Journal of Physics: Theories and Applications E-ISSN: 2549-7324 / P-ISSN: 2549-7316
J. Phys.: Theor. Appl. Vol. 5 No. 1 (2021) 37-43 doi: 10.20961/jphystheor-appl.v5i1.51855

Oxidation state analysis of $LiFeSi_xP_{1-x}O_4/C$ (x = 0.06) with X-ray absorption near edge structure (XANES) in Fe K-edge and Si K-edge

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Received 10 February 2021, Revised 26 March 2021, Published 30 March 2021

Abstract: The development of $LiFePO_4$ as a cathode materials on lithium-ion battery was increased with the use of additional techniques such as atomic doping and coating. The material used in this report was $LiFeSi_{0.06}P_{0.94}O_4/C$ (LFP Si-6%), synthesized with doping silicon 6% and 11wt% carbon coating by a solid state method. X-ray Absorption Spectroscopy (XAS) characterization was used to investigate the effect on electronic and atomic structure of LFP Si-6%, especially in X-ray Absorption Near Edge Strucuture (XANES) region. XANES data measured on Fe K-edge and Si K-edge. Fe foil, FeO, Fe_2O_3, $FePO_4$, Si powder, SiO, SiO_2 were used as a standard sample for comparison with the result of LFP Si-6%. XANES analysis showed that the energy absorption of Fe K-edge and Si K-edge in LFP Si-6% was 7124.94 eV and 1846.16 eV, respectively. The oxidation state of Fe was $Fe^{2.576+}$ between Fe^{2+} and Fe^{3+}, while Si was close to the estimation of Si^{4+}. In addition, the linear combination fitting (LCF) in XANES Fe K-edge was performed to show the ratio of Fe^{2+}/Fe^{3+} (FeO/Fe_2O_3).

Keyword : Fe K-edge, LFP Si-6%, Oxidation state, Si K-edge, XANES.

1. Introduction

$LiFePO_4$ material has been developed in many studies to investigate the electrochemical performance as a cathode material. Some techniques were used to improve the structural characteristic and electrochemical performance such as carbon coating, particle size reducing and atomic doping (Zainuri et al., 2020; Norouzi Banis et al., 2019; Chiang et.al., 2012; and Zhao et al., 2017). Atomic doping silicon in $LiFeSi_xP_{1-x}O_4/C$ possibly affect the Li^+ ion transport in cathode material (Zainuri et al., 2020). Furthermore, charge/discharge measurement also showed the enhancement of spesific capacity with increasing of Si composition (Zhao et al., 2017). Carbon coating in $LiFePO_4$

also showed that electrochemical performance has enhanced at initial charge/discharged capacities and efficiency. To investigate the structural characteristic of $LiFePO_4$ material, some measurements have been used previously, for instance X-ray Diffraction characterization (Zainuri et al., 2020). But in some cases, especially in atomic doping material, XRD can not explain more detail about doping phenomenon. Previous study used X-ray Absorption Spectroscopy (XAS) characterization to support the analysis in atomic doping in $LiFePO_4$ material which can determine the oxidation state (Norouzi Banis et al., 2019).

Banis et al used XAS characterization to determine the nature of Si doped $LiFePO_4$ to the P site sample and identifying impurity phases. X-ray Absorption Near Edge Structure (XANES) analysis showed the comparison spectrum of sampel $LiFePO_4$ with Si doped and SiO_2 sample standard. The result showed that Si atom primarily exists and aligned well with the standard spectrum (Norouzi Banis et al., 2019). Latif et al investigated the XANES spectrum in $LiFePO_4$ in Fe K-edge that showed pre-edge and edge regions to determine oxidation state of Fe from the energy absorption range (Latif et al., 2018). The absorption edge energy (E_0) is used to determine the oxidation state and can be seen clearly using the first derivative of normalized absorption (Chiang et.al., 2012). XANES analysis in $LiFePO_4$ with Cu doping is performed by comparing the spectrum of samples with those of standard-iron oxide (FeO, Fe_2O_3 and Fe_3O_4) and can be used to determine the oxidation state in Fe K-edge due to atomic doping (Cu in Fe) (Muyasaroh et al., 2019). Fitriana et al used interpolation linear technique to estimate the oxidation state of Fe (Fitriana et al., 2020). Husain et al measured XAS characterization in XANES Fe K-edge and analyzed it using linear combination fitting (LCF) to get a ratio of multivalent Fe atom (Husain et al., 2020). Based on all previous studies, XANES spectrum analysis can be used to determine the energy absorption and oxidation state of atom.

