

Use of carbon pyrolyzed from rice husk in $\text{LiFePO}_4/\text{V}/\text{C}$ composite and its performance for lithium ion battery cathode

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Abstract. The characteristics of activated carbon pyrolyzed from rice husk used in the synthesis of $\text{LiFePO}_4/\text{V}/\text{C}$ for the development of lithium ion battery cathode has been examined. The synthesis was begun by synthesizing LiFePO_4 (LFP) via hydrothermal route using the precursors in stoichiometric amounts of LiOH , $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The as-synthesized LFP was then added with variation of vanadium concentrations and a fix concentration of the carbon pyrolyzed from rice husk to form a composite of $\text{LiFePO}_4/\text{V}/\text{C}$. The composites were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), and electrochemical impedance spectroscopy (EIS). The XRD results showed that the $\text{LiFePO}_4/\text{V}/\text{C}$ has been successfully formed whereas SEM results showed a difference in morphology of vanadium and activated carbon addition. The EIS results showed that the conductivity of $\text{LiFePO}_4/\text{C}-0$ wt.% V is 1.0196×10^{-2} S/cm, $\text{LiFePO}_4/\text{C}-3$ wt.% V is 1.0302×10^{-2} S/cm, $\text{LiFePO}_4/\text{C}-5$ wt.% V is 6.1282×10^{-3} S/cm, and $\text{LiFePO}_4/\text{C}-7$ wt.% V is 8.3843×10^{-3} S/cm. The best performance for lithium ion battery cathode was given by $\text{LiFePO}_4/\text{V}/\text{C}$ at 3 wt.% vanadium. This result indicated that rice husk can be used as a cheap resource for activated carbon in the development of lithium ion battery cathode.

1. Introduction

Indonesia is the third largest rice producer in the world, after China and India [1]. In addition to producing rice, grain harvest will also produce rice husks. Assuming the grain-husk ratio is 1: 0.24, every ton of grain will produce 0.24 tons of rice husks. Hence, disposal of this vast amount of rice husk has been a major problem being faced by rice milling industry. The traditional method of disposing this rice husk is by burning it, however, other problem arises from this burning due to environmental issue.

Rice husk mostly contains cellulose and silica of around 20-25%, which when pyrolyzed under an inert atmosphere will produce carbon [2]. Many attempts have been performed by many investigators to make use of this rice husk such as precursors to produce zeolite [3], silica [4], concrete [5], activated carbon [6], and carbon for lithium ion battery anode [7].

Driven by the increasing need of energy demand in the midst of decreasing availability of the fossil fuel and the resulting emission of the fossil fuel that is not environmentally friendly, there is an



intensive research of material for energy storage. For this purpose, lithium ion battery has drawn much attention due to its good performance and relatively high capacity. The use of LiFePO_4 as a cathode has the advantage of low manufacturing cost, non-toxic, and quite high theoretical capacity, high charge-discharge cycles and environmentally friendly [8, 9]. The major problem is that it has slow lithium ions diffusion between the interface that results in low electrical conductivity ($\sim 10^{-9}$ S/cm) and thus low rate capability [10]. Many efforts have been carried out by many investigators to improve the conductivity of this LiFePO_4 such as metal doping [11, 12] and carbon coating [13].

Carbon is usually used to improve the conductivity of LiFePO_4 , and the most use material is carbon black. Carbon black is a material produced by the incomplete combustion of heavy petroleum products that has a high surface-area-to-volume ratio. However, the use of carbon black has been limited due to its carcinogenic effect [14]. Many efforts have been made to replace this carbon black with the one from natural resources such as table sugar and bamboo. In this work, rice husk was used as a precursor to produce activated carbon and the result was applied to increase the conductivity of vanadium doped LiFePO_4 in the form of $\text{LiFePO}_4/\text{V}/\text{C}$ composite for lithium ion battery cathode. The characteristic of the material was examined and the results are presented and discussed in detail.

