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Theoretical Assessment of the First Cycle Transition, Structural Stability and Electrochemical Properties of Li$_2$FeSiO$_4$ as a Cathode Material for Li-ion Battery

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P A P E R   I N F O

A B S T R A C T

Lithium iron orthosilicate (Li$_2$FeSiO$_4$) with Pmn2$_1$ space group was theoretically investigated as a cathode material of Li-ion batteries using density functional theory (DFT) calculations. PBE-GGA (+U^{SIC}), WC-GGA, L(S)DA (+U^{SIC}) and mBJ+LDA (GGA) methods under spin polarization ferromagnetic (FM) and anti-ferromagnetic (AFM) procedure were used to investigate the material properties including structural parameters, theoretical reaction voltage (TRV), magnetic state and electrical properties (based on density of states, DOS). Theoretical structural assessments implied electrochemical reversibility and structural stability of Li$_2$FeSiO$_4$. Based on DFT calculations, switching between magnetic states were proposed to account the experimental observations of the extra oxidation voltage in the first cycle.

1. INTRODUCTION

Due to the enhancing importance of energy storage devices in the human life, Li-ion batteries are one of the most important research issues in the scientific communities [1, 2]. Today, computational simulations provide a powerful method to evaluate the materials properties [3-5]. Li$_2$FeSiO$_4$ is one of the latest promising candidate cathode materials for lithium-ion batteries [6]. According to the some studies, Li$_2$FeSiO$_4$ has a large difference between charge and discharge voltages in the first cycle (about 3.1 and 2.8 V versus Li/Li$^+$, respectively) and it has been attributed to the irreversible reaction [7-12]. The first cycle phenomenon has been attributed to a phase transition [7] followed by a structural rearrangement of Fe/Li sites [8]. According to the density functional theory (DFT) calculations, this variation is caused by the difference between the lowest and the highest forming energy of three possible arrangements in delithiated structures [9].
Zaghib et al. [13] reported the totally reversible reaction for the first cycle with the oxidation and reaction peaks at 2.80 and 2.74 V versus Li/Li$^+$ for synthesized

Li$_2$FeSiO$_4$ by solid-state reaction, respectively. Dominko et al. [10] synthesized Li$_2$FeSiO$_4$ via three different techniques and concluded that the performance as a cathode depended on the synthesis conditions. In contrast to ref. [13] the first cycle, extra oxidation peak was observed in all samples. For assessing the structural and compositional changes associated with the first cycle extra voltage, in-situ X-ray diffraction (XRD) [7, 11, 12] and in-situ X-ray absorption spectroscopy (XAS) [11, 12] were employed. However, under cycling, the phase transition or the irreversible change was not found in the local environment of iron that wasreason for the presence of the extra voltage. The XAS results were confirmed by in-situ Mössbauer spectroscopy [12].
Three polymorphs had been established for Li$_2$FeSiO$_4$ material [14-17] including *Pmn2$_1$*, *P2$_1$/n* and *Pmnb* space groups. The extra oxidation peaks in the first cycle was observed for all polymorphs [17] and the *Pmn2$_1$* crystal was expected to be more stable structure [18, 19]. Furthermore, Armstrong et al. [20] investigated the phase transition from *P2$_1$/n* to an inverse-*β$_{II}$* (modified *Pmn2$_1$*) under the cycling. Studies based on DFT calculations, by Arroyo-de Dompablo and co-workers [19], have revealed although *Pmn2$_1$* structure was more stable than the inverse-*β$_{II}$* and the

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other polymorphs in the lithiated conditions, inverse-β_{II} structure was more energetically stable than others in delithiated condition. They had concluded the first cycle phenomenon was attributed to the phase transition. Also, Islam and co-workers [21] have revealed the first cycle extra oxidation voltage may be related to the transition to the lower energy configuration of the cycled structure. The problem was the cycled structure (inverse-β_{II}) was reported as a short range order [21]. In addition, inverse-β_{II} has been observed less stable phase [19] in the cycling of $P2_1/n$ [20] and there is no experimental evidence to prove that this structure may be produced by delithiation of $Pmn2_1$ and $Pmnb$ polymorphs. Although, transition can be progressed in other cycles, the first cycle extra voltage behaviour seems to be transient. Also, Islam and co-workers considered Fe-O bond length [21] since it could be important for the resulting voltage [22]. DFT has made an unparalleled impact on the application of quantum mechanics to exciting and challenging problems in chemistry [23] by describing the electronic states of atoms, molecules and materials in terms of the three-dimensional electronic density of the system [24]. DFT has been employed as a helpful method for evaluation and prediction of properties in many advanced materials such as Li-ion battery cathode materials [25]. However, several approximations exist for exchange-correlation in DFT framework and there are challenges on their validity for each material. An important benchmark for validation is experimental correspondence [24].

