An Insight into Crystal, Electronic, and Local Structures of Lithium Iron Silicate (Li$_2$FeSiO$_4$) Cathode for Li-ion Batteries

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Abstract Recently, orthosilicate, Li$_2$MSiO$_4$ (where $M$ = transition metal) materials have been attracting considerable attention for potential use as a new generation cathode for Li-ion batteries due to their safety, low toxicity, and low cost characteristics. In addition, the presence of two Li$^+$ ions in the molecule offers a multiple electron-charge transfer (M$^{2+}$/M$^{3+}$ and M$^{3+}$/M$^{4+}$ redox couples), thus allowing a high achievable capacity of more than 320 mAh/g per M unit. Good electrochemical properties of Li$_2$FeSiO$_4$ have been reported through several approaches such as downsizing of the particles, carbon-coating, etc. However, in addition to electrochemical performance, fundamental understanding regarding crystal, electronic and local structure changes during charge/discharge processes is also important and needs more rigorous investigation. In this work, lithium iron silicates (Li$_2$FeSiO$_4$/C) in space group of $Pnma$: $a = 10.6671(3)$ Å, $b = 6.2689(2)$ Å, $c = 5.0042(2)$ Å have been prepared by solid-state reaction. The synthesized as well as chemical delithiated samples have been characterized by XRD, HRTEM, AAS and XAS techniques. We will show the results focusing on Fe K-edge XANES, EXAFS, HRTEM and XRD of the Li$_{2-x}$FeSiO$_4$ samples and discuss how the crystal, electronic, and local structure changes upon Li$^+$ de-intercalation.

Acknowledgement

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Introduction

With world energy demand expected to increase by nearly half in the next twenty years, coupled with the growing demand for low- or even zero-emission sources of energy, there has been increasing awareness of the need for efficient, clean, and renewable energy sources. Of particular interest are energy sources based on electricity that can be generated from renewable sources such as solar and wind. However, the use of electricity generated from these intermittent, renewable sources requires efficient electrical energy storage such as batteries. High energy lithium-ion batteries have improved performance in a wide variety of mobile electronic devices such as cell-phones and laptop computers. However, new fields of applications such as power tools, electric vehicles, and large-scale stationary power require batteries that have high safety, high durable power, long life, and low cost. Materials selection and processing as well as understanding factors influencing the materials’ properties are central issues in the development of these batteries.

Today, researchers around the world are trying to find materials to be used as electrode materials for Li-ion batteries. Many families of ceramic compounds have been developed for use as cathode materials. The most common ceramics are layered oxides LiM0₂ (M = Co, Ni, Mn, or V), manganese spinel (LiMn₂O₄), and phospho-olivines LiMPO₄ (M = Fe, Mn, Co, or Ni). Lithium cobalt oxide (LiCoO₂) is the most common cathode used in Li-ion batteries today; however, the high cost of cobalt and safety concerns make it impractical for electric vehicle applications. Olivine-type and spinel cathodes have become of particular interest for transportation due to their low cost, high safety, and environmentally friendly characteristics. However, they are not yet a perfect material because the olivine cathodes have low intrinsic ionic and electronic conductivities, and the spinel materials have low specific capacity, rapid capacity-fading, and poor cyclic efficiency due to severe Jahn-Teller distortion effects.

Recently, Orthosilicate, Li₂M₄SiO₄ (where M = transition metal) materials have been attracting considerable attention for use as a new generation cathode for Li-ion batteries due to their safety, low toxicity, and low cost characteristics. In addition, the presence of two Li⁺ in the compound offers a multiple electron-charge transfer (M⁹⁺/M⁷⁺ and M⁷⁺/M⁵⁺ redox couples), thus allowing high achievable capacity of more than 320 mAh/g per M unit, 2 to 3 times higher than the above mentioned commercial cathode materials. Nyten et al. [1] have successfully prepared phase-pure lithium iron silicate (Li₃FeSiO₄) via a solid-state reaction method. The electrochemical performance of this ceramic compound also looks promising. The initial charge capacity is 165 mAh/g and stabilizes after a few cycles at around 140 mAh/g. With regard to the crystal structure, Nyten et al. suggested an orthorhombic Li₃PO₄ based structure with the Pmn2₁ symmetry. Recently, new polymorphic forms of Li₃FeSiO₄ have been reported by Sirisopanaporn et al. [2] and Nishimura et al. [3] indicating that structures with the orthorhombic Pmnb and monoclinic P2₁/n space groups are possible. The alternative material for high performance electrochemical performance is Li₂MnSiO₄. Dominko et al. [4] reported the local structure of Li₃FeSiO₄ and Li₂MnSiO₄ with in-situ XAS for electrochemically delithiated samples. The results suggested that the local symmetry of Fe cations could reversibly return to the initial one after cycling. However, in the case Mn cations, the process was not completely reversible after the first cycle suggesting its structure has poor structural stability, which can lead to poor energy storage capacity and short battery life. This, however, should not limit the use of their solid solutions such as Li₃Fe₄Mn₁, SiO₄ for potential use as cathode materials for Li-ion batteries.