2. Experimental Setup

2.1. Carbon pyrolysis

The raw material of rice husk was collected from local rice mill in Wonogiri, Central Java. The rice husk was thoroughly washed with tap water to remove any adhering dirt and dried under room temperature condition. The dried rice husk was heated at 700°C and the result in the form of rice husk charcoal was crushed into fine carbon fragments. The as-prepared charcoal was further blanched in NaOH (Merck) solution with a weight ratio of 1: 5 and stirred using a magnetic stirrer at 100°C for 2 hours. After the stirring, the carbon was allowed to stand for 22 hours before filtering it with filter paper and the carbon deposit was transferred to the crucible and was further heated at 450°C for 1 hour and cooled down to room temperature. After cooling down, the carbon was washed using distilled water to obtain a pH 7 and subsequently dried at 120°C for 12 hours before characterization using X-ray diffraction (XRD, ARL OPTX-2050) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$).

2.2. Synthesis of LiFePO_4

In this work, LiFePO_4 was prepared from the precursors of LiOH , $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. All of these precursors were analytical grade reagents from E-Merck. The preparation was in accordance to our previous work published elsewhere [15] and is explained as following. The stoichiometric amounts of the precursors were diluted with 30 ml distilled water in a separated glass beaker. After dilution, the three solutions of LiOH , $\text{NH}_4\text{H}_2\text{PO}_4$, and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were mixed into a glass beaker and stirred until homogenized under a magnetic stirrer for 30 minutes. The mixed solution was then transferred into a Teflon autoclave and hydrothermally heated at 180°C for 20 hours.

After the hydrothermal process, the solution was transferred into a beaker and left to form precipitates. The precipitates were then separated from the solution and washed with deionized water before being dried in an oven at 80°C for 18 hours. The characteristics of crystal structure of the obtained materials were examined by using X-ray diffraction (XRD, ARL OPTX-2050) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) and a scanning electron microscope (SEM, FEI Quanta-650).

2.3. Synthesis $\text{LiFe}_{1-x}\text{V}_x\text{PO}_4/\text{C}$

The synthesis was begun by preparing the as-synthesized LiFePO_4 powders from the previous step with variations of 0, 3, 5, and 7 wt.% $\text{H}_4\text{NO}_3\text{V}$ and 3 wt.% of activated carbon from the rice husk. Detail of the process has been published elsewhere [15] and is explained as following. A stoichiometric amount LiFePO_4 at various concentrations of $\text{H}_4\text{NO}_3\text{V}$ powders were ball-milled until homogenized. An amount of 3 wt.% carbon was then added into the mixture and the ball-milling process continued until a homogenized mixture was obtained.

After the milling process, a small amount of specimen was tested with a thermal analyser (PerkinElmer STA 6000) to examine the crystallization process. The results from the thermal analysis showed that the sintering process needs to be performed at 750°C. Therefore, all the samples were then sintered at 750°C for four hours under argon environment. The characteristics of the resulting cathode active materials were examined by using X-ray diffraction (XRD, Philips PW3020) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and a scanning electron microscope (SEM, FEI Quanta-650) equipped with energy dispersive X-ray spectroscopy (EDX).

2.4. Conductivity measurement

The cathode was prepared by mixing the material with poly-vinylidene fluoride (PVDF, MTI) in N-methyl pyrrolidone (NMP, MTI) solvent inside a vacuum mixer. The mixture in the form of paste was then applied onto a current collector of aluminium foil (MTI), dried, hot-rolled and heated in a vacuum oven at 80°C. The conductivity was measured using an electrochemical impedance spectroscopy (EIS, Hioki LCR 3532-50).

3. Results and Discussion

X-ray diffraction characterization was performed to confirm the crystal structure of the samples both for the activated carbon from the rice husk and LiFePO₄. The diffraction pattern for the activated carbon is shown in figure 1, whereas the diffraction patterns of the reference LiFePO₄, the commercial LiFePO₄, and the synthesized LiFePO₄/C with various vanadium concentrations are given in figure 2. For the activated carbon, as seen in figure 1, the diffraction pattern shows a crystalline structure indicated by the presence of several peaks at $2\theta = 26.50, 44.06, 64.41, 77.53,$ and 98.32 . The pattern is indexed to a rhombohedral R3 space group (JCPDS 026-1079).

