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Defect Engineering of Iron-Rich Orthosilicate Cathode Materials with Enhanced Lithium-Ion Intercalation Capacity and Kinetics

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Supporting Information

ABSTRACT: Defect engineering via nonstoichiometric composition control can serve as an effective strategy to tune the electronic and crystal structures of intercalation compounds, as has been recently evidenced in Li-rich cathode materials. To extend this strategy in another direction, Fe-richness as opposed to Li-richness is investigated in improving the electrochemical performance of a promising cathode material, Li₂FeSiO₄ (LFS). Nonstoichiometric LFS compounds in orthorhombic Pmn2, phase with up to 8% Fe-excess are successfully synthesized via controlled hydrothermal synthesis. It is demonstrated that, in addition to the higher electron capacity from the accessible Fe^{2+}/Fe^{3+} redox couple, the presence of excess Fe enhances the intercalation kinetics vis-à-vis the stoichiometric composition. From combined electrochemical evaluation and first-principles DFT calculations, the enhanced kinetics are rationalized by the introduction of the Fe^{\bullet}_{Li} + V'_{Li} defect pair and newly generated electron conducting states from the creation of local Fe-O-Fe configurations. Moreover, the Fe-rich structure facilitates Fe migration to the Li-site due to a lower energy barrier than that of stoichiometric LFS, hence apparently leading to faster phase



transformation from Pmn21 toward the cycled inverse Pmn21 phase. More generally, this study opens alternative defect and compositional engineering approaches in designing next generation intercalation materials with improved electrochemical performance.

KEYWORDS: nonstoichiometry, Fe-rich, Li₂FeSiO₄, Li diffusion, Li-ion batteries

1. INTRODUCTION

In the paradigm of intercalation cathode materials for Li-ion batteries, most research studies have focused on ordered and stoichiometric compounds, such as layered LiNi_xCo_yMn_zO₂ (NCM, x + y + z = 1), spinel LiMn₂O₄ (LMO), and olivine LiFePO₄ (LFP).^{1,2} In the recent decade, there has been increasing interest in developing nonstoichiometric oxides as an attempt to enable high energy density of the cathode materials.^{3–6} Reversible oxygen redox activity, thanks to the Lirich compositional design, adds extra capacity to what can be achieved with solely transition metal redox couple.^{3,7,8} It has been proven in these studies that compositional engineering can serve as an effective strategy for tuning the crystal and electronic structures and hence electrochemical properties of the intercalation materials.

Li₂FeSiO₄ (LFS) is a sustainable and promising high energy density intercalation cathode material with theoretical energy density of 1120 Wh kg⁻¹ because of having two Li per formula unit.^{9,10} Unfortunately, drawbacks such as low electronic and ionic conductivities and the difficulty in extracting reversibly more than one Li have hindered its development.¹¹ Performance of Li-ion batteries is highly correlated to the transport of electrons and Li-ions in the lattice of the electrodes. The lattice of stoichiometric LFS in Pmn21 structure can be viewed as an

assembly of corner-sharing tetrahedra of LiO₄, FeO₄, and SiO₄ occupying the hexagonal close-packed-based framework of oxygen.¹² Each FeO₄ is separated from the other by SiO₄ or LiO_4 . This results in a large bandgap of about 3 eV¹³ and a small electronic conductivity of about 6 \times $10^{-14}~S~cm^{-1}$ at room temperature and about 2×10^{-12} S cm⁻¹ at 60 °C.¹⁴ Within this framework, Li could transport along the *a*-direction with a migration barrier of 0.83 eV or along a zigzag *c*-direction with a migration barrier of 0.74 eV.¹⁵ Upon electrochemical cycling, LFS undergoes phase transformation to a cycled crystal structure with lower energy¹⁶ that is associated with an enlarged migration barrier to 0.91 eV along a zigzag cdirection.¹⁷ This Li migration barrier is high compared to those of other Fe-based cathode materials, for example, 0.55 eV for LiFePO₄¹⁸ and 0.47 eV for Li₂Fe(SO₄)₂.¹⁹ Meanwhile, it is also possible that the transport of electron and Li-ion is strongly coupled in LFS, referring to the formation of a small polaron that has been well-studied in LFP.²⁰⁻²³

To address the challenge of enhancing the electrochemical performance of LFS, introducing nonstoichiometric defects



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could serve as a powerful tool. There are two directions to tune the stoichiometry of LFS by varying Li/Fe ratio-either increase the content of Li while reducing Fe (Li-rich) or the other way around (Fe-rich). In the Li-rich direction, the chemical formula can be written as $Li_{4-2x}Fe_xSiO_4$ (0 < x < 1); thus, the total cations $(Li^+ + Fe^{2+})$ to be placed in the lattice are more than the original tetrahedral sites for Li and Fe. In a recent study on Li-rich LFS, Billaud et al.²⁴ proposed that the excess Li could occupy the interstitial octahedral sites. Interestingly, the presence of excess Li was found to promote the Li transport during (de)intercalation and thus enhance the rate performance. Yet, Li-rich LFS failed to deliver higher capacity because introducing Li-excess sacrifices the Fe²⁺/Fe³⁺ redox capacity. In the Fe-rich direction, denoted as chemical formula $Li_{4-2x}Fe_xSiO_4$ (1 < x < 2), the excess Fe could occupy the Li-site while forming a Li-vacancy to maintain charge neutrality. To the best of our knowledge, Fe-rich LFS compounds have not been reported, but as discovered in the present work this strategy can prove highly rewarding via alteration of the bonding and defect chemistry in terms of increased storage capacity, electronic conductivity, and Li transport kinetics.

