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Research Article

The Effect of Temperature Variation on Conductivity Value of Cathode Lithium Ferro Phosphate Carbon Composite

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Abstract

The lithium ferrous phosphate carbon composite (LFP/C) cathode material has been successfully synthesized using solid-state reaction method by utilizing one of the natural sources of iron rocks in Tanah Laut, Kalimantan, as the base material of Fe. Solid-state reaction method was done by using high energy ball milling tool. The LFP cathode material was prepared using a base material (Li_2CO_3), Fe_3O_4, *and* $(NH_4)_2HPO_4$ *in a ratio of 3:6:2 and 5% wt. of Citric acid as a carbon source. There were some variations of calcination temperature used under inert conditions at 400 °C, 500 °C, 600 °C, and 700 °C to determine the effect on the phase structure and electrical conductivity produced by LFP/C cathode composites. Characterization of phase structure was done by using X-ray powder diffraction (XRD), while the conductivity value of the sample was tested using Electrochemical Impedance Spectroscopy (EIS). The analysis of the diffraction pattern shows the largest composition of olivine structure formed at 700 °C at 93.3% wt. with* Fe_2O_3 *impurities of 6.7% wt. The highest conductivity value of LFP/C is shown by sampling with 500 °C calcination temperature with a total conductivity value of* 5.676×10^{-3} $S.cm^{-1}$.

Keywords: *iron rock, Cathode, solid-state reaction, LFP/C*

Pengaruh Variasi Temperatur Terhadap Nilai Konduktivitas Katoda Lithium Ferro Phosphat Carbon Composite

Abstrak

Material katoda lithium ferro phospat carbon composite (LFP/C) telah berhasil disintesis menggunakan metode solid-state reaction dengan memanfaatkan salah satu sumber alam batuan besi Tanah Laut Kalimantan sebagai sumber bahan dasar Fe. Metode solid state reaction dilakukan dengan menggunakan alat high energy ball milling. Material katoda LFP dibuat dengan menggunakan bahan dasar (Li_2CO_3), Fe_3O_4, *dan* $(NH_4)_2HPO_4$ *dengan perbandingan 3:6:2 serta ditambahkan asam sitrat 5%wt sebagai sumber karbon. Pada penelitian ini digunakan variasi temperatur kalsinasi pada 400°C, 500°C, 600°C, dan 700°C dalam kondisi inert untuk mengetahui pengaruh pada struktur fasa yang terbentuk dan konduktivitas listrik, yang dihasilkan komposit katoda LFP/C. Karakterisasi struktur fasa yang terbentuk dilakukan dengan menggunakan X-ray powder diffraction (XRD), sedangkan untuk mengetahui nilai konduktivitas yang dihasilkan sampel dilakukan pengujian Electrochemical Impedance Spectroscopy*

(EIS). Analisis pola difraksi sampel menunjukkan pada temperatur 700°C komposisi terbesar LFP dengan struktur olivine terbentuk sebesar 93.3 %wt dengan impuritas berupa Fe_2O_3 *sebesar 6.7 %wt. Nilai konduktivitas LFP/C paling tinggi ditunjukkan oleh sampel dengan temperatur kalsinasi 500°C dengan nilai konduktivitas total sebesar 5.676* 10^{-3} $S.cm^{-1}$.

Kata Kunci: *Batu besi, katoda, solid-state reaction, LFP/C*

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I. INTRODUCTION

The vast development of technology and electronic devices, such as laptops and other portable communication devices, even electric-based vehicles, is currently being intensively developed in developing countries, including Indonesia. The trend has led to the need for more efficient, environmentally-friendly, high-capacity, economical, and energy-efficient energy storage devices, which are primarily derived from readily available raw materials. One type of efficient battery is a secondary battery. Among the types of secondary batteries on the market, the most prominent is the Li-ion battery type. The $LiFePO_4$ has been attractive because of good cycle stability, high theoretical charging capacity, environmentally friendly, and excellent thermal stability. However, the $LiFePO_4$ is generally have much lower charge/discharge capacity than the theoretical value, especially at high current rates. Moreover, it has two major disadvantages, namely slow diffusion of lithium ions and poor electronic conductivity. The numerous researches have been carried out to develop both synthesis processes and modification methods to improve the performance of $LiFePO_4$ electrode. The most commonly used strategies to improve the electrochemical performance of the battery are: (1) surface coating with conductive material to improve value of electronic conductivity [1, 2, 3]; (2) increase the Li-ion diffusion rate used doping with guest ions [4-6]; and (3) shorten the diffusion distance of Li-ion bulk by minimizing particle size [7-9].

