X-ray Absorption Near Edge Structure (XANES) Spectrum Interpretation for LiFePO₄-Silicon Doped Cathode Material

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ABSTRACT

LiFePO₄-Silicon doped has been widely developed as a battery cathode material. Due to the doping of silicon atoms, this study aims to determine the peak energy (E_0), oxidation state and percentage of component composition for Fe K-edge. The experimental sample used are LFP Si-0%, LFP Si-1%, LFP Si-3% and LFP Si-6%. These samples were characterized using XAS (X-ray Absorption Spectroscopy). XANES spectrum showed the peak energy of Pre-edge area is 7113.08 – 7114.49 eV. The oxidation state of Fe atoms was increased and tend to be Fe^{3+} than Fe^{2+}. Moreover, Linear Combination Fitting (LCF) used to determine the ratio composition FeO/Fe_2O_3 in experimental samples. The ratio composition indicated Fe atom is multivalent, when the percentage of silicon-doped increases, the ratio of Fe^{3+} increased. It was found that the presence of silicon atoms in the LiFePO₄ structure has an effect in electronic structure.

I.   INTRODUCTION

LiFePO4 is a cathode material of lithium ion battery that has been widely developed with some special techniques, such as atomic doping (Banis *et al.*, 2018; Zainuri *et al.*, 2020; Liu *et al.*, 2020) and carbon coating (Zhao *et al.*, 2016; Wang *et al.*, 2021). X-Ray Absorption Spectroscopy (XAS) characterization was use to show the local electronic and atomic structure of material. XAS could provide good spectra of the impurities and doping elements in doped LiFePO4 material. However XAS has a chemical and an elemental sensitivity, that was required to determine the nature of doping elements in the LiFePO4 lattice and to identify possible impurities during the synthesis process (Banis *et al.*, 2018). X-ray Absorption Near Edge Structure (XANES) is one of characteristic that obtained from XAS. XANES data was used to get more detailed structural analysis and was analyzed to determine the information of the absorbing atom and its local environment. Furthermore, the pre-edge and main edge of the XANES spectra were analyzed qualitatively using ATHENA software (Husain *et al.*, 2020;Intifadhah *et al.*, 2021; Maghfirohtuzzoimah *et al.*, 2021;Astuti *et al.*, 2021). XANES data was performed to determine the absorption energy, oxidation number conditions and the ratio of oxidation composition (Husain *et al.*, 2020). From our previous study, the resulting data was performed in a normalized XANES spectrum that showing the relationship between the absorption coefficient (μE) and the absorption energy (eV), as shown in Figure 1 (Astuti *et al.*, 2021). The XANES spectrum is used for qualitative comparisons which are performed by overlaying or stacking the spectrum (Kelly, 2008).
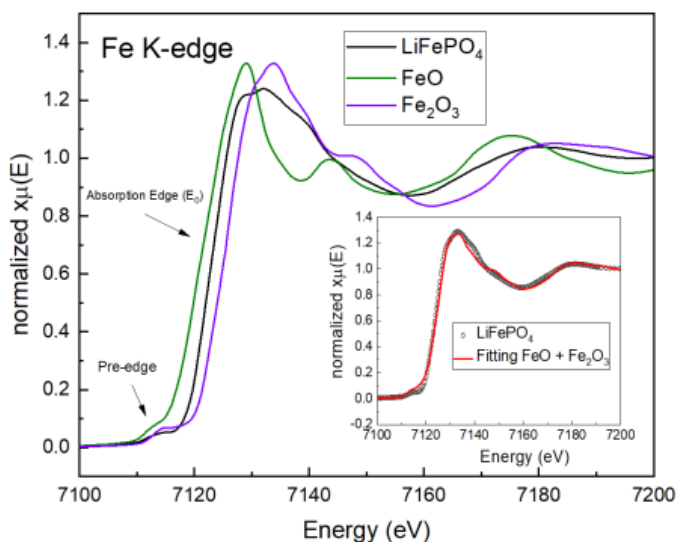

Figure 1 Fe k-edge XANES spectra of LiFePO4

For further analysis on the XANES data, Linear Combination Fitting (LCF) method was used to determine the ratio composition of oxidation state Fe^{2+} and Fe^{3+}. Linear Combination Fitting is a visual comparison technique of standard sample spectra and experimental sample spectra that can provide a representation of the chemical state of the sample (Kelly, 2008). LCF method was carried out to determine the oxidation composition of atoms which tend to be multivalent as shown in recent study, LCF method was used in nanoparticle magnetite material to investigate the ratio composition of oxidation state Fe^{3+}/Fe^{2+} for (Fe_2O_3/FeO) standard sample (Husain *et al.*, 2020). Multivalent atoms are atoms that have two or more valence states(Haas *et al.*, 2005).