Although, the occurrence of the first cycle extra oxidation voltage in Li_2FeSiO_4 cathode material is well established, systematic and comprehensive theoretical studies may be helped to recognizing the irreversible nature of the reaction. There are two published theoretical studies [19, 21] on this issue which are based on the phase transition to inverse-β_{II}. In this study, the other possible mechanisms were considered which were not based on the phase transition under cycling. Even though, phase transition may have a role in disappearing electrochemical properties of the material in the subsequent cycles, the first cycle phenomenon should be justified based on the variation of magnetic configuration instead of structure. In the present study, different DFT approaches have been used to evaluate the structural stability, electrical and electrochemical properties of Li_2FeSiO_4 with $Pmn2_1$ structure (the more stable polymorph), and describe the fundamental mechanisms for the irreversible nature of the first cycle reaction.

2. MATERIALS METHOD

All the calculations were performed using full-potential linear augmented plane wave (FP-LAPW) method as implemented in the WIEN2K code [26] within the framework of DFT [27]. Inside the non-overlapping spheres of muffin tin radius (R_{MT}) around the each atom, a linear combination of radial solution of the Schrödinger equation times the spherical harmonic were used and a basis set of the plane wave was used in the interstitial region. The R_{MT} values of 1.76 and 1.88 a.u were used for Li and Fe, respectively, and 1.50 a.u for Si and O. To expand the wave functions in the interstitial region, the plane wave cut-off value of $K_{max}=7.0/R_{MT}$ was used. The Fourier expanded charge density was truncated at $G_{max}=12(Ryd)^{1/2}$. The maximum value of the angular momentum (l_{max}) was set equal to 10 for the wave function expansion inside the atomic spheres. Convergence of the self-consistent iterations was performed within 0.0001 Ry.

The Li_2FeSiO_4 structure with $Pmn2_1$ space group (Fig. 1) suggested by Nyténet al. [7] was used as the initial structure for all DFT calculations in this study.

For the assessment of the structural and electrochemical properties, including structural parameters variation, theoretical reaction voltage (TRV), magnetic state and density of states (DOS), the calculations were carried out using the Perdew–Burke–Ernzerh generalized gradient approximation (PBE-GGA) [28], Wu-Cohen generalized gradient approximation (WC-GGA) [29], the local spin density approximation (LSDA) and the modified Becke-Johnson potential (mBJ) [30]. Two versions of the calculations, spin-polarized ferromagnetic (FM) and anti-ferromagnetic (AFM), were employed. Fe atoms in the unit cell were assumed to have a similar (up or down) spin polarization in the FM calculations. Also, Fe atoms were assumed to have no spin polarization in the AFM calculations. The electron and spin configurations were software defaults and for Fe atoms were Fe_{up}: [Ar] $3d^{6.5}(4.5\uparrow, 2\downarrow)$ $4s^{1.5}(1\uparrow, 0.5\downarrow)$, Fe_{down}: [Ar] $3d^{6.5}(2\uparrow, 4.5\downarrow)$ $4s^{1.5}(0.5\uparrow, 1\downarrow)$ and Fe_{non}: [Ar] $3d^7(3.5\uparrow, 3.5\downarrow)$ $4s^1(0.5\uparrow, 0.5\downarrow)$ for up, down and no spin polarization, respectively. No spin polarization was considered for the other non-magnetic atoms in the unit cell (calculations showed that, as expected, considering spin polarization for these atoms did not lead to any changes in the final results). Atomic configuration for these atoms were Li: [He] $2s^1$, Si: [Ne] $3s^2$ $3p^2$ and O: [He] $2s^2$ $2p^4$. The written states in the brackets were considered being the core states which were followed by the corresponding valence states.

For more comprehensive results, PBE-GGA and LDA plus an on-site Coulomb self-interaction correction potential (U^{SIC}) were applied, hereinafter called GGA+U^{SIC} and LDA+U^{SIC}, respectively. The U^{SIC} value in GGA+U^{SIC} method was considered being equal to 5 eV (based on [19, 31, 32]), and 1.67 eV based on Madsen and Novák method [33] for the relaxed structure under PBE-GGA calculations. Also, this value for LDA+U^{SIC} calculations was considered being 4.79,6.33 eV (calculated for tetrahedrally coordinated Fe^{+2} and Fe^{+3}, respectively, for magnetite material) [33], and 5 eV [19, 31, 32]. To obtain relaxed atomic

positions and crystal parameters, U^{SIC} was not applied since this parameter does not lead to significant change in the structural properties.

