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## Achieving High Capacity by Vanadium Substitution into $\text{Li}_2\text{FeSiO}_4$

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The feasibility of iron substitution by 50% vanadium in lithium iron silicates ( $\text{Li}_2\text{FeSiO}_4$ ) to improve the capacity is investigated by first-principles calculations based on density functional theory (DFT) within the generalized gradient approximation adding Hubbard-like correlation (GGA+U). The structural evolutions of  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  upon the selected delithiation states, namely  $x = 0, 0.5, 1.0, 1.5, 2.0$ , are analyzed in detail. It is demonstrated that 50% vanadium substitution of iron in  $\text{Li}_2\text{FeSiO}_4$  may be thermodynamically possible to achieve higher capacity corresponding to more than one lithium ion extractions and improve electronic conductivity with lower band gap. More importantly, minor local structural distortions resulted by vanadium substitution might be beneficial to stabilize the delithiated phases and to achieve better cycling performance.

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Improvement in the energy density of cathode materials is one of the most important subjects in the field of lithium ion batteries. The possible strategies mainly include the use of cathode materials with a high voltage or with a reversible exchange of more than one lithium ions per formula unit. Compared with lithium iron phosphates ( $\text{LiFePO}_4$ ) which possess the theoretical capacity of  $170 \text{ mAh g}^{-1}$ , lithium iron silicates ( $\text{Li}_2\text{FeSiO}_4$ ) would allow the exchange of two lithium ions in principle and result in delivering a nominal capacity of  $330 \text{ mAh g}^{-1}$ . The promising high capacities up to  $204 \text{ mAh g}^{-1}$  (C/20) at  $55^\circ\text{C}$ <sup>1</sup> and  $220 \text{ mAh g}^{-1}$  (C/16) at  $30^\circ\text{C}$  for the initial discharge capacity,<sup>2</sup> all correspond to the capacity more than one lithium ions ( $166 \text{ mAh g}^{-1}$  for one lithium ion), have been reported for  $\text{Li}_2\text{FeSiO}_4/\text{C}$  composites. However, the abovementioned large capacities obtained are either required a high temperature with only  $148 \text{ mAh g}^{-1}$  remained at  $25^\circ\text{C}$ <sup>1</sup> or accompanied by severe capacity fading with 29% capacity losses after 30 cycles at a low temperature.<sup>2</sup> It has been suggested, based on the first-principles calculations, that the capacity could be enhanced by  $\text{VO}_4^{3-}$  substitution for  $\text{SiO}_4^{4-}$  in  $\text{Li}_2\text{FeSiO}_4$  with the feasible substitution levels being less than 30%.<sup>3</sup>

Theoretically speaking, the capacity of  $\text{Li}_2\text{FeSiO}_4$  beyond one lithium ion extraction can be attained if iron is substituted by a transition metal (M) which could be oxidized from  $\text{M}^{2+}$  to  $\text{M}^{4+}/\text{M}^{5+}$  through delithiation. Based on the first-principles calculations, the lithium manganese/iron silicates are shown to be able to form a stable material with a reversible exchange of more than one lithium ions.<sup>4</sup> This is verified by the experimental results. An optimal composition of  $\text{Li}_2\text{Fe}_{0.5}\text{Mn}_{0.5}\text{SiO}_4$  was found to deliver an initial discharge capacity of  $214 \text{ mAh g}^{-1}$ , however, the severe capacity fading, more than 40% capacity losses after 10 cycles, was observed.<sup>5</sup> Similar phenomena were confirmed by Dominko et al.,<sup>6</sup> who reported an initial charge capacity as high as  $250 \text{ mAh g}^{-1}$  at  $60^\circ\text{C}$  with the rapid capacity dropping to  $0 \text{ mAh g}^{-1}$  after 15 cycles. It appears that the substitutions of iron by manganese in  $\text{Li}_2\text{FeSiO}_4$  are effective to improve the initial capacity but always accompany the severe capacity fading. To overcome this problem with manganese substitutions, other suitable transition metals should be searched. The substitution of vanadium is possible to enhance the capacity of  $\text{Li}_2\text{FeSiO}_4$  since several oxidized vanadium states up to pentavalent ( $\text{V}^{5+}$ ) are available. It is, therefore, necessary to know what the maximum capacity is and whether the capacity fading will occur by vanadium substitutions.

In this study, the first-principles calculations are carried out in an effort to examine the feasibility of achieving capacities beyond one electron reaction in  $\text{Li}_2\text{FeSiO}_4$  by vanadium substitution. By assuming that the vanadium substitution can fully exchange two lithium ions through the oxidations of vanadium from divalent to pentavalent states

( $\text{V}^{2+}$  to  $\text{V}^{5+}$ ), 50% vanadium substitution with a stoichiometric composition of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  is selected as a model compound for simplicity in computation. The structural evolutions of  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  upon the selected delithiation states, namely  $x = 0, 0.5, 1.0, 1.5, 2.0$ , are analyzed in detail.