A large number of studies have shown that LFP/C cathode materials having high porous/mesoporous and conductive structures can effectively strengthen the electrochemical performance of battery during high charge/discharge. Li and Kang [10] reported that LFP/C 3D network structures of multi-walled carbon nanotubes and such structures are believed to have better electronic conductivity and discharge capacity [11]. Some researchers employ polymers as the templates to create porous LFP/C with a pore size of 4-50 nm, indicating the capacity of discharge rates and excellent cycle stability [12]. However, the materials cannot withstand low and high temperatures. The release rate with a specific capacity decreased to 60 mAh g-1 at 14.7 ^{0}C. Furthermore, a new porous LFP/C microsphere has been developed by Sun and Rajasekhara [13] using a new hot solvent and the composite, and it has high tap density and exhibits excellent levels of ability, linking open 3D porous microstructure. In addition, the increasing energy density of LIBs has been a major focus of recent researches. A lot of scientists are developing and improving cathode materials for example with higher nickel contents and anode materials with silicon or tin composites for high voltage and high energy. Lithium-ion batteries structured nanotechnology porous electrode materials have been the key to high-performance rechargeable lithium batteries due to their sustained advantages in fast charge/discharge rate [14]. Concurrently, reducing LIB production cost without sacrificing cell performance is another focus especially for further implementation, such as electrical vehicles [15].

LFP/C is synthesized by many methods such as solid-state method, sol-gel, co-precipitation, microwave heating, and hydrothermal method [16-19]. In this study, the solid-state reaction method was employed by using high energy ball milling. The solid-state reaction has several advantages over other methods, such as it has simple synthesis process and it is easy to control the unsure concentration and suitable for mass production.

Another significant difference that has been used in this study is the iron rock of Tanah Laut, Kalimantan, which is used as a precursor source of Fe. Most of the elemental precursors usually use standard pro-analytical materials. This is due to an iron rock in Tanah Laut showed high Fe content, and according to XRD results, it has that natural iron rock contains Fe_3O_4 magnetite. The Fe_3O_4 mineral will have potentiality as the main source of Fe-source material for cathodes. Therefore, researchers tried to utilize Fe_3O_4 natural iron as a Fe source to form LFP/C to avoid high costs of Fe sources.

II. RESEARCH METHOD

Initially, the iron rock taken from Tanah Laut, Kalimantan, has been mechanically reduced to iron sand and sifted with size 170 Mesh; the iron sand was separated by the permanent magnet to obtain sand with high iron content. After the magnetic separation, the iron sand was washed with N-butanol to keep the surface clean of organic impurities. Fe element content is confirmed using X-ray Fluorescence (XRF), and its oxide phase was identified using X-Ray Diffraction (XRD). The LFP/C composite was made by a solid-state method using high energy ball milling with a base material composition according to the stoichiometry having 3:6:2 ratio for Li2CO3, (NH4) 2HPO4, Fe_3O_4, and citric acid as carbon source. The weight of carbon source is 5% wt. of the total composite raw material; the material was milled for 4 hours with a ball-to-powder ratio in ethanol set at 5:1 and at the rotational speed of 300 rpm. Calcination temperature based on temperature calcination vary by 500 °C, 600 °C, and 700 °C with a 10-hour hold time [20]. To prevent oxidation, composite preparation of LFP/C was performed in the N2 environment. After the process, the composite sample was observed using XRD to identify the formed phase, and the conductivity value of the sample was tested using Electrochemical Impedance Spectroscopy (EIS). The measurements of conductivity were carried out by certain procedures. The component must be in the form of a battery cell. The first step after obtaining an active sample of the material done was to make a salary, which is a mixture of *Polyvinylidene Fluoride* (PVDF) added with DMAC, acetylene black, and active material. The mixing of PVDF, DMAC, and acetylene black was performed using a magnetic stirrer at a rate of 150 rpm, while the active material was mixed using mortar. The mixed material was pasted on the grid or aluminum sheet and dried for 24 hours in the oven and compacted after that. The ready sample was inserted into the battery cell following with an anode (lithium metal), separator and electrolyte to test its conductivity used EIS.

III. RESULTS AND DISCUSSION

The diffraction pattern of four samples shows the qualitative and quantitative differences. The increasing of calcination temperature will increase the olivine phase and reduce the impurity phase. At the temperature of calcination 700 °C, the olivine phase amount reached 93% with slight hematite as impurities, while it is compared to a lower calcination at temperature 600 °C, the olivine ratio with impurities became 69% to 31%. The diffraction peak in the XRD pattern revealed higher impurities in the sample that was in at calcination temperatures of 400 °C and 500 °C. The hematite phase appeared along metastable phase of monoclinic $LiFeP_2O_7$ at 400 °C. When the temperature reached 500°C, the monoclinic $LiFeP_2O_7$ phase vanished but hematite remained, but the hematite phase completely was removed at 600°C. The peak of $LiFePO_4$ was obtained at the temperature of 700 °C (ICDD no. 04-016-0416) with slightly impurities of hematite [20]. The residual carbon in the LFP/C composite was amorphous because of carbon composite; apparently, it has no influence on the crystalline of the composite material.

