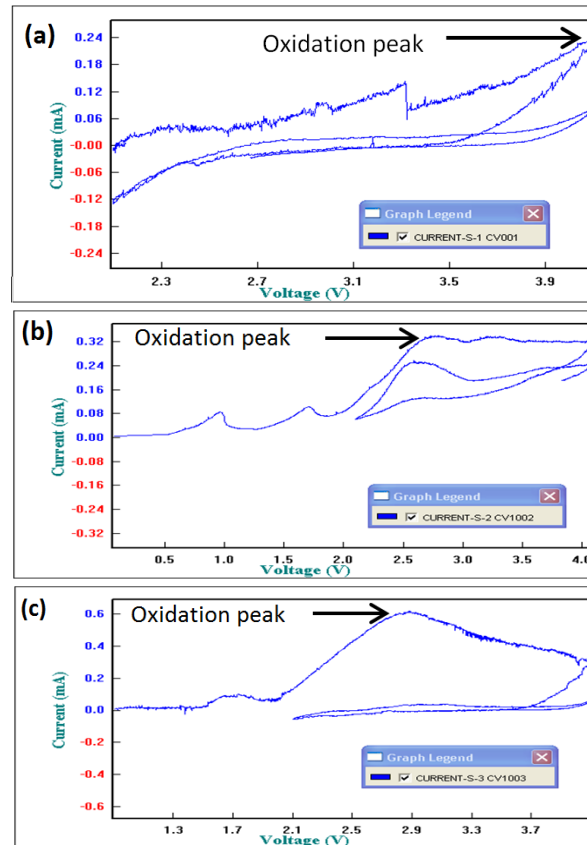


Figure 4. The voltammogram curves of S-1 (0% Fe₂O₃) (a), S-2 (0.5% Fe₂O₃) (b) and S-3 (1.5% Fe₂O₃) (c).

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**).

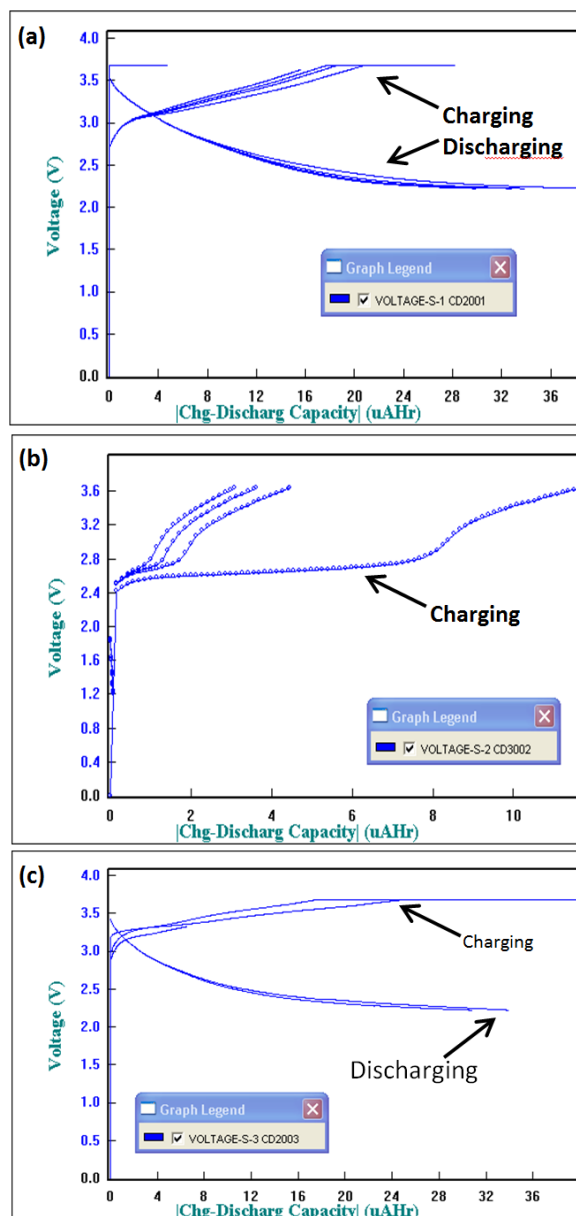


Figure 5. The charge-discharge curves of S-1 (0% Fe_2O_3) (a), S-2 (0.5% Fe_2O_3) (b) and S-3 (1.5% Fe_2O_3) (c).