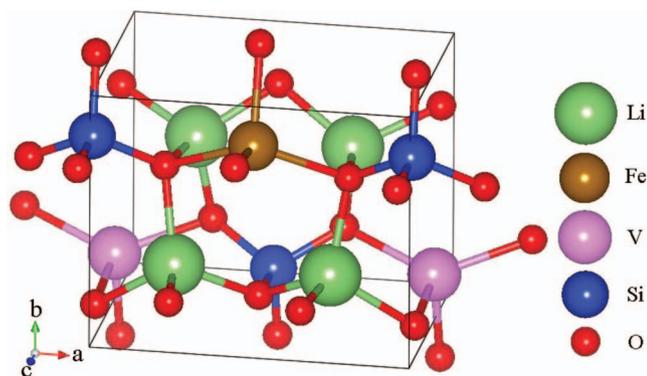
### Computational Details and Models

All of the calculations were performed using DFT with the exchange-correlation functional treated in the spin-polarized GGA as parameterized by Perdew-Burke-Ernzerhof (PBE)<sup>7</sup> using a projected augmented wave (PAW) method<sup>8</sup> as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>9–11</sup> The standard version of the PAW potentials for Li, Fe, Si and O supplied with VASP was used. Convergence with respect to both energy cutoff and  $k$ -point mesh was tested. As a result of the convergence, an energy cutoff of 600 eV was chosen to ensure that the total energies are converged within  $0.1 \text{ meV (f.u.)}^{-1}$ . The Brillouin zone was sampled with a mesh including the gamma point. A  $16 \times 16 \times 16$  mesh was selected for full structural relaxation using the Gaussian smearing method,<sup>12</sup> and a smearing parameter of 0.1 eV was chosen such that the error in the extrapolated energy at 0 K is less than  $0.1 \text{ meV (f.u.)}^{-1}$ . Since the optimization of polymorphs with different forms is usually very difficult and time consuming, we shall optimize the structure around the known forms and then compare their total energies for these forms. Thus, in all cases, the optimization was performed by setting the crystal structure according to the experimental data for  $\text{Li}_2\text{FeSiO}_4$  first for each structure, then by fully relaxing the atomic positions, cell parameters, cell volumes, and cell shapes to obtain the optimized structures for  $\text{Li}_2\text{FeSiO}_4$ . Finally, we replaced iron by vanadium in  $\text{Li}_2\text{FeSiO}_4$  to construct the model for  $\text{Li}_2\text{Fe}_{1-x}\text{V}_x\text{SiO}_4$ , and performed optimization again by fully relaxing the atomic positions, cell parameters, cell volumes, and cell shapes. The final energies for the optimized geometries were recalculated by using the tetrahedron method with Blöchl corrections. There are two magnetic spin orderings, i.e., ferromagnetic (FM) and anti-ferromagnetic (AFM), in  $\text{Li}_2\text{FeSiO}_4$ . However, the total energy difference between FM and AFM is only  $1 \text{ meV (f.u.)}^{-1}$  and the lattice parameters are almost the same.<sup>13</sup> Therefore, all the calculations in this work are spin-polarized with FM configuration unless stated otherwise.

There are large errors on the electronic structure of materials with strong Coulomb interaction<sup>14</sup> using the LDA and GGA methods. They usually underestimate the lithium ion deintercalation voltages ( $V_d$ ) with errors ranging from 0.25 to more than 1.0 V.<sup>15</sup> The GGA over LDA has previously been shown to be essential for correctly reproducing magnetic interactions.<sup>16</sup> It has been reported that for lithium intercalation compounds based on silicates, where due to a strong localization of the transition metal  $d$  orbital, the electronic structure

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**Figure 1.** The structural model of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ .

properties and  $V_4$  values would not be accurately reproduced by standard GGA calculations.<sup>13,17,18</sup> The GGA + U method was developed to more accurately describe strongly correlated materials with localized  $d$  orbital electrons.<sup>19–21</sup> To take into account the strongly correlated character of the  $d$  electrons of iron, a Hubbard-like correlation was added with values of  $U[\text{Fe}] = 5$  eV and  $U[\text{V}] = 4$  eV, and  $J = 1$  eV for all cases, because those have been recently reported as appropriated values for iron silicate compounds.<sup>17,22,23</sup>

