Robust diamond-like Fe-Si network in the zero-strain $\text{Na}_x\text{FeSiO}_4$ Cathode

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Abstract

Sodium orthosilicates Na_2MSiO_4 (M denotes transition metals) have attracted much attention due to the possibility of exchanging two electrons per formula unit. In this work, we report a group of sodium iron orthosilicates $\text{Na}_2\text{FeSiO}_4$. Their crystal structures are characterized by a diamond-like Fe-Si network. The Fe-Si network is quite robust against the charge/discharge process, which explains the high structural stability observed in experiment. Using the density functional theory within the GGA+U framework and X-ray diffraction studies, the crystal structures and structural stabilities during the sodium extraction/re-insertion process are systematically investigated.

Keywords: Battery; Cathode; First-principles calculations; Structure prediction; Structural evolution

1. Introduction

Transition metal lithium orthosilicates Li_2MSiO_4 ($M = \text{Fe}, \text{Mn}, \text{Co}$) have attracted much attention as promising candidates for cathode materials in rechargeable Li-ion batteries owing to their large theoretical capacities [1-7]. However, due to limited supply and high cost of lithium, alternatives are being sought and evaluated, including their sodium analogues, transition metal sodium orthosilicates Na_2MSiO_4 . The possibility of exchanging two electrons per formula unit (f.u.) is an outstanding property of the orthosilicates, which results in a high theoretical capacity of $\sim 275 \text{ mA h g}^{-1}$ and $\sim 330 \text{ mA h g}^{-1}$ for Na and Li systems, respectively. In 2011, Duncan *et al.* [8] first successfully synthesized $\text{Na}_2\text{MnSiO}_4$ with a *sol-gel* method and used it as the starting material to obtain a metastable polymorph (Space group, Pn) of $\text{Li}_2\text{MnSiO}_4$ *via* ion exchange. Chen *et al.* [9] also synthesized $\text{Na}_2\text{MnSiO}_4$ using the same method, and measured a reversible capacity of 125 mA h g^{-1} , which is the first evaluation of electrochemical properties for use of sodium silicate as a cathode material for Na secondary batteries. Besides, $\text{Na}_2\text{CoSiO}_4$ was prepared *via* hydrothermal method and used as positive electrode material for sodium-ion capacitors [10].

Table 1. Positions, relative position changes with respect to [open circuit potential \(OCP\)](#) measurements of the 2 major peaks in XRD patterns and relative volume changes when charging to different [potentials](#). The volume changes are calculated from the position changes of the 2nd major peak.

	1 st peak (2 θ /degree)	Change (%)	2 nd peak (2 θ /degree)	Change (%)	Volume change (vol%)
OCP	20.91	0	34.53	0	0
2.5 V	20.82	-0.4	34.59	0.2	-0.5
3.5 V	20.95	0.2	34.61	0.2	-0.6
4.0 V	20.94	0.1	34.65	0.3	-0.9

Table 2. Positions, relative position changes with respect to pristine measurements of the 2 major peaks in XRD patterns and relative volume changes after undergoing different numbers of cycles. The volume changes are calculated from the position changes of the 2nd major peak.

	1 st peak (2 θ /degree)	Change (%)	2 nd peak (2 θ /degree)	Change (%)	Volume change (%)
Pristine	20.90	0	34.68	0	0
10 th cycle	20.81	-0.4	34.60	-0.2	0.6
30 th cycle	20.81	-0.4	34.58	-0.3	0.8
50 th cycle	20.86	-0.2	34.61	-0.2	0.5
100 th cycle	20.75	-0.7	34.60	-0.2	0.6

Recently, a new material in this group, sodium iron orthosilicate Na₂FeSiO₄, was synthesized and reported to exhibit reversible electrochemical activity of 106 mA h g⁻¹ [11]. This material is attractive because of the natural abundance of sodium and iron. Interestingly, the major peaks of the X-ray diffraction (XRD) pattern remain at the same positions during the charge-discharge process (Table 1), indicating an anomalously high structural stability which is highly desirable for improved

mechanical stability in the cycle life and safety of batteries. This high structural stability is further confirmed by the XRD patterns measured after undergoing different numbers of cycles, as shown in Table 2. However, a thorough understanding of the structural stability against sodium ion extraction/re-insertion cannot be achieved without identification of the crystal structure of the material. The crystal structure is also the predominant information for material design and study of the extraction/re-insertion mechanism. In this work, the polymorphic behavior of $\text{Na}_x\text{FeSiO}_4$ are discussed and the high structural stability is explained by a robust diamond-like Fe-Si network that forms the common backbone of several families of structures and also the corresponding structures of the charged/discharged products.