An attempt to prepare Fe-rich LFS was made by Zhou et al. using sol-gel method with reactants containing excess Fe.²⁵ However, the excess Fe resulted in the formation of LiFeO_{2-x} as a secondary phase rather than being mixed in the LFS matrix. Li-rich Li₂MnSiO₄ was prepared by solid-state reaction via varying the stoichiometry of the reactants.²⁶ Yet Mn-rich composition was not achieved; one reason could be that both Mn and Li were in excess in the reactants, whereas the other reason could be the nature of the high-temperature solid-state reaction that does not favor the formation of certain defects such as Mn-Li antisites. For the purpose of preparing Fe-rich LFS, aqueous-based chemistry may open the possibility. Indeed, the presence of Fe on Li-site associated with Livacancy within a few atomic percentages has been typically observed in LFS or LFP prepared by aqueous synthesis.²⁷⁻ Fe-rich LFP was successfully produced by Axmann et al.³⁰ using co-precipitation method, and this nonstoichiometric structure remained stable after subsequent annealing. In our previous work, we demonstrated that the concentration of Fe-Li antisites can be tuned by manipulating the chemical potentials of Li- and Fe-species in hydrothermal synthesis.³¹

In this study, a series of new compounds of nonstoichiometric $Li_{4-2x}Fe_xSiO_4$ (target composition range, 0.8) $\leq x \leq 1.2$) are synthesized via hydrothermal crystallization featuring EDTA as a mesocrystal regulating agent.³¹ Structural analysis by Rietveld refinement of X-ray diffraction (XRD) and chemical analysis by inductively coupled plasma (ICP) are applied to determine the solubility limits of nonstoichiometric composition while understanding the effect of Fe-deficiency (used interchangeably with Li-rich) and Fe-excess on the crystal structure of LFS. Afterward, particular attention is given to Fe-rich LFS with the objective of elucidating the origin of enhanced electrochemical functionality by relating the defectengineered structure to properties such as charge-discharge capacity, voltage, and Li diffusion kinetics. Finally, firstprinciples DFT calculations are utilized to understand the change of local structure with excess Fe and its influence on the electronic conductivity as well as cation migration characteristics.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Pristine Materials. Stoichiometric and nonstoichiometric lithium iron silicates were synthesized by hydrothermal process using as starting materials lithium hydroxide monohydrate (98% LiOH·H₂O), fumed silica (99% SiO₂), and iron(II) sulfate heptahydrate (98% FeSO₄·7H₂O). Ethylenediaminetetraacetic acid calcium disodium salt (99% EDTA-Ca-2Na) was added as a chelating agent to control the reactive crystallization of lithium iron silicates.²⁷ All of the chemicals were purchased from Sigma-Aldrich and used without further purification. The detailed synthesis procedure can be found in our previous work.³¹ In a typical synthesis experiment, LiOH·H2O, SiO2, and FeSO4·7H2O were dissolved and mixed in degassed deionized water based on varied molar ratio of Li/Fe/Si as 4/x/1 (x = 0.8, 0.9, 0.95, 1, 1.05, 1.1, and 1.2). Hydrothermal syntheses were carried out in a 450 mL PTFElined stirred autoclave (Parr Instruments, Moline, IL, USA) at 200 °C for 6 h. The colors of the as-synthesized powders change from light beige to gray/brown from Li-richness to Fe-richness. After hydrothermal treatment, the obtained powders were annealed at 400 °C for 6 h under 5% H_2 + 95% N_2 atmosphere.

2.2. Characterizations. Powder X-ray diffraction (PXRD) patterns were collected on a Bruker D8 diffractometer with Nifiltered Cu K α radiation (λ = 1.5418 Å) and operated at 40 kV and 40 mA in a 2θ range between 10° and 100° with increment of 0.02° and a dwell time of 2.5 s per step. Phase quantification and crystal structures were determined from Rietveld refinement using TOPAS Academic V.5.0 program. Transmission electron microscope (TEM) and high-resolution TEM (HR-TEM) images were acquired using the FEI Tecnai 12 BioTwin at 200 kV. Brunauer-Emmett-Teller (BET) specific surface area measurements were performed using a TriStar 3000 analyzer (Micromeritics) in N2 (-196 °C). Inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Scientific iCAP 6500 ICP spectrometer) was applied for elemental analysis. Dissolved LFS for ICP measurements was prepared by fusion method. A 0.2 g amount of LFS powder was mixed with fusion flux (containing 2 g of $Na_2B_4O_7$, 0.02 g of NH_4NO_3 , and 0.2 g of KI) and heated at 1000 °C in a Pt crucible. The molten mixture was then diluted with 2 vol % HNO3 and subjected to ICP analysis thereafter.

2.3. Electrochemistry. Electrochemical measurements were performed in Swagelok type cells assembled in an Ar-filled glovebox. Chemicals used in the electrode fabrication included acetylene black (AB, Sigma-Aldrich), poly(vinylidene difluoride) (PVDF, Sigma-Aldrich), 1-methyl-2-pyrrolidone (99.5% NMP, Sigma-Aldrich), lithium metal foil (Sigma-Aldrich), and a standard electrolyte solution made of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 (v/v)) purchased from BASF. The composite electrode materials were prepared by mixing the as-synthesized powders with acetylene black (AB) in a weight ratio of 0.8:0.2 and ball-milling in isopropanol at 250 rpm for 3 h using a planetary micromill (Fritsch, Pulverisette 7 premium line). The working electrodes were prepared by spreading a slurry of the active material (ball-milled C-LFS), AB, and PVDF in weight ratio (C-LFS:AB:PVDF) of 0.8:0.1:0.1 onto aluminum foil. Li metal was used as the counter electrode. Two pieces of polypropylene film (Celgard 2200) were used as separator in each cell. Each electrode contained approximately 2.5 mg/cm² of active LFS material.

Galvanostatic charge–discharge profiles were measured on an Arbin cycler at varied current rates between 1.5 and 4.5 V. Galvanostatic intermittent titration technique (GITT) was conducted on the Arbin cycler by applying a constant current at 0.02 C rate (3.32 mA g⁻¹) for 5 h (corresponding to the removal of 0.1 Li), followed by relaxation for 24 h. Cyclic voltammetry (CV) measurements were performed by using an electrochemical workstation (Bio-Logic). CV was performed between 2 and 4.5 V at a scan rate of 0.05 mV s⁻¹ for five sweeps, followed by scanning at various rates from 0.1 to 0.5 mV s⁻¹. All of the electrochemical measurements were performed at 45 °C.

