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Crystal structure and multicomponent effects in Tetrahedral Silicate Cathode Materials for Rechargeable Li-ion Batteries

R.C. Longo*, K. Xiong, Santosh KC, K. Cho*

Departament of Materials Science & Engineering,The University of Texas at Dallas, 800 West Campbell Road, Richardson, TX 75080, USA

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ABSTRACT

A first principles investigation is performed to study the structural and electrochemical properties of four polymorphs of the $Li_2FeSiO4$ orthosilicate family ($Pmn2_1$, $Pmnb$, $P2_1/n$ and $Pbn2_1$), to predict the effect of the transition metal composition. Our results show that the inclusion of Mn and Ni cations helps to stabilize the layered structures, but the polymorphs with a 3D cation network arrangement ($P2_1/n$ and $Pbn2_1$) still have comparable energetic stability. We also show that the decrease of the cationic repulsion with the extraction of Li (found for these polymorphs during the discharge process) reduces the voltage step between the first and second Li extraction processes. The effect of multiple interactions between Li and the transition metals is examined, and the implications of multicomponent structures to improve the design of battery cathode are also addressed.

1. Introduction

Lithium metal orthosilicates, Li_2MSiO_4 (M=Mn, Fe and Co), are nowadays attracting much attention as an alternative positive electrode for Li-ion rechargeable batteries [1–19] (for a review see Ref. [3] and references therein). The Si-O bond is at least as stable as in any other polyoxyanion group, enhancing the necessary thermal and chemical stability for medium and large scale energy applications [20–24]. The most noteworthy property of this family of compounds is that the possibility of de-intercalation of two Li ions per Li_2MSiO_4 formula unit would give rise to a capacity almost twice than that of the current cathode materials [1,25–27]. However, the full-capacity that can be achieved from the reversible extraction of the two Li ions has not been obtained yet using standard synthesis methods for any transition metal (TM) or their alloys [13–15]. More recent works, using supercritical fluids as a reaction medium for the synthesis of nanomaterials [28] show capacity values for Li_2MSiO_4 (M=Mn and Fe) cathode materials in the form of nanosheets close to the theoretical limit, but only over a few number of cycles. The main reason is the wide variety of polymorphs that exists for this family of compounds and their proximity in energy, which leads to a phase transition and a shift in the voltage after the first cycle of charge and discharge [5]. Although for the Li_2MSiO_4 cathode material the capacity is maintained over a large number of cycles, such capacity corresponds only to one-ion cycling process. Moreover, the phase transformation upon cycling has structural, cycling rate and temperature dependence [7]. The extraction of the second Li atom also causes a severe structural distortion induced by the structural relaxation to minimize the cationic repulsions that appear upon the removal of all the Li ions from the host structure [10,13].

Li_2FeSiO_4 was the first compound synthesized among the orthosilicates family as a possible cathode material [1], and it is still considered one of the most promising candidates due to its good electrochemical activity and low cost. This and any other Li_2MSiO_4 polymorph are isostructural to the low or high temperature forms of Li_3PO_4, denoted as β- and γ-Li_3PO_4, respectively [29]. Their crystal structure consists of a distorted hexagonal packing of oxygen ions with half of the tetrahedral sites occupied by Li, Si, and TM cations. The arrangement of the cations in the tetrahedral sites leads to the different polymorphs [1–3]. In the β polymorphs all tetrahedra point in the same direction, perpendicular to the close-packed planes ("c" axis) and sharing only corners between each other, whereas in the γ family half of the tetrahedra point in the opposite direction to the other half, in all cases parallel to the c axis and sharing both corner and edges between each other [3]. In more detail; the first polymorph reported belongs to the β family (β_{II}) with the space group $Pmn2_1$, in which the tetrahedra only share their corners [1,2]. One variant reported for this polymorph interchanges Li and TM ions in the host structure, and has been observed for Li_2CoSiO_4 [4]. This cation exchange is the most favorable intrinsic defect for the

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* Corresponding author. Tel.: +19728832845.
E-mail addresses: roberto.longo@utdallas.edu (R.C. Longo), kjcho@utdallas.edu (K. Cho).