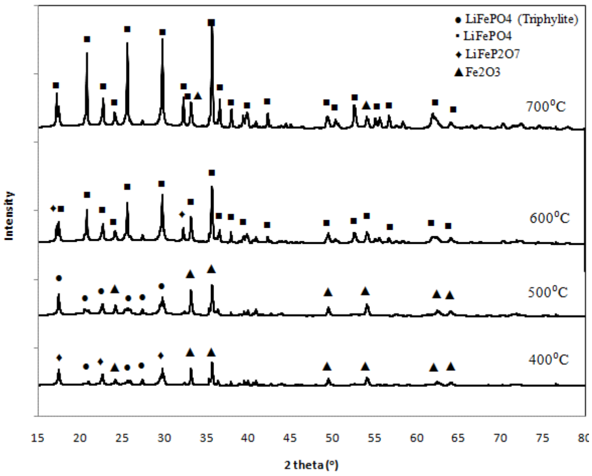

Figure 1. The XRD pattern of LFP/C composites by solid-state reaction methods at 400°C, 500°C, 600°C, and 700°C

The measurement of sample impedance values which has been given the variation of calcination temperature was conducted by using Electrochemical Impedance Spectroscopy (EIS). The EIS measurement employs small AC signal of 20 mV and a DC bias voltage of more than 3V in order to produce a curve that can form semi-circular arc patterns [3,21]. The frequency range used was at 0.1 Hz-10 KHz. The cole-cole curves of EIS testing of the four samples can be seen in Figure 2.

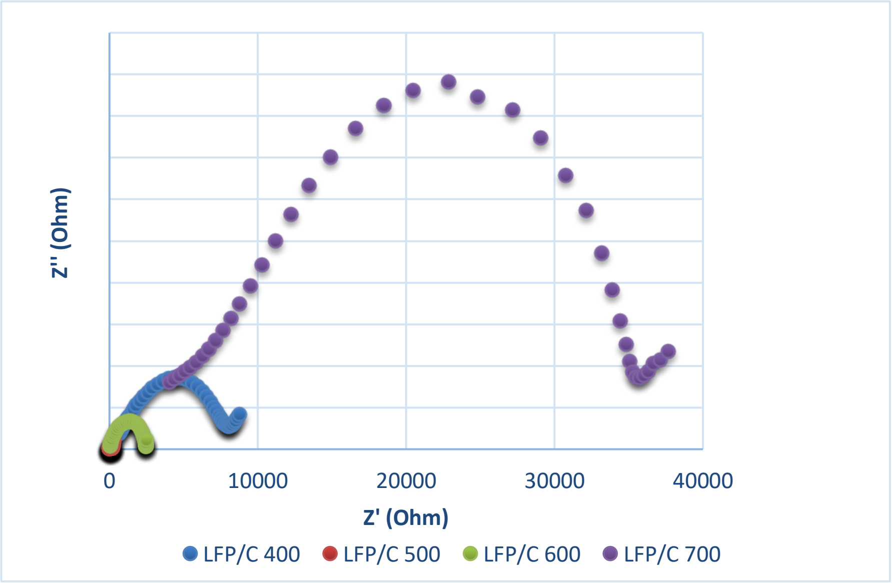

Figure 2. Total impedance value curve of LFP/C composite material at various calcination temperature (400 °C, 500°C, 600°C and 700°C)

Table 1. The conductivity value of LFP / C composite material at various calcination temperature

Temperatures of LFP/C	Total resistivity (Ω)	Total Permittivity (Ω)	Total Conductivity (10^{-6} S/cm)
400°C	9483	334954	155.57
500°C	322	11388	5676.53
600°C	2568	90706	781.34
700°C	41758	1474921	33.50

Based on Figure 2, it shows that for samples at each temperature variation form a single semicircle curve. The four samples have different semicircle diameters. The magnitude of the semicircle diameter of the graph shows the impedance value, the larger the diameter the higher the impedance value and the reverse. The highest impedance value is from the sample of 700 °C, while the lowest impedance value is from the sample of 500 °C.