In this study, we performed XAS characterization in Fe K-edge and Si K-edge to investigate XANES spectrum in $LiFeSi_xP_{1-x}O_4/C$ with doping silicon (x=0.06) and coating carbon 11 wt%. XAS characterization using two atomic absorber such as Fe K-edge and Si K-edge. XANES data used to investigate the energy absorption (E_0) and oxidation state (OS) of Fe and Si atoms. Furthermore, the oxidation state of Fe in can be calculated using interpolation linear technique. XANES data in Fe K-edge also used linear combination fitting (LCF) to explain the composition of multivalent atom Fe^{2+}/Fe^{3+}. In addition, Transmisson Electron Microscopy (TEM) is also reported to complete the SEM analysis that was studied previously (Zainuri et al., 2020).

2. Experiment

The $LiFePO_4$ material was prepared using a solid state method. $LiFeSi_xP_{1-x}O_4/C$ was synthesized in two processes. Firstly, material was synthesized by doping Si (x=0.06) to form $LiFeSi_{0.06}P_{0.94}O_4$ and then was coated with carbon 11 wt% to form $LiFeSi_{0.06}P_{0.94}O_4/C$ (LFP Si-6%) powder. Li_2O_3, Fe_2O_3, $(NH_4)_2HPO_4$ and SiO_2 were used as precursor of LFP Si-6%, while $C_6H_{12}O_6$ (glucose) was used as carbon source for coating process. Ball-milled process performed at 150 rpm for 10 hours after mixed all of precursor $LiFeSi_{0.06}P_{0.94}O_4$. Carboration process carried out at 450^0C for 2 hours under nitrogen atmosphere to form LFP Si-6% powder. The detail information of stoichiometric material and detail synthesis process can be referred in (Zainuri et al., 2020).

X-ray Absorption Spectroscopy (XAS) was performed at beam line 8 SLRI (Syncrotron Light Research Institute), Thailand (Klysubun et al., 2020). XAS measurement is used to investigate the XANES (X-ray Absorption Near Edge Structure) spectrum of LFP Si-6%. We performed XANES in 2 absorber atoms which was Fe K-edge using transmission mode and Si K-edge using fluorescence mode. XANES spectrum was analyzed by using Athena software (Ravel and Newville, 2005). XANES analysis used to determine the absorption energy and oxidation state. Oxidation state of Fe atom was calculated with linear interpolation techique (Fitriana et al, 2020). In addition, Transmission Electron Spectroscopy (TEM) used to determine the morphology of LFP Si-6% powder. TEM was performed at Laboratorium Mikroskop Elektron, Institut Teknologi Bandung (ITB) using HR TEM H9500.

3. Result and Discussion

Figure 1 shows LFP Si-6% spectrum compared with standard sample of Fe atom (Fe foil, FeO, Fe_2O_3 and $FePO_4$) which displays pre-edge and absorption edge region. Pre-edge describes a transition electronic Fe from 1s-state to 3d-state and absorption edge that shows an increasing line which corresponds to transition electronic Fe from 1s-state to 4s-state (Haas et al., 2005). Energy absorption (E_0) of Fe atom in LFP Si-6% is 7124.94 eV and has a good agreement with the previous study that observed in the range of 7121.7-7126.0 eV (Julien et al., 2012). The XANES spectrum show that LFP Si-6% is in energy range between FeO and Fe_2O_3 indicated in Fig.1.