This study focus on Fe K-edge which uses Fe as atom absorber from LiFePO4-silicon doped materials. Moreover, this study also focus on XANES spectrum analysis especially in peak energy of Pre-edge area, oxidation state of Fe atom and Linear Combination Fitting (LCF) method for LFP Si-0%, LFP Si-1%, LFP Si-3% and LFP Si-6%.

II.   METHOD

2.1   Material

LiFePO₄-silicon doped has a formula as $LiFeSi_xP_{1-x}O_4/C$ where a silicon atom was doped into a phosphate atom and carbon was used for coating. LiFePO₄-silicon doped or LFP-Si material was synthesized using the solid state method with additional techniques, such as doping of silicon (Si) atoms and coating of carbon. The variations of silicon atom doping were Si-0%, Si-1%, Si-3% and Si-6%. The basic materials used in the synthesis process are Li_2CO_4 powder (merck), Fe_2O_3 (technical), $(NH_4)_2HPO_4$, SiO_2 (merck) and $C_6H_{12}O_6$ (glucose). The final experimental samples were LFP Si-0%, LFP Si-1%, LFP Si-3% and LFP Si-6%. The details of experimental process can be referred in previous study (Zainuri *et al.*, 2020).

2.2   Characterization

XANES Fe K-edge data was obtained from XAS (*X-ray Absorption Spectroscopy*) characterization. XAS characterization was carried out at beamline 8 SLRI (Syncrotron Light Research Institute) in Thailand. Measurement was using an energy range of 1 - 13 keV (Klysubun *et al.*, 2021). This study was using Fe atom as absorber (Fe K-edge) from LFP Si-1%, LFP Si-3% and LFP Si-6%. and was using XAS transmission mode. FeO, Fe_2O_3 and $FePO_4$ were use for standard sample to comparison. Furthermore, XANES data were analyzed and fitted using *Athena* software (Intifadhah *et al.*, 2021; Muyasaroh *et al.*, 2019;Maghfirohtuzzoimah *et al.*, 2021).

III.   RESULTS AND DISCUSSION

The normalized XANES spectrum for the Fe atom is shown that there are two peak energy areas, absorption edge area and pre-edge area(Astuti *et al.*, 2021). Both of these areas show the XANES spectrum characteristics of absorber atom, which is Fe atom in this study. In previous study, the spectrum and peak energy value (E₀) of the Fe atom in the $LiFeSi_xP_{1-x}O_4/C$ material for absorption edge area were 7124 – 7125 eV (Maghfirohtuzzoimah *et al.*, 2021; Astuti *et al.*, 2021), while the spectrum of the Fe K-edge in Pre-edge area for standard sample and experimental sample is shown in Figure 2.