In this work, lithium iron silicates (Li₃FeSiO₄) in space group of Pnma were prepared by solid-state reaction. The synthesized as well as chemical delithiated samples were characterized by XRD, TEM, AAS and XAS techniques. We show and discuss how the crystal, electronic, and local structure changes upon Li⁺ de-intercalation.
Experimental

Li$_2$FeSiO$_4$/C was prepared by solid-state reaction from stoichiometric amounts of Li$_2$CO$_3$ (99%), Fe$_2$O$_3$ (99.6%), SiO$_2$ (99.9%) and 10 wt% ethylene glycol. The starting materials were first thoroughly mixed by ball-milling in isopropyl alcohol for 36 hrs. After that, the mixture was stirred at 80°C to evaporate the alcohol. The resulting powders were ground by a mortar grinder and calcined under flowing an Argon gas (99.999%) atmosphere to final temperatures for 5 hours. Chemical delithiation of the Li$_2$FeSiO$_4$ sample fired at 900°C were performed by using potassium persulfate (K$_2$S$_2$O$_8$) in an aqueous solution, as follows [5]:

$$\text{Li}_2\text{FeSiO}_4 + y(\text{K}_2\text{S}_2\text{O}_8) \rightarrow (1-y)\text{Li}_2\text{FeSiO}_4 + \text{FeSiO}_4 + y(\text{K}_2\text{SO}_4 + \text{Li}_2\text{SO}_4), \ 0 \leq y \leq 1$$

The K$_2$S$_2$O$_8$ K$_2$SO$_4$ redox couple has a Nernst standard potential of approximately 5 V vs. Li/Li$^+$, which is higher than the 4.5 V vs. Li/Li$^+$ for Li$_{0.0}$FeSiO$_4$/Li$_{2.0}$FeSiO$_4$ couple. Consequently, K$_2$S$_2$O$_8$ can oxidize Li$_2$FeSiO$_4$ to full delithiation. An aqueous solution of K$_2$S$_2$O$_8$ and Li$_2$FeSiO$_4$ was mixed at 50°C for 24 hours under an argon flowing atmosphere. By changing the molar ratio of K$_2$S$_2$O$_8$/Li$_2$FeSiO$_4$, the Li$_{2-x}$FeSiO$_4$ samples with different amounts of lithium were prepared.

The effects of chemical delithiation on the crystal structure of Li$_2$FeSiO$_4$ were studied by XRD measurement using a Bruker Model D5005 diffractometer with a rotating anode and Cu-Kα radiation. Structural parameters of the samples were refined by the Rietveld method using PANalytical X’Pert HighScore Plus software and Silicon NIST 640c as the external standard for particle size analysis. The chemical compositions of these samples were determined by performing atomic absorption spectroscopy (AAS). The morphology of samples was observed by a High Resolution Transmission Electron Microscope (HRTEM) using a JEOL JEM-2011 instrument.

The effects of chemical delithiation on the local structure of Li$_2$FeSiO$_4$ were studied by X-ray absorption spectroscopy (XAS) measurements carried out at Beamline 8 (BL8) of the Synchrotron Light Research Institute (SLRI) in Thailand [6]. X-ray absorption near-edge spectroscopy (XANES) and Extended X-ray absorption fine structure (EXAFS) of Li$_{2-x}$FeSiO$_4$ samples at various degrees of delithiation were measured at the Fe K-edge (7112 eV) at room temperature in transmission detection mode using a Ge (220) double crystal monochromator (energy range was 3440 – 10000 eV). All XAS spectra were averaged and normalized using IFFEFIT software version 1.2.11 Ravel & Newville [7].
Fig. 1. X-ray diffraction patterns refinement of Li$_{2.16}$FeSiO$_4$ phase indexed in the space group \textit{Pnma} corresponds to the orthorhombic structure with $a = 10.6671$ Å, $b = 6.2689$ Å, $c = 5.0042$ Å, $R_{wp} = 22.45\%$, $R_p = 17.58\%$, $R_{exp} = 21.43\%$, and Goodness of fit = 1.09. TEM image showing an average particle size for Li$_{2.16}$FeSiO$_4$ material prepared by solid state reaction at 900°C is shown. Conductive carbon layers on the surface of the particles are also visible in the image (inset).