2. Computational Methods

The crystal structures of $\text{Na}_2\text{FeSiO}_4$ were explored using random searching with experimental input, *i.e.*, lattice parameters determined from XRD measurements [11]. The XRD pattern from the sample of solid state reaction can be indexed to a cubic cell with $a = 0.7330(3)$ nm and a space group of $F\bar{4}3m$. A total number of 100 structures were generated randomly and relaxed using first-principles calculations. But no low-energy structures were found. However, when the space group restraint was lifted to primitive cubic, a low energy structure was found with $P2_13$ (No. 198) as shown in Fig. 1.

The first-principles calculations were carried out using the projector augmented wave (PAW) method [12] within density functional theory (DFT) as implemented in the Vienna ab initio simulation package (VASP) [13,14]. The exchange and correlation functional is treated within the spin-polarized generalized gradient approximation (GGA) and parameterized by Perdew-Burke-Ernzerhof formula (PBE) [15]. Wave functions are expanded in plane waves up to a kinetic energy cut-off of 500 eV. Brillouin zone integration was performed using the Monkhorst-Pack sampling scheme [16] over k-point mesh resolution of $2\pi \times 0.3 \text{ nm}^{-1}$. The ionic relaxations stop when the forces on all the atoms are smaller than 0.1 eV nm^{-1} . The effects due to the localization of the *d* electrons of the transition metal ions in the silicates are taken into

account with the GGA + U approach of Dudarev *et al.* [17]. Within the GGA + U approach, the on-site coulomb term U and the exchange term J are grouped together into a single effective interaction parameter $U-J$. In our calculations, $U-J$ value is set to 4 eV for Fe.

3. Results and Discussion

3.1. Crystal structures of $\text{Na}_x\text{FeSiO}_4$ polymorphs and zero-strain behavior with variation of Na occupancy

The structure with space group $P2_13$ is plotted in Fig. 1. The SiO_4 and FeO_4 tetrahedra are connected by sharing an O-vertex and form a three dimensional diamond-like framework. Sodium atoms are located within the channel of the $[\text{FeSiO}_4]$ framework and form another diamond sub-lattice. However, the sodium sub-lattice is disrupted when sodium ions are removed from the material during the battery charge process.

Based on the charge/discharge curves from experiments [11], the estimated number of Na atoms is 1~1.25 per f.u. in the as-produced samples, 1.5~1.75 when discharged to ~1.2 V, and 0.25~0.5 when charged to 4.5 V. To study the structural evolution of the $\text{Na}_x\text{FeSiO}_4$ crystal in the charge/discharge process, Na ions are removed one by one ($x = 1.75, 1.5, 1.25, \dots, 0$) from the parent structures $(\text{Na}_2\text{FeSiO}_4)_4$ as shown in Fig. 1. The resulting structures are then fully relaxed. Figure 2a summarizes the cell volumes *v.s.* the energies of the lowest-energy structures after removal of Na ions and relaxation from the parent structure. It is interesting to see that most of the lowest-energy structures have volumes within a small scope as indicated with the grey region. Only 2 structures around the large end of the x spectrum ($x \sim 2$) are located out of the grey region. This is consistent with experiments, where the estimated number of Na never reaches 0 or 2 per f.u. Figure 2(b) plots the formation energy per f.u. of $\text{Na}_x\text{FeSiO}_4$ *v.s.* x with respect to $\text{Na}_{0.25}\text{FeSiO}_4$ ($x_t = 0.25$) and $\text{Na}_{1.75}\text{FeSiO}_4$ ($x_i = 1.75$), which is defined as [4]:

$$E_f(x) = E(\text{Na}_x\text{FeSiO}_4)$$

$$- \left[\left(\frac{x-x_t}{x_i-x_t} \right) E(\text{Na}_{x_i}\text{FeSiO}_4) + \left(1 - \frac{x-x_t}{x_i-x_t} \right) E(\text{Na}_{x_t}\text{FeSiO}_4) \right] \quad (1)$$