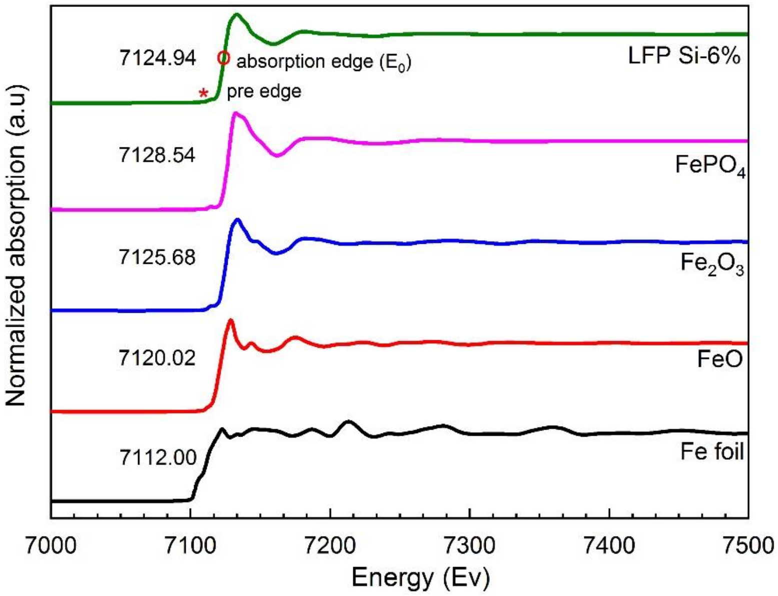


Figure 1. XANES spectrum of LFP Si-6% compare with standard sample after normalizing energy in Fe K-edge.

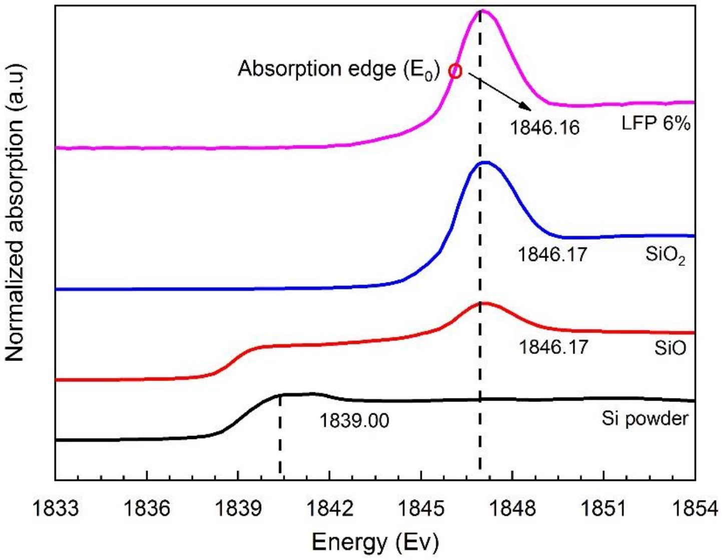


Figure 2. XANES spectrum of LFP Si-6% compare with standard sample after normalizing energy in Si K-edge.

Figure 2 shows the XANES Si K-edge spectrum compared with standard sample of Si atom (Si powder, SiO and SiO_2) with different peak position and intensity. Si powder has the lowest absorption energy in 1839.00 eV while SiO in 1846.17 eV, and SiO_2 in 1846.17 eV. Absorption energy (E_0) of Si atom in LFP Si-6% is 1846.16 eV that appropiate with previous study (Norouzi Banis et al., 2019). It was found from our result that SiO_2 and LFP Si-6% have almost the same XANES spectrum and absorption energy. Strong peak in Si K-edge associated with a transition electronic of Si atom from 1s-state to 3p-state and similar spectrum with SiO_2 standard at around 1847 eV showed that oxidation state is Si^{4+} (Norouzi Banis et al., 2019). In our study, LFP Si-6% spectrum has one strong peak that more similar to SiO_2 standard than the other standard spectrum. It also has a good agreement with the starting materials since SiO_2 was used as a source of Si in this study. Hence, the oxidation state of Si in LFP Si-6% is estimated to be Si^{4+}.