The XRD pattern of the Li$_2$FeSiO$_4$ sample prepared at 900°C by solid state reaction was measured, and Rietveld refinements were carried out. The XRD pattern of the Li$_2$FeSiO$_4$ sample, together with its Rietveld refinement, are shown in Fig. 1. The XRD pattern can be indexed on the basis of an orthorhombic unit cell in space group \textit{Pnma}. The lattice parameters are refined to be $a = 10.6671(3)$ Å, $b = 6.2689(2)$ Å, $c = 5.0042(2)$ Å. The starting parameters for the refinements were those of Sirisopanaporn et al. [2] for the Li$_2$FeSiO$_4$ phase and of Hirayama et al. [8] for the LiFeO$_2$ phase. The relative amount of each phase was determined and found to consist of 91.5\% Li$_2$FeSiO$_4$ and 8.5\% LiFeO$_2$ phases. The average particle size of the Li$_{2.16}$FeSiO$_4$ sample resulting from the refinements is 173 nm. The shape and morphologies of the particles are shown in the TEM image in Fig. 1. (inset). The average particle size estimated from the TEM image is found to be 200-300 nm, which is in agreement with the XRD data refinements. Conductive carbon layers resulting from residual carbon in the raw materials and ethylene glycol can be observed on the surface of the particles. Carbon coating is a common technique for preparing electrode materials with good electrochemical properties; therefore, we are expecting good electrochemical performance of this material.
Fig. 2. X-ray diffraction patterns of Li$_2$FeSiO$_4$ crystalline powders calcined at 600, 700°C, 800°C and 900°C for 5 h in an Argon atmosphere.

Fig. 3. X-ray diffraction patterns of chemically delithiated Li$_2$FeSiO$_4$ samples. Atomic mass microscopy study shows that the compositions are: Li$_{2.16}$FeSiO$_4$, Li$_{1.62}$FeSiO$_4$, Li$_{1.54}$FeSiO$_4$ and Li$_{0.12}$FeSiO$_4$, respectively.
The X-ray diffraction patterns of the Li$_2$FeSiO$_4$ powders prepared at 600°C to 900°C are shown in Fig. 2. All diffraction patterns show evidence of LiFeO$_2$ phase impurity formation (space group R-3m), which is common to this synthesis method as previously reported by Hirayama et al. [8]. This is because the starting materials, Li$_2$CO$_3$ and Fe$_2$O$_3$ are known to react to form LiFeO$_2$ phase in argon atmosphere above 600 °C. With an increase in temperature to 700°C, the phases Li$_2$FeSiO$_4$ and Li$_2$SiO$_3$ can be found. The typical peaks at 18.92, 27.00 and 38.60° are attributed to the diffraction of base-centered orthorhombic Li$_2$SiO$_3$ phase (JCPDS no. 29-0828 in S.G. Ccm21). The Li$_2$SiO$_3$ phase occurred at this temperature was a result from the reaction between Li$_2$CO$_3$ and SiO$_2$ used as starting materials. Besides, the observed peaks positions of the Li$_{2.16}$FeSiO$_4$ correspond to the full diffraction pattern of orthorhombic Li$_2$FeSiO$_4$ phase. The intensities of Li$_2$SiO$_3$ phase decrease as temperature increases and are found to diminish at 900°C.

The Li$_2$FeSiO$_4$ sample synthesized at 900°C was used to prepare chemically delithiated samples with various amounts of Li. XRD patterns of these chemically delithiated samples are shown in Fig. 3. The states of delithiation of the Li$_{2-x}$FeSiO$_4$ samples were analyzed by atomic absorption spectroscopy and found to be $x = 0.00, 0.38, 0.46$ and 1.88. The X-ray diffraction pattern for $x = 0$ (Li$_{2.16}$FeSiO$_4$) is shown, and indexed in the orthorhombic structure in the Pnma symmetry. As the degree of delithiation increases, the main peaks intensity of the Li$_2$FeSiO$_4$ structure decrease indicating structural changes upon removal of Lithium ion from its original occupied sites. The main peak intensity of the impurity (LiFeO$_2$) phase does not change indicating that there is no lithium extraction from this phase. Lithium removal from the structure of Li$_2$FeSiO$_4$ makes the structure become more and more disordered. This can be seen as we extract more Li-ions, the background of the X-ray diffraction patterns increase, which indicate that the crystalline structure transforms into amorphous materials. Finally, when Li-ions are fully extracted, for $x = 1.88$ (Li$_{0.12}$FeSiO$_4$), the structure becomes completely amorphous. The observed peaks are of the LiFeO$_2$ phase in the sample alone.
Fig. 4. TEM image with its corresponding electron diffraction (SAED) patterns of Li$_2$-$_x$FeSiO$_4$ compositions ($0 \leq x \leq 2$).