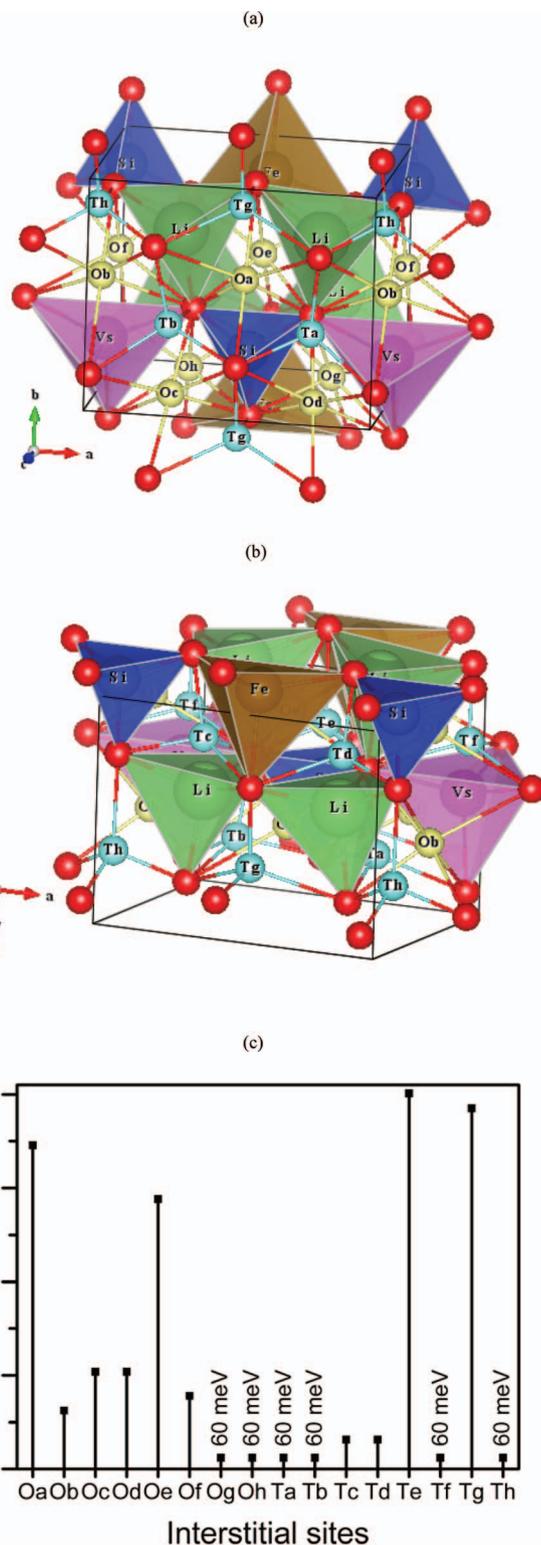
Three possible polymorphs in  $Pmn2_1$ ,<sup>24</sup>  $P2_1$ ,<sup>25</sup> and  $Pmnb$ <sup>26</sup> forms have been reported for  $\text{Li}_2\text{FeSiO}_4$  compounds. Our calculation shows that the total energies for the stable configurations of  $Pmn2_1$ ,  $P2_1$  and  $Pmnb$  are  $-54.512$ ,  $-54.521$  and  $-54.496$  eV (f.u.)<sup>-1</sup>, respectively, which indicates that  $P2_1$  is the stable form with mere 9 and 25 meV (f.u.)<sup>-1</sup> lower than those for the stable configurations of  $Pmn2_1$  and  $Pmnb$ . Since the energy differences among the three are small, the substitution of iron by vanadium may change the relative stabilities of these crystal structures. To verify this point of view, structural models of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  derived from the optimized cell of  $\text{Li}_2\text{FeSiO}_4$  are constructed by replacing a half of the Fe atoms with V in  $Pmn2_1$ ,  $P2_1$  and  $Pmnb$  forms, respectively, then the optimizations of these structures are performed and the corresponding total energies are calculated. The total energies associated with  $Pmn2_1$  are nearly 22 and 80 meV (f.u.)<sup>-1</sup> lower than those for  $P2_1$  and  $Pmnb$ , respectively, implying that the  $Pmn2_1$  becomes the most stable structure in  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ . Therefore, the structural model derived from  $Pmn2_1$  is selected. The optimized structure of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  is illustrated in Fig. 1. This structure belongs to monoclinic system, space group  $Pm$ . The Li, Fe, V, and Si ions in  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  locate in the central sites of the O tetrahedral, whereas each O ion has two Li, one Fe or V, and Si neighbors. There are two formula units per unit cell, i.e., each unit cell contains four Li, one Fe and one V, two Si, and eight O ions. When lithium ions are removed from the structure, various lithium-vacancy configurations can be formed.