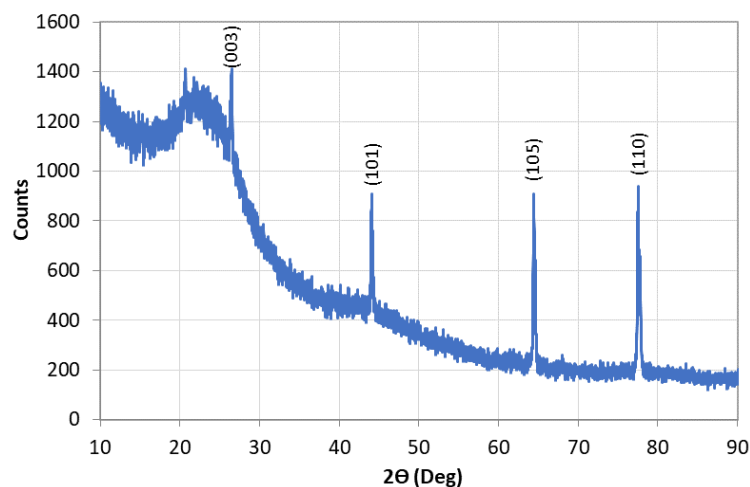


Figure 1. X-ray diffraction pattern of the activated carbon from the rice husk.

For the synthesized LiFePO₄ samples with carbon addition are still in agreement with that of LiFePO₄ reference with a structure crystal indexed to the Pnma orthorhombic (JCPDS No.083-2092). The same result has been obtained by other investigators [16, 17]. For the LiFePO₄ with carbon addition and various concentrations of up to 7 wt.% vanadium, there is no change in the structure as indicated by the diffraction peaks. Some differences in the diffraction intensities exist, however, due to the carbon and or vanadium addition as can be seen in figure 2(e) and (f). In all of vanadium-doped LiFePO₄/C, high crystallinity has been obtained with no typical diffraction patterns of carbon nor vanadium. The non-existence of carbon and vanadium diffraction patterns within the materials is an indication that carbon is in an amorphous form whereas vanadium has substituted and occupied Fe sites in LiFePO₄.