2.4. Computational Method. Spin polarized density functional theory (DFT) calculations were performed in the Vienna ab initio

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Figure 1. (a) Calculated phase diagram of the Li₂O-FeO-SiO₂ system. Nonstoichiometric compounds $Li_{4-2x}Fe_xSiO_4$ locates on the dashed lines in which the dashed red line represents Fe-rich compounds (1 < x < 2) whereas the short-dashed blue line represents Li-rich compounds (0 < x < 1). (b) Powder X-ray diffractograms (Cu K α radiation; $\lambda = 1.5418$ Å) of hydrothermal products synthesized from precursors with varied molar ratios of Li/Fe/Si = 4/x/1 (x = 0.8, 0.9. 0.95, 1, 1.05, 1.1, and 1.2). Black streaks at the bottom represent the Bragg peak positions of *Pmn2*₁ Li₂FeSiO₄ (Reference PDF No. 01-080-6279). Cross and star symbols represent second phases of Fe₂O₃ and Li₂SiO₃, respectively. Enlarged 2θ area on the right side illustrates peak shifts of the reflections corresponding to (020) and (002) lattice planes in Fe-rich and Fe-deficient compounds.

simulation package (VASP) using the projector augmented wave (PAW) method.^{32,33} Generalized gradient approximation Perdew–Burke–Ernzerhof (GGA-PBE) functional was employed.³⁴ Hubbard parameter correlation (GGA + U) was used to correct the interactions inside the d-orbitals of the transition metals. The U value used for Fe is 5.3 eV.^{35,36} The cutoff energy was kept at 700 eV for all of the calculations. Each calculation is treated as converged if the forces on all of the nuclei were smaller than 0.01 eV/Å. A reciprocal space discretization of 25 Å is adapted in all structural optimizations while 45 Å is applied for self-consistent calculations were performed by employing transition-state theory. The climbed image nudged elastic band (ci-NEB) method^{37–40} was adopted to compute the minimum reaction paths (MEPs) and associated energy barriers.

The starting atomic configurations of stoichiometric and Fe-rich LFS were based on $Pmn2_1$ Li₂FeSiO₄ adopted from Eames et al.⁴¹ All calculations were done in supercells containing 16 formula units (2 × 2 × 2 unit cells). For the investigation of Fe-rich LFS, one Li was substituted by one Fe along with one Li-vacancy on the adjacent site

for charge compensation, resulting in 6.25% Fe-richness (Li_{1.88}Fe_{1.06}SiO₄). Lattice parameters and atomic positions were fully relaxed prior to further calculations. To evaluate the phase stability of the Fe-rich structure, all of the competing phases under the Li₂O-FeO-SiO₂ compositional space were involved to build the energy convex hull. In this case, the energy above the hull represents the thermodynamic driving force for a compound to decompose into the competing phases at the hull. This will therefore offer more accurate description about the stability and the potential phase transition of the compounds during synthesis. The structures of all of the potential competing phases were taken from the Materials Project database³⁵ with followed-up convergence to ensure the higher precision criterion as described above.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Structures of Nonstoichiometric $Li_{4-2x}Fe_xSiO_4$. The phase diagram of the Li_2O -FeO-SiO₂ system (Figure 1a) was constructed by DFT calculations to

Table 1. Ta	arget and	Determined	Compositions	of	Hydrothermally	y S	ynthesized	Li_{4-2}	_x Fe _x Si	iO_4
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label of products	target x in $Li_{4-2x}Fe_xSiO_4$	Fe/Si molar ratio from ICP	weight percent from XRD	determined composition ^a	deviation from stoichiometry
LFS-Fe1.2	1.2	1.19	95.2%, 4.8% Fe ₂ O ₃	$\mathrm{Li}_{1.84}\mathrm{Fe}_{1.08}\mathrm{SiO}_4$	8% Fe-rich
LFS-Fe1.1	1.1	1.09	98.0%, 2.0% Fe ₂ O ₃	Li _{1.9} Fe _{1.05} SiO ₄	5% Fe-rich
LFS-Fe1.05	1.05	1.05	100%	Li _{1.9} Fe _{1.05} SiO ₄	5% Fe-rich
LFS-stoi	1	1.00	100%	Li ₂ FeSiO ₄	stoichiometric
LFS-Fe0.95	0.95	0.96	100%	Li _{2.08} Fe _{0.96} SiO ₄	4% Fe-deficient
LFS-Fe0.9	0.9	0.91	100%	Li _{2.18} Fe _{0.91} SiO ₄	9% Fe-deficient
LFS-Fe0.85	0.85	0.83	92.2%, 7.8% Li ₂ SiO ₃	Li _{2.26} Fe _{0.87} SiO ₄	13% Fe-deficient

^aThe composition of the LFS-based phase was determined by the Fe/Si molar ratio, the weight percentage of the phase, and consideration of charge neutrality.



