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EFFECT OF CARBON COATING ON CATHODE ACTIVE MATERIAL OF $LiFe_{0.9}Ni_{0.1}PO_4$ FOR LITHIUM BATTERY

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ABSTRACT

The $LiFe_{0.9}Ni_{0.1}PO_4$ was developed from active cathode material $LiFePO_4$ for Lithium ion Battery. Ni doping was used to increase lithium ion diffusion. This active material of $LiFePO_4$ has low conductivity approximately 10^{-9} S/cm. By having carbon coated on the surface of $LiFe_{0.9}Ni_{0.1}PO_4$ powder, the conductivity characteristic is expected to increase. Cassava powders, tapioca, as carbon sources were mixed and milled for 3 days with ball mill method. The process varied on the weight ratio between tapioca and $LiFe_{0.9}Ni_{0.1}PO_4$, which were 1:4; 1:5 and 1:6. The next step in mixed millings product was heating with pyrolisis method at a temperature of 800 ^{0}C and under gaseous nitrogen flow. From the XRD analysis, it is shown that the coated carbon is in a form of amorphous phase. Atomic Ni was well detected by using mapping mix SEM. The coating of carbon of the sample with weight ratio of 1:5 had sufficient carbon on its surface and a conductivity of 4.4 10^{-3} S/cm.

Keywords: lithium battery, cathode material, $LiFePO_4$, carbon, pyrolisis, tapioca, conductivty.

INTRODUCTION

In 1997, $LiFePO_4$ was proven by Goodenough and co-workers as an excellent material for the cathode of a low-power rechargeable lithium batteries [1]. Later on, some of researchers and engineers used $LiFePO_4$ as a cathode materials for lithium-ion batteries. Several advantages on the use of this material are inexpensive, nontoxic, and environmentally benign [1]. The specific capacity obtained was 100 to 110 mAh/g [1]. Many researchers have been trying to increase the specific capacity of $LiFePO_4$ through doping technology. The doping materials are usually metal-transition elements such as Ni, Co, and Mn [2]. These doping materials usually do not destroy olivine-type phase of $LiFePO_4$ since their atoms only occupy the Fe sites [2]. One of the useful doping element to improve electrochemical performance of $LiFePO_4$ is Nickel. The product of Ni doped $LiFePO_4$/C can obtain a specific capacity approximately 137 mAh/g at 0.5 C rate [3]. If C means the capacity, then 0.5 C means the charging velocity that is used is a half of the capacity. At the high rate of 10 C and 15 C, Ni doped $LiFePO_4$/C (the composite of $LiFePO_4$ and carbon) can obtain 130 mAh/g of specific capacity [4].

In general, $LiFePO_4$ synthesis is usually carbon coated. There are many advantages by having carbon coating on $LiFePO_4$ synthesis. The carbon coating plays an important role in reducing particle size, inhibit the formation of undesired impurity phase, and promote the electrochemical performance [5,6]. The carbon coating can also increase the conductivity characteristics of $LiFePO_4$ [7].

A lot of carbon sources are available for carbon coating. Sources mostly used are well-known commercial carbon sources such as citric acid [8], graphite [9], and graphene [10]. In this research, tapioca powder is used as the carbon source. The tapioca powder was chosen because it is widely available in Indonesia. Therefore, reduces the need to import raw material for synthesizing $LiFePO_4$/C. This research combines the doping technology and carbon coating for $LiFePO_4$ synthesis. The doping material is Nickel with 10% added to occupy 10% Fe sites. In order to create synthesis of LiFe0.9Ni0.1PO4, the material doping is then combine with carbon coating from tapioca powder. The outcome is to measure both effects on the LiFe0.9Ni0.1PO4 conductivity.

METHODOLOGY

Materials

Technical grade $LiOH.H_2O$, Fe_2O_3, and H_3PO_4 were all purchased from China. Pure Ni from Merck was used as a doping material source. Tapioca powder is used as carbon source for carbon coating.