Relaxation process was carried out in the following three modes:

1. Geometry minimization of the atomic positions according to the inter-atomic forces (mini. positions),
2. Optimization volume with constant a:b:c ratio,
3. Optimization volume with variable a, b and c for orthorhombic structure (number of the structure was set as 3×3×3=27).

In all three modes of relaxation, 2×3×3 Monkhorst–Pack (MP) mesh was used. In the calculation of mini. positions, force set at 0.001 and 0.01 Ry.au^{-1} for original structure (Li_2FeSiO_4 with *Pmn2$_1$* space group) and delithiated structure ($LiFeSiO_4$ with *P1* space group), respectively. In the case of second and third modes (optimization volume modes), convergence of the self-consistent iterations was performed within 0.001 Ry.

In order to obtain the total energies, magnetic state and DOS (so band-gap), integrals were calculated over the Brillouin zone with k-points based on 4×5×5 MP mesh. This grade contained 18 and 50 k-points in the irreducible Brillouin zone for *Pmn2$_1$* space group (Li_2FeSiO_4) and *P* space group (U^{SIC} calculations for Li_2FeSiO_4 and all calculations for $LiFeSiO_4$), respectively.

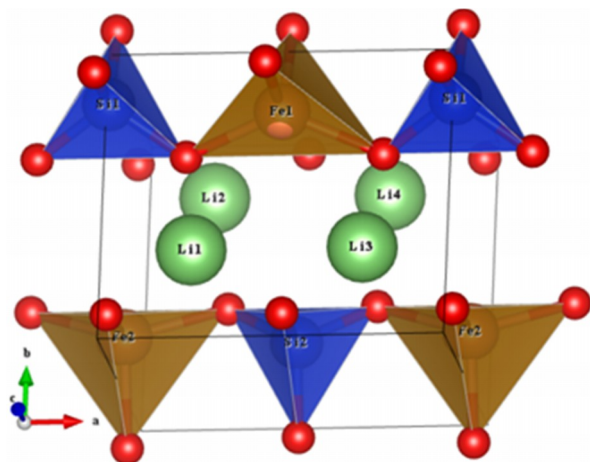**Figure. 1.** Schematic of the crystal structure of Li_2FeSiO_4 with Pmn2$_1$ space group

In order to calculate more accurate DOS, the modified Becke-Johnson exchange potential plus LDA(GGA)-correlation [30] was performed within LSDA ($U^{SIC}=0$), LDA+ U^{SIC} (U=6.33 eV) and GGA+ U^{SIC} (U=1.67 eV) frameworks.

It was assumed that the ionic condition of Fe atoms in Li_2FeSiO_4 can only change between State II and State III. To determine the most probable delithiated phase, Li_xFeSiO_4 were evaluated for x=0.5, 1, 1.5 and 2 under the AFM condition via both PBE-GGA and LSDA

methods. According to Fig. 1, there were three possible arrangements in the delithiated structure in the case of x=1 (extraction of two Li from unit cell). There was only one type of Li atom position and the other three positions were created by symmetry in space group of *Pmn2$_1$*. However, in delithiated structures with the space group of *P1*, no symmetry element existed and Li ions were differentiated by using subscripts. If Li ions were extracted from opposite positions (1 and 4, or 2 and 3), the resulting arrangement would be named A and if they were extracted from the same-side positions (1 and 2, or 3 and 4), it would be called C. Other arrangements would be called B. Arrangements A and C were the most stable and the least stable configurations, respectively [9]. Therefore, the total energy of $LiFeSiO_4$ crystal structure was calculated for the arrangement A.

An important electrochemical property that can be assessed directly from the difference of total energies before and after lithium extraction is the theoretical reaction voltage (TRV). This parameter is calculated from charge reaction (2-1) in this study and it is presented by equation (2-2).
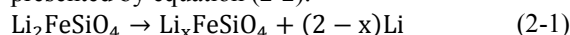
$$Li_2FeSiO_4 \rightarrow Li_xFeSiO_4 + (2-x)Li \qquad (2-1)$$
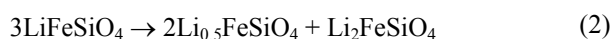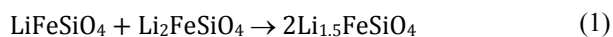$$TRV = E_{Li_2FeSiO_4} - E_{Li_xFeSiO_4} - (2-x)E_{Li} \qquad (2-2)$$

Where $E_{Li_2FeSiO_4}$, $E_{Li_xFeSiO_4}$ and E_{Li} are the calculated total energies of one unit formula for lithiated, delithiated structures and lithium metal (bcc structure), respectively. To determine E_{Li}, the relaxation process was carried out with optimization volume (k-points= 7×7×7 and E=0.0001) and then total energy (E_{Li}) was calculated based on 3094 k-points in the irreducible Brillouin zone (50×50×50 grid) setting energy convergence at E=0.00001 Ry.