### Results and Discussion

Before discussing properties of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ , it is necessary to investigate whether the V substitution or V interstice is more feasible in  $\text{Li}_2\text{FeSiO}_4$ . The energy difference between the interstitial and substituted V ( $\Delta E_{\text{IS}}$ ) may be calculated by

$$\Delta E_{\text{IS}} = E_{\text{I}} - E_{\text{S}} \quad [1]$$

where  $E_{\text{I}}$  and  $E_{\text{S}}$  are the total energies of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  formula units within V interstice and substitution, respectively. As shown in Fig. 2, there is only one type of V substitution site, denoted as “Vs”. On the other hand, there are sixteen V interstitial sites, including eight octahedral interstitial sites labeled as “Oa, Ob, Oc, Od, Oe, Of, Og, and Oh” (Fig. 2a), and eight tetrahedral interstitial sites “Ta, Tb, Tc, Td, Te, Tf, Tg, and Th” (Fig. 2b). The calculated  $E_{\text{IS}}$  between interstice and substitution are presented in Fig. 2c. It is evident that  $E_{\text{IS}} > 0$ ,



**Figure 2.** Schematic representations of V interstitial and substitution sites in  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ . (a) Along the  $c$ -axis (b) Along the  $b$ -axis (c) The calculated energy difference between the V interstice and V substitution. The “Vs” denotes the substitution site; “Oa, Ob, Oc, Od, Oe, Of, Og, and Oh” the octahedral interstitial sites; “Ta, Tb, Tc, Td, Te, Tf, Tg, and Th” the tetrahedral interstitial sites.

**Table I.** The calculated parameters and unit cell volumes ( $V_c$ ) for  $\text{Li}_2\text{FeSiO}_4$  and the selected delithiated states in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  compounds. For comparison, the experimental results of  $\text{Li}_2\text{FeSiO}_4$  from literature Ref. 24 (italic) and the calculated volume changes with the selected delithiated states in  $\text{Li}_x\text{FeSiO}_4$  (bold) are given in parenthesis.

Compound	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	$\alpha / ^\circ$	$\beta / ^\circ$	$\gamma / ^\circ$	$V_c / \text{\AA}^3 (\text{f.u.})^{-1}$	$\Delta V_c / V_c / \%$
$\text{Li}_2\text{FeSiO}_4$	6.326 (6.266)	5.388 (5.330)	4.987 (5.015)	90.0 (90.0)	90.0 (90.0)	90.0 (90.0)	85.00 (83.73)	–
$\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$	6.504	5.342	4.919	90.4	90.0	90.0	85.47	–
$\text{Li}_{1.5}\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$	6.273	5.514	4.978	89.6	89.5	88.9	86.08	0.7 ( <b>0.7</b> )
$\text{LiFe}_{0.5}\text{V}_{0.5}\text{SiO}_4$	6.131	5.660	5.023	90.1	90.9	90.5	86.15	0.8 ( <b>1.4</b> )
$\text{Li}_{0.5}\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$	6.110	5.825	5.044	84.0	90.0	75.6	86.44	1.1 ( <b>1.2</b> )
$\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$	5.882	5.984	5.336	88.6	90.0	90.0	93.86	9.8 ( <b>11.5</b> )

i.e.,  $E_I > E_S$ , indicating that the structure with V substitution is more stable than that with V interstice.

The relations among the formation free energy ( $G_f$ ), internal energy ( $E_f$ ) and configurational entropy ( $S$ ) is expressed as

$$\Delta G_f = \Delta E_f - T\Delta S \quad [2]$$

where the ideal configurational entropy is  $0.69 k_B (\text{f.u.})^{-1}$ ,<sup>4</sup> and  $\Delta E_f$  of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  solid solution can be calculated from the following equation.

$$\Delta E_f = E[\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4] - \left\{ \frac{1}{2} E[\text{Li}_2\text{FeSiO}_4] + \frac{1}{2} E[\text{Li}_2\text{VSiO}_4] \right\} \quad [3]$$

where  $E[\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4]$ ,  $E[\text{Li}_2\text{FeSiO}_4]$  and  $E[\text{Li}_2\text{VSiO}_4]$  are the total energies per  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ ,  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{VSiO}_4$  formula units, respectively. The  $\Delta G_f$  values are evaluated to be  $-55 \text{ meV (f.u.)}^{-1}$ , and  $-75 \text{ meV (f.u.)}^{-1}$  at 298 K if the configurational entropy is considered. The negative  $\Delta G_f$  values indicate that the formation of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  solid solution is thermodynamically feasible.

The predicted lattice parameters and unit cell volumes ( $V_c$ ) for both  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  compounds are given in Table I. The available experimental data<sup>24</sup> are also included for comparisons. As can be seen in the first two rows in Table I, the predicted  $V_c$  values for  $\text{Li}_2\text{FeSiO}_4$  are  $85.00 \text{ \AA}^3$ , with a slight overestimation (1.5%) compared with the experimental values, which is expected from the calculations based on GGA + U exchange and correlation potentials.<sup>27</sup> Since the errors between the experimental and calculated results are less than 2%, it is reasonable to believe that the method provides a good reproduction of the cell parameters and is reliable in the subsequent substitution calculations. It is interesting to note that the substitution of 50% vanadium in  $\text{Li}_2\text{FeSiO}_4$  results in small changes in the cell parameters (mainly increasing  $a$  and  $\alpha$ ), which leads to minor local structural distortions (approximately 0.6% in volume expansion).

