Ionic conductivity enhancement by particle size reduction in Li$_2$FeSiO$_4$

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**Abstract**

Li$_2$FeSiO$_4$ is an important alternative cathode material for the next generation Li-ion batteries due to its high theoretical capacity (330 mA h/g). However, its development has faced great challenges arising from its structural complexity and its poor ionic conductivity. In the present study, the energetics of surface structures and nano particles of the Pmn2$_1$ polymorph of Li$_2$FeSiO$_4$ are studied by means of first-principles calculations based on density functional theory. The present study demonstrates that, by tailoring the particle size of the Li$_2$FeSiO$_4$, one can increase the diffusion coefficient above 10$^{-8}$ cm$^2$/s, which is comparable to the typical one reported for the current generation state-of-the-art material.

1. Introduction

Energy storage is unquestionably one of the greatest challenges of the twenty-first century. In response to the needs of the modern society and of the emerging ecological concerns, it is crucial that novel, low-cost, and environmentally friendly systems for energy conversion and storage are discovered; hence the rapid development of research in this field. Nanostructured materials have attracted great interest in recent years because of their unusual mechanical, electrical, and optical properties endowed by confining the dimensions of such materials, and because of the combination of bulk and surface properties to the overall behavior. Nanostructured materials are becoming increasingly important for the storage of electrochemical energy [1,2]. Although such batteries are commercially successful, we are reaching the limits in performance using the current electrode and electrolyte materials [3].

Further breakthroughs in materials are therefore essential for the new generations of rechargeable lithium batteries, not only for applications in consumer electronics but especially for clean energy storage and use in hybrid electric vehicles. The nanomaterials for lithium-ion batteries have several potential advantages and disadvantages associated with the development of nano-electrodes for lithium batteries. Li$_2$FeSiO$_4$ (hereafter referred as LFS) is a new kind of polyoxy anion cathode material based on the ortho silicates family, it has a theoretical specific capacity of 330 mA h/g, with lower irreversible capacity [4]. In addition, iron and silicon are very abundant material, and their cost is consequently low. Since LFS was firstly synthesized and characterized by Nytén et al. [4] it has been attracting increasing interest from the scientific community, as a potential candidate for next-generation cathode material in lithium ion batteries. Unfortunately, LFS have several defects, including a poor electronic conductivity [5] and a slow diffusion rate of lithium ions [6], which has become an obstacle to its extensive application in electric vehicles (EV) and hybrid EV. Many efforts have been therefore made to optimize the properties of LFS cathodes. Reducing the LFS into nano scale was proven to be an effective approach [7–9]. In this article we studied how the particle size affects the electrochemical properties of LFS using first-principles calculations.

1.1. Computational details

Total energies have been calculated by the projected-augmented plane-wave (PAW) implementation of the Vienna ab initio simulation package (VASP). More computational details of the modelling of the bulk phases can be found in Ref. [10]. Periodic slab models are used to simulate the surfaces. All slabs used in the present work are constructed from a $2 \times 2 \times 2$ optimised supercell, containing 16 LFS formula units. For slabs of such a large size, both the atomic and the electronic properties of the central atoms are similar to the bulk references. The thickness of the vacuum layer is set to be larger than 14 Å, thick enough to ensure that the interactions between the surfaces are negligible. The slab models are extracted directly from the bulk using the theoretical equilibrium bulk lattice constants. The atomic positions in the slab are
fully optimized until the force exerted on each atom is smaller than 0.05 eV/Å. During the relaxation, the thickness of the slab and the in-plane lattice constants are kept fixed. Different sizes of the nano particles (NP) have been constructed from optimized bulk LFS-Pmn21 phase through different supercell sizes. The k-points were generated using the Monkhorst-Pack method with a grid size of 2 × 2 × 1 and 1 × 1 × 1, for structural optimization for thin film and nano-clusters/particles, respectively. During the thin film and nano-clusters construction, the LFS stoichiometry was always maintained and the dangling bonds are terminated with H atom. For the surface and NP models considered, we have included an integer number of LFS formula units, and they are thus stoichiometric. This will avoid generating surface and NP models that are significantly polar and that would consequently be artificially stable due to long-range electrostatic forces. The Li+ diffusion barrier heights in the bulk and in the np models were investigated using the climbing-image nudged elastic band (cNEB) method [11]. By removing a Li atom in the lithiated systems, we are properly modeling the oxide-reduction reaction that occurs in the cathode during the discharging processes of the battery. To determine the minimum energy path (MEP) through the cNEB method, seven replicas of the system were created, in each of which the diffusing Li atom was moved by equidistant steps to positions between the initial and final states for the path obtained from linear interpolation.

