Multicomponent Silicate Cathode Materials for Rechargeable Li-ion Batteries: An Ab Initio Study

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Multicomponent Silicate Cathode Materials for Rechargeable Li-Ion Batteries: An Ab Initio Study

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A first principles investigation is performed to study the structural and electrochemical properties of new multicomponent silicate materials that can be suitable for the cathode of rechargeable Li-ion batteries. The distribution of different transition metals in the silicate structure alters the structural and electronic properties of the crystal, affecting its kinetics, redox potentials and both ionic and electronic conductivities. We also explain the effect of the multiple interactions between Li ions and the transition metals. These multicomponent structures represent a very powerful strategy to control the electrochemical performance of the silicates. In this work, we finally address the implications of such strategy on the design of Li-ion batteries.

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Electrochemical energy storage devices are nowadays the focus of numerous research efforts, in an attempt to solve the growing environmental and sustainability problems associated to fossil fuels.1,2 Among them, rechargeable Li-ion batteries have been widely used in several small electronic devices. The possibility of extending their usage to all type of large scale applications (electric vehicles or grid energy storage) has raised a new “golden age” to the study and development of new electrode materials for Li-ion batteries. Stability, energy and power density, and low cost are the main characteristics pursued in any suitable electrode material.3,4 In recent years, polyoxyanion compounds are attracting considerable interest to be used as cathode materials because the strength of the bond between the oxygen and the corresponding cation (P, Si or V) enhances the stability substantially, thus showing a way to solve the well-known safety issues of the intercalation oxides, which are the main current cathode materials.5 It is a well-known issue of these materials that the release of oxygen can react with the electrolyte, causing a short-circuit of the battery. In this sense, the polyoxyanion cathode materials make more “safe” Li-ion batteries.5

Within this context, Fe phosphate Li2FePO4 with an olivine structure has been extensively studied, and still appears to be a promising alternative to the current cathode materials due to its remarkable stability.6–9 Nevertheless, its low voltage makes it inappropriate for usage to all type of large scale applications (electric vehicles or grid energy storage).10,11 The redox couple of the transition metal in the olivine silicates is Mn2+/Mn3+ (M=Mn, Fe, Co), showing the possibility of extracting and inserting two Li atoms in the consecutive electron redox processes (Mn++/Mn3+ and Mn2+/Mn3+), giving rise to a capacity of about 330 mAh/g, much higher than that of current electrodes (layered oxides, 200 mAh/g) and Fe phosphate (170 mAh/g). The main shortcomings reported for these tetrahedral silicates are the poor reversibility and cycling performance (Li2FePO4)15 or low electronic conductivity and amorphization (Li2MnSiO4).16 Moreover, previous theoretical studies10 seem to indicate that the stability of the silicates with the olivine morphology is larger than that of the semi-delithiated phase of Li2MnSiO4 tetrahedral silicates (Li2SiO4), which constitutes another issue that needs to be addressed to achieve a good electrochemical performance over a large number of cycles of the charge/discharge process.

With all these issues in mind, our main goal in this paper is to perform an in-depth study of both olivine and tetrahedral silicate morphologies using first principles method, to achieve a comprehensive understanding of their structural and electronic properties and to compare their electrochemical characteristics to examine if both silicate morphologies are promising materials for the cathode of Li-ion batteries. In order to develop possible new cathode materials overcoming the limitations of current silicates, we investigate the effect of combining multiple transition metals on the structural and electronic properties of these compounds. Multiple transition metals are expected to allow simultaneous optimization of multiple redox couples to address current limitations of silicate cathodes. Although several theoretical studies have been reported for the tetrahedral silicates, there are few investigations on the effect of multiple transition metals on the electrochemical performance of these compounds and, to our knowledge, nothing about the olivine silicate morphology. The inclusion of more than one type of transition metal in a cathode material shows new and interesting phenomena, like shift of the redox potential of the transition metal, different rate behavior, mixed two-phase and one-phase Li de/intercalation reactions at different Li compositions, etc.18,19

Computational Details

We performed our first principle calculations using density-functional theory (DFT) with plane-wave basis sets and projector augmented wave (PAW) pseudopotentials, as implemented in VASP code.20,21 The exchange and correlation interactions were included by the spin-polarized generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof parameterization.22 The electronic wave functions are represented by plane waves with a kinetic energy cutoff of 500 eV. For the silicates with an olivine-type structure, we started from the previously reported olivine phosphate morphology and built the silicate from it. We used a unit cell of 28 atoms (4 formula units, f. u.) for the single-component silicates and a unit cell of 168 atoms (24 f. u.) for the multicomponent structures. The structure of the tetrahedral silicates was taken from the experiments reported in Ref. 12. For this morphology, we used a unit cell of 32 atoms (4 f. u.) for the single-component silicates and 192 atoms (24 f. u.) for the multicomponent compounds.