Figure 2. (*a*, *b*) Rietveld refinement of LFS-stoi and LFS-Fe1.2. Red scatters are experimental XRD results, black lines are calculated XRD results from Rietveld refinement, blue steaks at the bottom belong to the reference pattern of $Pmn2_1$ Li₂FeSiO₄ (PDF No. 01-080-6279), and gray lines are the differences between experimental and calculated results. Miller indices of major peaks are shown on the top. (c) Variation of unit cell volumes of Li_{4-2x}Fe_xSiO₄ with *x*. *x* represents the measured amount of Fe in Li_{4-2x}Fe_xSiO₄ compounds. Red dashed arrows are shown as a guide for view.

represent thermodynamic solid phase equilibria in the corresponding chemical system. Thermodynamically stable solid compounds under the given conditions are labeled as gray nodes in the phase diagram. The positions of nonstoichiometric compounds Li_{4-2x}Fe_xSiO₄ are marked as dashed lines and can be separated to Li-rich (short-dashed blue line) and Fe-rich regions (dashed red line). In the Li-rich region, i.e., 0 < x < 1, the potential decomposition phases for Li_{4-2x}Fe_xSiO₄ are Li₂FeSiO₄ and Li₄SiO₄. In the Fe-rich region, i.e., 1 < x < 2, the potential decomposition phases for $Li_{4-2x}Fe_xSiO_4$ are Li_2FeSiO_4 and Fe_2SiO_4 . It must be noted that the phase diagram in Figure 1a was constructed for systems at 0 K and 0 atm, which is different from actual experimental conditions (higher temperature and pressure, presence of aqueous solution, and oxidizing or reducing environment, etc.). Thus, some differences between the calculations and the experiments are expected. Nonetheless, this phase diagram serves as a guide in understanding the compositional spaces of Li₂O-FeO-SiO₂ and gives insights into impurity phases that might be obtained from synthesis. Examples of constructing and interpreting these types of phase diagrams can be found elsewhere.^{42,43}

Stoichiometric and nonstoichiometric LFS compounds, $Li_{4-2x}Fe_xSiO_4$ (target composition range, $0.8 \le x \le 1.2$), with deficiency or excess in Fe, were synthesized by hydrothermal method. In the nominal formula Li_{4-2x}Fe_xSiO₄, the stable polyanion unit SiO₄ is used as the reference to determine the elemental composition of the nonstoichiometric compound. The content of Fe in the crystallized compound was adjusted by tuning the concentration and therefore the chemical potential of Fe^{2+} in the precursor mixture. Figure 1b shows the measured powder XRD patterns of seven compounds from Li-rich to Fe-rich. It reveals that pure Pmn2₁ LFS phase can be obtained when the precursors contained Fe concentrations ranging from 10% deficiency (x =0.9) to 5% excess (x = 1.05). When Fe in precursor was 20% deficient (x = 0.8) from the stoichiometry, Li₂SiO₃ formed as the secondary phase. On the other side, when Fe in precursor was 10% or 20% excess (x = 1.1 or 1.2), small quantities of Fe₂O₃ formed. It is noted that the experimentally observed secondary phases, namely, Li₂SiO₃ and Fe₂O₃, are different from those predicted from DFT (Li₄SiO₄ and Fe₂SiO₄ as shown in Figure 1a). This can be attributed to the difference between the applied experimental conditions (hydrothermal at 473 K) and the calculation conditions (0 K and 0 atm) that could result in changes in total energies of solid compounds. To have a better understanding of the current solution system, Pourbaix diagrams in terms of the stability of Li2SiO3 and Fe_2SiO_4 in aqueous solutions at room temperature were constructed via the Materials Project.44 As presented in



Figure 3. TEM and high-resolution TEM images of (a-c) LFS-stoi and (d-f) LFS-Fe1.2. High-resolution TEM images in panels c and f show lattice fringes with spacing of 3.7 Å, corresponding to the (011) lattice planes in orthorhombic $Pmn2_1$ LFS. Insets in panels c and f are the corresponding FFT patterns.

Supporting Information Figure S1, under the experimental condition in aqueous solution with pH = 11-12, Li_4SiO_4 is unstable relative to Li_2SiO_3 . While for Fe_2SiO_4 , a trace of oxygen could readily induce its decomposition to Fe_2O_3 and soluble SiO_4^{4-} -species.

Rietveld refinement of XRD data combined with ICP elemental analysis were applied to quantify the phase fractions and hence determine the composition of $\text{Li}_{4-2x}\text{Fe}_x\text{SiO}_4$ in the synthesized products. The deduced purity and compositions of seven compounds are listed in Table 1. According to these analyses, the solubility limits of Fe-deficient and Fe-rich regions are about 13% and 8%, respectively, in the crystal lattice of $Pmn2_1$ LFS. That is to say, the composition range of synthesizable nonstoichiometric compounds $\text{Li}_{4-2x}\text{Fe}_x\text{SiO}_4$ at 200 °C is $0.87 \le x \le 1.08$. We also calculated the energy above the hull of one Fe-rich composition $\text{Li}_{1.88}\text{Fe}_{1.06}\text{SiO}_4$ (i.e., 6.25% Fe-richness) and found it to be 15.97 meV/atom. According to Boltzmann distribution⁴⁵ for calculating the defect concentration, theoretically 4.5% of Fe-excess could be accommodated in the structure of LFS at 200 °C.

Figure 2a shows the Rietveld refinement result of LFS-stoi refined by the reference structure of Pmn21 Li2FeSiO4. The lattice parameters of LFS-stoi were found to be a = 6.2660 Å, b = 5.34789 Å, c = 4.96323 Å, and V = 166.317 Å³. Figure 2b presents the Rietveld refinement result of LFS-Fe1.2, which contains the highest level of Fe-excess in the products synthesized in this study. The refined lattice parameters of $Li_{1.84}Fe_{1.08}SiO_4$, the dominant phase in LFS-Fe1.2, are a =6.26762 Å, b = 5.33556 Å, c = 4.96026 Å, and V = 165.878 Å³. It is also resolved that 8% of Li-sites are partially occupied by Fe, whereas Fe-sites are fully occupied by Fe. Rietveld refinement results of other products are presented in Figure S2 with their corresponding lattice parameters. Figure 2c shows the variation of unit cell volumes with the deviation of Fe content from stoichiometry. In the Fe-rich region, the unit cell volume of $Li_{4-2x}Fe_xSiO_4$ decreases as x increases. LFS-Fe1.1 and LFS-Fe1.05 were found to have similar unit cell