2. Result and discussions

2.1. Surface geometry structure

Experimental and theoretical studies on LFS have reported several stable structures, all characterised by cations located in the tetrahedral interstitials of a nearly hexagonally close-packed framework of oxygen atoms. The most known polymorphs are Pmn21 (orthorhombic at low temperature), P21/m (monoclinic at 700 °C), and Pmn2 (orthorhombic at 900 °C). However, the orthorhombic space group Pmn21 is found (see Fig. 1a) to be the most stable polymorph according to first-principles calculations [12–15]. In this study, we have concentrated mainly on the Pmn21 polymorph. Before studying the surface models, we first optimize the lattice parameters and the magnetic ordering of the bulk structures. Our results show that the optimized bulk system is ferromagnetic and the theoretical lattice constants are 6.3250 Å, 5.3842 Å and 4.9731 Å for a, b and c, respectively. These values are slightly larger than the experimentally observed one of 6.2950 Å, 5.3454 Å and 4.9624 Å [16]. This overestimation of the lattice parameters is typical of the GGA approximation we applied in our calculations. In the present work, the slab models are constructed with Li atoms at the outmost layer of the surface, as Li atoms are fully ionized in the material and have low mobility in the bulk. We have considered only 3 nonpolar (0 0 1), (0 1 0) and (1 1 0) surfaces. The surface energy of a crystal can be calculated using

\[
\text{Esurf}(n) = E_{\text{slab}}(n) - E_{\text{bulk}}(n)/2S,
\]

where \(E_{\text{slab}}(n)\) is the total energy of the slab and \(E_{\text{bulk}}(n)\) is the total energy of bulk which has the same number of atoms with the super cell and \(S\) is the surface area. The factor “2” denotes the total surfaces of the supercell. The calculated surface energies for the (0 0 1), (0 1 0) and (1 1 0) surfaces are 60.3, 31.9, and 24.6 meV Å\(^2\) respectively. The magnitude of the calculated surface energies are following sequence (1 1 0) < (0 1 0) < (0 0 1). This finding is consistent with recent theoretical reports [17]. It should be noted that large relaxations of the outermost Li atoms are observed at the LFS (1 1 0), (0 1 0) and (0 0 1) surfaces, especially for the case of (1 1 0) and (0 0 1) surfaces. Fig. 1b compares the side view of bulk LFS and (0 1 0) slab model after relaxation. Although atoms relaxed inward and outward alternatively, the whole thickness of atom slabs became smaller than the bulk reference. It is very interesting to note that the outmost Li and O layers do not relax much for the case of (0 1 0) surface slab relaxation, being in accordance with the stable (0 1 0) termination. The calculated Li-Li, Fe-Li, Si-Li, Li-O, Si-O, and Fe-O distances at the surface of the slabs differs considerably from the bulk, and these distances are very scattered. On the other hand, in the inner part of the slabs these distances are identical to the bulk reference.