In all cases, we used appropriate k-meshes up to 72-k points per reciprocal lattice vector, to ensure a convergence of 5 meV/f.u. of...
the energy during the self-consistent electronic optimization. We performed structural relaxations without including any type of constraint or spin symmetry, to take into account possible Jahn-Teller distortions (specially important if Mn TM cations are present), to a tolerance of $10^{-4}$ eV in the total energy and 0.01 eV/Å in all the components of the forces acting on the system. 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 generally 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 the adjacent layers.

Although PAW potentials have been extensively used in the study of positive electrode materials for Li-ion batteries, GGA is known to show large errors for the electrochemical properties of these materials.\textsuperscript{23–25} 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 explicitly including an onsite Coulomb, $U$, and exchange, $J$, terms in the Hamiltonian (GGA+$U$ approach), we can partially correct the electron overdelocalization (and the self-interaction errors this leads to) and accurately calculate the electrochemical properties of the silicates.\textsuperscript{23} The $U$ parameters have been obtained by means of a linear response method,\textsuperscript{11} and we have averaged them over the values of the $M^3+/M^4+$ redox states of the different TM for the olivine-type silicates and over the $M^{2+}/M^{3+}/M^{4+}$ redox states for the tetrahedral silicates. The $J$ value was set to 1 eV in all cases, as only the $U$-$J$ difference is relevant for the calculation.

Results and Discussion

Starting from the two silicate morphologies aforementioned (olivine and tetrahedral), we carried out structural optimizations taking Mn, Fe, Co or Ni as TM of the cathode. With the aim of developing an in-depth insight into the effects of multicomponent TMs on the properties of the cathode material, we have also considered binary (LiMn$_{1/2}$Fe$_{1/2}$SiO$_4$ and LiMn$_{1/2}$Ni$_{1/2}$SiO$_4$) and ternary (LiMn$_{1/3}$Fe$_{1/3}$Ni$_{1/3}$SiO$_4$, LiMn$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$SiO$_4$ and LiMn$_{1/3}$Fe$_{1/3}$Ni$_{1/3}$SiO$_4$) olivine systems, and the ternary Li$_2$Mn$_{1/3}$Fe$_{1/3}$Ni$_{1/3}$SiO$_4$ tetrahedral compound. The olivine structure belongs to the P$nma$ space group and the tetrahedral silicate morpholo
gy originally synthesized belongs to the P$nma$$_2$$_1$ space group.\textsuperscript{12} Although slightly different experimental morphologies have been synthesized and reported very recently,\textsuperscript{26,27} we have focused in our calculations in the original P$nma$$_2$$_1$, because it is supposed to be the most stable configuration at room temperature and it is enough for our comparative purposes. Figure 1 shows the crystal structure of both morphologies.

Structural properties and bond characteristics.— In the olivine morphology, the TM atoms are in the middle of an octahedron formed by six oxygen atoms, which share a corner between each other and form a two-dimensional square lattice. The Li ions are also in oxygen octahedral sites, sharing their edges and forming parallel chains. Finally, the Si atoms are in tetrahedral oxygen sites, connecting neighboring planes.\textsuperscript{3} The difference with respect to the tetrahedral morpholo
gy is that in this case Si, TM and Li atoms are all in tetrahedral oxygen sites. The Si tetrahedra share their four corners with four neighboring TM tetrahedra. Li ions also occupy tetrahedral sites between two of these layers.\textsuperscript{12} The most important characteristic about these two types of silicates is that there is a clear path for Li diffusion in both cases, due to the arrangement of the Li ions in rows, thus forming a one-dimensional channel for motion with low diffusion barriers, as it has been previously shown for olivine phosphates.\textsuperscript{28} Problems with the ionic conductivity stem from defects and impurities that appear on cycling, blocking these one-dimensional channels.