3. RESULTS AND DISCUSSION

3.1. Possible crystal phases

Based on the total energy calculations, extraction of two Li per formula was needed a charge voltage over 6 V. This value of charge voltage was clearly beyond the maximum tolerance limit of the currently available electrolytes. Based on the other investigations, it was well established that the extraction of two Li per formula caused collapsing the structure [19, 34]. Also, two iron ions (Fe^{+2} and Fe^{+3}) were detected in lithiated and delithiated structures by using in-situ Mössbauer spectroscopy detected [12]. Therefore, the final formula of delithiated structure was assumed to be $LiFeSiO_4$ in this study. However, the from crystal structure point of view, appearing $LiFeSiO_4$ formula was possible in the crystal phases and mixtures, for example $Li_2FeSiO_4+FeSiO_4$. In order to assess the possibility of different values of x (2, 1.5, 1, 0.5 and 0) in this structure, the possible reaction energies were calculated from the differences between the calculated total energies of reactants for one formula. Since the dynamic condition under cycling was considered for these

reactions, LiFeSiO$_4$ structure was assumed to have the most stable arrangement, i.e., arrangement A. This was justified since Li ions were assumed to diffuse out of the Li$_2$FeSiO$_4$ structure due to the applied charge potential and the kinetic barriers had already been surmounted. The possible reactions were assumed to be according to the equation (3-1), (3-2) and (3-3):

$$LiFeSiO_4 + Li_2FeSiO_4 \rightarrow 2Li_{1.5}FeSiO_4 \qquad (1)$$

$$3LiFeSiO_4 \rightarrow 2Li_{0.5}FeSiO_4 + Li_2FeSiO_4 \qquad (2)$$

$$2LiFeSiO_4 \rightarrow FeSiO_4 + Li_2FeSiO_4 \qquad (3)$$

3.2. Structural properties

The calculated lattice parameters and cell volume by various methods are shown in Table 1 (atomic positions are given by electronic supplementary information). For comparison, experimental[7, 10, 15-17, 36] and theoretical values [19, 21, 31, 32] by various investigators are given in this table. Relative differences among the calculated volumes of this study experimentally and theoretically obtained volumes of the literatures are shown in Table 2. According to this table, the calculated volume with LSDA method is the most similar to the experimentally measured values. The most similar values to the calculated volume were published in the references [15, 16, 17, 36]. The sign of Δ[x] are different in our calculations (-) and the other DFT calculations (+) and attributed to the different used program package.

TABLE 1. Calculated lattice parameters (a, b and c) and cell volume (Ω) of Li$_2$FeSiO$_4$ (*Pmn2$_1$* space group) with experimental (E) and calculated (T) values presented in the literature

Method	a (Å)	b (Å)	c (Å)	Ω (Å³)
PBE-GGA	6.221	5.290	4.979	163.858
WC-GGA	6.170	5.247	4.938	159.881
LSDA	6.241	5.308	4.995	165.449
E [7]	6.26615	5.32955	5.01484	167.474
E [10]	6.26538	5.34371	5.01393	167.868
E [17]	6.26955	5.34546	4.96244	166.305
E [16]	6.26746	5.33527	4.96535	166.029
E [15]	6.26800	5.34163	4.96013	166.072
E [36]	6.2711	5.3361	4.96079	166.004
T [19]	6.32	5.384	4.998	170.066
T [21]	6.259	5.402	5.027	169.968
T [31]	6.3246	5.3817	4.9967	170.073
T [32]	6.331	5.391	4.992	170.379

One of the important parameters for computational assessment of the structural stability is the volume change after the extraction of lithium from the unit cell of cathode material. The calculated change of the lattice parameters and volume via various methods are given in Table 3. According to this table, Li$_2$FeSiO$_4$ is a stable structure as a cathode material in Li-ion batteries due to a low volume changes (less than 3%). These results are in agreement with the experimental results that especially were obtained via in-situ XRD [11].