To examine the structural evolution of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  during the lithium deintercalation/intercalation process, the formation energy for a given Li-vacancy arrangement with a composition  $x$  in

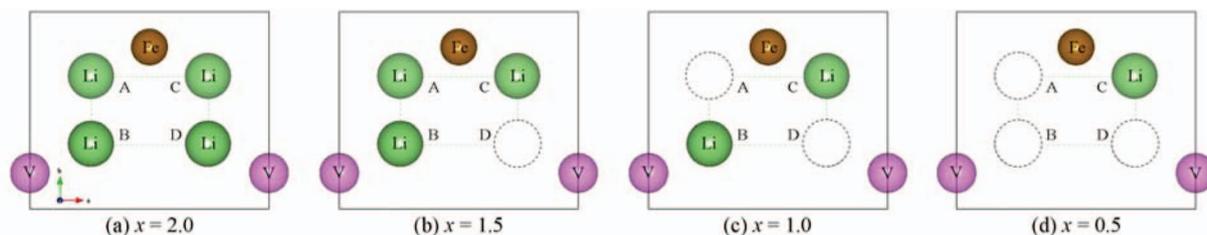
$\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  ( $\Delta_f E_x$ ) is defined as

$$\Delta_f E_x = E[\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4] - \left\{ \frac{x}{2} E[\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4] + \left(1 - \frac{x}{2}\right) E[\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4] \right\} \quad [4]$$

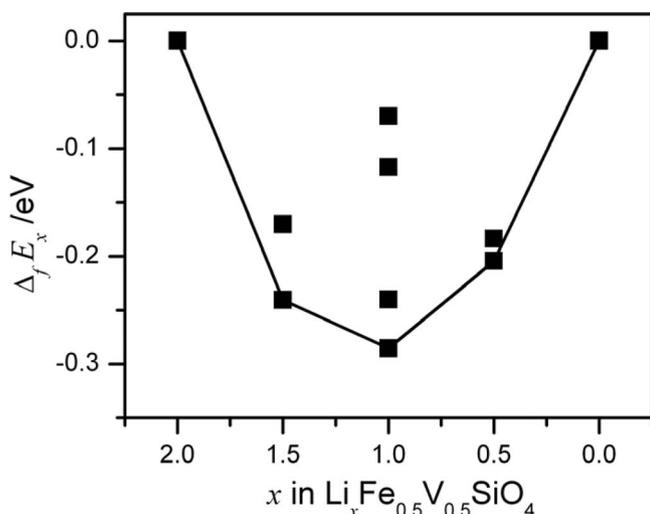
where  $E[\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4]$  is the total energy of the configuration per  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  f.u.,  $E[\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4]$  and  $E[\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4]$  are the energies of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  and  $\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ , respectively. The magnitude of  $\Delta_f E_x$  defined in Eq. 4 reflects the relative stability of  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  with respect to the phase separation into a fraction  $x/2$  of  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  and a fraction  $(1-x/2)$   $\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ .

The lithium ion arrangements in  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  are presented in Fig. 3a, and the most stable lithium-vacancy configurations in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  for  $x = 1.5$ , 1.0 and 0.5 are shown in Fig. 3b–3d. The stable configurations are defined as the lithium-vacancy ordering configurations associated with the lowest formation energies ( $(\Delta_f E_x)_{\text{min}}$ ). Since the  $\text{Li}_2\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  compound has only one symmetry operation of a mirror plane perpendicular to  $a$ -axis, it is not difficult to show that there exist two equivalent sites, namely, A-C and B-D sites, for Li ions (cf. Fig. 3a). In general, there are multiple configurations for each  $x$  in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  at  $0 < x < 2$ . For example, a vacancy and three Li ions exist in the unit cell for  $x = 1.5$ , which corresponds to two independent Li-vacancy ordering configurations. For  $x = 0.5$ , there are three vacancies and one Li ion in the unit cell, similar to the case of  $x = 1.5$  with two Li-vacancy ordering configurations. For  $x = 1.0$  two vacancies and two Li ions in the unit cell lead to four Li-vacancy ordering configurations. The values of  $\Delta_f E_x$  calculated by Eq. 4 are provided as a function of  $x$  in Fig. 4. It is clear that the contours of  $(\Delta_f E_x)_{\text{min}}$  are convex, which implies the attainable configurations for  $0 \leq x \leq 2$ . The selected  $x$  values in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  represent the following typical lithiated/delithiated states during the extractions of the first and second lithium ions:

- $x = 2.0$ : fully lithiated state (no extraction of Li ion)
- $x = 1.5$ : first half delithiated state during the extraction of the first Li ion



**Figure 3.** The lithium ion arrangement and the most stable lithium-vacancy configuration for the selected delithiated states in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  within the unit cell (Si and O atoms omitted).

