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Density functional theory insights into the structural stability and Li diffusion properties of monoclinic and orthorhombic Li_2FeSiO_4 cathodes

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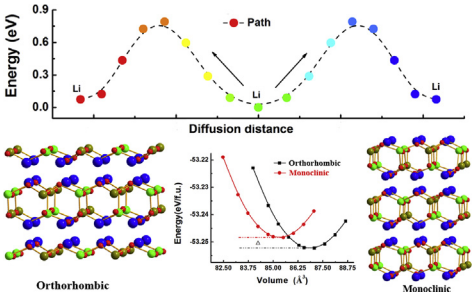
HIGHLIGHTS

- Thermodynamic properties of monoclinic and orthorhombic Li_2FeSiO_4 are investigated.
- Delithiation energy profiles and structures of $Li_{2-x}FeSiO_4$ are calculated.
- Charge compensation mechanism is discussed accordingly.
- Li diffusion trajectories and energy barriers are derived in both Li_2FeSiO_4 phases.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium iron orthosilicate (Li_2FeSiO_4) is an important alternative cathode for next generation Li-ion batteries due to its high theoretical capacity (330 mA h/g). However, its development has faced great challenges arising from significant structural complexity, including the disordered arrangement/orientation of Fe/Si tetrahedra, polytypes and its poorly understood Li storage and transport properties. In this context, ab-initio calculations are employed to investigate the phase stability and Li diffusion profiles of both monoclinic ($P2_1$) and orthorhombic ($Pmn2_1$) Li_2FeSiO_4 orthosilicates. The calculations demonstrate that formation of Li–Fe antisites can induce a metastability competition between both phases, with neither dominating across nearly the entire discharging profile from Li_2FeSiO_4 through to $LiFeSiO_4$. Furthermore, structural instability is shown to be a serious concern at discharge concentrations below $LiFeSiO_4$ (1 Li extraction) due to the shared occupation of Li donated electrons with oxygen 2p orbitals – rather than the hypothesized transition to a tetravalent Fe^{4+} state. This finding is further supported by diffusion calculations that have determined a high activation energy barrier towards fast charging and rapid phase transitions. In summary, these theoretical results provide critical and timely insight into the structural dynamics of lithium iron orthosilicate, in pursuit of high energy density cathodes.

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1. Introduction

Lithium metal orthosilicate materials $Li_2\boldsymbol{M}SiO_4$ ($\boldsymbol{M}$ = Fe, Mn, *etc.*) are promising cathode alternatives for next generation Li-ion batteries due to their high theoretical capacity (~330 mA h/g *vs.* 2 Li exchange) [1–4]. However, great challenges remain to take full advantage of their theoretical capacity in a reversible manner due to their complex structure and Li diffusion kinetics. In particular, the occurrence of disordered arrangements in the form of Li–Fe antisites and the co-existence of many polymorphs interfere with the Li ion exchange process, are likely responsible for capacity loss upon electrochemical cycling [5–11]. Hence there is a need to further investigate these phenomena in order to fully understand the dynamics of Li storage and transport in the prototype Li_2FeSiO_4 material (LFS) – a necessary condition in our pursuit of a higher charge capacity (>1 Li capacity) cathode. Crystallographically, lithium metal orthosilicates can be indexed into two crystal families to describe its structural symmetry and atomic occupations, namely monoclinic and orthorhombic phases. These two phases, at least according to simulation results in the case of Li_2MnSiO_4 [12], are reported to have very close Gibbs free energies, a situation that complicates both their synthesis as well as the interpretation of their electrochemical performance. A similar situation exists for the less energetically favorable metastable Li_2FeSiO_4 phases [13]. Thus without an in-depth understanding of the role of each phase in the observed capacity fading and structure instability during cycling [10], it is unlikely that significant progress will be made towards realizing the full Li-ion storage potential of lithium metal orthosilicate cathodes.

In early reports [5,12] less than one Li was extracted from each Li_2FeSiO_4 unit cell upon cycling, far below the maximum theoretical capacity, and this low capacity level was ambiguously ascribed to interior structural distortions [14,15]. More specifically the observed lowering of the potential plateau from 3.10 to 2.80 V during the first cycle was explained by a structural rearrangement in which some of the Li ions (in the 4b site) and Fe ions (in the 2a site) become interchanged [15]. However further clarifications are needed to confirm the formation and the role of the Li–Fe interchange taking place during electrochemical cycling in these cathodes. Then by *in-situ* XRD, Dominko *et al.* demonstrated a structural collapse of Li_2MnSiO_4; the observed structural stability is completely different for Li_2FeSiO_4, which undergoes a fully reversible two-phase transition, but a clear identification of the two-phase structure has not yet been achieved [16,17]. Subsequent structural analysis implies intricate atomic occupations in $Li_2\boldsymbol{M}SiO_4$ ($\boldsymbol{M}$ = Fe, Mn, *etc.*), including the orthorhombic $Pmn2_1$ phase by Nyten *et al.* [5], monoclinic lattice with $P2_1$ or $P2_1/m$ symmetry by Nishimura *et al.* [18], and the orthorhombic *P*mnb phase and monoclinic $P2_1$/n phase by Sirisopanaporn *et al.* [7], the electrochemical performance of which demonstrates strong structure-dependence. However, Saracibar *et al.* have identified monoclinic ($P2_1$) and orthorhombic ($Pmn2_1$) Li_2FeSiO_4 to be the most energetically favorable, which has been supported by our recent experimental work [10], and these two phases shall be the focus of the present study [13].

