

Synthesis of C-LiFePO₄ composite by solid state reaction method

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Abstract. In this research, the enhancement of LiFePO₄ conductivity was conducted by doping method with carbon materials. Carbon-based materials were obtained from the mixture of sucrose, and the precursor of LiH₂PO₄ and α -Fe₂O₃ was synthesized by solid state reaction. Sintering temperature was varied at 700°C, 800°C, 900°C and 1,000°C. The results showed that C-LiFePO₄ could be synthesized by using solid state reaction method. Based on the XRD and FTIR spectrums, C-LiFePO₄ can be identified as the type of crystal, characterized by the appearance of sharp signal on (011), (211) and typical peak of LiFePO₄ materials. The result of conductivity measurement from C-LiFePO₄ at sintering temperature of 900°C and 1,000°C was 2×10^{-4} S/cm and 4×10^{-4} S/cm, respectively. The conductivity value at sintering temperature of 700°C and 800°C was very small ($< 10^{-6}$ S/cm), which cannot be measured by the existing equipment.

1. Introduction

LiFePO₄ has been known as lithium battery cathode material that has a high theoretical capacity (170 mAh/g), a stable potential voltage of 3.5 V vs Li⁺, and environmental friendliness. However, LiFePO₄ have weaknesses, those are a slow kinetic diffusion of lithium ion and a low electronic intrinsic conductivity. Therefore, it needs a modification to improve its electrochemical performance [1,2].

One of the attempts to increase the low kinetic diffusion of lithium ion is coating the surface of LiFePO₄ with carbon, copper, and silver [3]. Enhancing electronic conductivity can be conducted by minimizing the particle size with modification in the sintering process. One of the methods for synthesizing LiFePO₄ is solid state reaction. The solid state reaction is more effective than sol-gel method. In addition, doping process with carbon can be conducted simultaneously in the solid state reaction. Therefore, with solid state reaction [3, 4], the results of synthesizing LiFePO₄ are expected to produce a material with a fairly high conductivity.

The purpose of this study was to synthesize C-LiFePO₄ composite by solid state reaction method. The present method used carbon for enhancing and getting excellent LiFePO₄ material. Carbon was selected because carbon is easily produced. [5]

2. Experimental Method

The materials used are aquades, LiH₂PO₄ p.a. (Aldrich, 99%), α -Fe₂O₃ p.a. (Aldrich, 99%), sucrose (C₁₂H₂₂O₁₁), N-metilpirolidinon (NMP), polivinildene fluoride (PVDF), and nitrogen gas (N₂).

The initial step for synthesizing C-LiFePO₄ was preparing the precursor from the material LiH₂PO₄, α -Fe₂O₃ and sucrose. Those three precursors were made by the molar ratio Li: Fe: P: C = 1:1:1:1,2. After weighing those three precursors and mixed it into mortar containing aquades, the mixture was crushed by ball mill for 2 hours. After that, drying process was conducted at temperature 80°C, using

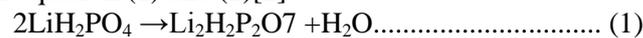


oven. After the three precursors were dried, it was heated at temperature of 520°C for six hours in furnace without flowing N₂ gas, then the powder was crushed again in mortar for 2 hours. The powder which had subtle was heated with temperature variation of 700°C, 800°C, 900°C and 1,000°C in the furnace for 16 hours with flowing N₂ gas. The physical characteristics of cathode materials were analysed by using the x-ray diffractometer(XRD), infrared spectrophotometer (FTIR).

The production of Film C-LiFePO₄ was conducted by mixing C-LiFePO₄, and PVDF as an adhesive with weight composition of 92%:8% in total weight of 2 gram. The mixture was put in 5 mL of NMP solvent while stirred by magnetic stirrer for 16 hours until the homogenous LiFePO₄ liquid were produced. The production of LiFePO₄ film is conducted by printing the homogenous liquid of LiFePO₄ on glass substrates with size of 2cm x 2cm. The film of LiFePO₄ was dried in the oven at temperature of 80°C for 4 hours. Then, each thickness and conductivity of the dried film was measured by four line probe method.

3. Result and Discussion

During the calcination process, a reduction in the mass of the precursor from 28.8992 gram to 23.4556 gram was observed. This is caused by the releasing of water on calcinations process which occurred at temperature of 100°C until 300°C, chemical reaction which occurred on calcinations process was written in equation (1) and (2)[2].



During the sintering, there were three stages of microstructural processes which contained expansion on the initial condition, there was no reaction yet, and particle composition did not change. During the initial stage of sintering, rearrangement occurred, there was a little moves or particle rotation to enhance the number of contacts between the particles and the formation of linkages between the particles, C-LiFePO₄ composite materials were still red, it indicated that there was no reaction of formation a perfect C-LiFePO₄ composite.