The value of the impedance value can affect the value of the conductivity of the materials; the higher the impedance value, the smaller the conductivity of the materials. From the graph, it can be interpreted that the sample with the highest conductivity value is from the sample of 500°C as it has the least impedance value compared to other samples. Despite the fact that at the temperature of 700 °C also reaches highest purity, but it has a lower conductivity value compared to the sample 500 °C because at higher temperatures, there will be grain growth in LFP materials. Therefore, coatings will usually be carried out using carbon as in addition to increase the conductivity, and carbon can also prevent or minimize the grain growth. But as the temperature is increased, there will be a lot of carbon that will oxidize to form CO2, so less carbon is available to cover the LFP which in turn leads to decrease the conductivity.

In addition, based on the peak height of the semicircle curve, the capacitive properties of each sample can be identified. The higher the peak of the semicircle curve, the lower the capacitive properties it possesses (1/jωC). Therefore, from the above cole-cole curves, the material with the best capacitive properties is the sample with a 500 °C calcination temperature. Capacitive properties are related to the ability of materials to store Li ions in their structure. Furthermore, the conductivity value is shown in Table 2. Based on the table, it is known that the sample with the largest conductivity value is shown by the sample at the temperature of 500 °C with a conductivity value of 5.676 x 10^{-3} S.cm-1. This value is higher than the LFP material without carbon which has low conductivity value (10^{-9} S.cm-1) [3, 4, 6]. In the table, there is a tendency to decreasing conductivity value along with the increase of calcination temperature. The findings of this study have significant implications in the field of material physics. The success of the synthesis of LFP/C by using raw material as a source of Fe will certainly be one of the beneficial alternatives to start utilizing natural resources in Indonesia. Based on the results, further research is expected to develop further in relation with the use of other natural resources, for example, the raw material used as a carbon source, which is known that carbon has a significant influence on the level of material conductivity.

IV. CONCLUSION

Lithium Ferro Phosphate Carbon Composite (LFP/C) has been successfully made using solid-state reaction methods by utilizing one of the natural sources of iron rocks of Tanah Laut, Kalimantan, as the base material of Fe in inert condition. Based on the research, temperature variations influence the formation of LFP/C crystallization but do not have a significant effect on the conductivity [9-10]. The conductivity level of LFP/C tends to be influenced by the homogeneity of carbon coatings on the sample.

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REFERENCES

[1] Zuo D, Tian G, Li X, Chen D, and Shu K. Recent Progress in Surface Coating of Cathode Materials for Lithium Ion Secondary Batteries. *Journal of Alloys and Compounds*. 2017; **706**: 24-40. DOI: https://dx.doi.org/10.1016/j.jallcom.2017.02.230.

[2] Shim JH, Lee S, and Park SS. Effects of MgO Coating on the Structural and Electrochemical Characteristics of LiCoO2 as Cathode Materials for Lithium Ion Battery. *Chemistry of Materials*. 2014; **26**(8): 2537-2543. DOI: https://dx.doi.org/10.1021/cm403846a.

[3] Song J, Sun B, Liu H, Ma Z, Chen Z, Shao G, and Wang G. Enhancement of the Rate Capability of $LiFePO_4$ by a New Highly Graphitic Carbon-Coating Method. *ACS Applied Materials and Interfaces*. 2016; **8**(24): 15225-15231. DOI: https://dx.doi.org/10.1021/acsami.6b02567.

[4] Satyavani TVSL, Kumar AS, and Subba Rao PSV. Methods of Synthesis and Performance Improvement of Lithium Iron Phosphate for High Rate Li-ion Batteries: A Review. Engineering Science and Technology. *Engineering Science and Technology, an International Journal*. 2016; **19**(1): 178-188. DOI: https://dx.doi.org/10.1016/j.jestch.2015.06.002.

[5] Ruan YL. Effect of Doping Ions on Electrochemical Properties of $LiFePO_4$ Cathode. *Advanced Materials Research*. 2011; **197-198**: 1135-1138. DOI: https://dx.doi.org/10.4028/www.scientific.net/AMR.197-198.1135.

[6] Zhang DY, Zhang L, Zhang PX, Lin MC, Huang XQ, Ren XZ, and Xu QM. Modification of $LiFePo_4$ by Citric Acid Coating and Nb^{5+} Doping. *Advanced Materials Research*. 2011; **158**: 167-173. DOI: https://dx.doi.org/10.4028/www.scientific.net/AMR.158.167.

[7] Uddin MJ, Alaboina P, Cho S. Nanostructured Cathode Materials Synthesis for Lithium-ion Batteries. *Materials Today Energy*. 2017; **5**: 138-157. DOI: https://doi.org/10.1016/j.mtener.2017.06.008.