An investigation using High Resolution Transmission Electron Microscopy (HRTEM) further showed the structure of several of Li$_2$FeSiO$_4$ particles. Fig. 4 (a), shows a lattice image and the corresponding selected area electron diffraction (SAED) pattern (inset) of the orthorhombic (Pnma) Li$_{2.16}$FeSiO$_4$ composition, where all of the spots were evaluated to represent d-spacing of 3.65, 3.15 and 2.70 nm, which can be clearly indexed as $hkl$ referred to the crystallographic planes of (201), (211) and (220) in the [112] zone axis, respectively. These results are also consistent with the standard information provided by the XRD patterns. Fig. 4 (b) demonstrates the corresponding selected area electron diffraction pattern (inset) of the Li$_{1.62}$FeSiO$_4$ composition. The spots were calculated to represent d-spacing of 5.34, 3.91 and 3.14 nm, which can be indexed to the crystallographic planes of (200), (011) and (020) in the [011] zone axis, respectively. In addition, Fig. 4 (c) illustrates the lattice bordered with carbon coating on the Li$_{1.54}$FeSiO$_4$ composition. The lattice image is clearly visible and distinguished from carbon coated layers on the surface. The electron diffraction pattern (inset) displayed spots to represent d-spacing of 3.91, 3.65 and 3.15 nm, which can be indexed to the crystallographic planes of (011), (201) and (211) in the [122] zone axis, respectively. Moreover, the resulting lattice image and carbon layer are observed clearly in this zone axis. Furthermore, Fig. 4 (d) presents a high resolution TEM (HRTEM) image in which lattice fringes of Li$_{0.12}$FeSiO$_4$ crystals can be seen. This sample exhibits all of the ring spots to represent d-spacing of 2.43 and 2.10 nm consistent with previous reported [10], which can be clearly referred to the crystallographic planes of (012) and (104) in the [421] zone axis, respectively. These results are consistent with provided by XRD patterns. Fig. 5 illustrates the FT-IR (Fourier transform infrared) of the samples at different states of delithiation, the FT-IR range 1150-1050 represent to Si-O bond. Cluster analysis resolves the sample into 2 clusters using Ward’s method. The IR spectrum of Li$_{0.14}$FeSiO$_4$ shows that the peak occurs around 1072 cm$^{-1}$, which can be assumed to be the Si-O bond. This silicate structural bonding is enhanced by the lithium extraction process. Alternately, in Li$_{2.16}$FeSiO$_4$ and Li$_{1.54}$FeSiO$_4$ samples, the Si-O peak is not quite clear because the intensity of the last peak (890 cm$^{-1}$) is quite high. Moreover, lithium extraction from the structure distorts SiO$_4$ symmetry. Then Li$_{0.14}$FeSiO$_4$ becomes SiO$_4$ changing its symmetry as the volume of structure decreases [12].

Comment [JN1]: I am having a little trouble understanding here.
Fig. 5. [a] FT-IR spectra of Li$_{2-x}$FeSiO$_4$ sample at different parts of the delithiation process, the FT-IR range 1150-1050 represented SiO$_2$ or silicate bonds. [b] Cluster analysis of Li$_{2-x}$FeSiO$_4$ sample with different delithiation processes.
Fig. 6. Normalized Fe K-edge spectra of a series of Li$_{2-x}$FeSiO$_4$ compositions (0 ≤ x ≤ 2), as prepared by chemical delithiation of Li$_{2.16}$FeSiO$_4$, reference compounds such as Fe$_2$O$_3$ (Fe$^{3+}$), Fe$_3$O$_4$ (Fe$^{2+}$/3+) and LiFePO$_4$ (Fe$^{2+}$).

Fig. 7. Pre-edge structure of Fe K-edge XANES spectra of Li$_{2.16}$FeSiO$_4$, Li$_{1.53}$FeSiO$_4$, Li$_{0.14}$FeSiO$_4$ and all reference compounds represent structural symmetry of different oxidation states.