2.1.1. Nano particles

It should be noted that the (0 0 1) derived (0 1 0), and (1 1 0) derived nano structures are quite similar due to the layered nature of the bulk phase. From the calculated total energy as a function of particle size (see Fig. 2a) we found that NP with 33 f.u. of LFS the energy becomes stable. Hence, for the cNEB study we have used this 33 f.u. of LFS NPs. The optimized stable Pmn21-LFS derived NPs with the size of ca. 2.5 nm is displayed in Fig. 3a. From the variation in the interatomic distances of the nanoparticles compared with that of the bulk phases, it should be anticipated that the nanophase materials have different physical and chemical properties with respect to the bulk materials. The calculated interatomic distances versus number of bonds (i.e., the pair distribution function, see Fig. 2b) for the optimized nanoparticles indicate that the values are very scattered compared to that in the...
corresponding bulk phases. The corresponding Li-Li, Fe-Li, Si-Li, Li-O, Si-O, and Fe-O distances in the bulk phases are denoted in red (see Fig. 2b) and these distances are very scattered. Especially, several Li-Li bonds in the nanoparticles have very shorter bond distances than that in the corresponding bulk phases (in the bulk phase 3.016 Å). This type of structural arrangement is expected in nano and amorphous phases, not presenting three-dimensional crystallinity. In the present calculation the temperature effect was not taken into account. Because of the large number of atoms involved in the calculation, it is not possible to test the dynamical stability. A closer inspection of the interatomic distances in the NP reveals that the inter atomic distances at the center of the NP is still maintained as that of the bulk. On the other hand, the Li-Li distances in the surface are much shorter than in the bulk phase. This clearly indicates that the bonding interactions in the surface layers are considerably weaker than at the center of the NP. As a result, one can expect that the transport of Li ions from the surface of the NP is easier than that in the bulk or in the inner part of the NP.

2.2. Diffusion coefficient

The lithium diffusion coefficient can be calculated as $D = d^2 \Gamma$, where $d$ is the hopping distance and $\Gamma$ is the hopping rate being defined in the transition state theory as $\Gamma = v_0 \exp(-E_a/k_BT)$. In this case, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant, $T$ is the temperature, and $v_0$ is the attempt frequency. All calculations for the diffusion coefficient were performed considering $v_0$ about $10^{13}$ Hz, which is in the range of the phonon frequencies and consistent with typical values for the attempt frequency [18]. We considered temperatures between 300 K and 1000 K. Table 1 summarizes the diffusion coefficients for the bulk LFS, the thin films and the free standing nanoparticles of LFS. Since we have plotted the natural logarithm of the diffusion coefficient against $1/T$ (see Fig. 3c), we can see that the activation barrier is proportional to the slope of each straight line. The calculated energy barrier for the bulk structure Pmn2₁ symmetry is 0.83 and 1.06 eV for linear and zig-zag pathways respectively (see Fig. 3a, b). This finding is in good agreement with other theoretical works [19]. However, the values listed in Table 1 are considerably higher than that of ca. 0.30 eV, typically reported for the LiFePO₄ olivine cathode [20], which directly reflects the poor ionic conductivity of LFS. On the other hand, it can be seen in Table 1 that the activation energy of the surface models (ranges from 0.48 eV to 0.91 eV) and NP (vary from 0.37 to 0.722 eV) are much closer to that of the state-of-the-art-materials. Fig. 3c summarizes the obtained results for the natural logarithm of the diffusion coefficient in the selected Li migration in NP of LFS as a function of $1/T$. The coordination
number of the Li atoms at the surface of the NP are lower than that in the inner part of the NP. This is the main reason for the higher Li conductivity at the NP surface. The diffusion coefficient calculated in NP of LFS at room temperature, ranging from $10^{-18}$ cm$^2$/s up to $10^{-8}$ cm$^2$/s (lower value in the surface and higher value in the middle of the NP). On the other hand diffusion coefficient in currently used materials (e.g. Li$_x$CoO$_2$) typically ranging from $10^{-13}$ cm$^2$/s to $10^{-7}$ cm$^2$/s, it is seen clearly that NP of LFS can be provide as an alternative high density cathode material for Li ion battery with the kinetic closure to the state-of-the-art materials.

2.2.1. Conclusion

In summary, the energetics of surface structures and NP and of the Pmm2$_1$ polymorph of the electrode material LFS are studied by first-principles calculations based on density functional theory. We have also studied the surface energies of different surface terminations of LFS, a promising material for battery electrodes. The diffusion coefficients in bulk LFS at room temperature are calculated, their values ranging from $10^{-10}$ cm$^2$/s to $10^{-21}$ cm$^2$/s and therefore suboptimal with respect to the current generation of state-of-the-art materials. We have demonstrated for the first time that the NP of LFS with the size ca 2.5 nm have the diffusion coefficients ranging from $10^{-16}$ cm$^2$/S to $10^{-8}$ which is comparable to the commercialized cathode materials. Therefore, we believe that electrode materials based on the NP should be ideal candidates for the expansion of Li ion battery technology in automobile, aerospace, and power-grid applications that demand the development of lightweight, long-lasting batteries.

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References