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Effect of Ti modification on Structural, Electronic and Electrochemical properties of Li_2FeSiO_4—A DFT study using FPLAPW approach

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ABSTRACT

We report the effect of Ti modification on structural, electronic and electrochemical properties of Li^+ ion battery cathode material Li_2FeSiO_4. A density functional theory (DFT) study based on full potential linearized augmented plane wave (FPLAPW) approach has been performed on Li_2FeSiO_4 of $Pmn2_1$ polymorphic phase. Simulation of geometric, electronic structure and electrochemical characteristics of Li_2FeSiO_4 are performed prior to Ti modification. Ti doping is done by replacing either 50% Fe or 50% Si in Li_2FeSiO_4 with Ti. The optimized Ti-doped geometric structures are used to evaluate electronic structure and electrochemical properties in terms of density of states (DOS), and Li de-intercalation voltage. Effect of de-intercalation on structural stability, density of states and hence band-gaps are also analyzed. Feasibility of de-lithiation of more than one Li^+ ion per formula unit of Li_2FeSiO_4 of $Pmn2_1$ polymorphic phase without and with Ti modification is estimated using FPLAPW approach. It is observed that, Ti doping by replacing 50% Fe would be suitable for more than one (1.5 Li ion) Li^+ ion de-intercalation from $Pmn2_1$ polymorphic phase of $Li_2Fe_{0.5}Ti_{0.5}SiO_4$.

1. Introduction

Impending energy crisis and present emphasis on search for clean and green energy sources has increased the relevance and importance of materials research for device applications such as; high energy density lithium batteries, supercapacitors, fuel cell, photovoltaics etc. [1]. Suitable electrodes (cathode/anode) are the essential components of these devices. Conventionally, transition metal oxides having layered structure such as $LiCoO_2$, $LiNiO_2$ or oxides having spinel structure such as $LiMn_2O_4$ etc., have been rated as potentially viable cathodes for commercial applications. However, these options for cathodes have serious inherent limitations [2] in view of strong oxidizing activity in the presence of an organic electrolyte, safety issues due to toxicity of Co, complex chemistry of Mn causing phase instability and problems of lifetime/passivation etc.

However, a low cost material phosphate (i.e.; $LiFePO_4$) having olivine structure [3], has been emerged as the next generation cathode. It offered advantages, such as; lattice stabilization due to strong P—O bond, chemical and electrochemical safety in a voltage domain, freedom from the requirements of a passivation layer and reasonably acceptable reversible capacity etc. The only known drawback of $LiFePO_4$ as a cathode is its poor electronic conductivity which affects overall power rating of the device. Several approaches for an improvement of this limitation have been proposed and the subject is under an extensive research process [2,3].

The ongoing quest, for a low cost and stable cathode material with acceptable properties, has created significant interest in silicate structure alternatives based on Li-Fe-Si-O combination [4–11]. It is expected that lower electro-negativity of Si (2.03) vs. P (2.39) [4] would reduce de-intercalation voltage for $Fe^{(II)} \rightarrow Fe^{(III)}$ redox couple formation [4], lower electronic band gap and increase electronic transport. Earlier reports in literature [4–11] on this system confirmed the presence of inactive impurity as well as unreacted components (e.g.; $Li_2SiO_3 + FeO_x$) affecting phase purity and suitability of Li_2FeSiO_4 as an electrode material. Attempts are, therefore, going on to optimize the conditions of synthesis process for achieving pure phase of Li_2FeSiO_4. Further, the mechanism of voltage reduction after first cycle is yet to be understood clearly [5]. The problem is linked directly with the stability of the structural phase formation of Li_2FeSiO_4 and energetics related to it [4–11].

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However, serious attempts have been made to control the limitations on this account using recently evolved concept of particle size engineering and novel coating strategies. A state-of-the art review [12–18] of the theoretical work on Li_2FeSiO_4 suggested that density functional theory (DFT) [19,20] calculations based on generalized gradient approximation (GGA) associated with Hubbard U (GGA + U approach) would provide accurate values of structural parameters (e.g.; bond length etc.) as well as electronic structure (e.g.; band gap) [21] and de-intercalation voltage. In fact, the predicted voltage (vs. Li/Li^+) for Li_2FeSiO_4 is 2.66, 2.79 and 2.88 volts for three structures obtained with GGA approach [12], while this value is 3.30 [13] and 3.16 volt [14] with GGA + U (SIC) approach depending on different values of U used for DFT studies on polymorphs of Li_2FeSiO_4 having $Pmn2_1$ symmetry.

A state-of-the art survey suggests that all the theoretical calculations reported in literature till now are based on mainly "pseudopotential" [12–17] approach. Kalantarian et al. [18], however, simulated density of states of Li_2FeSiO_4 with $Pmn2_1$ symmetry using FPLAPW code [20] Wien2k [24] and analyzed them to predict rate capability of this material. However, they have not reported Li de-intercalation voltage of Li_2FeSiO_4 in their work. Wu et al. [13] reported de-intercalation voltage (V) = 3.3 V for Li_2FeSiO_4 of $Pmn2_1$ symmetry using pseudopotential code with U = 5 eV. On the other hand, Dompablo et al. [14] obtained V = 3.16 V with U = 4 eV. This value is more close to the actual experimental Li^+ de-intercalation voltage ~3.1 V [4] for Li_2FeSiO_4. A careful comparison of literature, therefore, suggests that theoretical calculations based on GGA or (GGA + U) methodologies exhibit divergent results depending on choice of Hubbard potential (U). A more realistic value of electrochemical parameters can be ensured via tunability of Hubbard potential (U) term. Therefore, any theoretical prediction based on energy of the unit cell, electronic structure and cathode characteristic of Li_2FeSiO_4 needs a revisit to check the accuracy of earlier results considering full potential (FPLAPW) approach.