The local structural variations around Fe ions during chemical delithiation process are illustrated in Fig. 6. The spectra of the samples at different states of delithiation show pre-edge and edge positions which are obviously from contributions of the change of the local environment.
around Fe-ions. Table 1 shows the fitting results for the pre-edge and edge positions of the Li$_{2-x}$FeSiO$_4$ samples along with the results from standard materials. Here we use LiFePO$_4$ and Fe$_2$O$_3$ as the standard materials for calibrating the positions of Fe$^{2+}$ and Fe$^{3+}$ peaks, respectively. Fe$_3$O$_4$ is known to have both oxidation states Fe$^{2+}$ and Fe$^{3+}$ co-existing so the pre-edge feature appears between these two positions. As can be seen, the main edge peak (Fe 1s → 4p transition and 1s→continuum transition) of XANES spectrum is slightly shifted to higher energies when the number of lithium ions is decreased. This indicates that the valence state of Fe changes from Fe$^{2+}$ to Fe$^{3+}$ [13,15] and as Li content decreases, structural distortion occurs during the transformation of Fe$^{2+}$ to the Fe$^{3+}$ state. The pre-edge feature is related to 1s → 3d transition of Fe ions. The pre-edge of Fe also shifts to a higher energy when the number of Li-ions is reduced during charging process (Fig.7). Shifting to higher energy of the pre-edge means that the nuclear bonding around the core ion is stronger; therefore, we can see that the fully delithiated sample (Fe ion has the Fe$^{3+}$ state) has stronger nuclear bonding than the fully lithiated sample (Fe ion has the Fe$^{2+}$ state). The pre-edge peak of the synthesized sample appears at 7112.7 eV which is slightly higher than the edge energy of the standard Fe$^{2+}$ of LiFePO$_4$. This may be due to the fact that our sample also contains a small amount of LiFeO$_2$ impurity. The pre-edge peak of the partially delithiated sample (Li$_{1.53}$FeSiO$_4$) is intense and approximately at 7114 eV with respect to Fe$_3$O$_4$ which indicates the mixed Fe$^{2+/3+}$ oxidation state. For the fully delithiated sample, the weak pre-edge peak appears at approximately 7114 eV. This is the same pre-edge peak position of Fe$_2$O$_3$, meaning that the valence of the Fe ion in this sample has the Fe$^{3+}$ state. Ideally, the valence of Fe ion for the full delithiated sample, FeSiO$_4$, should be the Fe$^{3+}$ state in order to ensure the charge balance condition. However, in the case of Li$_{0.14}$FeSiO$_4$, the Fe$^{3+}$ state occurs. This means that full delithiation of Li$_2$FeSiO4 may not be possible without changing the structure of this compound.

Table 1

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Fig. 8. Fourier transformed spectra of $k^3$-weighted $|k^3 \chi(k)|$ series of $Li_{2+x}FeSiO_4$ compositions (0 ≤ x ≤ 2) calculated in the $k$ range of 2.0-10 Å⁻¹. Comparison of the experiment - (dashed line) and IFEFF fit theoretical analysis of the $k^3$-weighted Fe EXAFS - (solid line) is shown.