Figure 2 shows the Pre-edge spectrum of Fe K-edge that was obtained using normalized Gaussian Function, which is available on the fitting analysis features in *Athena* software. The spectrum consists of the experimental sample (black line), peak fitting (dot line), error function (blue line) and
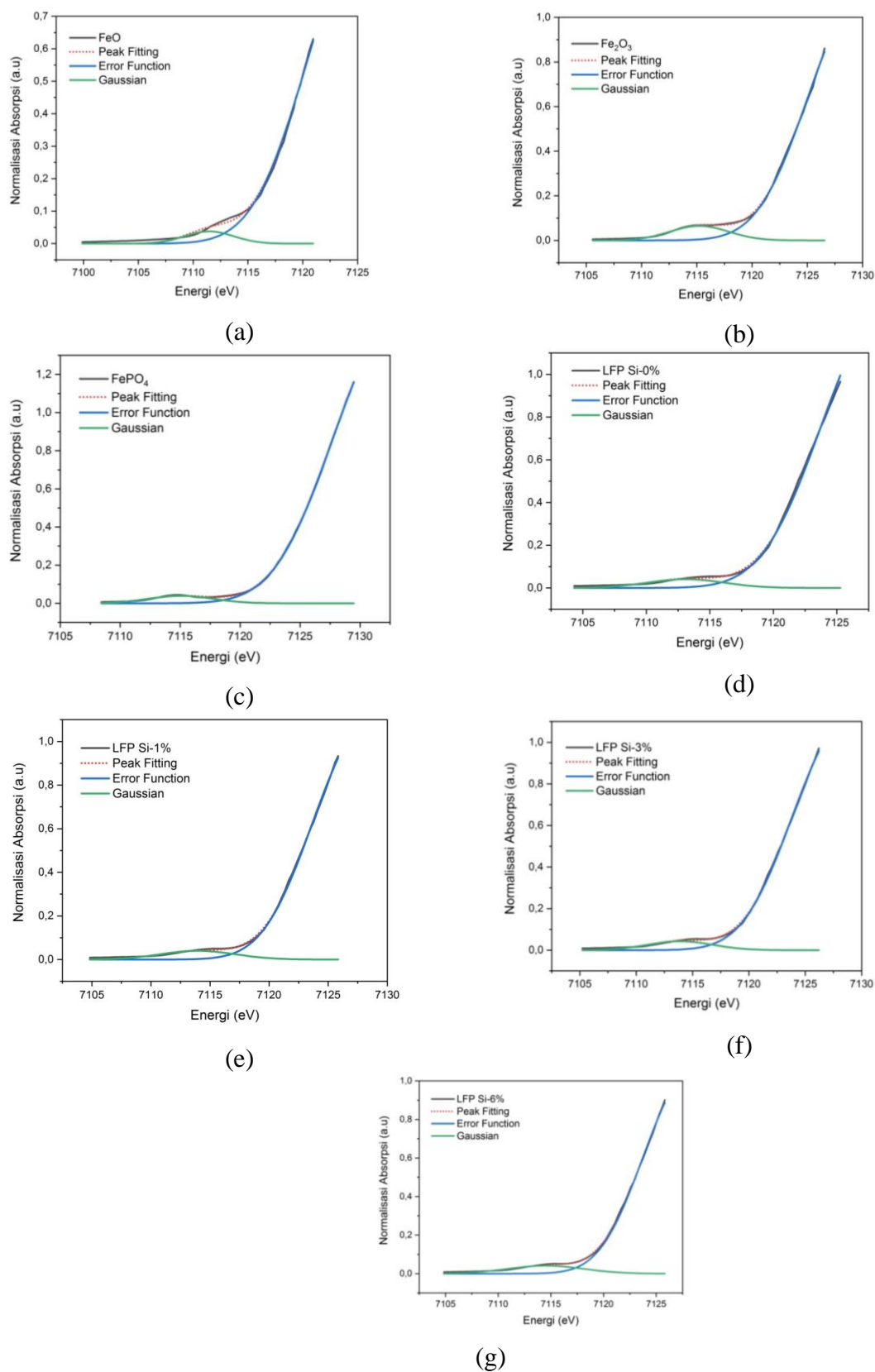
Figure 2 XANES Pre-edge spectrum of Fe K-edge using Gaussian function fitted on standard samples (a) FeO; (b) Fe2O3; (c) FePO4; and experimental samples (d) LFP Si-0%; (e) LFP Si-1%; (f) LFP Si-3%; (g) LFP Si-6%.

Gaussian spectrum (green line). The gaussian spectrum is used to bring out the energy peaks in the pre-edge area. Pre-edge area describes an electronic transition of Fe atom from 1s-state to 3d state (Astuti *et al.*, 2021) when the XAS characterization process occurs on the Fe atom. The peak energy (E$_0$) in the absorption edge and pre-edge regions have different energy ranges as previously mentioned. Comparison of Pre-edge peak energy values (E$_0$) and oxidation state are shown in Table 1.

Table 1 Peak energy (E$_0$) in the pre-edge area of Fe K-edge from standard samples and experimental samples.

Sample	E$_0$ (*eV*)	Oxidation State
FeO	7111.46	2
Fe$_2$O$_3$	7115.30	3
FePO$_4$	7115.05	3
LFP Si-0%	7113.08	2.31
LFP Si-1%	7113.96	2.55
LFP Si-3%	7113.89	2.53
LFP Si-6%	7114.49	2.70

The range of peak energy (E0) in Pre-edge area is 7111.46 – 7115.05 eV for standard samples and 7113.08 – 7114.49 eV for experimental samples (LiFePO$_4$ - silicon doped). Peak energy of LFP Si-1%, LFP Si-3% and LFP Si-6% are still in the standard energy range of Fe K-edge. Furthermore, for oxidation state analysis was used linear interpolation technique to calculate the value of oxidation state Fe atom(Fitriana *et al.*, 2020) . The linear interpolation technique was carried out using data on peak energy values (E$_0$) and theoretical oxidation state from standard samples (FeO, Fe$_2$O$_3$ and FePO$_4$). The data will be used to generate linear interpolation's equation that obtained from Microsoft Excel program. The linear interpolation equation is shown in equation 1.

$$y = 0.2716x - 1929.6 \tag{1}$$

where (*x*) is peak energy value (*E$_0$*) and (*y*) is oxidation state.