Materials synthesis

The 26.54 g $LiOH.H_2O$, 45.47 g Fe_2O_3, 3.71 g Ni, 61. 99 g H_3PO_4 were mixed and milled homogenously. The precursor were calcinated at 700 ^{o}C for about 2 hours flowed by inert gas. The calcinated precursor then sintered at 800 ^{o}C for about 8 hours flowed by inert gas. The sintered precursor then mixed with tapioca powder with different mass ratio. The variation of mass ratio between tapioca powder and sintered precursor were 1:4, 1:5, and 1:6. The three mixed samples then were milled using ball millers for about 3 days. The three mixed samples then were sintered again at 800 ^{o}C for about 2 hours.

Sample characterization

The three variation samples were then characterized using Rigaku SmartLab X-ray diffractometer (XRD) with 2 theta rate from 20o to 80o to determine the synthesized phases. If there is only $LiFePO_4$ phase, it is indicated that the precursor has been successfully synthesized. The three strongest lines d-spacing analysis by comparing the structure to the ICDD/PDF 4+ database was used to examine the $LiFePO_4$ structure.

Hitachi SU3500 Scanning Electron Microscope (SEM) with EDX added was used to detect carbon coating and elements distribution. EIS was used to determine sample conductivity values.

RESULTS AND DISCUSSION

There are three variation of the samples. Each sample has a difference in carbon added composition. The carbon source was tapioca powder from cassava. All the samples has been calcinated by 700 ºC temperature and sintered at 800 ºC. The mass compositions between tapioca powder and LiFe0.9Ni0.1PO4 precursor powder before final sintering are 1:4 for first sample, 1:5 for second sample, and 1:6 for third sample. These ratios of 1:4, 1:5, and 1:6, are used as the codes of the samples. Figure-1 shows the X-ray diffraction (XRD) pattern of the samples. LiFePO4 phase is the target of the synthesis. All the three samples consist of LiFePO4 phase. According to PDF4+ No. 01-078-7909 of ICDD database, LiFePO4 has three strongest lines values i.e. 2.51924 Å, 3.48061 Å, and 3.00342 Å. The XRD results must be compared with the ICDD standard. The three strongest lines values consist of three d-spacing values as the requirement values to indicate a phase. The tolerance are ± 0.01 Å for first d-spacing value and ± 0.02 for second and third d-spacing value. There are 2.5222 Å, 3.4879 Å, and 3.0061 Å d-spacing values at sample 1:4; 2.5212 Å, 3.4823 Å, and 3.0046 Å d-spacing values at sample 1:5; 2.5199 Å, 3.4837 Å, and 3.0046 Å at sample 1:6. It means that all the three samples consist of LiFePO4 phase. There is only LiFePO4 phase at sample 1:4 and 1:5. On the other hand, there is a trace in sample 1:6 that was indicated by 2.0518 Å, 1.19978 Å, and 1.4525 Å d-spacing values that were matched with PDF4+ No. 04-017-1577 of ICDD database as Fe phase which has 2.05061 Å, 1.18392 Å, and 1.45 Å d-spacing requirement values. Besides the main function for increasing conductivity of $LiFePO_4$, carbon coating has another function that is as a $LiFePO_4$ phase stabilizer during the sintering process. From the XRD analysis, only sample 1:6 that has a trace (Fe), it means that the mass composition between tapioca powder and LiFe0.9Ni0.1PO4 precursor at sample 1:6 is not recommended because the composition of tapioca powder as carbon source is not enough to stabilize $LiFePO_4$ phase. The next step of XRD analysis after finding phases is refining XRD pattern. The XRD pattern was refined by Rietveld method using Rigaku PDXL software. The reliability statistical parameters that indicated pattern convergence are chi2 and Rwp. Sample 1:4 shows chi2 = 1.0268 and Rwp = 5.83%, sample 1:5 shows chi2 = 1.0527 and Rwp = 8.09%, sample 1:6 shows chi2 = 1.0009 and Rwp = 7.69%. All the refinements of the samples shows that chi2 is almost 1 and Rwp value is below 10%. It is indicated that all the sample was convergent and reliable to be used. The quantitative analysis shows that sample 1:6 included 95.5 wt.% $LiFePO_4$ phase and 4.5 wt.% Fe phase. The target phase is LiFe0.9Ni0.1PO4. Since Ni only substituted 10% of Fe atom occupations, the basic phase is still $LiFePO_4$. From the three samples that were investigated, there were no Ni phase indicated. It can be stated that Ni succeeded to substitute Fe atom without changing $LiFePO_4$ basic crystal structure. The carbon phase was not indicated from all diffraction patterns. This means that the carbon from tapioca powder is amorphous. However, this finding cannot be confirmed through XRD analysis only. We have to compare with EDX analysis to make sure that there exist Ni and carbon, although there are no Ni and carbon phase from the XRD analysis. EDX analysis can be done using SEM.