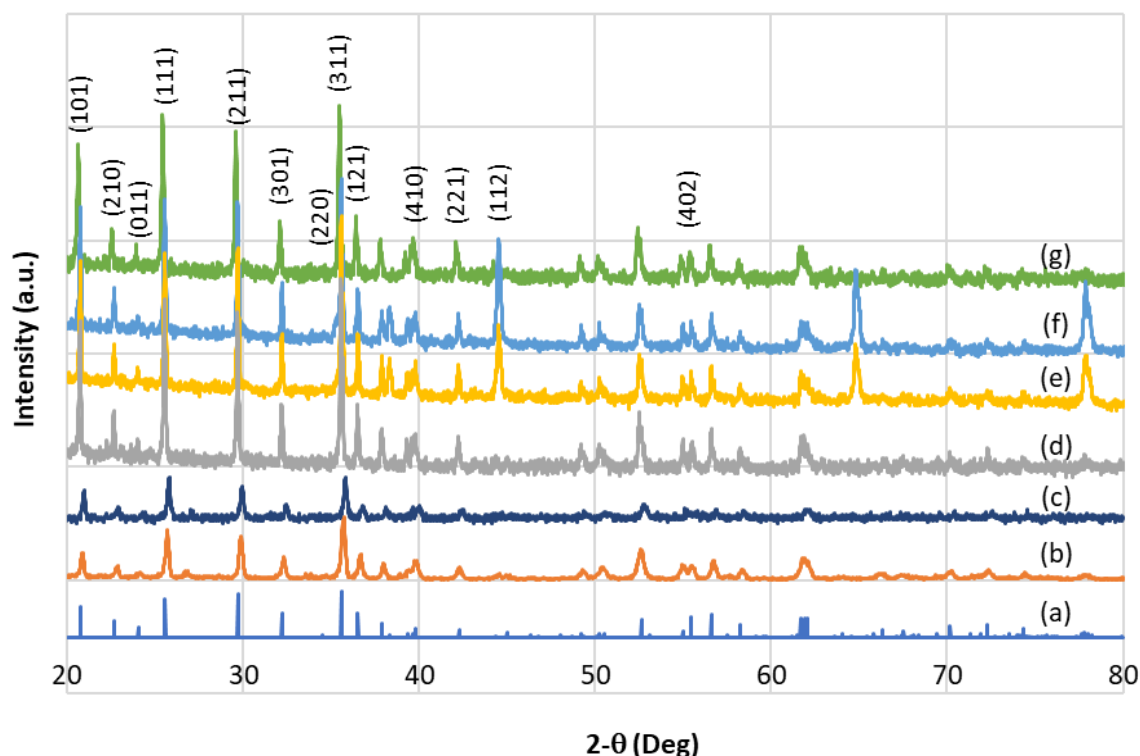


Figure 2. Diffraction patterns of (a) reference LiFePO_4 (JCPDS No.083-2092), (b) commercial LiFePO_4 , (c) as-synthesized LiFePO_4 , (d) 0 wt.% V-doped LiFePO_4/C , (e) 3 wt.% V-doped LiFePO_4/C , (f) 5 wt.% V-doped LiFePO_4/C , and (d) 5 wt.% V-doped LiFePO_4/C .

In order to support the results from the X-ray diffraction investigation, scanning electron microscope observation was performed to reveal the surface morphology of the samples. The results from the secondary electron image for $\text{LiFePO}_4/\text{V}/\text{C}$ composites are given in figure 3. As seen in the micrograph, figure 3(a) is at 0 wt.% V-doped LiFePO_4/C , figure 3(b) is at 3 wt.% V-doped LiFePO_4/C , figure 3(c) is at 5 wt.% V-doped LiFePO_4/C , and figure 3(d) is at 7 wt.% V-doped LiFePO_4/C . In all of the micrographs, most of the particles show the morphology of flake shape and the particles distribute homogeneously.

Electrical conductivity was measured using electrical impedance spectroscopy to reveal the change in conductivity through a plot diagram depicting the material's capacitance. The results in the forms of Cole plots are shown in figure 4. Analysis of this diagram shows that the resulting conductivity of LiFePO_4/C -0 wt.% V is 1.0196×10^{-2} S/cm, LiFePO_4/C -3 wt.% V is 1.0302×10^{-2} S/cm, LiFePO_4/C -5 wt.% V is 6.1282×10^{-3} S/cm, and LiFePO_4/C -7 wt.% V is 8.3843×10^{-3} S/cm. These results indicate that the addition of activated carbon alone could increase the conductivity as compared to the pure LiFePO_4 . In the case of vanadium, at 3 wt.% V, the conductivity increases; however, at 5 wt.% V and 7 wt.% V results in decreasing the conductivity. It seems that when vanadium concentration is higher than 3 wt.%, it is suspected that the particles tend to agglomerate results in more pores formation and thus decreases the conductivity. See the surface morphology of the composite from the secondary electron image in figure 3 for more detail.

The cyclic voltammetry and charge/discharge testing were performed for 3 wt.% V and 7 wt.% V only and the curves are given in figure 5. As seen in figure 5, cyclic voltammetry curves shown at the top have reduction-oxidation peaks at 3.59 and 3.22 volts for 3 wt.% V (left) and at 3.59 and 3.20 volts for 7 wt.% V (right), respectively.