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orthosilicates, as identified by atomistic simulations in Li_2MnSiO_4 [5]. Another β-polymorph similar to the last one (with the *Pbn*2$_1$ space group) can be built up with parallel chains of alternating LiO_4 and TMO_4 tetrahedra, but with a different link between each other in the *xy* plane. A different type of polymorphs experimentally synthesized, γ_S, with the space group $P2_1$ (later simplified as $P2_1/n$), shows two symmetrically different LiO_4 tetrahedra sharing an edge with an FeO_4 and another LiO_4, respectively [6]. More recently, a γ_{II} polymorph with the space group *Pmnb* has been reported [7]. It shows FeO_4 tetrahedra sharing edges with two LiO_4 tetrahedra. All these polymorphs have similar formation energies, which cannot rule out the possibility of another structures based on Li_3PO_4 being synthesized [9–11]. The $Pmn2_1$, $P2_1$ and *Pmnb* polymorphs have 2D arrangement of FeO_4-SiO_4 and LiO_4 tetrahedra, whereas the modified $Pmn2_1$, $Pbn2_1$, and $P2_1/n$ polymorphs are based on a 3D cation network arrangement of Li, Fe, and Si tetrahedra. This seems to be a more convenient distinction to describe the differences in their electrochemical properties, rather than a mere structural classification into β and γ families [10].

Only the 2D polymorphs have been experimentally synthesized for Li_2FeSiO_4. The reported results show slightly different equilibrium potentials during the first charge cycle, around 3.1 V [7]. This equilibrium potential drops to 2.76 V after the first cycle, showing an irreversible phase transformation. Such a transformation from $P2_1$ to the modified $Pmn2_1$ polymorph has been shown by means of neutron diffraction scattering experiments [19]. In addition to the phase transformation, the high voltage associated to the removal of the second Li atom remains as another issue that hinders the silicates from achieving their potential full-capacity. In a similar manner to the strategy adopted for layered oxides or Fe phosphates [30,31], an alternative to stabilize the layered-2D silicates is the doping with larger TM cations, such as Mn. Some attempts have been made experimentally: a mixed solid solution of $Li_2Fe_{0.5}Mn_{0.5}SiO_4$ seems to be the ideal composition. The basic idea was to stabilize the Mn^{3+} of the intermediate step ($LiTMSiO_4$) introducing Fe as an external “stabilizer” [13]. A capacity of 214 mAh/g was reported but, again, with serious fade during cycling [14]. Studies on $Li_2Fe_{0.8}Mn_{0.2}SiO_4$ show good reversibility but due only to oxidation of Fe^{3+}. No tetravalent Fe or Mn was detected, which implies that no more than one electron was exchanged [15]. Previous theoretical works [13,32] on the stability of Mn-doped $Pmn2_1$ Li_2FeSiO_4 polymorph seem to indicate that the Mn/Fe mixture will not separate during the delithiation process [13], giving rise to a 0.7 V step in the extraction of more than 1 Li ion per formula unit (f. u.). Such mixed structure should be stable up to the extraction of 1.5 Li ion/f. u. For low concentrations of Mn doping (12.5%, [32]), the delithiation induces structural distortion at the Mn-sites, correlating with the reported cycling instability of the Mn silicate [33].

In this paper, we report a density-functional theory (DFT) study on the effects of doping on the Li_2FeSiO_4 silicate. Taking two polymorphs with 2D cation arrangement ($Pmn2_1$ and *Pmnb*) and another two with a 3D cation network ($Pbn2_1$ and $P2_1/n$) as an example, we investigate the effects of several concentrations of Mn and Ni on the formation energy, phase stability, electronic structure and electrochemical properties of the $Li_{2-x}FeSiO_4$ silicate, as a function of the Li concentration ($x = 0 - 2$). Even though divalent Ni can not be stabilized in a tetrahedral morphology, the use of Ni as a dopant can definitely improve some of the weaknesses of the silicates, especially the low electronic conductivity. Our results will help to elucidate if the use of mixed solid solutions of late TM cations can stabilize some of the host compounds to avoid phase transformations during cycling with the resulting fade in the capacity.