TABLE 2. Comparison of calculated cell volume (Ω) with experimentally (E) or theoretically (T) published cell volume for Li$_2$FeSiO$_4$ structure; Δ[x] =100× (Ω$_{row}$-Ω$_{Ref. x}$)/Ω$_{Ref.x}$

Method	Δ [7]	Δ [10]	Δ [17]	Δ [16]	Δ [15]	Δ [36]
PBE-GGA	-2.16	-2.39	-1.47	-1.31	-1.33	-1.29
WC-GGA	-4.53	-4.76	-3.86	-3.70	-3.73	-3.69
LSDA	-1.21	-1.44	-0.51	-0.35	-0.37	-0.33
T [19]	1.55	1.31	2.26	2.43	2.41	2.45
T [21]	1.49	1.25	2.20	2.37	2.35	2.39
T [31]	1.55	1.31	2.27	2.44	2.41	2.45
T [32]	1.73	1.50	2.45	2.62	2.59	2.64
E [7]	-	-0.23	0.70	0.87	0.84	0.89
E [10]	0.24	-	0.94	1.11	1.08	1.12
E [17]	-0.70	-0.93	-	0.17	0.14	0.18
E [16]	-0.86	-1.10	-0.17	-	-0.03	0.01
E [15]	-0.84	-1.07	-0.14	0.03	-	0.04
E [36]	-0.88	-1.11	-0.18	-0.01	-0.04	-

TABLE 3. Calculated change percentage (%) of the lattice parameters (a, b and c) and cell volume (Ω) for a transition from Li$_2$FeSiO$_4$ to delithiated LiFeSiO$_4$ (arrangement A) structure

Method	Δa/a	Δb/b	Δc/c	ΔΩ/Ω
PBE-GGA	0.322	0.322	0.322	0.971
WC-GGA	0.332	0.332	0.332	0.971
LSDA	-0.334	-0.334	-0.334	-0.999

3.3. Theoretical reaction voltage (TRV)

The obtained TRV by various methods of DFT calculations for two versions (FM and AFM) are given in Table 4, As aforementioned, many researchers have observed two oxidation voltages in the cyclic voltammogram (the first cycle was different from the others). In the some studies, the first oxidation peak (Li

extraction) and the other one were occurred at about ~3.1 and 2.8 V, respectively. Also, the reduction peaks were occurred at ~2.72 V [7, 11, 17, 37]. The first and the other oxidation voltage values could be found (for space group of *Pmn2₁*) in literatures, were 3.23, 2.86 [38]; 3.2, 2.8 [39]; 4.4, 3 [40] and 4.6-, 3.8 (for nano-sheets) [41], respectively. In contrast, the obtained voltammogram by Zaghib et al. [13] did not contain any extra oxidation peak in the first cycle and the oxidation and reduction peaks were occurred at 2.8 and 2.74 V, respectively. It was concluded that the high purity of the sample caused the absence of the first cycle phenomena. By comparison to the recently employed Rietveld method [15], these sample seems to contain the impurities.

Table 4 clearly shows that the calculated TRV values via LSDA, PBE-GGA and WC-GGA methods without SIC in FM state are always higher than of the value in AFM state. In contrast, in framework LDA (GGA)+U^{SIC} the AFM and FM calculations always led to the similar total energies. This is expected because U^{SIC} is applied to *3d* orbitals of Fe atoms which are also responsible for the magnetic properties. However, equal total energies (in U^{SIC} methods) imply the similar magnetic stability which might not be correct with this material (see e.g. Refs. [13, 42]). Therefore, the calculation methods without SIC may be more reliable for obtaining TRV. The transition energy transition from non-magnetic to magnetic states for the lithiated and delithiated materials are shown in Table 5. In contrast to the method with SIC, these values could not be neglected.

TABLE 4. Calcultaed theoretical reaction voltage (TRV) from various methods in two versions of calculations: FM and AFM

Method	U^{SIC} (eV)	FM	AFM
PBE-GGA	0	2.6945	2.3374
WC-GGA	0	2.9144	2.4891
LSDA	0	3.2046	2.7942
GGA+ U^{SIC}	1.67	2.7685	-
GGA+ U^{SIC}	5	2.8624	-
LDA+ U^{SIC}	5	3.1374	-
LDA+ U^{SIC}*	4.79-6.33	3.8521	-
LDA+ U^{SIC}	4.79	3.1332	-
LDA+ U^{SIC}	6.33	3.1628	-

* Lithiated and delithiated structures were calculated using U^{SIC} = 4.79 and 6.33 eV, respectively, based on Ref. 33.

According to Table 4, the differences between FM and AFM voltage values are 0.36, 0.42 and 0.41 for PBE-GGA, WC-GGA and LSDA calculations, respectively.

This value for PBE-GGA method is compatible with the experimentally observed differences between the first cycle oxidation and reduction voltages (0.3 [7, 11, 17, 37] and 0.37 [36]). Also, the obtained values by LSDA and WC-GGA are supported by other experimental data (0.37 [38], 0.4 [39] and 1.4 [40]). The calculated values of TRV (Table 4) and cell parameters (Table 2) by LSDA seem to be more agreeable to the experimentally measured values. The accuracy of LSD approximation, especially in the case of 3d transition metals, is challengeable. DFT calculations with LSD approximation in different compounds of Fe and other *3d* metals show various validities. It may be related to Fe environment or s/d electron orbitals. However, this discussion is out of the scope of this paper (for more information see Ref. [24] and its references).