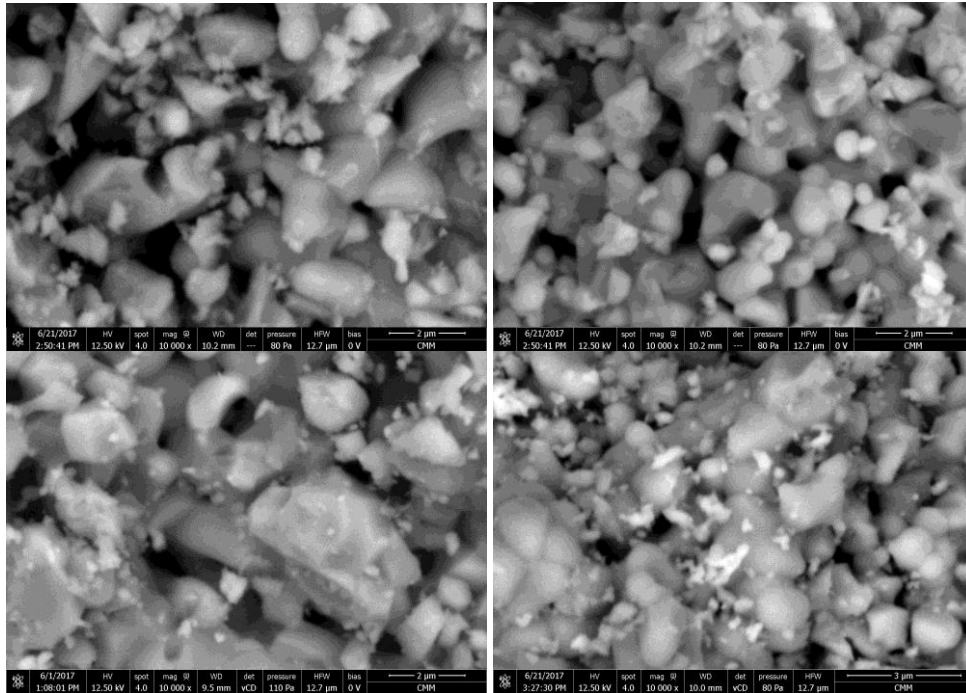


Figure 3. Secondary electron images of (a) 0 wt.%, (b) 3 wt.%, (c) 5 wt.%, and (d) 7 wt.% vanadium-doped LiFePO₄/C.

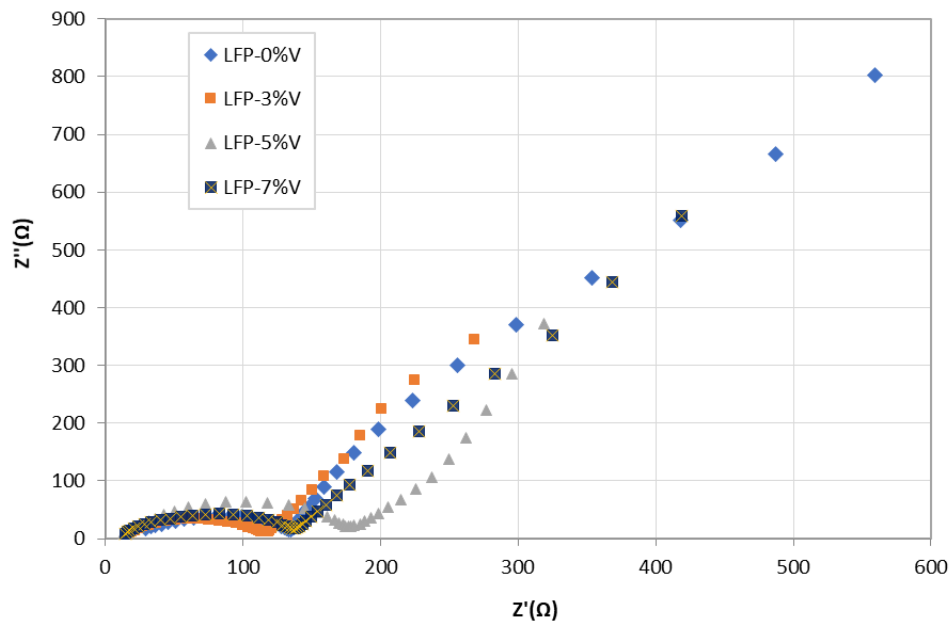


Figure 4. Nyquist plots for the LiFePO₄/C (blue diamond), 3 wt.% V (red square), 5 wt.% V (green triangle), and 7 wt.% V LiFePO₄/C (blue square).

The charge/discharge testing was performed at the potential range of 2.5–4.2 V at two capacities, i.e. 0.5C and 4C, and the curves are shown at the bottom in figure 5 for the LiFePO₄/V/C at 3 wt.% V (left) and 7 wt.% V (right). The initial charge and discharge capacities of both 3 wt.% V (left) and 7 wt.% V (right) at 0.5C are almost the same (8 mAh g⁻¹), however, the charge and discharge capacity of

7 wt.% V drops below 3 mAh g⁻¹ at 4C. It seems that, as has been mentioned previously, when the vanadium concentration is higher than 3 wt.%, the particles tend to agglomerate. This agglomeration results in more pores formation that decreases the conductivity and thus the performance.