Figure 3 shows the calculated XRD patterns of the lowest-energy structures for each x in Fig. 2, along with the atomic structures of 4 selected configurations: $(\text{Na}_2\text{FeSiO}_4)_4$, $(\text{Na}_{1.25}\text{FeSiO}_4)_4$, $(\text{Na}_{0.75}\text{FeSiO}_4)_4$, and $(\text{FeSiO}_4)_4$ according to the $P2_13$ parent structure. It is worth noting that Fe and Si form a diamond-like backbone that is quite robust against sodium ion extraction/re-insertion. As a consequence, the material attains a high structural stability resulting in a nearly zero volume change during the charge-discharge process. This is consistent with experiment measurements [11] where the 2 major peaks at 20° and 34° (2θ) do not shift as Na ions are being extracted/re-inserted. The 2nd major peak at 34° (2θ) is initially broadened and eventually splits into multiple peaks. This behavior is also observed in the experimental XRD spectra [11].

As shown in Fig. 3a, there are some minor peaks in the calculated XRD pattern which are not seen in the experiment. The discrepancy comes from the fact that the current modelling does not involve the disordered distribution of sodium ions when they are randomly extracted or inserted. In our modelling, sodium ions are randomly removed from ONE unit cell and relaxed. The resulting structure inherits some characteristics from the $P2_13$ parent structure $(\text{Na}_2\text{FeSiO}_4)_4$, which results in the extra minor XRD peaks. In contrast, the real structure is an ensemble of numerous unit cells with sodium ions randomly extracted/re-inserted. The sodium ions are randomly distributed, while the Fe and Si form the aforementioned diamond-like network. The positions of oxygen anions are also disrupted to accommodate the extraction/re-insertion of sodium cations, creating disorder in the oxygen lattice. Consequently, the averaged structure of the ensemble displays a higher cubic symmetry, characteristic of the robust Fe-Si network in the crystal, while the disorder in the sodium and oxygen positions remove the extra minor peaks in the experimental XRD spectra. For illustration, we approximate such random structures by constructing $2 \times 2 \times 2$ supercells $(\text{Na}_2\text{FeSiO}_4)_{32}$ and randomly removing 0.25~1.75 sodium ions per

f.u. The XRD patterns for the corresponding fully-relaxed structures are shown in Fig. 4. The supercell structures have similar XRD patterns with the single-cell structure (Fig. 3a), except that the extra minor peaks are greatly reduced, as expected. The minor peaks do not completely disappear, as the supercell represents a random sampling of only 8 unit cells.

3.2. Robust diamond-like Fe-Si network responsible for the zero-strain behavior

Since the single cell structure may not have the cubic symmetry, more comprehensive searches were performed with no space group restraint and only the cubic unit cell being enforced. In this case, random searches are not effective. So we applied the motif-network scheme [18] to search possible configurations with such a cubic unit cell and no restraint of symmetries. Two low-energy structures in space group $C2$ and $C222_1$ are found after relaxation to have XRD patterns similar to experiments. They are shown in Fig. 5a and 5b, respectively. It can be seen from Figs. 1 and 5 that all the 3 structures ($P2_13$, $C2$, and $C222_1$) can be characterized by 2 penetrating diamond sub-lattices of Na and Fe-Si cations. However, the different local arrangements of FeO_4 and SiO_4 tetrahedra result in slightly different orientations of the diamond sub-lattices in the 3 different structures.

Same calculations as shown in Fig. 2 are repeated for the 2 new structures and the results are plotted in Fig. 6. It can be seen by comparing Fig. 2 and Fig. 6 that the parent $P2_13$ structure has a much higher energy and a larger cell volume than the $C2$ and $C222_1$ structures to accommodate the FeO_4 and SiO_4 tetrahedra that satisfy the higher symmetry. However, the lowest-energy structures after removal of Na ions has almost the same energies and cell volumes for all the 3 structures, indicating a common Fe-Si network underlying the 3 different parent structures through the Na extraction/re-insertion. This robust Fe-Si diamond framework contributes to the nearly zero volume change during the charge-discharge process.