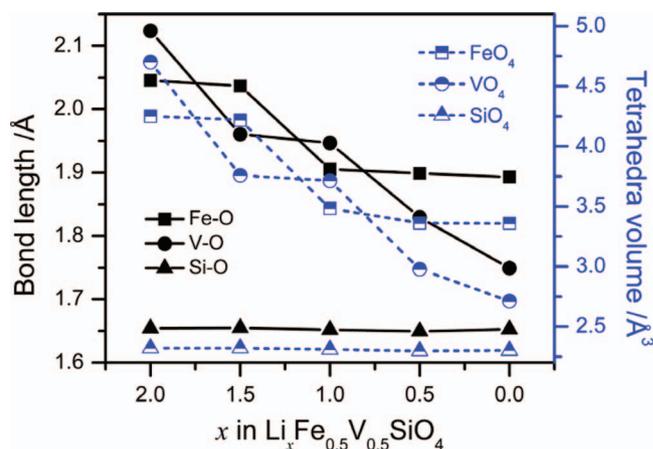


**Figure 4.** The calculated formation energies for the selected delithiated states in  $\text{Li}_x \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$ .

- $x = 1.0$ : first delithiated state (complete extraction of one Li ion)
- $x = 0.5$ : second half delithiated state during the extraction of the second Li ion
- $x = 0$ , fully delithiated state (complete extraction of two Li ions)

The calculated cell parameters and  $V_c$  values for the stable configurations of  $\text{Li}_x \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$  are included in Table I. It is evident that for  $0.5 \leq x \leq 2.0$  all the  $V_c$  values of the V substituted compounds slightly expand with a maximum increase of 1.1%. However, at the fully delithiated state ( $x = 0$ ), the compound shows a rather significant volume expansion up to 9.8%. In particular, the volume changes with the fully delithiation of V substituted compounds are 17% smaller than those of  $\text{Li}_2 \text{FeSiO}_4$ , suggesting that the V substitution could notably reduce the structure deformation for the delithiated phase, which might become possible to avoid severe capacity fading observed previously from the manganese substitutions.

The V substituted compound,  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$ , may be regarded as a network of corner shared tetrahedra of  $\text{SiO}_4$ ,  $\text{FeO}_4$ , and  $\text{VO}_4$  with properly located Li ions. Deintercalating Li ions to the states with  $x < 2.0$  may imply that these tetrahedra are able to evolve, which would relate to the structural stability of the compounds. Thus, the capability of delithiation/lithiation for the  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$  compounds depends upon the deformation behaviors such as bond lengths of M-O and volume changes of these tetrahedra. It is, therefore, important to understand how these tetrahedra deform during the process of deintercalation/intercalation. The calculated average bond lengths of Fe-O, V-O and Si-O, as well as the volumes of  $\text{SiO}_4$ ,  $\text{FeO}_4$ , and  $\text{VO}_4$  tetrahedra for  $x = 2.0, 1.5, 1.0, 0.5$  and 0 are compared in Fig. 5. It is observed that the significant reductions in the volumes of  $\text{VO}_4$  tetrahedron and average bond lengths of V-O occur as  $x$  varies from 2.0 to 1.5, from 1.0 to 0.5, and 0.5 to 0.0, which may accompany with redox reactions



**Figure 5.** The calculated average bond lengths and volumes in  $\text{FeO}_4$ ,  $\text{VO}_4$  and  $\text{SiO}_4$  tetrahedra for the selected delithiated states in  $\text{Li}_x \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$ .

changed as  $x$  varies from 2.0 to 0, confirming that the  $\text{SiO}_4$  tetrahedron is very stable during the delithiation/lithiation process.

The calculated FM spin-polarized total density of states (DOS) and their projections onto the  $d$ -shell of Fe and V ions and the  $p$ -shell of O ion for the stable configurations of  $\text{Li}_x \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$  are given in Fig. 6. It may be seen that the highest occupied band is mainly the up-spin V-3d band at  $x = 2.0$ . As Li ions are extracted out from the  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$  compound to the states of  $x = 1.5, 1.0, 0.5$ , and 0, the electrons are removed from the up-spin V-3d band, the down-spin Fe-3d band, the up-spin V-3d band, and finally the up-spin V-3d band, respectively. These observations suggest that the order of redox reactions occurred during the delithiation process is  $\text{V}^{2+}/\text{V}^{3+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{V}^{3+}/\text{V}^{4+}$ , and  $\text{V}^{4+}/\text{V}^{5+}$  for the selected five lithiated/delithiated states. In addition, preliminary information on electron conductivity can be obtained from the DOS of  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$ . As shown in Fig. 6, the band gap ( $E_g$ ) of  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$  is 1.7 eV, which is only half of  $\text{Li}_2 \text{FeSiO}_4$  (3.4 eV),<sup>13</sup> indicating that the V substitution would improve the electronic conductivity of  $\text{Li}_2 \text{FeSiO}_4$ . The Fermi level resides in a gap between the filled V-3d states and the unfilled Fe-3d states. It is likely that the filled V-3d states will participate in the electron transfer in this material.

