Performance of Vanadium Doped and Carbon Bamboo/ Carbon Black Coated Lithium Iron Phosphate for Battery Cathode

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Abstract. Synthesis of lithium iron phosphate (LiFePO4) via wet chemical followed by a hydrothermal method has been carried out. The preparation of LiFePO4 was begun with the precursor of LiOH, NH4H2PO4, and FeSO4·7H2O mixed stoichiometrically. After the synthesis, LiFePO4 was doped using vanadium and then coated using two types of carbon sources, i.e. carbon black blended with activated carbon pyrolyzed from bamboo, through a solid-state reaction. The materials were mixed using a ball-mill and subsequently characterized using a thermal analyzer (STA) to determine the sintering temperature. The result shows that LiFePO4 formation temperature is at 639°C. The sintering process was performed for 4 hours and the characterization was done using X-ray diffraction (XRD) and electron microscope (SEM) equipped with energy dispersive x-ray spectroscopy (EDX). The electrochemical impedance spectroscopy (EIS) testing was performed to show the conductivity of the formed materials. XRD result showed that LiFePO4/V/C phase has formed with an olivine structure, while the SEM result showed fair distribution and small particle size with some agglomerated microstructures. The EIS results showed that carbon coating on the active material increases the conductivity, whereas the addition of vanadium increases the conductivity of up to 5 wt.% vanadium but decreases at 7 wt.% vanadium.

Keywords: LiFePO4, hydrothermal, bamboo carbon, carbon black, battery cathode

1. Introduction
Currently, environmentally friendly energy sources such as water, wind, and solar radiation has been widely used. To store this kind of energy, a material with a large capacity such as lithium ion battery is required [1]. One kind of lithium ion battery active materials is lithium iron phosphate (LiFePO4). This material has received much attention due to its simple olivine-based structure, in addition to its environmentally friendly, low material cost, good chemical stability, high theoretical capacity of 170 mAh/g and good potential (~ 3.45 V vs. Li/Li+) [2]. However, there are some drawbacks of this material, such as low intrinsic electronic conductivity (about 10⁻⁹-10⁻¹¹ S/cm) and low diffusion coefficients (about 10⁻¹¹-10⁻¹³ cm²/s) depending on Li⁺ concentration and characterization method used [3]. Because of that, there has been considerable development in improving the electrochemical performance of LiFePO4 cathodes, among them with conductive materials to improve its electrical conductivity [4], wherein the carbon layer is a promising and effective method [5]. The effect
of carbon coating alone, however, decreased its tap density, therefore doping with the supervalent cation is commonly used to improve tap density [6].

In this study, a combination of carbon layer source (activated carbon from bamboo and carbon black) was performed. Activated carbon from bamboo as a reducer, mixed with raw materials, forming a mixture of precursors. Carbon black acts as a carbon coating source, added in the second step, wrapping the precursor particles. The addition of a supervalent cation element such as vanadium is also performed to form a number of active electrochemical compounds that can intercalate/deintercalate reversible lithium.

2. Experimental

2.1 LiFePO₄ cathode synthesis
Firstly, LiOH, NH₄H₂PO₄, and FeSO₄.7H₂O powder were prepared stoichiometrically. The powders were diluted using distilled water up to 30 mL into a separate beaker glass. Further, the three solutions were mixed and stirred for homogenization in a magnetic stirrer for 30 minutes. The solution was then move to a Teflon autoclave and was heated at 180°C for 20 hours. The solution was move to a beaker glass to settle until the solids were separated from the solution. The solid was filtered and washed with deionized water to obtain a pH of 5. After all the process was completed, the precipitate was put in an oven at 80°C for 18 hours. Finally, the powder was ready for the next treatment.

2.2 LiFePO₄/V/C fabrication
The previously prepared LiFePO₄ powder was mixed with activated carbon pyrolyzed from bamboo, and carbon black, and H₄NO₃V with a composition of 92:2:2:5% wt. LiFePO₄ and H₄NO₃V powder were inserted into a ball miller. After the milling process, activated carbon powder was then fed into the LiFePO₄ and H₄NO₃V powders. The same procedure was carried out for other percentage variations of 0, 3, 5, and 7 wt.% of H₄NO₃V. After all the process of milling were set, thermal test on 4 variations of the sample was carried out. Thereafter, the materials were calcined at 750°C for 4 hours. The samples were then subjected to characterization using SEM, XRD, and EIS.

2.3 Battery fabrication and testing
All of these manufacturing processes were performed in a glove box on the split test cell. The electrode sheets were prepared and circular cut using a disc puncher. The material was arranged in sequence from below; bottom casing, cathode, separator, anode, and top casing. Further, the battery was filled with LiPF₆ electrolyte solution and tested using split test cell to obtain a potential difference in the component.