In second stage, size of linkages between particles grew and its porosity decreased due to the particles which come closer each other. On this stage, grain growth started, formed the pore, the distance between the particles became smaller, and shrinkage occurred as shown in Figure 1(b), and (c), C-LiFePO₄ composite begun to form and characterized by changing into blackish, it indicated that reaction stage was at intermediate stage.

On this stage, the pore became a round pore eventually, size of particle increased and the rate of shrinkage pores became smaller as shown in Figure 1(d), C-LiFePO₄ composite material had been formed then compaction and hardening occurred. It showed that effect of the higher sintering temperature would change form structures material of C-LiFePO₄ composite became more solid and the color turn into blackish. The reaction on the sintering process $\text{Li}_2\text{H}_2\text{P}_2\text{O}_7 + 2\text{FeO} (\text{Fe}_3\text{O}_4 + \text{Fe}) \rightarrow 2\text{LiFePO}_4 + \text{H}_2\text{O}$ [2].

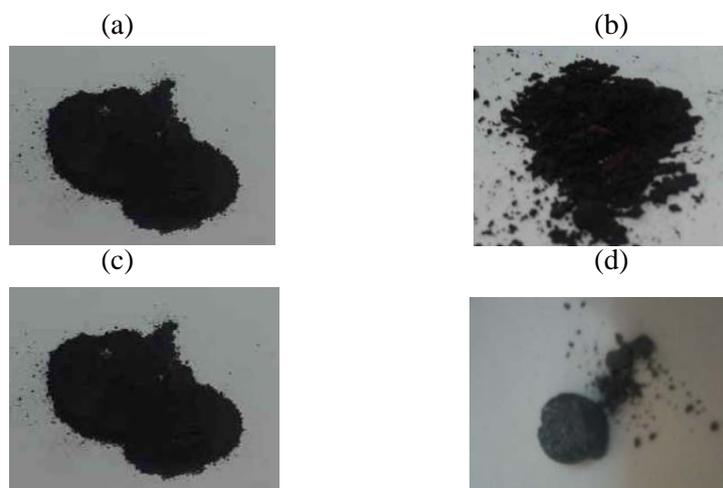


Figure 1. Powder as the result of *sintering* (a) 700°C (b) 800°C (c) 900°C (d) 1000°C

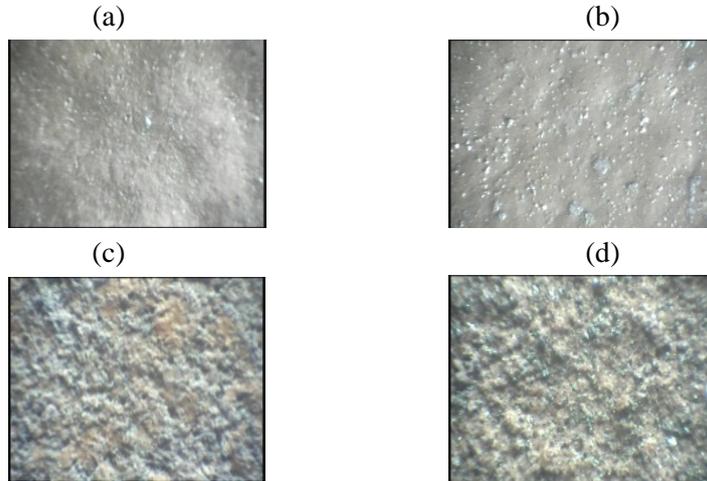


Figure 2. Profile of C-LiFePO₄ surface with 100x of magnification, formed in *sintering* film (a)700°C (b) 800°C (c) 900°C (d) 1,000°C

Figure 2 shows the surface of C-LiFePO₄ cathode material on the addition of the sintering temperature (a) 700°C (b) 800°C (c) 900°C (d) 1000°C. The surface of LiFePO₄ cathode on heating the sintering temperature of 700°C looked still subtle but the heating at sintering temperature of 800°C looked to start rough and coarsening occurred, then hardening occurred on heating at the sintering temperature of 900-1000°C. It occurred due to the heating of the sintering temperature, the higher sintering temperature, then the more formation of the perfect C-LiFePO₄ would be formed, otherwise at the temperature of 700-800°C, C-LiFePO₄ had not formed completely. It showed that the higher sintering temperature, then the more perfect C-LiFePO₄ would be formed.

Each thickness and conductivity of dried film would be measured by four line probe method. Table 1 showed that increasing of conductivity occurred along with the enhancing of the sintering temperature. It occurred because the enhancing of the sintering temperature then the crystal structure had been formed, which the bonding between the powder particles bind each other in these conditions. The conductivity of C-LiFePO₄ composite materials at temperature of 700-800°C was not detected on the equipment, the ability of the equipment was only capable of reading up to 10⁻⁶ S/cm.