Based on the delithiation reaction of  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$ ,



the required energy ( $\Delta E_r$ ) for Reaction 5 can be calculated by

$$\Delta E_r = G[\text{Li}_x \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4] - G[\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4] + (2-x) G(\text{Li}) \quad [6]$$

The average lithium ion deintercalation voltage ( $V_d$ ) can be determined by

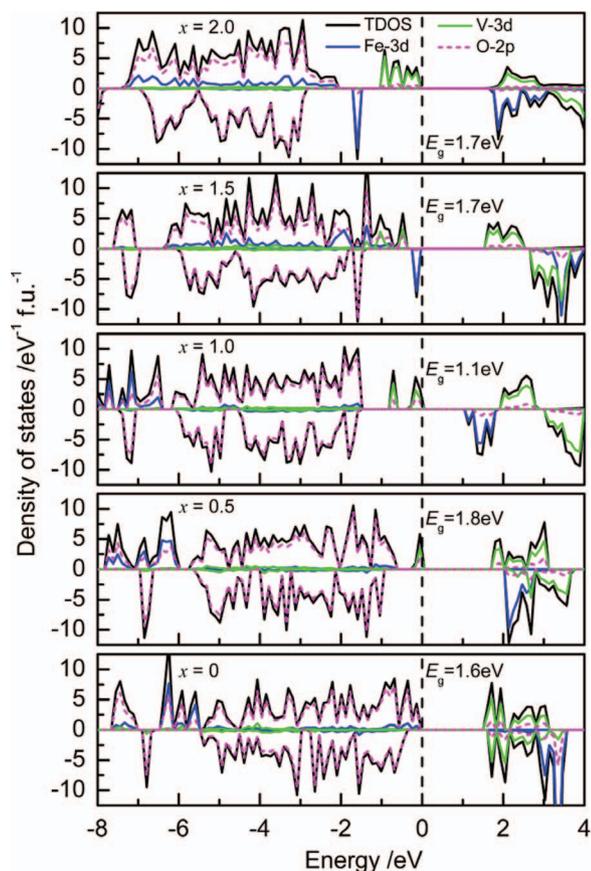
$$V_d = - \frac{G[\text{Li}_{x_2} \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4] - G[\text{Li}_{x_1} \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4] - (x_2 - x_1) G(\text{Li})}{x_2 - x_1} \quad [7]$$

The specific energy density ( $E_m$ ) is defined by<sup>28</sup>

$$E_m = - \frac{G[\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4] - G[\text{Li}_x \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4] - (2-x) G(\text{Li})}{m} \quad [8]$$

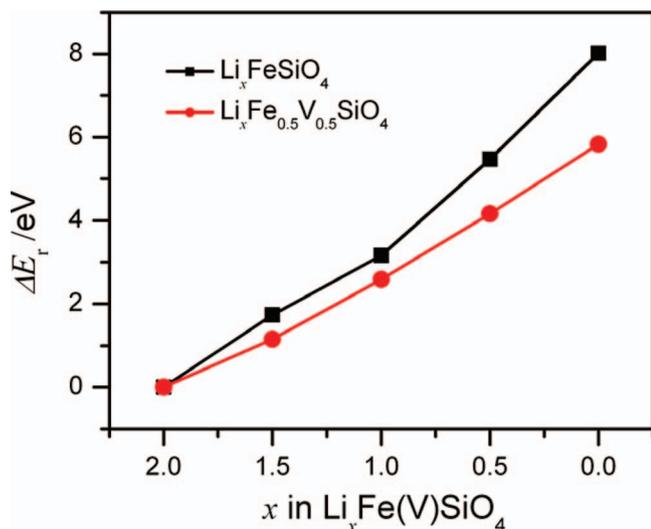
of  $\text{V}^{2+}/\text{V}^{3+}$ ,  $\text{V}^{3+}/\text{V}^{4+}$ , and  $\text{V}^{4+}/\text{V}^{5+}$ , respectively. On the other hand, the remarkable decreases in the volumes of  $\text{FeO}_4$  tetrahedron and the average bond lengths of Fe-O take place when  $x$  varies from 1.5 to 1.0 with a redox reaction of  $\text{Fe}^{2+}/\text{Fe}^{3+}$ . As expected, the volume of  $\text{SiO}_4$  tetrahedron and the average bond lengths of Si-O remain almost un-

Typically, the free energies ( $G$ ) may be replaced by the ground state energies ( $E$ ) with little error.<sup>29</sup> The  $G(\text{Li})$  is the energy of metallic lithium calculated at the  $bcc$  structure, which corresponds to the structural phase of Li anode. The quantity  $m$  in Eq. 8 denotes the mass with one molecular formula unit of  $\text{Li}_2 \text{Fe}_{0.5} \text{V}_{0.5} \text{SiO}_4$ .

