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Editor's Choice

First principle study of the electrochemical properties of Li_2FeSiS_4

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ABSTRACT

First principle calculations have been performed to evaluate the effect of S substitution for O on the electrochemical performance of Li_2FeSiO_4. Basing on the Li_2FeSiO_4 structure, the hypothetical models of Li_2FeSiS_4 have been analyzed. The deinsertion voltage associated to Fe^{3+}/Fe^{4+} redox couple is predicted to decrease from 4.80 V (Li_2FeSiO_4) to 3.24 V (Li_2FeSiS_4). From the point of view of electronic conductivity, Li_2FeSiS_4 is expected to have a better current rate capacity than Li_2FeSiO_4. The calculations also indicate that S substitution significantly improve the material ductility, preventing the probable structural collapse of silicate materials during charge–discharge cycles. In the light of our calculated results the high electrochemical performance of silicate cathode materials would be achieved in Li_2FeSiS_4.

1. Introduction

For the past decade, silicate materials Li_2MSiO_4 (M = Mn, Fe, Co, Ni) have been extensively studied as cathode materials for Li-ion batteries [1–9]. The Li_2MSiO_4 group has attracted considerable interests due to the possibility of utilizing two Li ions per formula unit (FU) during the battery operation, which could yield higher specific capacity. Among these materials, Li_2FeSiO_4 exhibits reversible electrochemical activity and is considered as the most promising candidate. The inherent disadvantage of Li_2FeSiO_4 is the high operating voltage associated to Fe^{3+}/Fe^{4+} redox couple, which exceeds the stability window of conventional electrolyte (ca. 4.8 V) [4,5]. To attain a high performance, Armand et al. [6,7] proposed that the substitution of more covalent Fe—N for Fe—O bonds would destabilize the Fe-d antibonding states leading to a voltage decrease. Their computational results predicted that the voltage (Fe^{3+}/Fe^{4+}) can be decreased from 4.86 V in Li_2FeSiO_4 to 4.1 V in Li_2FeSiO_3N. The deinsertion of two Li ions per FU in Fe-based silicates can thus be implemented.

It is noted that a ductile–brittle transition with Li deinsertion was observed in the elastic properties calculations of Li_2MSiO_4 (M = Mn, Fe, Co, Ni) [10]. During charge–discharge cycles, the brittle $MSiO_4$ structure would probably collapse under significant cell expansion/contraction, which induces structure amorphism and drastic capacity fading of Li_2MnSiO_4 [11,12]. The stable cycle performance of Li_2FeSiO_4 lies in only one Li ion per FU being deinserted under the high operating voltage. If the deinsertion of two Li ions is possible within the limit of electrolyte, the brittle $FeSiO_4$ would also probably damage the cycle performance.

N substitution for O can decrease the deinsertion voltage to achieve the full deinsertion of two Li ions [6,7]. However, whether the reversible electrochemical activity can be achieved by the substitution is questionable. Recent elastic properties calculation of $Li_{2-x}FeSiO_{4-y}N_y$ showed that the Pugh ratio B/G (quotient of bulk to shear modulus) of delithiated $FeSiO_3N$ is 0.96 [13], significantly lower than the critical value 1.75 which separate ductile and brittle materials [14], and even lower than the values 1.02 of $FeSiO_4$ and 1.26 of $MnSiO_4$ [10]. Therefore $Li_2FeSiO_{4-y}N_y$ would experience structure amorphism and capacity fading during charge–discharge cycles, as observed in Li_2MnSiO_4 [11,12]. Simple doping modification for Li_2FeSiO_4 with the aim of decreasing the deinsertion voltage does not definitely improve the electrochemical performance.

N and S locate near O in the periodic table, they are often employed to substitute O to improve the performance of materials [6,7,15]. In the present work, we perform first principles calculations of the virtual Li_2FeSiS_4 compound to investigate the effects of S substitution for O on the crystal structure, deinsertion voltage, rate capacity and structural stability of Li_2FeSiO_4.

2. Computational details

The calculations were performed using the projector augmented wave (PAW) method [16], within the framework of density functional theory (DFT), as implemented in the Vienna *ab initio* Simulation Package (VASP) [17,18]. The exchange–correlations were treated by the generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [19]. To address on-site

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Coulomb interactions in the localized d electrons of transition-metal ions, additional Hubbard parameter correction was taken [20]. *U* and *J* parameters were adopted as 5 eV and 1 eV respectively, in accordance with previous calculations [4,10,13]. The energy cut-off for the plane wave basis set was kept at a constant value of 520 eV and the reciprocal space sampling done with k-points grid of 4 × 5 × 5. Structure optimization was achieved until the force on each atom is less than 0.01 eV $Å^{-1}$.

The lattice stability of Li_2FeSiS_4 was evaluated by the phonon dispersion spectrum. Phonon calculations were carried out using the finite displacement method and PHONONPY package [21]. 2 × 2 × 2 supercell with 128 atoms and 3 × 4 × 4 k-points mesh were applied to calculate the force constants.

To calculate the elastic properties, a set of normal and shear strains was applied to fit the energy-strain curves of deformed structures. The polynomial coefficients were used to solve the linear equations to determine the elastic constants. The bulk modulus B, shear modulus G and Pugh ratio B/G were calculated according to Voight-Reuss-Hill approximation [22–24].

3. Results and discussion

3.1. Crystal structure

The crystal structure of Li_2FeSiS_4 was constructed on the basis of Li_2FeSiO_4 with the orthorhombic lattice (space group: $Pmn2_1$) [1] by the relaxation of lattice parameters and atom positions, as shown in Fig. 1a. It can be described as being built up of the infinite layers of $[FeSiS_4]_\infty$ lying on the *ac*-plane, and linked by LiS_4 tetrahedra along the *b*-axis.