Fig. 9. Fourier transforms of Fe EXAFS spectra of the $Li_{2+x}FeSiO_4$ compositions (0 ≤ x ≤ 2) during the delithiation process calculated in the $R$ range of 1.3-3.2 Å. Comparison of the experiment - (dashed line) and IFEFF fit theoretical analysis using the data from Rietveld refinement of the $Li_{2.16}FeSiO_4$ sample is shown - (solid line).
The short-range order around Fe ions in the Li$_2$FeSiO$_4$ cathode materials during delithiation was directly probed using the information obtainable from the K-edge EXAFS spectrum analysis with the IFEFFIT program package [8]. The structural parameters used at the beginning of the fitting process were from the XRD refinements. Fig. 8 shows the $k^2 \chi(k)$ function of the Fe K-edge EXAFS spectra after performing background subtraction, energy calibration, normalization and weighting of the data with $k^2$ of the different states of delithiation. Fig. 9 shows the corresponding radial structure function as a function of the inter-atomic distance, $R$ (Å). A very good agreement between the Li$_{2.14}$FeSiO$_4$ model and experimental spectra is found in the $R$ range from 1.3-3.2 Å near the Fe atom. This was obtained by Fourier transformation of $k^2 \chi(k)$ over the limited $k$-space range between 2.0-10 Å$^{-1}$. The structural parameters are shown in Table 2. As can be seen, the first shell around Fe ion contains oxygen and second shell contains silicon atoms. The best fits show that there were three different Fe-O bond distances in case of Li$_{2.16}$FeSiO$_4$ and Li$_{1.15}$FeSiO$_4$ and two different Fe-O bond distances for Li$_{0.14}$FeSiO$_4$ as shown in Table 2. EXAFS results for the local Fe environment in the synthesized Li$_{2.14}$FeSiO$_4$ were also in agreement with XRD Rietveld refinement. In this case, Fe is located in the FeO$_4$ tetrahedron symmetry with two oxygen atoms at 1.99 Å, one oxygen atom at 2.02 Å and one oxygen atom at 2.13 Å. The local environment of the second shell is the Fe-Si bond at 3.19 Å forming Si-O bonds. During the chemical delithiation, Fe-O and Fe-Si distance decreases with the increasing relative amount of Fe$^{3+}$. For Li$_{0.14}$FeSiO$_4$, the structure change from Li$_{2.15}$FeSiO$_4$ to FeSiO$_4$ was found and that Fe-O is located at 1.90 and 2.04 Å, Fe-Si at 3.13 Å. The XRD data indicated that Li$_{0.14}$FeSiO$_4$ is an amorphous structure. Nevertheless, XRD cannot identify its structural symmetry. The EXAFS data can be used to identify that the amorphous structure has the SiO$_4$ tetrahedral symmetry. This result is also consistent with our FT-IR finding as shown previously. Fig. 10 demonstrates structural changes in Li$_2$FeSiO$_4$ cathode batteries as lithium is extracted. Results were obtained for the stages of the charging process: Li$_{2.14}$FeSiO$_4$ → LiFeSiO$_4$ → FeSiO$_4$. Comparing Li$_{2.14}$FeSiO$_4$ and FeSiO$_4$, the bond distances decrease and result in a volume change of approximately 9%. Even though this material becomes amorphous upon lithium extraction, this small volume change of only 9% may be beneficial for Li-ion batteries that use the silicate ceramics as the cathode because the materials will be highly stable after several rounds of charging and discharging, enabling a long Li-ion battery life.

Fig. 10. Schematic of model structure change of Li$_2$FeSiO$_4$ to FeSiO$_4$ as delithiation progresses [a] Li$_{2.14}$FeSiO$_4$ structure (Pnma) representing LiO$_6$, FeO$_4$ and SiO$_4$ tetrahedral symmetry, [b] FeSiO$_4$ structure representing the SiO$_4$ tetrahedral symmetry.
Table 2

Structural parameters of the nearest coordination shells around Fe atoms in samples from the IFEFF fits at different states of the lithium extraction process: CN is the coordination number of nearest neighbor atoms (oxygen), R is the inter-atomic distance, $\sigma^2$ is Debye-Waller factor. Best fit in the k-range = 2-10 Å$^{-1}$ and R range of 1.3-3.2 Å is obtained with the amplitude reduction factor $s_0^2 = 1.0$.

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</table>

Conclusion

In this work, Lithium iron silicate (Li$_2$FeSiO$_4$) materials were prepared by a solid-state reaction method. Crystal structure refinements indicate that the materials have an orthorhombic structure with the Pnma space group symmetry and a = 10.6671(3) Å, b = 6.2689(2) Å, c = 5.0042(2) Å. The materials prepared by this method have a narrow particle size distribution with an average size of approximately 200 nm. The HRTEM confirms that this structure is orthorhombic structure (Pnma) by using compared hkl indices. The crystal and local structures of the chemically delithiated samples were studied. AAS was used to measure the Li content in the chemically delithiated samples. XRD and HRTEM results show that the materials become amorphous as the lithium extraction progresses. FT-IR shows that the amorphous structure of the delithiated sample has the SiO$_4$ symmetry and there is a volume reduction upon delithiation. The XAS measurements can be used to study the local structure around Fe ions. XANES data reveal oxidation state of Fe ions changes from Fe$^{2+}$ to Fe$^{3+}$ upon lithium extraction. There is no evidence of the formation of the Fe$^{4+}$ state even for the fully delithiated sample. EXAFS results show the best fit for the local environment of Fe slightly changes by less than 0.01 Å, which result in a reduction of approximately 9% of the volume upon lithium extraction. This may be beneficial for the silicate ceramics as it will be highly stable during cycling, ensuring a long life Li-ion battery.
References


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