TABLE 5. Calculated reaction energies by various methods for transition of Li_2FeSiO_4 and $LiFeSiO_4$ from the non-magnetic to the magnetic state. The negative sign meams the stability of the magnetic state. Subscript "f" in ΔU_f means per formula

Structure	Method	ΔU_f (eV)	ΔU (kJ/mol)
Lithiated	PBE-GGA	-2.1044	-202.7614
	WC-GGA	-1.9517	-188.0545
	LSDA	-1.749	-168.5268
Delithiated	PBE-GGA	-1.7473	-168.3556
	WC-GGA	-1.5264	-147.0759
	LSDA	-1.3386	-128.983

This study suggests that the first oxidation cycle voltage is attributed to the FM state and the AFM state is efficient in the subsequent cycles. This means that as-synthesized Li_2FeSiO_4 have sensitive magnetic property and the magnetic state of the material changes after a cycle of lithium extraction. Therefore, the transition between the two phases is not required in the first cycle. Based on this discussion, the structure of Li_2FeSiO_4 may remain stable with noremarkable change in the atomic positions or the crystal parameters in all cycles but electron configuration may be varied. Credible experimental evidences confirmed this idea. The in-situ XAS measurements showed the reversible oxidation/reduction process for iron analogue [12]. Therefore, iron environment did not change after delithiation. In-situ Mössbauer spectroscopy measurements had indirectly shown that no irreversible reactions had taken place in the first cycle[12]. Unfortunately, in-situ Mössbauer spectroscopy had not been considered for hyperfine magnetic point of view but it showed the differences between the first and second cycles [8]. In-situ XRD for *Pmn2₁* polymorph suggested that no remarkable changes of the structure

and the lattice parameters occurred in the first cycle [8, 12]. It is concluded that the phase transition was very unlikely [12]. Electrochemical measurements at the moderate rates (>C/10) showed that the change of structure was a rather slow process evolving principally over the first 2–3 cycles [8]. Although the range of 2θ in the published XRD patterns[8, 12] was only up to 40 degrees, the XRD peaks were quite different from the obtained pattern by Armstrong et al. [20]. It is noteworthy that Armstrong et al. used *P21/n* polymorph as the starting material and obtained inverse-β_{II} (modified *Pmn2₁*) after ten cycles, and Dominko [12] used *Pmn2₁* polymorph for experiments. In this study, the well-documented switching from ~3.1 to ~2.8 was occurred as a result of the inter-structural switching in Fe magnetic configuration due to extraction of lithium atoms. This transition may have occurred due to the sensitive difference between the two magnetic states. The NMR results showed that the materials have the substantial anisotropy of the bulk magnetic susceptibility [42]. In comparison, another lithium iron cathode material compound of $LiFePO_4$ (that do not show this behavior) have collinear antiferromagnetic ground state that is very robust and do not change against imperfections [43]. Also, indirect experimental evidence exists for this proposal. Zaghib et al. [13] emphasized that the Li_2FeSiO_4 magnetic ground state was sensitive to the various imperfections of the structure. Therefore, the state could be easily switched from the magnetic to a weak ferromagnetic state. If the proposed mechanism was valid, the phenomenon of magnetic ground state sensitivity might lead to the switch in the magnetic state by the presence of crystal imperfections due to lithium extraction in the presence of the electric field. The switching between the two states may be occurred by the external magnetic fields which leads to the lack of the first cycle extra oxidation peak in the voltammogram (see[13]). Furthermore, applying an external magnetic field during the preparation process may change the electrochemical properties. Based on this discussion, the influence of adding elements such as Zn, Cu, Ni and Cr on the electrochemical properties of Li_2FeSiO_4 could be predicted (see [41, 44]). For example, doping of Zn as an element with diamagnetic property [42] and Cu had led to decrease the first cycle oxidation voltage of the material [41]. In addition, a similar behaviour had been observed for Li_2MnSiO_4 as a cathode material [45].
For the first time, Nyten et al. [8] suggested that the first cycle phenomenon was due to the rearrangement of Li/Fe sites. If it caused more stable structure in the lithiated condition, this suggestion would be agreeable. However, calculations showed that the miss-fit structure was thermodynamically less stable [19] that would cause higher voltage. Also, transition between magnetic states was more coherent with the first cycle extra voltage than a transition to the cycled phase (such as

inverse-β_{II} [20]). Transition to another phase could be caused the diminishing the properties in the subsequent cycles because this kind of transition hada kinetic barrier. If the most stable lithiated phase (*Pmn2₁*) transitioned to the most stable delithiated phase (inverse-β_{II}) in the delithiated condition [19] without kinetic problem, an inverse transition could be carried out in the lithiated condition. Furthermore, the first cycle phenomenon has been observed in the ultrathin nanosheets of this material [41] and this observation has not justified by the phase transition approach.