Table 1. The conductivity of C-LiFePO₄

The sintering temperature /oC	Conductivity/S/cm
700	-
800	-
900	2 x10 ⁻⁴
1000	4 x10 ⁻⁴

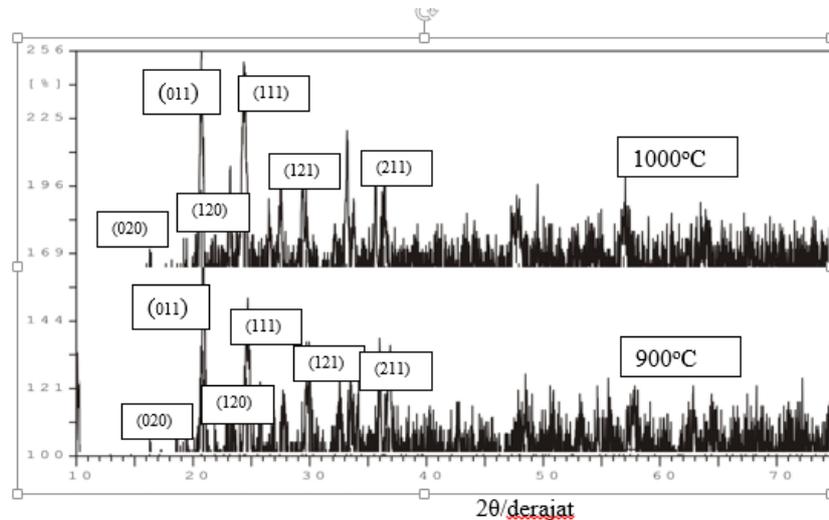


Figure 3. The result of XRDC-LiFePO₄

Figure 3 shows that x-ray diffractogram pattern from the variation of sintering temperature. All the products were identified as the type of olivine crystal LiFePO₄, marked by the appearance of sharp signal on (020), (011), (120), (101), (111) and (211) but the relative intensities of the peak numbers were different among samples, due to the effect on the size of the crystal. There were also signals that did not match and it was possible of the existence of impurities.

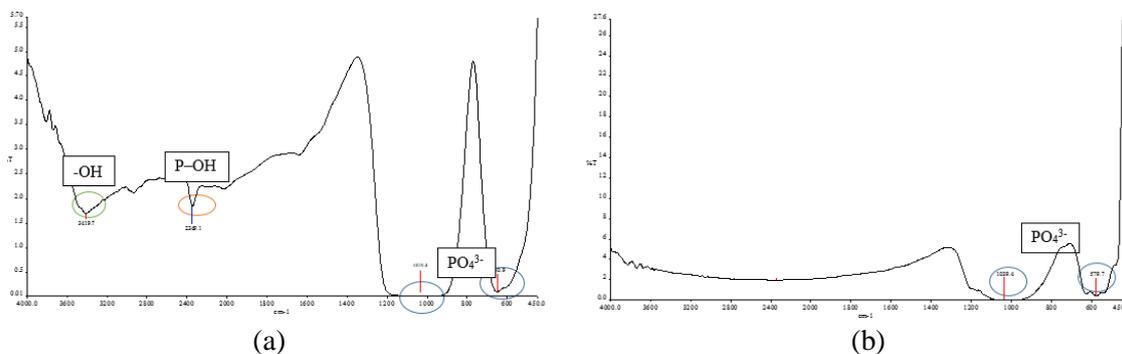


Figure 4. Spectrum infrared C-LiFePO₄ sintering at (a) 700 and (b) 800°C

To determine the functional groups contained in the C-LiFePO₄, the characterization by FTIR. Figure 4.(a) is an FTIR spectrum measurement results of C-LiFePO₄ sintering 700°C. On the spectrum, formed in wave numbers 3419,7 cm⁻¹, 2349,1 cm⁻¹, 1039,4 cm⁻¹, and 650,9 cm⁻¹ that each identifies -OH stretch vibration, Un-deprotonated P-OH, and shows PO₄³⁻ functional groups. Figure 5(b) is an FTIR spectrum measurement results of C-LiFePO₄ sintering 800°C. On the spectrum, formed in wave numbers 2344,4 cm⁻¹, 1039,4 cm⁻¹, and 579,1 cm⁻¹ identifies each functional group PO₄³⁻. At 800°C sintering visible loss of OH and P-OH, the high temperature heating leads to loss of impurities such as OH. From the results of FTIR, two samples identified as PO₄³⁻ functional groups.

4. Conclusion

C-LiFePO₄ composite material can be synthesized by using solid chemical reaction method. Based on the XRD and FTIR characterization, it can be identified as C-LiFePO₄ which has the olivine crystal structure with the appearance of sharp signal on (011), (020), (011), (120), (101), (111) and (211). The composite materials of C-LiFePO₄ on the sintering temperatures of 900°C and 1,000°C were 2×10^{-4} S/cm and 4×10^{-4} S/cm, respectively. The sintering temperature of 700°C and 800°C provided a very small conductivity ($<10^{-6}$ S/cm). Therefore, it cannot be measured by the existing equipment.

5. References

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