Recently an intersite-exchange of Li (initially at 4b sites) and transition-metal (initially at 2a sites) was reported for Li_2CoSiO_4 [25] and N-substituted Li_2FeSiO_4 [13]. The similar behavior was also observed in the structure of Li_2FeSiO_4 after the first charge–discharge cycle [1]. In view of the possibility of Li/Fe site-exchange, additional six possible configurations are considered in the pursuit of the ground state structure of Li_2FeSiS_4. They are labeled as Li1 – Li2, Li1 – Li3, Li1 – Li4, Li2 – Li3, Li2 – Li4 and Li3 – Li4 according to the locations of two Fe atoms. For convenience the configurations with and without Li/Fe site-exchange being considered are classified as site-exchanged (SE) and initial (INIT) respectively.

Table 1 lists the calculated total energies for various possible configurations of Li_2FeSiS_4. The corresponding data of Li_2FeSiO_4 are also given for comparison. The calculated results show that the most stable configuration of Li_2FeSiO_4 is INIT ($Pmn2_1$), being the energy difference with SE configurations for at least 20 $meVFU^{-1}$. However, the hypothetical Li_2FeSiS_4 prefers to form a β-Li_2CoSiO_4 type structure with the space group $Pbn2_1$ (see Fig. 1b), in which two Fe atoms locate as far as possible from each other at 4b sites. This configuration lowers the energy by at least 56 $meVFU^{-1}$ in comparison with the less stable INIT configuration.

Table 1
Calculated total energies ($meVFU^{-1}$) of Li_2FeSiO_4 and Li_2FeSiS_4 with various possible configurations. The INIT configuration are derived from the ground state structure of Li_2FeSiO_4 with $Pmn2_1$ symmetry. The Li/Fe site-exchange are included in the SE configurations characterized by the locations of Fe atoms at 4b sites. Among the SE configurations, Li1 – Li2, Li1 – Li3 and Li1 – Li4 are energetically degenerate with Li3 – Li4, Li2 – Li4 and Li2 – Li3 respectively. Bold value represents the smallest value in that group.

	INIT	SE		
		Li1 – Li2 (Li3 – Li4)	Li1 – Li3 (Li2 – Li4)	Li1 – Li4 (Li2 – Li3)
Li_2FeSiS_4	−39.401	−39.355	−**39.457**	−39.325
Li_2FeSiO_4	−**53.285**	−53.120	−53.265	−53.098

To evaluate the lattice stability, we calculated the phonon dispersion spectrum of Li_2FeSiS_4 with the most stable Li/Fe SE configuration as given in Fig. 2. The occurrence of imaginary frequency is often a sign of lattice instability. Usually the imaginary frequency is contributed by 3 low frequency acoustic branches which reflect the vibration of mass center. The locations of heavier Fe atoms would play an important role in the lattice stability. As seen in the figure, the calculated vibrational spectrum has no imaginary frequency, which suggests that the energetically favored Li/Fe SE configuration is dynamically stable.

Li ions are selectively removed according to energy minimization to derive the delithiated structures from the possible one INIT and six SE lithiated structures. During this process, Fe atoms keep sitting at 4b sites and as far as possible from each other due to the strong electrostatic repulsion between Fe atoms which is consistent with the calculated results of Li_2MSiO_4 and $Li_2FeSiO_{4-y}N_y$ [10,13].

3.2. Deinsertion voltage

The voltage-composition profiles of Li_2FeSiO_4 and Li_2FeSiS_4 are marked with two-plateau structures associated to Fe^{2+}/Fe^{3+} and Fe^{3+}/Fe^{4+} redox couples, as shown in Fig. 3. The first (Fe^{2+}/Fe^{3+}) and the second (Fe^{3+}/Fe^{4+}) deinsertion voltages for Li_2FeSiO_4 on the basis of $Pmn2_1$ structure (without site-exchange) are 3.08 V and 4.80 V, while the counterparts for Li_2FeSiS_4 are 3.07 V and 3.14 V.

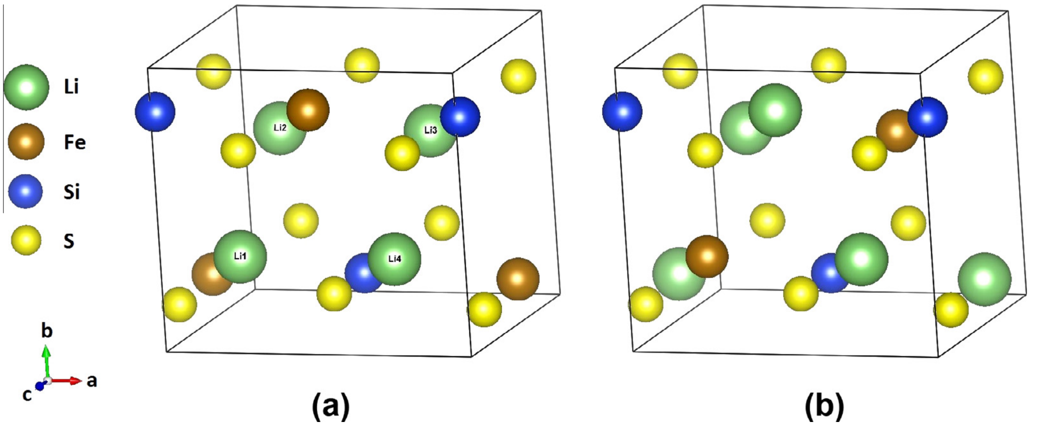

Fig. 1. Crystal structures of Li_2FeSiS_4 with $Pmn2_1$ (a) and $Pbn2_1$ (b) space groups.