2. Computational methods

We performed our first principles calculations using DFT with plane-wave basis sets and projector augmented wave (PAW) pseudopotentials, as implemented in VASP code [34,35]. The exchange and correlation interactions were included by using the spin-polarized generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof parameterization [36]. The electronic wave functions are represented by plane waves with a kinetic energy cutoff of 500 eV. The structure of the $Pmn2_1$ tetrahedral silicate was taken from the experiments reported in Refs. [1,2], the *Pmnb* from Ref. [7], and the $P2_1/n$ from Refs. [6,7]. In all cases we used a $2a \times 2b \times 2c$ supercell of 128 atoms (16 f. u.) for the silicates with two different TM cations and $2a \times 2b \times 3c$ supercell of 192 atoms (24 f. u.) for the compounds with a ternary solid solution of TM cations.

In all cases, we used appropriate *k*-meshes (4×4×4 for $Pmn2_1$ and $Pbn2_1$, and 4×2×4 for $P2_1/n$ and *Pmnb*) to ensure a convergence of 5 meV/f.u. We performed structural relaxations without including any type of constraint or symmetry, to take into account possible Jahn-Teller distortions, to a tolerance of 10^{-4} eV in the total energy. All our calculations were spin-polarized and, in all cases, they have been performed with both initial ferromagnetic (FM) and antiferromagnetic (AFM) spin ordering configurations. The energy of the AFM configurations is always lower than that of the structures with initial FM spin ordering, with the magnetic moments of the TM cations antiparallel to those of the cations of adjacent layers.

Although PAW potentials have been extensively used in the study of positive electrode materials for Li-ion batteries [37–44], GGA is known to show large errors for the electrochemical properties of these materials [41–43]. The main reasons are the different chemical environment the electrons “see” during the redox processes: from metallic Li to a transition metal (TM) in a oxyanion group; and the known tendency of the GGA to overestimate the delocalization of these *d*-redox electrons of the TM and their hybridization with the *p* O states, which is the main driving force for the energy differences between the lithiated and delithiated phases. By explicitily including an on-site Coulombic, *U*, and exchange, *J*, terms in the Hamiltonian (GGA+U approach), we can partially correct the electron overdelocalization (and the corresponding self-interaction errors) and accurately calculate the electrochemical properties of the silicates [41]. The U parameters have been obtained by means of a linear response method [38], and then averaged over the values of the $M^{2+}/M^{3+}/M^{4+}$ redox states of the TM in the tetrahedral silicates (5.825, 4.765, and 6.885 eV for Mn, Fe and Ni, respectively). The *J* value was set to 1 eV in all cases, as only the $U - J$ difference is relevant for the calculation.

3. Results and discussion

The relative phase stabilities and electrochemical properties of the different Li_2FeSiO_4 polymorphs have been investigated previously [9–11]. The $Pmn2_1$ polymorph is the most commonly observed for the Mn silicates [3], whereas it was the first one synthesized for the Li_2FeSiO_4 silicate [1]. Afterwards, it has been shown that $P2_1/n$ polymorph is formed in a typical ceramic synthesis route [6] and the $Pmn2_1$ morphology is not stable above 800 K [7]. It has a layered 2D network of Li, Fe, and Si tetrahedra. Upon delithiation, and to minimize the electrostatic repulsion energy between the different cations, the polymorphs with a 3D cation network appeared to be the most stable ones, because the distance between the different cations is larger than that of the polymorphs with a 2D arrangement of the Si, Li, and TM tetrahedra [9–11]. In this study, our main goal is to explore the effect of larger TM cations like Mn on the stability of the polymorphs with a 2D network. Furthermore, another