It was already known that the Fe atom has a multivalent atom from Fe^{2+} and Fe^{3+}. The calculation result that using equation 1, experimental samples LFP Si-1%, LFP Si-3% and LFP Si-6% show the enhancement in their oxidation state with increasing percentage of silicon atoms. So it was found that the doping of silicon atoms in the LiFePO$_4$ structure showed the influence in the electronic structure especially in peak energy (E$_0$) and oxidation state. The oxidation state of all experimental samples tend to be Fe^{3+} than Fe^{2+}. This might because during the synthesis of the LiFePO$_4$-silicon doped material, the basic material used as Fe precursor is Fe$_2$O$_3$ which is in theory has Fe^{3+} (Azzahra, 2019). Moreover, in previous study, the peak energy of Pre-edge area of the Fe atom (Fe K-edge) is about 7114 eV. This result corresponds to the phase identification with XRD, that the iron stone sample contains dominant Fe^{3+} ions from Fe$_3$O$_4$ and Fe$_2$O$_3$ (Latif *et al.*, 2018).

The next worth analysis is the ratio composition of the oxidation state Fe atoms using the Linear Combination Fitting method. Linear Combination Fitting (LCF) method analysis was using *Athena* software with normalized XANES spectra. LCF method allows for the determination of a compound composition and useful when two compounds construct a different structure (Husain *et al.*, 2020). In this research LCF analysis was carried out on experimental samples of LFP Si-0%, LFP Si-1%, LFP Si-3% and LFP Si-6% using 2 standard samples, FeO and Fe$_2$O$_3$ which represent the oxidation states of Fe^{2+} and Fe^{3+}. The energy range in LCF was used for -20 eV to 80 eV from normalized XANES spectrum. The results of fitting analysis of the XANES Fe K-edge spectrum with the LCF method are shown in Table 2.

Table 2 The linear combination fitting parameters from experimental samples

Experimental Sample	Atomic Standard Percentage		R-factor	Ratio Fe^{2+}/Fe^{3+}
	FeO	Fe_2O_3		
LFP Si-0%	$0,450 \pm 0,011$	$0,550 \pm 0,011$	0,008	45,0/55,0
LFP Si-1%	$0,267 \pm 0,009$	$0,733 \pm 0,009$	0,005	26,7/73,7
LFP Si-3%	$0,261 \pm 0,008$	$0,739 \pm 0,008$	0,004	26,1/73,9
LFP Si-6%	$0,209 \pm 0,008$	$0,791 \pm 0,008$	0,004	20,6/79,1

The result of LCF method was shows in Table 2. The reliability factor (R-factor) is a parameter that indicated the LCF fitting route is acceptable(Husain *et al.*, 2020). R-factor parameters are obtained in a good value while the requirements value is in the range of 0.02-0.003 (Cholsuk, 2019). The atomic standard percentage parameter indicates a change in the percentage of FeO and Fe_2O_3 in each experimental sample. It has been found that the ration compositions of Fe_2O_3 for Fe^{3+} were increase and the compositions of FeO for Fe^{2+} were decrease, while the silicon percentage is increasing. This is also has a good agreement with the interpolation calculations that was discussed before, Fe atoms in the experimental samples have multivalent atoms. Moreover, the tendency of experimental samples (LFP Si-0%, LFP Si-1%, LFP Si-3% and LFP Si-6%) to have an oxidation state of Fe^{3+} could be due to the fact that the basic material's synthesize in this study is used Fe_2O_3 for Fe precursor in LiFePO₄ – Silicon doped.

IV.   CONCLUSION

LiFePO₄-Silicon doped materials have been analyzed with XANES spectrum especially in the Pre-edge area. Peak energy (E_0) of experimental samples were in the range 7113.08 – 7114.49 eV which shows a slight change with the increasing the percentage of silicon atoms. Oxidation state of Fe atom was tend to be Fe^{3+} than Fe^{2+} which is showed from the linear interpolation's calculation. One of the change's factors in peak energy and oxidation state of Fe atoms might be caused by the presence of silicon atoms in the LiFePO₄ structure. Furthermore, the result LCF analysis was obtained that all of experimental samples have a larger oxidation state composition of Fe^{3+} than Fe^{2+}. From this study, it has been found that the presence of silicon atoms in the LiFePO₄ structure has an effect in electronic structure.

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