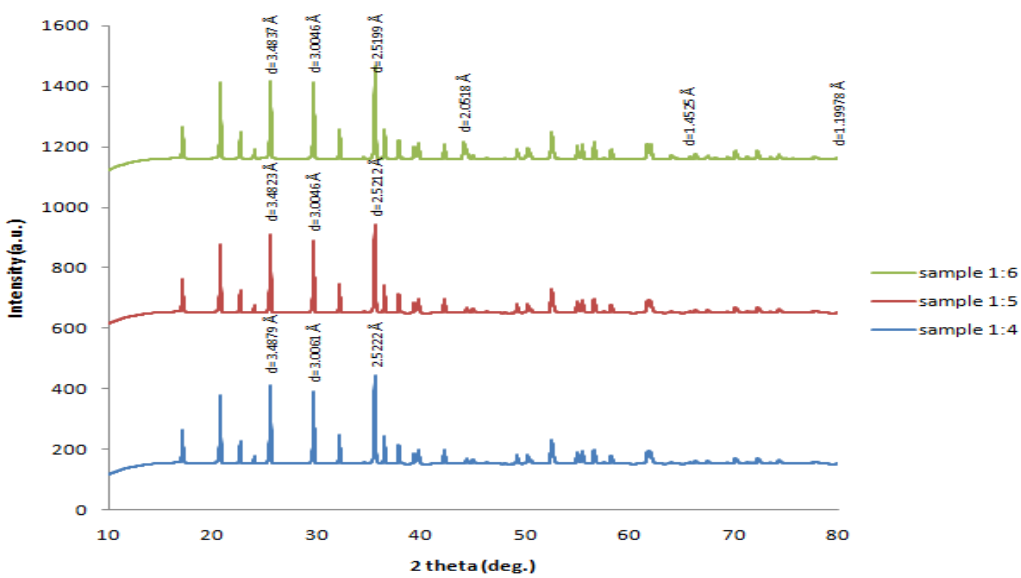


Figure-1. X-ray diffraction pattern of the samples.

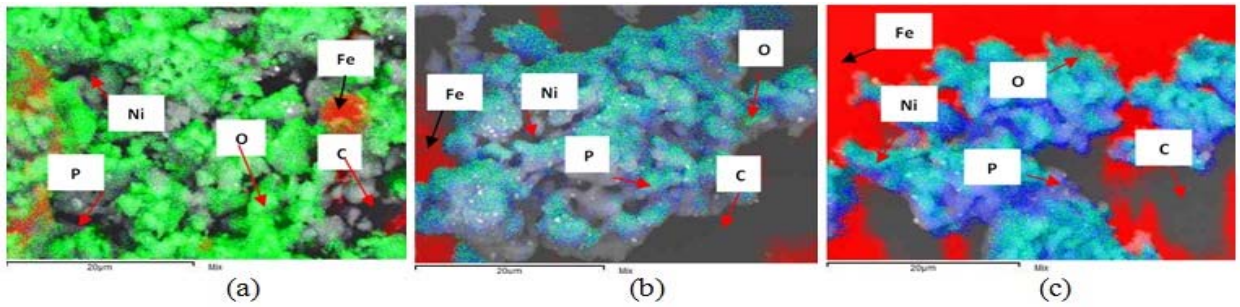
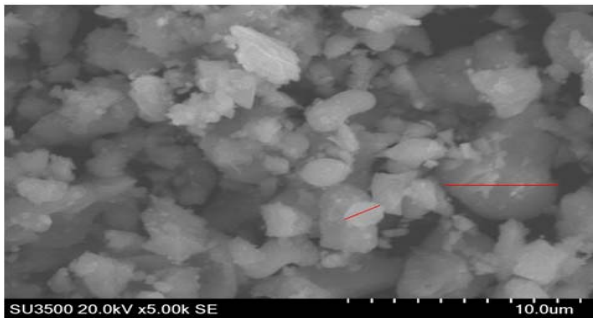