The strong Si-O bond provides an extraordinary stability to these compounds, as stated previously, and the Si polyhedra (tetrahedron in both cases) are not very much structurally affected during the delithiation process. The well-known stability issues of the tetrahe
dral silicates arise from the instability of the TM tetrahedra with Li extraction/insertion during the charge/discharge processes.\textsuperscript{15–16} To estimate the stability of the silicates, we have obtained the volume of the unit cell and the bond distortion of the TM polyhedra indicated by volume change (octahedron for the olivine silicates and tetrahedron for the tetrahedral silicates). We estimate the bond distortion from the volume change of the polyhedra between the relaxed structures and the starting configurations. Our starting configurations were the experimental ones in the case of tetrahedral silicates\textsuperscript{12} and the olivine Fe phosphate for the olivine silicate.\textsuperscript{6} Table I lists the results obtained for the olivine morphologies LiMn$_x$SiO$_4$ ($M=$Mn, Fe, Co, Ni) and Table II the results obtained for the tetrahedral silicates Li$_2$MnSiO$_4$ ($M=$Mn, Fe, Co, Ni). In both cases we have included the lithiated and delithiated structures and, for the tetrahedral silicates, the semi-delithiated intermediate state Li$_2$MnSiO$_4$. Table I shows that the volume decreases upon delithiation for the olivine silicates (except Ni, whose volume remains practically unaltered) because the TM octah
dra share one corner with each other, while the Li octahedra share one edge with each other and another one with the TM octahedra. During the charge process, the Li atoms are extracted from the host system, leaving free space between the TM octahedra, which are then tilted over themselves, reducing the corresponding length of the lattice vector and, consequently, the cell volume. Table I also shows that...
the volume change of the octahedra is always bigger for the lithiated systems, which basically means that the volume of such octahedra increases during the discharging process (upon Li insertion). This can be understood in terms of the TM oxidation states. The redox couple for these systems is \( M^{2+}/M^{4+} \) and, as \( r_{M^{2+}} > r_{M^{4+}} \), the average distance between the TM and the oxygen atoms is bigger for the lithiated structures.

Table II lists the results obtained for the \( P_{6}m2_{1} \) tetrahedral silicates. The situation now is notably different. For the same reason mentioned above, the distortion of the TM polyhedra (a tetrahedron in this case) decreases with delithiation (i.e., as we remove Li ions from the supercell). In this case the redox states are consecutively \( M^{2+}/M^{4+} \) and, the TM-O distance decreases as we extract Li ions. However, the volume of the unit cell increases during the Li extraction in all cases, except for Fe. On the basis of size reduction of the octahedra, one would expect a cell contraction. This unexpected behavior has already been pointed out, but it still remains as an open question. One possible explanation is that there are two opposite effects in competition: one is the already mentioned shortening of the \( M-O \) bond with oxidation. The other one is that along one axis of the unit cell, \( SiO_{4} \) and \( MO_{4} \) tetrahedra alternate by corner-sharing. Since Li ions link these \( Si-M \) layers together, as we extract Li ions, the forces between two consecutive layers become weak if they were extracted. As a result, the layers will separate. Another structural rearrangement occurs in these \( Si-M \) layers. The \( SiO_{4} \) and \( MO_{4} \) tetrahedra share one oxygen atom, in order to form a chain. As we extract Li, the angle \( Si-O-M \) opens up, in order to diminish the strong cationic repulsion and the cell also expands along this direction. If these two combined expansions are predominant over the shortening of the \( M-O \) bond, the volume of the unit cell will increase upon delithiation. In the fully delithiated state, another mechanism has to be taken into account, because the \( MSiO_{4} \) configurations may not be the most stable ones, as \( Mn^{4+} \) and \( Co^{4+} \) ions with tetrahedral coordination are a rarity. That is easier to see if we have more than one type of TM atom in the cathode material, as we will discuss in the next paragraph.

Table II. Unit cell Volume (Å\(^3\)) and \( M-O \) (\( M=Mn,Fe,Co,Ni \)) bond distortion (Å\(^3\)) of the single compound \( P_{6}m2_{1} \) tetrahedral silicates \( Li_{2}MSiO_{4}, LiMnSiO_{4} \) and \( MSiO_{4} (M=Mn,Fe,Co,Ni). \)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Unit cell Volume (Å(^3))</th>
<th>( M-O ) bond distortion (Å(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li2MnSiO4</td>
<td>348.84</td>
<td>1.2262</td>
</tr>
<tr>
<td>LiMnSiO4</td>
<td>352.26</td>
<td>0.0444</td>
</tr>
<tr>
<td>MnSiO4</td>
<td>358.16</td>
<td>−0.4978</td>
</tr>
<tr>
<td>Li2FeSiO4</td>
<td>339.26</td>
<td>0.8206</td>
</tr>
<tr>
<td>LiFeSiO4</td>
<td>344.48</td>
<td>0.0184</td>
</tr>
<tr>
<td>FeSiO4</td>
<td>289.34</td>
<td>−0.5872</td>
</tr>
<tr>
<td>Li2CoSiO4</td>
<td>336.64</td>
<td>0.6541</td>
</tr>
<tr>
<td>LiCoSiO4</td>
<td>338.14</td>
<td>−0.1828</td>
</tr>
<tr>
<td>CoSiO4</td>
<td>348.46</td>
<td>−0.3627</td>
</tr>
<tr>
<td>Li2NiSiO4</td>
<td>330.94</td>
<td>0.4383</td>
</tr>
<tr>
<td>LiNiSiO4</td>
<td>359.26</td>
<td>0.1306</td>
</tr>
<tr>
<td>NiSiO4</td>
<td>344.12</td>
<td>−0.4794</td>
</tr>
</tbody>
</table>

