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Density functional theory study of $LiFeTiO_4$

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HIGHLIGHTS

- $LiFeTiO_4$ exhibits 4% volume strain accompanying 1.5 Li^+ exchange in a cycle.
- Mott-Hubbard and charge-transfer insulator type band-gap exist in $LiFeTiO_4$.
- Estimated voltage plateaus are 2.6 V and 3.7 V.
- The redox active couple are Fe^{+3}/Fe^{+2} and $Fe^{+3}/Fe^{+(3+\delta)}$, $O^{-2} \rightarrow O^{-2+\gamma}$ for the plateaus.

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ABSTRACT

Electrochemical characteristics of spinel cubic $LiFeTiO_4$ are evaluated through Density Functional Theory (DFT) study. Li^+ intercalation/de-intercalation behavior of $LiFeTiO_4$ is studied in accordance to the electrochemical relation; $LiFeTiO_4+Li \rightarrow Li_2FeTiO_4$ and $LiFeTiO_4-0.5Li \rightarrow Li_{0.5}FeTiO_4$ respectively. Effect of Li^+ ion exchange on geometrical and electronic structure in terms of volume strain and density of states are respectively studied. It is found that there would be 4% volume strain in charge-discharge cycle accompanying 1.5 Li^+ ions exchange per cycle producing high structural rigidity and hence electrochemical safety. The intercalation/de-intercalation voltages are estimated to be 2.6 V and 3.7 V respectively, and are in accordance with earlier experimental reports. The redox active couple corresponding to the intercalation reaction is identified to be Fe^{+3}/Fe^{+2} while those corresponds to the de-intercalation reaction are identified to be $Fe^{+3}/Fe^{+(3+\delta)}$ and $O^{-2}/O^{-2+\gamma}$. The electrochemical capacity is estimated to be 230 mA h g^{-1} per cycle enabling 1.5 Li^+ exchange.

1. Introduction

Research on different Li-oxide composites are going on for decades [1] in search of new efficient materials to be used as electrodes in Li batteries. Especially olivine [2], spinel [2] and layered silicate [3] type structures are of primary interest among researchers due to the presence of suitable Li-diffusion path in these materials. Whether a Li-oxide can be used as a cathode or an anode depends on the oxidation state of the transition metals presents in these composite oxides. Among electrode materials $-SiO_4^{-4}$ [3,4], $-PO_4^{-3}$ [5–7] and $-TiO_4^{-4}$ [8,9] are considered as the next generation of cathode materials and are under extensive research process in different labs. Although these materials have lower electronic conductivity than commercial cathode materials $LiCoO_2$, they have several advantages also; viz. (i) materials are nontoxic, (ii) Presence of strong bonds like -Si–O, –P–O, –Ti–O make them electrochemically safer, (iii) capacity enhancement may be possible by de-intercalating more one Li^+ ions per formula units [2]. While as anode materials, graphite or MCMB are mostly used in Li batteries [10]. Although these materials can show high capacity (360–400 mA h g^{-1}) [2]) and good electronic conductivity (~10^3 S cm^{-1}) [2]), they have disadvantage in terms of volume expansion-contraction during charge-discharge cycle that causes capacity fading [11]. An alternative titanate based anode material is $Li_4Ti_5O_{12}$ which shows zero strain during [12] charge-discharge process and hence electrochemically safer than usual graphite anode. However, it has lower capacity (165–170 mA h.g^{-1} [13]) and very low electronic conductivity (~10^{-10} S cm^{-1} at room temperature [14]). There have been many studies on spinels of general formula $Li_{0.5+0.5x}Fe_{2.5-1.5x}Ti_xO_4$ for $x = 0$ to 1.5 [15]. These materials have created considerable interest because they show structural

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and magnetic transitions with variations of x. Among them, $LiFeTiO_4$ (corresponding to x = 1) resides at an intermediate phase between 3D magnetic ordering and spin glass state. $LiFeTiO_4$ show canted spin states with ferrimagnetic ordering between tetrahedral (A) and octahedral (B) sites [16].

Structural studies show that $LiFeTiO_4$ has same spinel crystal structure [17] as $Li_4Ti_5O_{12}$ with Fd3m space group symmetry and hence could be of interest as an alternative anode material. $LiFeTiO_4$ with a different polymorph having calcium ferrite ($CaFe_2O_4$) type tunnel structure [18] has been studied electrochemically; however that polymorph was seen to be unstable and converts into the known spinel $LiFeTiO_4$ with Fd3m symmetry at higher temperature. Recently Chen et al. [19] have shown that $LiFeTiO_4$ can even be used as cathode material with extraction of 1.6 Li^+ (with 244 $mAhg^{-1}$) ion per formula unit during charging. However, Chen at al [19]. also showed that excess electrochemical capacity can be achieved due to the presence of pseudo-capacitance in $LiFeTiO_4$ as has also been seen in our earlier experimental work on this material [20]. In this work we have modeled $LiFeTiO_4$ as an intercalating/de-intercalating electrode material for Li ion battery application without bringing the complexity of pseudo-capacitance. Henceforth, in this work, the calculated electrochemical capacity corresponds only to the intercalation/de-intercalation of Li^+ ion inside the lattice host.

It was seen from thorough literature survey that there were few structural, dielectric, magnetic and electrochemical studies on spinel $LiFeTiO_4$ have been carried out [15–20] already, however, it lacks any theoretical study using atomistic simulation process via either density functional theory or any other electronic structure methods like monte-carlo simulation. A complete understanding of electrochemical properties requires knowledge of correlation and changes in geometric as well as in electronic structure with Li^+ intercalation/de-intercalation in the material and that is still undone. With an aim to complete this study, structural, electronic properties and Li intercalation/de-intercalation voltage and the effect of ion-exchange on geometric and electronic structure of $LiFeTiO_4$ was studied and estimated theoretically through density functional theory (DFT) simulation for the first time and is reported in the present work.