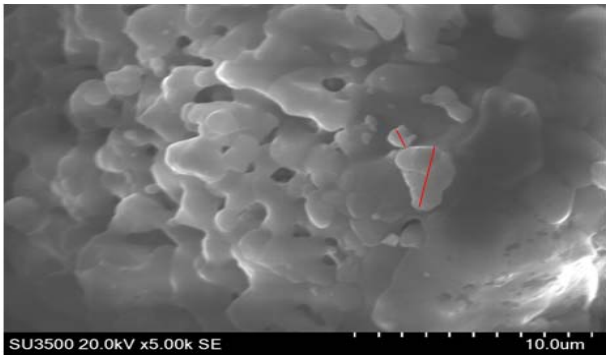
Figure-2. EDX mapping of the SEM images. (a) sample 1:4. (b) sample 1:5. (c) sample 1:6.

Figure-2 shows EDX mapping of the SEM images. Unfortunately, Li element cannot be detected by EDX and only Fe, P, O, Ni, and C that can be indicated by EDX. The EDX mapping of sample 1:4 shows Fe, Ni, P, O, and C elements. Meanwhile, using the XRD analysis of sample 1:4, the Fe, Ni, P, and O indicated LiFe0.9Ni0.1PO4 phase and C indicated amorphous carbon due to the tapioca source. The EDX mapping of sample 1:5 shows Fe, Ni, P, O, and C elements and comparing with XRD analysis; Fe, Ni, P, O tend to create a LiFe0.9Ni0.1PO4 phase and C indicate amorphous carbon from tapioca powder source. The EDX mapping of sample 1:6 shows Fe, Ni, P, O, and C indicated elements. Comparing with XRD analysis, some of the Fe tend to Fe phase, other Fe with Ni, P, O are parts of LiFe1-xNixPO4 phase. The x value of LiFe1-xNixPO4 is not 0.1 because there is Fe phase as a trace that reduce number of substitution and might be bigger than 0.1 since there are reduction occupation value of Fe less than 0.9. Same as with sample 1:4 and 1:5, the C indicated element has the tendency to create amorphous carbon given the tapioca powder source.

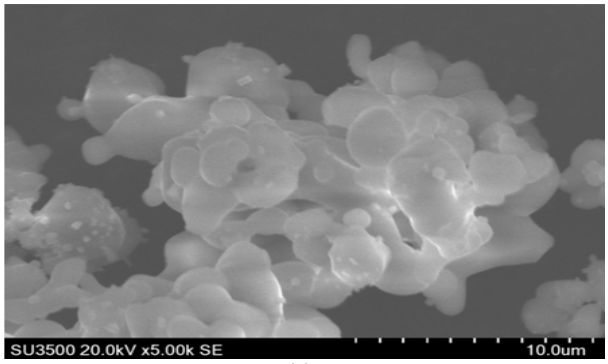
As shown in Figure-3, with the assumption that the SEM electron beam arrived at the sample vertically from the top, it can be stated that all the three samples indicated a growth of carbon coating in a vertical direction, during the sintering process. It was indicated by pores shown in the SEM images. If the carbon coating grows horizontally perpendicular with electron beam direction, there are no pores indicated. After confirming XRD analysis and SEM analysis, the analysis to determine sample conductivities and trace or impurity effect to the sample conductivity using EIS was done.