Table III shows the results obtained for the multicomponent cathode materials. The last three columns show directly the volume of the polyhedra, to allow a direct comparison between them. The first column tells us that the volume always decreases with Li extraction, in both the five olivine and the tetrahedral multicomponents studied in this work. The Mn-Fe olivine lithiated silicate shows a larger Mn-O than Fe-O bond distance. Interestingly, the situation is reversed on delithiation, as the redox state changes from \( M^{2+} \) to \( M^{4+} \). The volume of the Mn-O octahedron is smaller in the Mn-Ni cathode, reflecting a stronger repulsion between Mn and Ni cations. This effect is in part counteracted in the “sandwich” structure Mn-Ni-Mn, reflecting a way to avoid possible structural instabilities. The ternary Mn-Fe-Ni olivine silicate shows similar bond distances compared to the binary compounds, but without the reduction of the volume of the Mn-O octahedron. For the ternary tetrahedral silicate, however, the delithiation shows a very different effect. If the TM is in an \( M^{2+} \) redox state (lithiated phase), the average distances follow the order \( Mn-O > Fe-O > Ni-O \). In the semi-delithiated phase, the TM atoms become fivefold coordinated in the regions where Li ions have been removed, thus increasing the volume of the TM polyhedra. Finally, once all the Li atoms have been removed, all the TM atoms are six-fold coordinated, reflecting a change in the structure, as one can see comparing the volumes of the TM polyhedra with those of the lithiated and semi-delithiated phases. We can conclude that the delithiated tetrahedral silicates are in a metastable state.

Electronic structure and electrochemical performance.— All our calculations have been performed with both initial ferromagnetic (FM) and antiferromagnetic (AFM) configurations. Figures 2 and 3 show
the average magnetic moments per TM ion of the olivine and tetrahedral silicates, respectively, together with their most stable magnetic configurations. The pictures show the results obtained for the lithiated (discharged) and delithiated (charged) states, together with the semi-delithiated state (LiMnSiO4) of the tetrahedral silicates. Most of the configurations are stabilized in AFM configurations, and in the cases where the FM polymorph is more stable, the magnetic exchange energies are always small (e.g., for the olivine Mn this difference is 0.08 eV). The magnetic moments shown in Figs. 2 and 3 drop, in general, with the increase of the redox valence state of the TMs, as expected (the outer electronic d-shell becomes more populated). The smallest magnetic moment corresponds to the Ni, in both lithiated and delithiated phases, due to its almost closed (with 9 electrons in its d-shell) electronic configuration) electronic d-shell. Interestingly, the magnetic moments are hardly altered if more than one type of TM is present in the cathode, which means that the magnetic exchange interactions are short-range, because they are mostly screened by the presence of Li and Si cations.

As an example of the electronic structures, and also to show how they change when we have a combination of different TM ions in the silicate cathode material, Figs. 4 and 5 show the projected density of states (PDOS) onto the d-orbitals of the TM ions of the tetrahedral silicates. Most of the configurations are stabilized in AFM configurations, and in the cases where the FM polymorph is more stable, the magnetic exchange energies are always small (e.g., for the olivine Mn this difference is 0.08 eV). The magnetic moments shown in Figs. 2 and 3 drop, in general, with the increase of the redox valence state of the TMs, as expected (the outer electronic d-shell becomes more populated). The smallest magnetic moment corresponds to the Ni, in both lithiated and delithiated phases, due to its almost closed (with 9 electrons in its d-shell) electronic configuration) electronic d-shell. Interestingly, the magnetic moments are hardly altered if more than one type of TM is present in the cathode, which means that the magnetic exchange interactions are short-range, because they are mostly screened by the presence of Li and Si cations.

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For the tetrahedral silicates, Fig. 7 shows the two voltages corresponding to the extraction of two Li ions in two consecutive redox processes, corresponding to the $(x = 2,1)$ and $(x = 1,0)$ transitions of the $\text{Li}_x\text{TMSiO}_4$ silicate. These results show that, although the tetrahedral morphology seems to be more promising as a cathode material, the olivine morphology is much more stable, especially in the charged state, up to the point that the semi- and fully-delithiated phases of the tetrahedral silicates are in metastable configurations. On delithiation, the TM, Si and Li (if any) cations lose their original oxygen tetrahedral coordination, relaxing to five- and six-fold coordinated structures for the semi- and fully-delithiated phases, respectively.

Our results also show that, despite of the fact that these silicates are medium-gap insulators, they present favorable features to allow polaron (hole) movement as a mechanism for the electronic conductivity.

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