volume, which gives further evidence that the LFS phase in LFS-Fe1.1 contains the same Fe content as LFS-Fe1.05 (both are 5% Fe-rich) in the compounds. The residual Fe in LFS-Fe1.1 from precursor formed the secondary phase, Fe_2O_3 . The shrinking of unit cell associated with Fe-excess can be attributed to the Li-vacancies created by substitution of Fe in Li. These Fe-rich compounds have less cations to be arranged than the available cation sites in the lattice. To keep the charge neutrality, the presence of excess Fe (x > 1 in Li_{4-2x}Fe_xSiO₄) requires formation of defects with a negative effective charge, which could be a cation vacancy or an excess oxygen on interstitial site. In a close-packed oxygen sublattice, interstitial oxygen is expected to have a large free energy of formation compared to cation vacancy. Therefore, charge compensation of Fe-excess is most likely to be accomplished by Li⁺-vacancies, generating defect pairs $Fe_{Li}^{\bullet} + V'_{Li}$ based on Kröger–Vink notation.⁴⁶ The solubility limit of these defect pairs in $Pmn2_1$ Li_{4-2x}Fe_xSiO₄ prepared by hydrothermal process were found to be approximately 8% as aforementioned. In the case of LiFePO₄, the same type of defect pairs (i.e., $Fe_{Li}^{\bullet} + V'_{Li}$) was found to have a concentration limit of 6.8%³⁰ when synthesized via a room-temperature co-precipitation route with subsequent annealing at 725 °C.

In the Fe-deficient region, the unit cell volume decreases with reducing Fe content (Figure 2b). This variation is consistent with that reported by Billaud et al.,²⁴ in which the unit cell volumes of Li-rich (i.e., Fe-deficient) LFS compounds in both *Pmnb* and *P*2₁/*n* phases were found to decrease with reducing Fe content. Because the total number of cations (Fe²⁺ + Li⁺) is more than the original cation sites, the extra Li may occupy the interstitial Li octahedra sites which are not occupied in the stoichiometric LFS, as pointed out by Billaud et al.²⁴ The excess in Li could generate defect pairs of Li-ions occupying an Fe-site plus an interstitial Li-site, denoted as Li[']_{Fe} + Li^{*}₀. The solubility limit of this type of defect in Fe-deficient (Li-excess) Li_{4-2x}Fe_xSiO₄ (*x* < 1) in *Pmn*2₁ polymorph is about 13% based on the present study. In comparison, the Li-



Figure 4. Electrochemical performance of LFS-stoi and LFS-Fe1.2. Galvanostatic charge-discharge profiles of (a) LFS-stoi and (b) LFS-Fe1.2 at 0.02, 0.1, and 1 C cycled from 1.5 to 4.5 V at 45 °C. For clarity, only the fifth cycle at each cycling rate is shown. (c) Cycling performance of LFS-stoi (black) and LFS-Fe1.2 (red) in 50 cycles. Charge capacities are shown in solid symbols, whereas discharge capacities are shown in open symbols.

excess $\text{Li}_{4-2x}\text{Fe}_x\text{SiO}_4$ synthesized at high temperature in a mixed $Pmnb-P2_1/n$ phase was found to accommodate excess Li up to 30%.²⁴ The larger Li-excess solubility compared to the present study could be attributed to higher processing temperatures that favor the formation of defects as well as the difference in crystal structures.

Panels a and d of Figure 3 show that LFS-stoi and LFS-Fe1.2 have similar particle size and shape. Under the hydrothermal conditions applied in the present study, LFS with either stoichiometric or Fe-rich composition crystallizes as hollow mesocrystals that are assembled by smaller elongated nanocrystals aligned in the same crystallographic direction. Detailed analyses have been reported in a previous study.³¹ High-resolution TEM images (Figure 3b,e) on the edges of particles demonstrate the characteristics of nanocrystals stacking on each other and having the same lattice fringe. The spacing of these lattice fringes is about 3.7 Å, corresponding to the (011) lattice planes in orthorhombic *Pmn*2₁ LFS (Figure 3c,3f).

3.2. Electrochemical Performance. Figure 4 presents the electrochemical performance of LFS-stoi and LFS-Fe1.2 evaluated via galvanostatic charge–discharge measurements. Half-cells using Li-metal as the counter and reference electrodes were first cycled at a low current rate of 0.02 C for five cycles, which were followed by cycling at 0.1 and 1 C for five cycles at each rate, and finally at 0.1 C until 50 cycles were completed. As shown in Figure 4a, the stoichiometric LFS delivered a discharge capacity of 128.9 mAh g⁻¹ in the fifth cycle at 0.02 C (77% of the theoretical capacity), while this value decreased to 92 mAh g⁻¹ at 0.1 C and 40.5 mAh g⁻¹ at 1 C. The difference between the average charge and discharge voltages increases with the current rate due to

increasing overpotential. As a comparison, Fe-rich compound LFS-Fe1.2 (Figure 4b) exhibited discharge capacities of 161.8 mAh g^{-1} (97% of the theoretical capacity), 125.2 mAh g^{-1} , and 65.3 mAh g⁻¹, respectively, at 0.02, 0.1, and 1 C. From LFSstoi to LFS-Fe1.2, the discharge capacity increased by 25%, 36%, and 61% at 0.02, 0.1, and 1 C, respectively. Figure 4c presents the cycling performance of LFS-stoi and LFS-Fe1.2. While both cells went through capacity fading, LFS-stoi faded by 33% from the sixth to the 50th cycle at 0.1 C, which is almost double that of LFS-Fe1.2 (17%). The deterioration of capacity upon cycling could be mainly attributed to the side reactions between LFS and the LiPF₆-based electrolyte.⁴⁷ Nonetheless, Fe-rich LFS-Fe1.2 shows an improved cyclability which can be also confirmed when cycled at 0.02 C for the first five cycles (see Figure S3). The improved electrochemical performance of Fe-deficient (namely, Li-rich) LFS vis-à-vis the stoichiometric LFS studied by Billaud et al.²⁴ had been attributed to enhanced Li-ion transport. However, the Fedeficient compounds are limited in terms of theoretical specific capacities. Thus, the reported capacity of Li_{2.6}Fe_{0.7}SiO₄ studied by Billaud et al.,²⁴ was only ~120 mAh g^{-1} in the first cycle and quickly dropped to 105 mAh g^{-1} between 1.5 and 3.7 V at 0.06 C rate at 60 °C. In this regard the superiority of Fe-rich LFS in terms of intercalation capacity and retention is really remarkable.