Delithiation of inverse-β_{II} cycled phase can be caused the significant changes in the structure volume under the cycling (+5.6% [21]) and the extraction/insertion of Li-ions can be irreversible. If this kind of transition takes place significantly, orthosilicate material will not be an appropriate cathode. However, there is no evidence for supporting the idea that the transition to the cycled structure occurs in large magnitude [21], so Li_2FeSiO_4 may still be considered as a promising cathode for Li-ion batteries.

TABLE 6. Calculated Band Gaps (BG), magnetic moments (μ_B) for the iron atom (m_{Fe}) and the total unit cell (m_{cell}) via various calculation methods

Structure	Method	U (eV)	BG (eV)	m_{Fe}	m_{cell}
Lithiated	PBE-GGA	0	0.31	3.14	4.08
	LSDA	0	0	3.12	4.03
	mBJ+LDA	0	0.73	3.24	4.00
	GGA+ U^{SIC}	1.67	1.31	3.30	4.00
	mBJ+GGA	1.67	1.83	3.33	4.00
	GGA+ U^{SIC}	5	2.63	3.41	4.01
	LDA+ U^{SIC}	5	2.04	3.37	4.01
	LDA+ U^{SIC}	4.79	1.98	3.36	4.01
	LDA+ U^{SIC}	6.33	2.36	3.40	4.00
	mBJ+LDA	6.33	3.88	3.45	4.00
Delithiated	PBE-GGA	0	0.71	3.79	5.01
	LSDA	0	0	3.68	5.02
	mBJ+LDA	0	0.86	3.74	5.00
	GGA+ U^{SIC}	1.67	1.4	3.85	5.00
	mBJ+GGA	1.67	1.62	3.87	5.00
	GGA+ U^{SIC}	5	2.55	4.02	5.01
	LDA+ U^{SIC}	5	2.44	3.98	5.03
	LDA+ U^{SIC}	4.79	2.27	3.95	5.00
	LDA+ U^{SIC}	6.33	2.88	4.03	5.02
	mBJ+LDA	6.33	3.36	4.08	5.00

3.4. Band Gap and Magnetic Moment

Calculated DOS by selected methods are illustrated in Fig. 2 for structures of Li_2FeSiO_4 and delithiated