Figure 7a and 7b show the calculated XRD patterns of the lowest-energy structures in Fig. 6a and 6b with Na ions removed from the parent $C2$ and $C222_1$ structure, respectively. The positions of the 2 major peaks are exactly like the $P2_13$

structure. However, the *C2* structure has fewer minor peaks than the other 2 structures. The simulated XRD spectra for the $2 \times 2 \times 2$ supercell of the *C2* and *C222₁* structures are plotted in Fig. 7c and 7d. In the XRD pattern of the *C2* structure, the 2nd major peak is almost as sharp as the 1st one even in the random supercell structure. It is found that Na extraction causes less disruption in the positions of the remaining Na atoms in this structure. Interestingly, the $\text{Na}_x\text{FeSiO}_4$ sample prepared by solid state reaction also has a similar sharp 2nd major peak [11], while the sample synthesized by sol-gel method has a broadened 2nd major peak. Different processing methods probably create slightly different structures associated with different XRD patterns. However, these structures share a very similar Fe-Si network, as indicated from the fixed positions of the 2 major XRD peaks. As Fig. 1a and the top of Fig. 5a & 5b show, the 2 penetrating diamond sub-lattices of Na and Fe-Si cations are the best neatly lined up for the *C2* structure. This may explain why the Na extraction causes less disruption in the positions of the remaining Na atoms in this structure during discharge process. The oxygen anions are differently distributed in the 3 structures. Nevertheless, the detailed arrangement of oxygen ions cannot be determined unless XRD patterns with very high resolutions are acquired.

All the 3 $\text{Na}_2\text{FeSiO}_4$ polymorphs are similar in structure: the SiO_4 and FeO_4 tetrahedra are connected by sharing an O-vertex and Na's are located within the channel of the $[\text{FeSiO}_4]$ framework. To characterize the structural evolution in the charge/discharge process, the bond lengths of Fe-O and Si-O and distortions of FeO_4 and SiO_4 tetrahedra for the 3 $\text{Na}_x\text{FeSiO}_4$ polymorphs are calculated as functions of x ($0.25 \leq x \leq 1.75$). For all 3 structures, the bond lengths increase as x increases, as expected. The distortion parameter Δ of a FeO_4 (SiO_4) tetrahedron with an average Fe-O (Si-O) distance $\langle d \rangle$ is defined as $\Delta = \frac{1}{4} \sum_{n=1}^4 [(d_n - \langle d \rangle) / \langle d \rangle]^2$. Figure 8a plots Δ of FeO_4 tetrahedra for the stable structures as indicated in the convex hull in Fig. 2 and Fig. 6 and 2 additional configurations $\text{Na}_2\text{FeSiO}_4$ and FeSiO_4 . The 3 polymorphs have similar values of Δ all of which are within a reasonably small range.

As emphasized before, the Fe-Si diamond-like network is responsible for the nearly zero volume change during the charge-discharge process. It is thus interesting to analyze the stability of the Fe-Si network. The bond length of Fe-Si for the 3 $\text{Na}_x\text{FeSiO}_4$ polymorphs as a function of x is plotted in Fig. 8b. The Fe-Si bond length varies within a very small range of $\sim 1\%$, which results in a small volume change during the charge-discharge process.

3.3. Influence of crystal structure in the electrochemical properties

The average [potentials](#) of sodium deintercalation/intercalation can be predicted with first-principles calculations. Following the well-established methods, the average deintercalation [potential](#) V v.s. Na/Na^+ can be calculated using the following equation,

$$V = - \frac{E_{coh}[\text{Na}_{x_2}\text{Host}] - E_{coh}[\text{Na}_{x_1}\text{Host}] - (x_2 - x_1)E_{coh}[\text{Na}]}{x_2 - x_1} \quad (2)$$

where x_2 and x_1 are the Na composition before and after the sodium extraction from the host, respectively. Fig. 9 shows the calculated average [potentials](#) for the 3 $\text{Na}_2\text{FeSiO}_4$ polymorphs. They have similar calculated [potentials](#), except that the $P2_13$ structure has an additional stable structure at $x = 0.5$. As a comparison, a value of 1.9V and 4.0V are experimentally observed during the charge/discharge process, corresponding to the $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{Fe}^{3+}/\text{Fe}^{4+}$ redox reaction, respectively.