2. Computational details

DFT calculation was done using a full potential linearized augmented plane wave (FPLAPW) [21] code wien2k [22].

The scheme of calculation adopted for $LiFeTiO_4$ comprises GGA+U approach with a U = 6 eV has been employed for Fe-d orbitals in order to simulate approximate Li intercalation voltage [23–25]. Ferrimagnetic alignment of Fe spins was considered by setting opposite spin directions of Fe resides at octahedral (16d) and tetrahedral sites (8a) respectively. For all the calculations we have considered $R_{MT}*K_{max} = 7$ where K_{max} is the cutoff for the plane wave basis set in the interstitial region. A minimum value of (1.5–1.6) for oxygen atom for different calculations has been used and it gave K_{max} ranging from 4.66 a.u.$^{-1}$ to 4.38 a.u.$^{-1}$ for all the calculations. Simulation was done using 14 reciprocal lattice points (k-points) in the irreducible Brillouin zone for all the cases.

3. Results and discussion

3.1. Structural optimization

Simulation of $LiFeTiO_4$ structure was carried out using our experimentally determined structural parameters (Table 1) obtained from Rietveld analysis of XRD pattern of $LiFeTiO_4$. A 56 atom unit cell (1 × 1 × 1 primitive unit cell) was generated for incorporating the partial occupancies in the simulated structure. This was done by mapping the structural coordinates corresponding to $LiFeTiO_4$ structure having space group Fd3m (Table 2) on a primitive lattice with space group P1 (by keeping all 56 atoms inequivalent). The experimental lattice parameters were further relaxed. Atomic coordinates were also relaxed to obtain ground state structure having minimum energy per unit cell volume and minimum force per atoms. Simulated lattice parameter and atomic coordinates of the 56 atom cell are listed in Table 2. The structural parameters of simulated primitive unit cell generates comparable XRD pattern (Fig. 1(a)–(b)) (generated using software Powdcell [26]) with experimental XRD along with slight variation in intensity due to little difference in atomic coordinates originated from atomic relaxation with primitive mapping. However, the same simulated structure has predicted very accurate Li intercalation/de-intercalation voltage as described in Section 3.4.

Table 1
Experimental structural parameters obtained from Rietveld fitting of $LiFeTiO_4$.

Atom	Wyckoff positions	x	y	z
Ti	16d	0.5	0.5	0.5
Li	16d	0.5	0.5	0.5
Fe	16d	0.5	0.5	0.5
Li	8a	0.125	0.125	0.125
Fe	8a	0.125	0.125	0.125
O	32e	0.258	0.258	0.258

Experimental lattice parameter a = 8.355(8) Å, space group = Fd3m, R_{wp} = 7.067(2), R_e = 7.044(9), R_p = 5.644(3), **GOF** = **1.006(4);** in which R_{wp} → weighted R profile, Re → expected R profile, R_p → R profile, GOF → Goodness of fit, Profile function used → Pseudo Voight.

$LiFeTiO_4$ unit cell contains 8 Ti, 4 Fe and 4 Li atoms at octahedral lattice site 16d, 4 Fe, 4 Li at tetrahedral lattice site 8a and 32 oxygen atoms at lattice site 32e with details in the Table 2. An earlier report [17] showed that tetrahedral and octahedral occupancy of Fe atom in $LiFeTiO_4$ are respectively 53% and 47%, incorporation of those occupancies need larger unit cell (2 × 2 × 2 primitive unit cell). In the present calculations, we have considered equal occupancy (50%) of Fe atoms at both the sites. However, this approximation has not caused a huge deviation from actual structure, as is also evident from simulated XRD pattern in Fig. 1. Average bond lengths in $LiFeTiO_4$ (both theoretical and experimental) are depicted in Table 3. There are two types of triatomic bonding present in $LiFeTiO_4$. They are B–O–B and B–O–A where B are the atoms at octahedral lattice site 16d (Ti, Fe, Li) and A are the atoms at tetrahedral lattice site 8a (Li, Fe) whereas no A–O–A bond is present in the material.

3.1.1. Effect of Li^+ ion intercalation/de-intercalation on structural parameters

Effect of Li^+ ion intercalation on structural parameters were studied by intercalating one Li ion in $LiFeTiO_4$ leading to Li_2FeTiO_4 as the final structure. It was simulated according to our experimentally determined structural models (Table 4) as obtained from Rietveld analysis of XRD pattern of Li_2FeTiO_4 by considering 8 Ti, 4 Fe and 4 Li atoms at octahedral lattice site 16d; 4 Fe, 12 Li at octahedral lattice site 16c and 32 oxygen atoms at lattice site 32e. This is also in accordance with existent literature reports on Li_2FeTiO_4 structure [9,27]. The simulated XRD pattern corresponding to Li_2FeTiO_4 and its experimental XRD pattern are shown in Fig. 2. In experimental XRD pattern there are some extra peaks which correspond to Fe_2TiO_4 as being prepared as an impure phase in our experimental synthesis and also been identified from Rietveld analysis. Average bond lengths in Li_2FeTiO_4 (both theoretical and experimental) are described at Table 5. There are three types of triatomic bonding present in Li_2FeTiO_4. They are B–O–B, B′–O–B′