3. Results and discussion

3.1 Hydrothermal Synthesis Phase Formation LiFePO₄
Figure 1 shows STA test results from the LiFePO₄ cathode. It appears that the heat flow increases with the addition of temperature. This is because the sample continues to oxidize due to the absence of nitrogen or argon gas so that the test conditions are not inert. Then, on another graph or on the TGA there is a continuous weight increase at 10.71 at 242°C to 11.12 mg at 493°C. Then, rise slowly to 11.91 mg when the temperature is 639.18°C. Then it drops to 11.01 mg at 959.7°C.
3.2 Diffraction Patterns

It can be seen in Fig. 2 that the diffraction pattern of the LiFePO$_4$ cathode sample with the various variables of carbon coating difference and the addition of vanadium having a peak corresponding to the reference PDF2 diffraction pattern is the olivine structure with the orthorhombic Pmnb space group. However, a shift in the LiFePO$_4$/V 7% sample was not significant due to the formation of a new phase Li$_3$V$_2$(PO$_4$)$_3$ in which the amount of vanadium addition would result in a peak shift. This vanadium content can only be seen with a TEM (Transmission Electron Microscopy) due to its very little percentage which only serves as a doping on LiFePO$_4$.

3.3 Morphological and Distribution of LiFePO$_4$

Figure 3(a) is a result of a pure LiFePO$_4$ cathode having angular crystal structure and agglomerated by heterogeneous sizes. This is because the effect of sintering temperature is high enough to change the amorphous structure into crystalline so that the surface area is...
smaller and the particles are stick together and form particles of large size. For Fig. 3(b) EDS results where the three spectra show the same result, composed LiFePO$_4$ compounds. But there is little difference in the amount of its element content. In the first spectrum there is a considerable amount of Fe content and on the third spectrum the content of the oxygen element sufficiently affects the color of the image.

**Figure 3.** SEM results of the synthesized LiFePO$_4$ cathode and EDS point with magnification (a) 120X (b) 2500X

**Figure 4.** SEM LiFePO$_4$ cathode with carbon without vanadium doping and EDS point with magnification 2500X

**Figure 4.** SEM results of LiFePO$_4$ cathode material of carbon coating without vanadium doping. At 2500X magnification, there are some irregular shapes but a fairly homogeneous size, a small white sphere. Figure 6. EDS results where spectrum 1 and 2 show the presence of carbon that does not coat LiFePO$_4$. Spectrum 3 shows LiFePO$_4$ coated by carbon.
Figure 5. SEM LiFePO₄ cathode with carbon and doping 5% vanadium and EDS point with magnification 2500X

Figure 5. shows SEM results of LiFePO₄ cathode material with carbonaceous coating and 5% vanadium doping show reduced particle size and more evenly where vanadium reduces the carbon content to decrease the valence from V⁵⁺ to V³⁺ [6]. Figure 8. shows no significant difference where both spectra indicate LiFePO₄ which has been coated by carbon. However, in spectrum 2 it does not show the presence of vanadium in LiFePO₄ whereas in spectrum 1 there is little vanadium content.

3.4 EIS characterization of LiFePO₄ electrodes

Figure 6. EIS test results on LFP samples with various variables

Figure 6 shows LiFePO₄ sample results without vanadium doping (LFP-V0%) has a greater resistance value, which is 119 Ω. For samples of LiFePO₄ with vanadium doping (LFP-V3%, LFP-V5%, and LFP-V7%) had a smaller resistance value of 92 Ω, 77 Ω, and 105 Ω, respectively. This can be proven by the diameter of semicircle on the graph. In theory, the addition of vanadium will increase the conductivity of the active material, but the excessive addition of LFP-V7% may carry an impurity phase such as Li₃V₂(PO₄)₃ and block the diffusion channel Li⁺, which will adversely affect the electrochemical performance [7]. Table 1. shows the comparison between carbon black or activated carbon from bamboo with using a
mixture of both [8,9]. As a result, LFP-V0% with an activated carbon mixture of bamboo and carbon black has a larger conductivity value and has a larger Li rate as well, but at LFP-V5% the results look somewhat different.

**Table 1.** Comparison of total resistance and conductivity with different carbon coatings and vanadium doping

| Sample                           | Rct (Ω) | t (cm) | A (cm²) | σ (S/cm) |
|---------------------------------|---------|--------|---------|----------|
| Carbon Black                    |         |        |         |          |
| LiFePO4/C/0V                    | 158     | 0.008  | 2.01   | 2.52 x 10⁻⁵  |
| LiFePO4/C/5V                    | 59      | 0.008  | 2.01   | 6.75 x 10⁻⁵  |
| Activated Carbon Bamboo        |         |        |         |          |
| LiFePO4/C/0V                    | 197     | 0.008  | 2.01   | 2.02 x 10⁻⁵  |
| LiFePO4/C/5V                    | 91      | 0.008  | 2.01   | 4.37 x 10⁻⁵  |
| Mixed Carbon Black and Activated Carbon Bamboo |         |        |         |          |
| LiFePO4/C/0V                    | 119     | 0.008  | 2.01   | 3.34 x 10⁻⁵  |
| LiFePO4/C/5V                    | 77      | 0.008  | 2.01   | 5.17 x 10⁻⁵  |

4. Conclusion
The carbonization process of bamboo was successful and produced high crystallinity so that when mixed with carbon black yielded a low resistivity value of about 119 Ω of vanadium 0% addition. While the addition of vanadium 5% showed higher resistance value than using only carbon black and lower than using only bamboo activated carbon alone. The SEM test results show smaller and homogeneous particle size although some of the agglomerated particles are compared with pure LiFePO₄.

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