The charge-discharge curves (**Figure 5**) describe that the ceramic glass cathodes base on lithium phosphate material doped by Fe_2O_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).

Sampel	Vocp (V)	Current (μA)	Charge time (minutes)	Discharge time (minutes)	Capacity (μAhr)
S-1	3.128	100	12	17 – 13	38.5
S-2	1.500	50	15 – 32	-	-
S-3	3.206	100	24 – 32	14 – 12	32.0

Base 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 Li₂CO₃ : 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 10⁻⁵ 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.

ACKNOWLEDGEMENTS

Acknowledgements and high appreciation were submitted to the Directorate General of Higher Education of the Indonesian Ministry of Research, Technology and Higher Education for the financial support through the research scheme of Penelitian Fundamental. Acknowledgments were also conveyed to Ahmad Subhan, Researcher of Research

Center for Physics, Indonesian Institute of Sciences. Thanks are also due to all colleagues who provided assistance in this research.

REFERENCES

- Effendi, M., Yokoi, H., & Kuroda, N., (2010). Optical study on electronic transport properties of single-walled carbon nanotubes at high temperature. *J Nanosci Nanotechnol*, 10 (6): 4074-7
- Khopkar S.M. (1990). Konsep Dasar Kimia Analitik, Terjemah A. Saptokaharjo. Jakarta, Indonesia: UI Press (Penerbit Universitas Indonesia)
- Nisa, A. S., & Iskandar, F. (2013). Studi Awal Sintesis Material Katoda Lithium Besi Fosfat (LiFePO₄) dengan Metode Solvotermal pada Konsentrasi Tinggi. *Prosiding Simposium Nasional Inovasi dan Pembelajaran Sains 2013 (SNIPS 2013)*. Bandung, Indonesia: ISBN 978-602-19655-4-2.
- Striebel, K., Shim, J., Srinivasan, V., & Newman, J. (2005). Comparison of LiFePO₄ from Different Sources. *J.Electrochem, Soc.*, 152, A664.
- Subhan, A., Rohman, F., Lestariningsih, T., & Purawardi, R. I. (2014). Pengujian Serbuk Komersial LiFePO₄ Sebagai Bahan Aktif Katoda Baterai Lithium Untuk Mobil Listrik Nasional. *Simposium Fisika Nasional*, (SFN XXVII) (S. 325-329). Denpasar-Bali: Universitas Udayana.
- Tatsumisago, M., & Hayashi, A. (2008). Preparation of lithium ion conducting glasses and glass-ceramics for all-solid-state batteries. *Journal of Non-Crystalline Solids*, 354(12-13), pp.1411–1417.
- Waluyo, H., & Noerochiem, L. (2014). Pengaruh Temperatur Hydrothermal terhadap Performa Elektrokimia LiFePO₄ sebagai Katoda Baterai Ion Lithium Type Aqueous Elektrolit.

- Jurnal Teknik Pomits*, Vol. 3, No. 2, ISSN: 2337-3539.
- West, A. R. (1984). *Solid State Chemistry and Its Application*. USA: Wiley.
- Widanarto, W., Sahar, M.R., Goshal, S.K., Arifin, R., Rohani, M.S., & Effendi, M., (2013), Thermal, structural and magnetic properties of zinc-tellurites glasses containing natural ferrite oxide, *Material Letters* 108, pp. 289-292.
- Widanarto, W., Jandra, M., Goshal, S.K., Effendi, M., & Cahyanto, W.T., (2015), BaCO₃ mediated modifications in structural and magnetic properties of natural nano ferrites, *Journal of Physics and Chemistry of Solids* 79, pp. 78-81.
- Wungu, T. D., Kurniawan, G., Yulianto, B., Kasai, H., & Iskandar, F. (2014). Studi Sifat Elektronik pada Bahan Katoda untuk Baterai. *Research and Development on Nanotechnology in Indonesia*, Vol.1, No.1, pp. 1-4 ISSN : 2356-3303.
- Zhang, Y., Huo, Q.-Y., & Du, P.-p. (2012). Advances in new cathode material LiFePO₄ for lithium-ion batteries, *Synthetic Metals* 162, 1315-1326.
- ZHU, C. (2013). *Size Effects on Lithium Storage and phase Transition in LiFePO₄/FePO₄ System*. Stuttgart : von der Fakultät Chemie der Universität Stuttgart zur Erlangung der Würde eines Doktors der Naturwissenschaften (Dr. rer. nat.). Max-Planck-Institut für Festkörperforschung.