One may notice that nanosized LFS in monoclinic $P2_1/n$ structure with conductive carbon coating could deliver capacity corresponding to exchanging over one-electron per formula unit and show better rate capability than what have been achieved in the present study.^{48,49} However, it remains unclear whether the extra capacity is from LFS redox activity or



Figure 5. Cyclic voltammograms (CVs) of (a) LFS-stoi and (b) LFS-Fe1.2 between 2 and 4.5 V at scan rates from 0.05 to 0.5 mV s⁻¹. (c) Comparison of CVs between LFS-stoi and LFS-Fe1.2 scanned at 0.05 mV s⁻¹. The solid line represents the fourth scan, while the dashed line represents the fifth scan.

electrolyte degradation as such capacity was typically obtained when the cell was charged to a rather high voltage, e.g., 4.8 V vs Li⁺/Li.⁵⁰ Using a high-voltage electrolyte is necessary for confirming the achievability of extraction/insertion of more than one Li from/to LFS and the associated charge compensation mechanism.⁵¹ As for the rate capability of stoichiometric or Fe-rich *Pmn2*₁ LFS, there is still room for improvement by surface modification with conductive coating.

To compare Li diffusion kinetics between LFS-stoi and LFS-Fe1.2, cyclic voltammetry (CV) at different scan rates was performed to determine the apparent chemical diffusion coefficient of Li^{+,52} Figure 5a shows CV of LFS-stoi scanned between 2 and 4.5 V at various rates $(0.05-0.5 \text{ mV s}^{-1})$. It is noted that the lower cutoff was chosen at 2 V for CV scans, which is different from the 1.5 V that was applied for galvanostatic charge-discharge tests. One reason is that the peak positions for both oxidation and reduction reactions during CV scans are above 2 V; thus a lower voltage is unnecessary. The other reason is that some unknown cathodic reactions may occur below 1.8 V, as observed in a recent study.⁵³ Considering that the main purpose of CV tests in the present study is to understand the kinetics of Li-ion diffusion, we chose 2 V as a more appropriate cutoff voltage. Two oxidation peaks, denoted as I_{A1} and I_{A2} , are observed, with their intensities increasing with the scan rate, while I_{A2} increases faster than I_{A1} . In contrast to the oxidation process, only one peak, denoted as I_C, is seen in the reduction process. This might be explained by different diffusion kinetics between delithiation and lithiation processes, so they lead to different responses in the CV characteristics. LFS-Fe1.2 (Figure 5a), although showing some similar features with LFS-stoi, has lower I_{A2}/I_{A1} intensity ratio at all of the scan rates. Particularly, at the lowest scan rate 0.05 mV s⁻¹, only I_{A1} shows up in the

oxidation curve of LFS-Fe1.2. Figure 5c compares CV of LFSstoi to that of LFS-Fe1.2 at the same scan rate 0.05 mV s⁻¹. It is clearly shown that LFS-Fe1.2 exhibits more symmetric shape between oxidation and reduction peaks, as opposed to the asymmetric behavior of LFS-stoi, suggesting a better reversibility of Fe-rich LFS. Moreover, LFS-Fe1.2 has larger area under the current curve than LFS-stoi, indicating more capacity can be delivered. This is consistent with the galvanostatic charge—discharge measurements (Figure 4). Peak currents of the redox reaction are proportional to the square root of the scan rates if Li⁺ diffusion is the ratedetermining step, according to the Randles–Sevčik equation (eq 1) shown as follows:⁵⁴

$$I_{\rm p} = 0.4463 \left(\frac{F^3}{RT}\right)^{1/2} n^{3/2} A D_{\rm Li^+, CV}^{1/2} \Delta C_{\rm Li^+} v^{1/2}$$
(1)

where I_p is the peak current (A), v is the scan rate (V s⁻¹), F is Faraday's constant (96,485 C mol⁻¹), R is the gas constant of 8.314 J K⁻¹ mol⁻¹, T is absolute temperature (318.15 K), n is the number of electrons involved in the redox reaction (n = 1for Fe²⁺/Fe³⁺), and A is the surface area of the electrode (0.785 cm²). ΔC_{Li^+} is the change in concentration of Li⁺ before and after a sweep, which is approximately 0.0185 mol/cm³ for either the anodic or the cathodic reaction assuming a complete one Li⁺ insertion/extraction reaction per formula unit. $D_{\text{Li}^+,\text{CV}}$ is the chemical diffusion coefficient of Li⁺ (cm² s⁻¹) determined by CV.

The calculated values of $D_{\text{Li}^*,\text{CV}}$ are listed in Table 2. For both anodic and cathodic reactions, $D_{\text{Li}^*,\text{CV}}$ of LFS-Fe1.2 are larger than those of LFS-stoi. This indicates that the diffusion kinetics during lithiation and delithiation are enhanced by introducing excess Fe in the crystal lattice. It should be mentioned that the value of $D_{\text{Li}^*,\text{CV}}$ determined by CV method