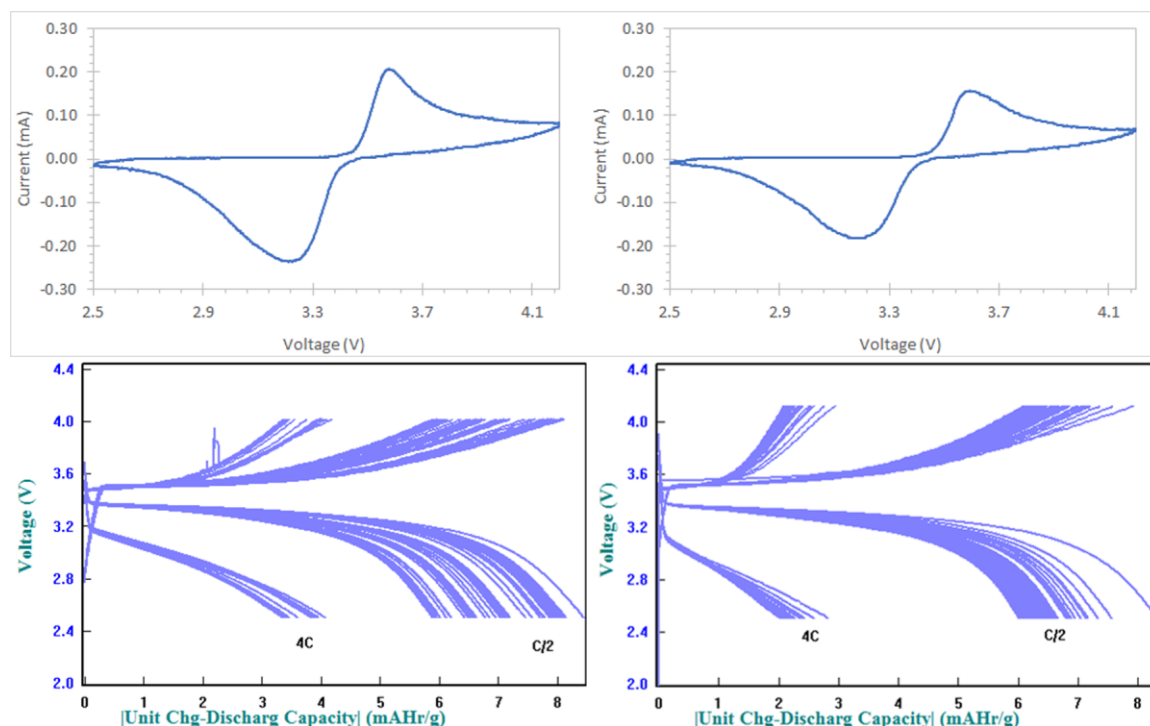


Figure 5. Cyclic voltammetry (top) and charge and discharge (bottom) testing for the LiFePO₄/V/C at 3 wt.% V (left) and 7 wt.% V (right).

4. Conclusion

In this work, a relatively high purity of LiFePO₄ has been obtained from the hydrothermally synthesis. The addition of activated carbon from the rice husk did not affect the purity of the LiFePO₄ particles. The electrochemical impedance spectroscopy test results showed that the conductivity of LiFePO₄/C-0 wt.% V is 1.0196×10^{-2} S/cm, LiFePO₄/C-3 wt.% V is 1.0302×10^{-2} S/cm, LiFePO₄/C-5 wt.% V is 6.1282×10^{-3} S/cm, and LiFePO₄/C-7 wt.% V is 8.3843×10^{-3} S/cm., respectively. These results indicate that the addition of carbon increases the conductivity whereas the vanadium addition also increase the conductivity but decreases at vanadium concentration >3 wt.%. The best performance was given by LiFePO₄/V/C at 3 wt.% vanadium.

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