[8] Eftekhari A. $LiFePO_4$/C Nanocomposites for Lithium-ion Batteries. *Journal of Power Source*. 2017; **343**: 395-411. DOI: https://doi.org/10.1016/j.jpowsour.2017.01.080.

[9] Chunli G, Zhigang X, Sheng W, Yunsheng Y, and Xiaolin X. Advanced Carbon Materials/ Olivine $LiFePO_4$ Composites Cathode for Lithium Ion Batteries. *Journal of Power Source*. 2016; **318**: 93-112. DOI: https://doi.org/10.1016/j.jpowsour.2016.04.008.

[10] Li XL, Kang FY. Bai X and Shen W. A Novel Network Composite Cathode of LiFePO4 / Multiwalled Carbon Nanotubes with High Rate Capability for Lithium Ion Batteries. *Electrochemistry Communications*. 2007; **9**(4): 663-666. DOI: https://doi.org/10.1016/j.elecom.2006.10.050.

[11] Zhang H, Xu Y, Zhao C, Yang X, and Jiang Q. Effects of Carbon Coating and Metal Ions Doping on Low Temperature Electrochemical Properties of $LiFePO_4$ Cathode Material. *Electrochimica Acta*. 2012;

83: 341-347. DOI: https://doi.org/10.1016/j.electacta.2012.07.128.

[12] Sinha NN. High Rate Capability of a Dual Porosity $LiFePO_4$/C Composite. *ACS Applied Materials & Interfaces*. 2010; **2**(7): 2031-2038. DOI: https://dx.doi.org/10.1021/am100309w.

[13] Qian JF. Template-Free Hydrothermal Synthesis of Nanoembossed Mesoporous LiFePO4 Microspheres for High-Performance Lithium-Ion Batteries. *The Journal of Physical Chemistry C*. 2010; **114**(8): 3477-3482. DOI: https://dx.doi.org/10.1021/jp912102k.

[14] Sun CW, Rajasekhara S, Goodenough JB, and Zhou F. Monodisperse Porous $LiFePO_4$ Microspheres for a High Power Li-Ion Battery Cathode. *Journal of the American Chemical Society*. 2011; **133**(7): 2132-2135. DOI: https://dx.doi.org/10.1021/ja1110464.

[15] Wood DL, Li J, and Daniel C. Prospects for Reducing the Processing Cost of Lithium Ion Batteries. *Journal of Power Source*. 2015; **275**: 234-242. DOI: https://doi.org/10.1016/j.jpowsour.2014.11.019.

[16] Hong SA, Kim SJ, Kim J, Lee BG, Chung KY, and Lee YW. Carbon Coating on Lithium Iron Phosphate (LiFePO4): Comparison Between Continuous Supercritical Hydrothermal Method and Solid-state Method. *The Chemical Engineering Journal*. 2012; **198-199**: 318-326. DOI: https://doi.org/10.1016/j.cej.2012.05.058.

[17] Wang L, Sun W, Tang X, Huang X, He X, Li J Zhang Q, Gao J, Tian G, and Fan S. Nano Particles $LiFePO_4$ Prepared by Solvothermal Process, *Journal of Power Sources*. 2013; **244**: 94-100. DOI: https://doi.org/10.1016/j.jpowsour.2013.03.101.

[18] Huang X, He X, Jiang C, and Tian G. Morphology Evolution and Impurity Analysis of LiFePO4 Nanoparticles via a Solvothermal Synthesis Process. *RSC Advances*. 2014; **4** (99): 56074-56083. DOI: https://doi.org/10.1039/C4RA09484KAaaa.

[19] Park KS, Son JT, Chung HT, Kim SJ, Kim CH, Lee CH, and Kim H. Synthesis of LiFePO4 by Coprecipitation and Microwave heating. *Electrochemistry Communications*. 2003; **5**(10): 839-842. DOI: https://doi.org/10.1016/j.elecom.2003.08.005.

[20] Mauliana M and Zainuri M. Characterization of Lithium Ferro Phosphate Carbon Composite by Solid-State Reaction Methods in Various Temperature Calcination. *Proceeding of International Conference on Research, Implementation and Education of Mathematics and Sciences 2015*. Yogyakarta: Yogyakarta State University; 2015; P-55-P-60. Available from: https://eprints.uny.ac.id/21054/1/08%20-%20Metatia%20Intan%20Mauliana.pdf.

[21] Subhan A. *Fabrikasi dan Karakterisasi Li4Ti5O12 untuk Bahan Anoda Baterai Lithium Keramik*. Master Thesis. Unpublished. Jakarta: Universitas Indonesia; 2011.