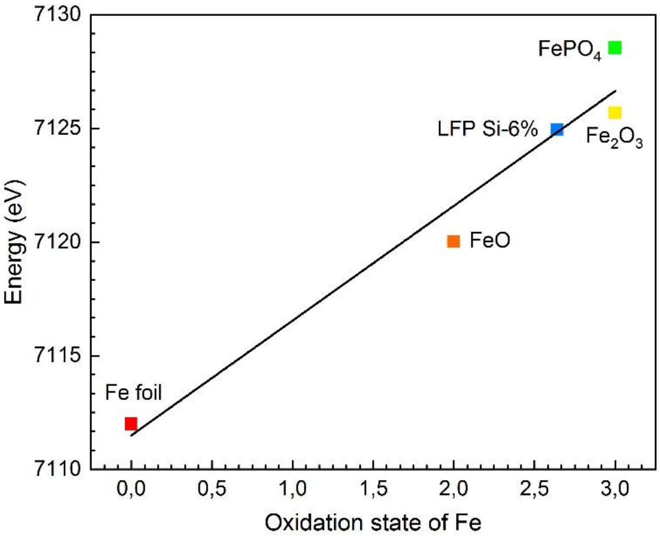


Figure 3. The oxidation state of LFP Si-6% compare with standard sampel Fe K-edge (Fe foil, FeO, Fe_2O_3 and $FePO_4$).

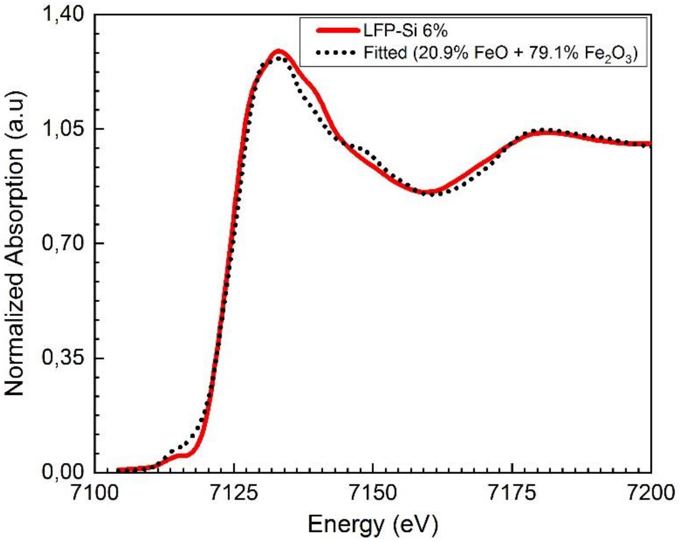
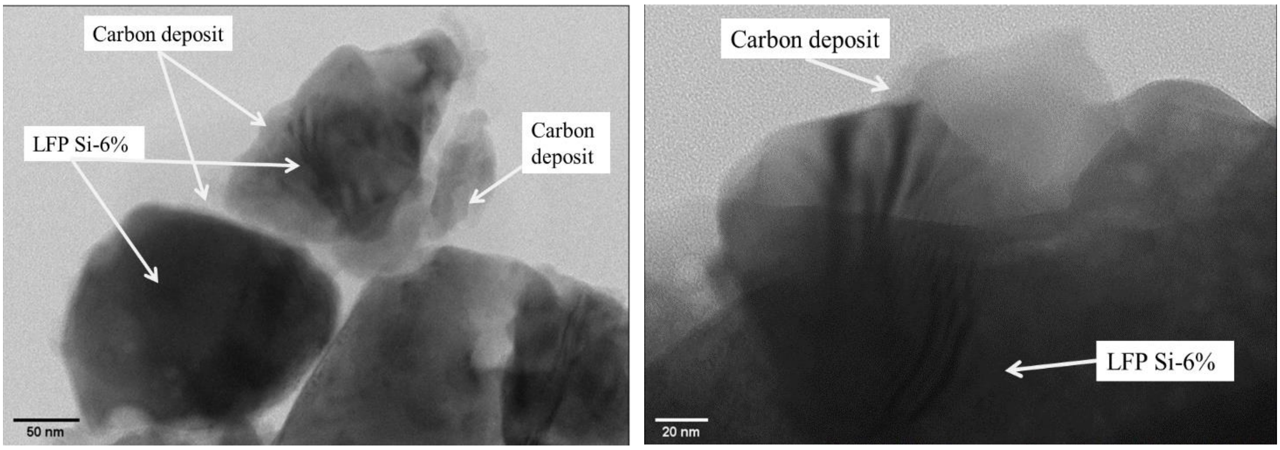


Figure 4. Linear combination fitting (LCF) of LFP Si-6% in FeO and Fe_2O_3.