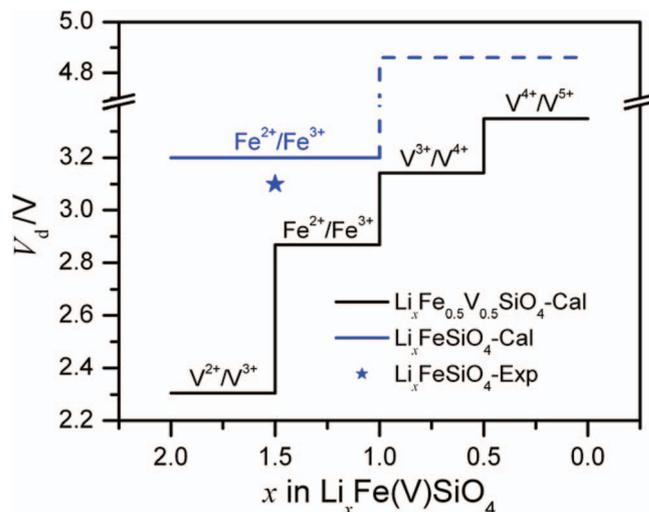


**Figure 6.** Density of states for the selected delithiated states in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ . The positive/negative directions in the Y-axis represent the majority/minority spin directions. The Fermi level is set at 0 eV and the values of energy gap ( $E_g$ ) are provided.

The calculated  $E_r$  values for  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  are plotted in Fig. 7. The  $E_r$  values for delithiation from  $\text{Li}_2\text{FeSiO}_4$  obtained using the identical computational scheme are also included for comparison. It is apparent that the  $E_r$  values for delithiation from  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  are substantially smaller than those from  $\text{Li}_2\text{FeSiO}_4$ , indicating that



**Figure 7.** A comparison of the required energies for different delithiated states in  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ .



**Figure 8.** The calculated deintercalation voltages for the selected delithiated states in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ . For comparison, the calculated values and available experimental data for  $\text{Li}_2\text{FeSiO}_4$  are also included.

V substitution is beneficial to the delithiation from  $\text{Li}_2\text{FeSiO}_4$ , in particular, to the full delithiation by removing second Li ions.

The calculated  $V_d$  values for  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  are depicted in Fig. 8. The  $V_d$  values of  $\text{Li}_x\text{FeSiO}_4$  obtained using the same computational method and from the available experimental data<sup>24</sup> are also included for comparison. Apparently, there exist four platforms at 2.30, 2.87, 3.14 and 3.35 V, corresponding to the  $\text{V}^{2+}/\text{V}^{3+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{V}^{3+}/\text{V}^{4+}$  and  $\text{V}^{4+}/\text{V}^{5+}$  redox couples, respectively, for  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ , which are lower than those for  $\text{Li}_x\text{FeSiO}_4$ , particularly at  $0 \leq x \leq 1$ . This suggests that the  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  cathode materials can function within the stability window of conventional electrolytes. Compared with  $\text{Li}_x\text{FeSiO}_4$ , the reduction of 0.33 V in the redox potentials of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  by V substitution results in the decrease of 87 Wh (kg)<sup>-1</sup> in  $E_m$  during the delithiation by removing the first Li ions. However, it is almost impossible to remove the second Li ions from  $\text{Li}_x\text{FeSiO}_4$  in the conventional electrolytes with such high  $V_d$  values as 4.86 V observed in Fig. 8. The significantly lower  $V_d$  values achieved with V substitution (3.14 and 3.35 V) made  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  more readily to delithiating the second Li ions. Thereby, the calculated total  $E_m$  in  $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$  would be  $\sim 978$  Wh (kg)<sup>-1</sup>, which is appreciably larger than that of  $\text{Li}_2\text{FeSiO}_4$  ( $\sim 521$  Wh (kg)<sup>-1</sup>).

## Conclusions

Based on the first-principles calculations, the 50% vanadium substitution for iron in  $\text{Li}_2\text{FeSiO}_4$  is thermodynamically more feasible than vanadium interstice. The higher capacity may be obtained with vanadium substituted compound by exchanging more than one lithium ions. The calculated redox potentials of  $\text{V}^{2+}/\text{V}^{3+}$ ,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{V}^{3+}/\text{V}^{4+}$ , and  $\text{V}^{4+}/\text{V}^{5+}$  are 2.30, 2.87, 3.14 and 3.35 V versus Li, respectively, indicating that the vanadium substituted compound ( $\text{Li}_x\text{Fe}_{0.5}\text{V}_{0.5}\text{SiO}_4$ ) can function within the stability window of conventional electrolytes. The detrimental capacity fading might be minimized with the improved structural stability in delithiated phases of vanadium substituted compounds due to smaller changes in the cell parameters and lower degree of volume expansions during the delithiation processes.

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