Aside from the reported two-phase reaction of Li storage mechanism other issues remain unresolved as is the charge compensation from Fe^{2+} oxidation to Fe^{4+} suggested by Lv *et al.* [8] in the case of $P2_1$/n phase Li_2FeSiO_4 cathode and the associated phase transition phenomena. The latter have been primarily investigated on postmortem [9] and/or *in situ* – electrochemically [10] or structurally [19] – lithium iron orthosilicate electrodes. However these studies have led to many controversial results, including the Li-extraction-induced phase transition process [8–10,20] and the existence of tetra-valent iron that is not convincing due to its instability and short lifetime during the electrochemical reaction [8,19]. Therefore the key problem remains as to the unclear relationship between structure, charge compensation and the electrochemical performance, which has a profound influence on the Li storage and transport properties of LFS cathodes, thus in turn limiting their real battery applications.

In addition to its phase complexity, LFS also suffers from low electronic conductivity of no higher than 10^{-14} S/cm [17] and similarly poor Li-ion conductivity. Theoretical simulations and experimental measurements have placed the Li-ion diffusion activation energy in the Li_2FeSiO_4 at approximately 1.0 eV [6,21,22], which is more than three times higher with respect to that of the same polyanion cathode of $LiFePO_4$ (0.3 eV) [23]. To understand the coupled phase evolution and ionic/electronic diffusion properties of LFS, it is necessary to fundamentally examine the atomic occupation, structure evolution and Li diffusion trajectory in $Li_{2-x}FeSiO_4$ lattice. Here, first-principles calculations are performed to explore the crystal structure, defects, electronic structure and Li diffusion kinetic properties to elucidate the Li/Fe antisite formation, charge compensation and Li transport mechanisms in both monoclinic ($P2_1$) and orthorhombic ($Pmn2_1$) phase Li_2FeSiO_4. The results indicate that monoclinic ($P2_1$) and orthorhombic ($Pmn2_1$) phases may persist throughout the intercalation process and that the extraction of more than one Li-ion from LFS may require greater control of oxygen bonding induced structural instabilities. In general, it is anticipated that this work will contribute a lot to the developments and optimization of stabilized LFS structures for a > 1 Li exchange cathode.

2. Calculation methodology

All spin-polarized total energy calculations were performed using Vienna *Ab initio* Simulation Package (VASP) [24,25] within the projector augmented-wave (PAW) approach [26–29] in the framework of density functional theory (DFT). Generalized gradient approximation (GGA) was adopted in the parameterization of Perdew, Burke, and Ernzerhof (PBE) [30,31]. To describe the exchange–correlation interaction and a Hubbard-type correction U was taken into account to deal with the strongly correlated Fe 3*d* electrons [32,33]. Following previous reports, the effective U value was set to 4.50 eV [34–36]. The configurations Li $2s^1 2p^0$, Fe $3d^7 4s^1$, Si $3s^2 3p^2$ and O $2s^2 2p^4$ were treated as the valence electrons. A kinetic energy cutoff of 600 eV was used throughout the simulations. Geometry optimizations were performed using a conjugate gradient minimization until all the forces acting on ions were less than 0.01 eV/Å per atom for all the static calculations and 0.02 eV/Å per atom for all the kinetic calculations. K-point mesh with a spacing of *ca.* 0.03 $Å^{-1}$ was adopted [37]. The minimum energy pathways and saddle points of Li migration were calculated using the nudged elastic band (NEB) method [38,39]. This method duplicates a series of images (seven images here) between the starting point and the end point of diffusing ion to simulate the intermediate states, with the positions of the starting point and the end point fixed during kinetic calculations.

For monoclinic (S.G. $P2_1$, denoted as *m*-LFS) and orthorhombic (S.G. $Pmn2_1$, denoted as *o*-LFS) Li_2FeSiO_4 structures, there are 4 and 2 formula units (f. u.) in each unit cell (u-cell, see Fig. 1a and b as well as supporting info Fig. S1). Then for better optimization and calculation of the electronic structure and Li diffusion kinetics, the extended cells (e-cell, see supporting info Fig. S1) were re-built using the transformation matrixes of [100; 020; 001] and [10$\bar{1}$; 020; 101], respectively acting on the primitive cell (p-cell) of the *m*-LFS and *o*-LFS phases to arrive at an e-cell containing 8 Li_2FeSiO_4 formula units. Furthermore, $2\boldsymbol{a} \times 2\boldsymbol{b} \times 1\boldsymbol{c}$ of *m*-LFS and $2\boldsymbol{a} \times 2\boldsymbol{b} \times 2\boldsymbol{c}$ *o*-LFS supercells with 16 formula units were utilized to simulate the