Figure 3 shows the oxidation state of Fe atom in LFP Si-6% and standard samples. The result of Fe oxidation state in LFP Si-6% was compared with standard sample (Fe foil (Fe^0), FeO (Fe^{2+}), Fe_2O_3 (Fe^{3+}) and $FePO_4$ (Fe^{3+})). From the calculation using linear interpolation technique, oxidation state of Fe atom in LFP Si-6% was estimated in $Fe^{2.576+}$. Oxidation state of Fe also indicated the mixing of multivalent atom Fe^{2+} and Fe^{3+}. Oxidation state of Fe in LFP Si-6% is in range of oxidation state of FeO and Fe_2O_3 showed in Fig.3. Fe atom in Fe_2O_3 has a higher energy and oxidation state than FeO.

The linear combination fitting (LCF) used to determine the ratio composition Fe^{2+}/Fe^{3+} (Muyasaroh et al., 2019) [6]. LCF of LFP Si-6% sample is shown in Fig 4. LCF analysis was performed using normalized absorption energy in Fe K-edge from XANES data (see Fig. 1) and used energy range from -20 to 80 eV, when the XANES energy range of Fe K-edge is in the range of 7100-7200 eV. This fitting used FeO and Fe_2O_3 as standard sample because LFP Si-6% has similar characteristic with FeO and Fe_2O_3 with the best fitting result. The result showed that ratio of FeO:Fe_2O_3 is 20.9%:79.1%. It shows that the composition of Fe_2O_3 (Fe^{3+}) is higher than FeO (Fe^{2+}). This result also proved the calculation of oxidation state Fe in this study was $Fe^{2.576+}$ (larger than Fe^{2+}).

Transmission Electron Microscopy (TEM) images are shown in Fig. 5 (a) and 5(b) with different magnification. TEM images show the morphology which indicated that the LFP Si-6% powders are not homogeneous, it might be caused by a mixed system indicated by the presence of more than one phase. It corresponds to the presence of mixed oxidation state from Fe^{2+} and Fe^{3+}. The LFP Si-6% indicated the presence of two coexisting phase such as olivine and nasicon that has been reported previously (Zainuri et al., 2020). Fig. 5(a) and 5(b) also show morphology of LFP Si-6% which have different brightness. It can be assumed that carbon coating was deposited surrounding the LFP Si-6% material with greyish region, while the LFP Si-6% was in a darker region. This is appropriate with previous study that used carbon coating on $LiFePO_4$ material (Julien et al., 2012).



(a) (b)

Figure 5. TEM images of LFP Si-6% powder with different magnification (a) 377,000x; (b) 753,000x.

4. Summary

$LiFeSi_xP_{1-x}O_4/C$ (x = 0.06) was characterized using XAS in Fe K-edge and Si K-edge. XANES spectrum of normalized absorption showed in Fe K-edge and Si K-edge were compared with standard samples. Oxidation state of Fe indicated the electronic structure of LFP Si-6% was $Fe^{2.576+}$. Oxidation state of Si was close to the estimation of Si^{4+}. Linear combination fitting (LCF) in Fe K-edge showed the best fitting that LFP Si-6% was mixed between Fe^{2+} (FeO) and Fe^{3+} (Fe_2O_3). Ratio composition FeO:Fe_2O_3 was 20.9%:79.1%, indicated that the composition of LFP Si-6% has more dominant Fe^{3+}. In addition, TEM image confirmed that LFP Si-6% has been coated with carbon from the presence of grayish region surronding the LFP Si-6% material.

Acknowledgement

This work was supported by Dana Lokal ITS Penelitian Doktor Baru No.:855/PKS/ITS/2020. The authors would like to thank Lembaga Ilmu Pengetahuan Indonesia (LIPI) at Serpong Tangerang and the staff at beamline 8 (BL-8), Syncrotron Light Research Institute (SLRI), Thailand for support during XAS data collection.

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