(a)

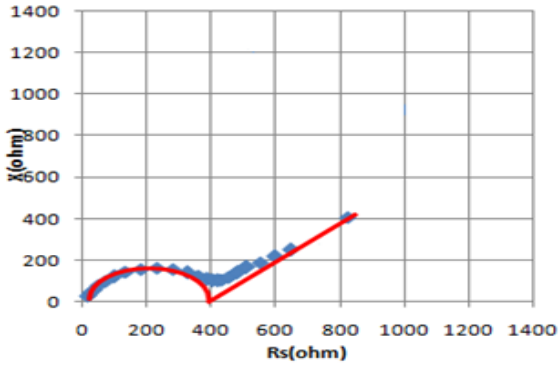


(b)

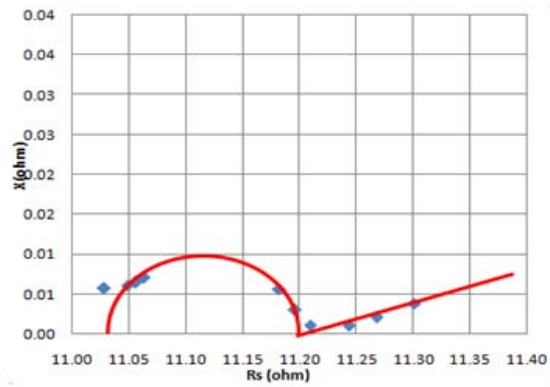


(c)

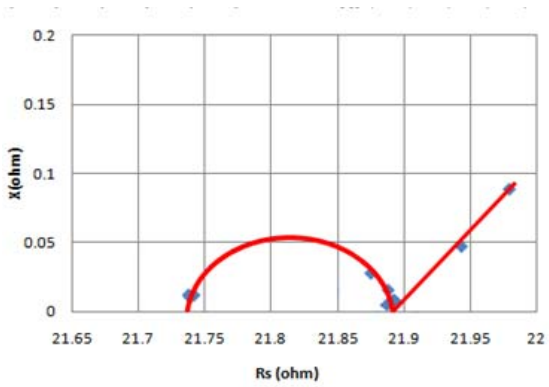
Figure-3. SEM images with 5000x magnification of the samples. (a) sample 1:4. (b) sample 1:5. (c) sample 1:6.



(a)



(b)



(c)

Figure-4. The EIS diagram of the three samples. (a) Sample 1:4. (b) Sample 1:5. (c) Sample 1:6.

Table-1. Conductivity test result of the samples.

Sample	σ (10^{-3} S/cm)
1 : 4	0.01
1 : 5	4.44
1 : 6	1.51

Figure-4 shows the EIS diagram. One half circle indicate one phase that effected the conductivity value. All the three samples showed that there are only one half circle. Sample 1:4 and 1:5 consist of only LiFe0.9Ni0.1PO4 phase and this was also indicated by only one half circle. As for sample 1:6, that consists of two phases i.e. LiFe1-xNixPO4 and Fe based on the XRD and EDX analysis, also has only one half circle in the EIS diagram. It is indicated that 4.5 wt.% Fe does not effect to the sample conductivity. If the trace or impurity effected the samples conductivity, then there will be more than one half circle indicated in the EIS diagram. The conductivity of the samples are shown in Table-1 with sample 1:5 having the most optimum conductivity.

CONCLUSIONS

Carbon coating creates effect to the conductivity value of LiFe0.9Ni0.1PO4. The optimum mass composition between tapioca powder as the carbon source and LiFe0.9Ni0.1PO4 precursor 1:5 with an optimum conductivity of 4.44 x 10-3is S/cm. This composition enable the carbon coating to increase the conductivity value of LiFe0.9Ni0.1PO4.

Carbon coating also has an effect to the LiFe0.9Ni0.1PO4 synthesis process. Carbon coating can inhibit the undesired impurity phase. There is undesired Fe phase at sample 1:6 and less carbon composition without producing undesired phase in sample 1:5. It can concluded that the optimum mass composition between tapioca powder as carbon source and LiFe0.9Ni0.1PO4 precursor to prevent undesired phase is in the ratio of 1:5.

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