Table 2. Calculated Chemical Diffusion Coefficient $(D_{\text{Li}^+,\text{CV}})$ of LFS-stoi and LFS-Fe1.2 Based on Cyclic Voltammetry

electrode	peak	slope of $I_{\rm p}$ vs $\upsilon^{1/2}$	$D_{\mathrm{Li}^+,\mathrm{CV}}$ cm ² s ⁻¹
LFS-stoi	$I_{\rm A1}$	0.0057	2.28×10^{-13}
	I_{A2}	0.0090	5.69×10^{-12}
	$I_{\rm C}$	0.0118	9.68×10^{-12}
LFS-Fe1.2	$I_{\rm A1}$	0.0200	9.48×10^{-12}
	$I_{\rm A2}$	0.0246	1.44×10^{-11}
	$I_{\rm C}$	0.0285	5.69×10^{-11}

represents an average performance of the whole lithiation/ delithiation process. Using the same determination method, the calculated $D_{\text{Li}^+,\text{CV}}$ of LFS-Fe1.2 (5.96 × 10⁻¹¹ to 9.48 × 10^{-12} cm² s⁻¹) is higher than that reported on 3DOM LFS/C composite (1.17 × 10^{-12} cm² s⁻¹)⁴⁸ and LFS/C nanocrystals (~6 × 10^{-12} cm² s⁻¹).⁵⁵

Galvanostatic intermittent titration technique (GITT) was conducted to gain insights into the diffusion kinetics at different Li⁺ compositions and the difference between delithiation and lithiation processes in LFS-stoi and LFS-Fe1.2. The GITT curves show considerably less voltage polarization (voltage relaxation after each charge or discharge step) in LFS-Fe1.2 (Figure 6b) than in LFS-stoi (Figure 6a), particularly at the beginning of charging. This suggests that the mass-transfer resistance of Li⁺ is decreased in the Fe-rich compound. For both cells, the largest polarization was observed at the end of charge and discharge. In the end of the first charge process, 1.1 Li was extracted from LFS-Fe1.2, whereas less than 0.8 Li was extracted from LFS-stoi. In addition, more Li-ions were inserted back to LFS-stoi than those extracted, indicating that the pristine LFS-stoi material may have been partially oxidized due to exposure to air during handling or to spontaneous reaction with the electrolyte.⁵⁶

The chemical diffusion coefficient of Li^+ can be deduced from GITT according to the following equation: $^{57-59}$

$$D_{\text{Li}^+,\text{GITT}} = \frac{4}{\pi} \left(\frac{IV_{\text{M}}}{ZFS} \right)^2 \left[\frac{dE(x)}{dx} / \frac{dE(t)}{dt^{0.5}} \right]^2$$
$$(t \ll L^2 / D_{\text{Li}^+,\text{GITT}})$$
(2)

where I is the applied current (A), $V_{\rm M}$ is the molar volume of the electrode material (about 54 cm³/mol for Li₂FeSiO₄), Z is the charge number of active species $(Z = 1 \text{ for } \text{Li}^+)$, F is the Faraday constant (96,485 $C \mod^{-1}$), and S is the electrochemical active area between the electrode and electrolyte (cm²) that can be estimated by BET surface area measurements (21 m² g⁻¹ for both products). $\frac{dE(x)}{dx}$ is the change of the steady-state voltage vs the change of Li^+ composition. E(t) is the transient voltage during the constant current intervals, t is the time (s) when current is applied, and L is the characteristic length (cm) of the electrode material. The value of $\frac{dE(t)}{dt^{0.05}}$ was determined from the slope of the linear part of E vs $t^{0.5}_{0.5}$ in the fisrt 10-100 s after applying a current pulse. This time domain corresponds to the diffusion process.^{60,61} It should be noted that the employment of eq 2 in solving the chemical diffusion coefficient depends on multiple assumptions.^{52,62} Therefore, deviation of the investigated electrochemical system from the assumptions may lead to inaccuracy in the obtained values of $D_{\text{Li}^+,\text{GITT}}$ for the studied electrochemical system. Nevertheless, the scope of applying CV and GITT measurements in this study is not to quantify the absolute values of diffusivity but rather to characterize the impact of Fe-rich composition on Li diffusion kinetics in comparison to that of the stoichiometric LFS. The variation of $D_{\text{Li}^+,\text{GITT}}$ with the LFS composition is presented in Figure 6c. As it can be seen, $D_{\text{Li}^+,\text{GITT}}$ ranges from



Figure 6. (a, b) GITT curves of the first charge–discharge cycle of LFS-stoi and LFS-Fe1.2. (c) Calculated diffusion coefficients $D_{\text{Li}^+,\text{GITT}}$ for the first charge (solid symbols) and discharge (open symbols) cycle based on GITT measurements. For LFS-stoi, a = 2 and b = 1; for LFS-Fe1.2, a = 1.84 and b = 1.08.

apporximately 10^{-17} to 10^{-22} cm² s⁻¹ for LFS-Fe1.2, while it is as low as 10^{-23} to 10^{-27} cm² s⁻¹ for LFS-stoi. These results indicate that Fe-rich compostion enhances the mass transfer of Li⁺. This could be attributed to the presence of Li-vacancy sites generated by introducing extra Fe. These vacancies facilite the transport of Li⁺, particularly in the beginning of charge when the lattice is supposed to be fully occupied in the stoichiometric LFS.

3.3. Electronic Structure and Fe Migration. In order to understand the influence of nonstoichiometry on the electronic structure of Fe-rich LFS, the projected density of states (PDOS) are calculated by DFT. The exact PDOS of LFS and Fe-rich LFS plotted in Figure 7a,b show a distinct gap between



Figure 7. Effect of local Fe-rich configuration on the electronic structure of LFS. (a) Projected density of states (PDOS) of stoichiometric LFS. (b) PDOS of Fe-rich LFS. Insets in panels a and b are the corresponding images of the as-synthesized powders of LFS-stoi and LFS-Fe1.2. (c) Merged PDOS of LFS and Fe-rich LFS. Inset in panel c is the isosurface of the charge density around Fe-O–Fe coordination in Fe-rich LFS, which is found to contribute to the highlighted peak in the conduction band close to the Fermi level. (d) Atomic configuration of Fe-rich LFS (orthorhombic $Pmn2_1$) with highlighted region corresponding to the Fe–O–Fe coordination shown in panel c.