4. Conclusions

In this work, we have studied the structural characteristics, stability and evolution of the 3 $\text{Na}_x\text{FeSiO}_4$ polymorphs crystallizing in the space group $P2_13$, $C2$ and $C222_1$, respectively. All the polymorphs are characterized by a common Fe-Si diamond-like network that is quite robust against the Na extraction/re-insertion. This structural characteristic is responsible for the nearly zero volume change observed experimentally during the charge/discharge process. Different processing methods probably create polymorphs with very similar arrangement of cations but different distribution of oxygen anions. The experimentally observed polymorphs are very stable in structure resulting in a very small volume change during the

charge/discharge process, which is highly desirable for improved mechanical stability for rechargeable Na-ion batteries. The idea of the Fe-Si diamond-like network that is robust in the charge/discharge process may be generalized to other transition metal sodium orthosilicates and/or other polyanion compounds to achieve the zero-strain for cathode materials.

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Figure Captions

Figure 1. Crystal structure in space group $P2_13$ (No. 198) that is characterized by 2 penetrating diamond sub-lattices of Na and Fe-Si cations. (a) & (b) The Na and Fe-Si networks are indicated in gold and blue, respectively. (c) Polyhedral representations of the crystal structures. The Na, Fe, Si and O atoms are shown in gold, brown, blue and red balls, respectively, whereas FeO_4 and SiO_4 tetrahedra are represent in brown and blue.

Figure 2. (a) Scatter plot of the total energy versus the volume per unit cell for the lowest energy structures with sodium ions removed from the parent structures $(\text{Na}_2\text{FeSiO}_4)_4$ (marked with red star) of space group $P2_13$. The grey region indicates the volume scope where most low energy structures locate. (b) Formation energy versus the Na composition. The solid line forms the convex hull of all the structures.

Figure 3. (a) Calculated XRD patterns of low-energy $(\text{Na}_x\text{FeSiO}_4)_4$ ($x = 0\sim 2$) structures obtained from extracting Na from parent $(\text{Na}_2\text{FeSiO}_4)_4$ structure of space group $P2_13$ as shown in Fig. 2(a). (b)-(d) atomic structures of $(\text{Na}_2\text{FeSiO}_4)_4$, $(\text{NaFeSiO}_4)_4$, and $(\text{FeSiO}_4)_4$, which depict a diamond-like Fe-Si network that is quite robust against sodium ion extraction/re-insertion.

Figure 4. Calculated XRD patterns of $2\times 2\times 2$ supercell structures $\text{Na}_x\text{FeSiO}_4$ ($x=0.25\sim 1.75$) of space group $P2_13$.

Figure 5. Crystal structures in space group (a) $C2$ (No. 5) and (b) $C222_1$ (No. 20). (top) The Na and Fe-Si networks are indicated in gold and blue, respectively. (bottom) Polyhedral representations of the crystal structures.

Figure 6. (a) & (b) Scatter plots of the total energy versus the volume per unit cell for

the lowest-energy structures with sodium ions removed from the parent structures $(\text{Na}_2\text{FeSiO}_4)_4$ (marked with red star) of space group $C2$ and $C222_1$, respectively. The grey region indicates the volume scope where most low energy structures locate. (c) & (d) Formation energy versus the Na composition for $C2$ and $C222_1$ structures, respectively. The solid line forms the convex hull of all the structures.

Figure 7. (a) & (b) Calculated XRD patterns of low energy $(\text{Na}_x\text{FeSiO}_4)_4$ ($x = 0\sim 2$) structures of space group $C2$ and $C222_1$, respectively. (c),(d) Calculated XRD patterns of $2\times 2\times 2$ supercell structures $\text{Na}_x\text{FeSiO}_4$ ($x = 0.25\sim 1.75$) of space group $C2$ and $C222_1$, respectively.

Figure 8. (a) The distortion parameter Δ of FeO_4 (SiO_4) tetrahedral, and (b) the averaged Fe-Si bond lengths as a function of x for the diamond-like Fe-Si network.

Figure 9. Deintercalation [potential](#) versus the Na composition for $P2_13$, $C2$ and $C222_1$ structures, respectively.

Figure 1

Figure 2

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Figure 9