Doping of foreign element in Li_2FeSiO_4 to enhance its electrochemical property is not a new approach. Mn, Ni [25], Ti, Sn [26], S [27] N [28] doping have already been documented. In this paper, we have reported structural, electronic and electrochemical properties of Li_2FeSiO_4 before and after Ti modification; effect of delithiation on structural, electronic and electrochemical properties and feasibility of delithiation of more than one Li^+ ion per formula unit of Li_2FeSiO_4 were studied.

2. Computational details

The present study aims to carry out simulation to determine structural and electrochemical properties using full potential approach, based on linearized augmented plane waves (LAPWs) [29] as the basis states instead of plane waves [19]. This approach considers a realistic crystal potential with no particular shape approximation giving very accurate result for total energy of the unit cell [20] and hence is very useful for calculating Li^+ de-intercalation voltage with greater reliability. A full potential approach [29], as implemented in DFT code Wien 2k [24] is used for this study. In order to achieve the target objectives defined as above, coulomb interaction (U) due to orbital electrons and exchange interaction (J) arising out of electron spin-states has been taken into consideration for a strongly correlated system like Li_2FeSiO_4. GGA + U type interaction which is consistent with earlier work of Anisimov et al. [21](a) & (b)] has been adopted. A Hubbard U(or U_{eff}) = U–J with U = 5 eV and J = 0, so that U_{eff} = 5 eV [13] has been used for Fe d-orbital in this calculation. For Ti^{+2} doping by replacing 50% Fe in Li_2FeSiO_4 a U value of 0.72 eV [30] was used. However, for doping of Ti^{+4} replacing 50% Si in Li_2FeSiO_4, no U_{eff} was used for Ti^{+4} in accordance with earlier work on Ti^{+4} based compound like Li_2FeTiO_4 [31]. Further, for all the calculations we have considered $R_{MT} * K_{max} = 7$ [29] where R_{MT} is the radius of muffin-tin spheres of Oxygen atoms and K_{max} is the cutoff for the plane wave basis set in the interstitial region. Simulation was done using 24 reciprocal lattice points (k-points) in the irreducible Brillouin zone for all the cases.

3. Results and discussion

3.1. Structural Analysis of Li_2FeSiO_4 and $LiFeSiO_4$

The origin of the present *ab initio* calculations on Li_2FeSiO_4 is based on the structural symmetry ($Pmn2_1$ space group) reported by Nyten et al. [4]. Nishimura et al. [7] showed that Li_2FeSiO_4 should be assigned monoclinic $P2_1$ symmetry while Sirisopanaporn et al. [8] reported different polymorphic forms of Li_2FeSiO_4 at different temperatures having space groups Pmnb and $P2_1/n$. In another work of Sirisopanaporn et al. [10], it was shown that among the polymorphs of Li_2FeSiO_4 prepared at different temperatures, the phase prepared at 200 °C can be assigned $Pmn2_1$ space group. It exhibited the same charging voltage (3.1 V) for the first cycle as reported by Nyten et al. previously. The aforesaid polymorphs of Li_2FeSiO_4, as have been reported in literature, were prepared under different synthesis conditions using different methods. Simulations of properties of different polymorphs of Li_2FeSiO_4 have already been performed through computational studies using pseudopotential approach [12–17].

In the present calculation, the input parameters have been taken from the experimental data of Li_2FeSiO_4 reported for the first time by Nyten et al. [4]. Optimized lattice parameters for each interaction were calculated by calculating energy (E) for different unit cell volume (V) and fitting the data in Birch–Murnaghan equation of states [32,33]. However, for further accuracy of structural model of Li_2FeSiO_4, the lattice parameters of the optimized volumes were further optimized by varying b/a ratio and c/a ratio. The results are compared with experimental lattice parameters obtained by Nyten et al. [4,5] and also with earlier results obtained by PAW calculations [13] in Table 1.

The ground state energy was recalculated on the basis of optimized structure as a corrective exercise for the change in basis sets during structure optimization [34]. The input structural

Table 1
Lattice parameters of Li_2FeSiO_4 and $LiFeSiO_4$ after optimization of *b/a* and *c/a* ratio.

Lattice parameters (Å)	Li_2FeSiO_4 Experimental [4]	Li_2FeSiO_4 Simulated	$LiFeSiO_4$ Experimental [5]	$LiFeSiO_4$ Simulated
a	6.2661	6.3602 (6.331[13])	6.508	6.1669 (6.138[13])
b	5.3295	5.4202 (5.391[13])	5.216	5.4263 (5.584[13])
c	5.0148	5.0392 (4.992[13])	5.002	4.8861 (5.021[13])