LiFeSiO$_4$. DOS plots for one category of calculation (i.e., FM or AFM for lithiated or delithiated structure) are similar except for band gaps. The calculated band gaps are given in Table 6.
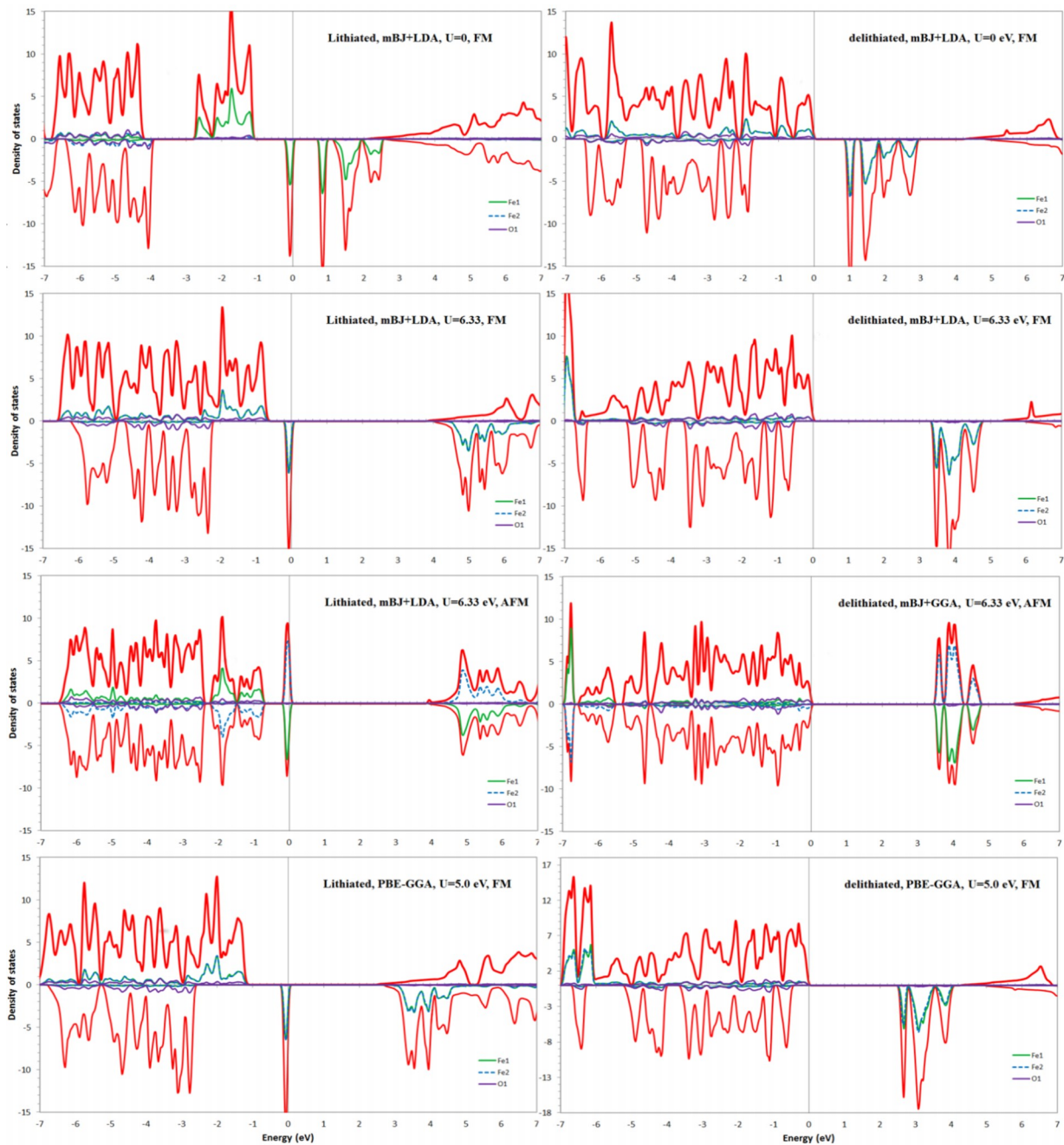

Figure 2. Diagrams of selected total DOSfor lithiated Li$_2$FeSiO$_4$ (left column) and delithiated LiFeSiO$_4$ (right column) structures obtained via various methods. The Fermi level is set at zero energy and marked by vertical lines. Negative values of vertical axes are related to the spin down DOS

It is worthy of note that the obtained band gaps for AFM versions were similar to FM versions and are not listed in this table. However, the limitation of this method is the uncertainty of U^{SIC} values. Unfortunately, the experimental data are not currently available for the band gap of this material. However, the calculated band gaps via mBJ+LDA+U methods are expected to be more accurate since different methods of carbon activation have been used by researchers. The value of band gap, in U^{SIC}=6.33 eV, is equal to 3.88 eV which is higher than the previously reported values. In our opinion, the main problem is the low electron

conductivity of this material. Various polymorphs have shown similar electrochemical properties [17, 19, 21] and it is expected that more comprehensive investigations will be carried out to overcome this problem.

4. CONCLUSIONS

In this study, *Pmn2₁* polymorph of Li_2FeSiO_4, a candidate cathode material for Li-ion battery applications, was investigated by DFT using PBE-GGA, WC-GGA and LSDA methods. Based on the calculated energies for possible reactions of delithiated structures, the arrangement A was chosen as the stable configuration for LiFeSiO₄ unit cell. Then, the considering structural parameters, TRV and DOS of Li_2FeSiO_4 were investigated by PBE-GGA (+U^{SIC}), WC-GGA, LSDA and LDA+U^{SIC} methods. Also, mBJ+ LDA (GGA)+U^{SIC} method was employed for the more accurate calculation of band gap. According to the structural parameters and TRV, the obtained structure by LSDA was the most similar value to the experimental values. All calculations proved the stability of Li_2FeSiO_4 structure (space group of *Pmn2₁*) after delithiation. The value of TRV in U=0 was employed for calculation of the total energy although the calculations in U≠0 have more importance for band gap prediction. Also, it was purposed that the calculated value of TRV by spin-polarized FM was related to the first cycle and the AFM was attributed to the subsequent cycles. Also, extraction of lithium atoms in the first cycle was caused the switching of magnetic states. Finally, the comparison of available experimental data suggested that the proposed approach based on the switching of magnetic states was more comprehensive compared to the other approaches offered for justifying the the first cycle extra oxidation voltage. Also, the variety of the electrochemical properties of Li_2FeSiO_4 was caused by dopants could be interpreted through the magnetic states.

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