the conduction band minimum (CBM) and the valence band maximum (VBM). To make a direct comparison, PDOS of the two materials are merged in the same figure (Figure 7c). For clarity, PDOS of majority and minority spins are summed up while the energy of the Fermi level is placed on the top of the VBM of both materials. It should be noted that since we are trying to visualize the difference of energy level alignment, the absolute value of energy level does not matter. As indicated in Figure 7c, the bandgap of Fe-rich LFS (2.6 eV) is narrower than that of stoichiometric LFS (3.1 eV), mainly attributed to the emergence of a new peak at the conduction band. By projecting the charge density into the highlighted region of PDOS, it is clearly shown in Figure 7c, d that the new electron

states in the conduction band originate from the Fe[•]_{Li} defect and its immediate neighboring Fe atoms. These findings clearly demonstrate that Fe[•]_{Li} defects in Fe-rich LFS are responsible for narrowing the bandgap of LFS. This is further confirmed by the darker color of the as-synthesized Fe-rich powders (LFS-Fe1.2) than the beige LFS-stoi, shown in the insets in Figure 7a,b.

During the initial charge–discharge, LFS experiences phase transformation to a new cycled phase associated with a ~ 0.3 V voltage drop.^{16,17,41} This phase transformation has been proposed to be triggered by Fe migration to a Li-site. When all of the Fe migrate to Li-sites, the reintercalated Li will occupy the Fe-sites to form a new phase such as the so-called inverse $Pmn2_1$. Thus, Fe migration is an important factor for understanding the behavior of LFS upon cycling. Transition metal migration is also a key characteristic in other Licontaining compounds that affects their structural stability and Li storage kinetics.^{63–65} Here, DFT calculations are performed to evaluate the change of Fe migration barrier in different local environments. The minimum diffusion pathways of Fe are demonstrated in Figure 8a,b respectively for LFS and Fe-rich



Figure 8. (a, b) Fe migration paths in LFS and Fe-rich LFS and (c) the corresponding energy barriers. The simulation is based on crystal structures in which one Li is extracted from a $2 \times 2 \times 2$ supercell (i.e., $Li_{32}Fe_{16}Si_{16}O_{64}$ for LFS and $Li_{30}Fe_{17}Si_{16}O_{64}$ for Fe-rich LFS). Fe migrates from a Fe-site to an adjacent Li-site. In Fe-rich LFS, an antisite defect Fe^L_{Li} and a Li-vacancy V'_{Li} are pointed out.

LFS. The energy evolution during Fe migration is demonstrated in Figure 8c. As can be inferred from Figure 8c, the activation barrier of Fe migration in LFS is about 1.18 eV, whereas when it comes to Fe-rich LFS, this barrier diminishes to 0.64 eV. The reduction of the Fe activation barrier can be attributed to the presence of extra Fe- and Li-vacancies. By comparing Figure 8a with Figure 8b, it shows that one of the immediate neighboring Li at the initial state of Fe migration is replaced by Fe as a result of nonstoichiometry. This results in a greater electrostatic repulsion that would destabilize the initial state. Similarly, the transition state and the final state would be stabilized by the adjacent Li-vacancy due to less electrostatic repulsion. As the Fe migration barrier is lowered, the phase transformation toward the cycled structure would be facilitated, consuming less energy for the migration process.

4. CONCLUSION

Nonstoichiometric $Li_{4-2x}Fe_xSiO_4$ compounds were synthesized via hydrothermal method by varying the concentration ratio of

precursors. Pure 5% Fe-rich and pure 10% Fe-deficient (Lirich) compounds in $Pmn2_1$ structure were obtained, while the higher extent of Fe-richness and Fe-deficiency resulted in the formation of secondary phases of Fe₂O₃ and Li₂SiO₃, respectively, as indicated by XRD. Rietveld refinement combined with compositional analyses revealed that the solubility limits of Fe-richness and Fe-deficiency in Pmn21 LFS are about 8% and 13% under the applied hydrothermal synthesis condition. As a result of Fe-rich composition, the formation of $Fe_{Li}^{\bullet} + V'_{Li}$ defect pair was induced which in turn leads to improvement of electrochemical performance in terms of higher capacity and facilitated Li⁺ transport. This thesis was corroborated from the galvanostatic charge-discharge measurements that showed the Fe-rich LFS delivering higher capacity than the stoichiometric LFS from low to high current rates (161.8 mAh g^{-1} vs 128.9 mAh g^{-1} at 0.02 C; 65.3 mAh g^{-1} vs 40.5 mAh g^{-1} at 1 C). Furthermore, enhanced diffusion kinetics in Fe-rich LFS were observed by CV and GITT. Firstprinciples DFT calculations revealed that the bandgap of LFS was narrowed from 3.1 to 2.6 eV by introducing excess Fe that generates local Fe-O-Fe configuration. In addition, the energy barrier for Fe migration to a Li-site was found to be diminished in the Fe-rich compound, thus facilitating phase transformation from Pmn21 toward the electrochemically cycled inverse Pmn21 phase. This study shows that the electrochemical performance of LFS can be largely improved by compositional engineering. Future work could be undertaken to investigate the effect of Fe-richness or Li-richness on the capacity beyond Fe²⁺/Fe³⁺ redox reaction if a compatible and stable high-voltage electrolyte is available. It would be also interesting to synthesize LFS with even higher Fe-rich composition to further increase the Fe²⁺/Fe³⁺-based capacity (e.g., 203 mAh g^{-1} for 33.3% Fe-rich composition) if the solubility limit can be elevated.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsaem.9b01869.

Figure S1 showing Pourbaix diagrams of the Li–Fe–Si– O systems, Figure S2 presenting the Rietveld refinement results of nonstoichiometric LFS compounds, and Figure S3 showing the charge–discharge curves at slow current rate 0.02 C (PDF)

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Notes

The authors declare no competing financial interest.

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