



Li Conductivity in Li_xMPO_4 ($\text{M} = \text{Mn, Fe, Co, Ni}$) Olivine Materials

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Materials with the olivine Li_xMPO_4 structure form an important class of rechargeable battery cathodes. Using first-principles methods, activation barriers to Li ion motion are calculated and an estimate for Li diffusion constants, in the absence of electrical conductivity constraints, is made. Materials with $\text{M} = \text{Mn, Fe, Co, Ni}$ are considered. Li diffuses through one-dimensional channels with high energy barriers to cross between the channels. Without electrical conductivity limitations the intrinsic Li diffusivity is high.

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Li_xMPO_4 materials with the olivine structure have become some of the most promising cathode materials for rechargeable Li and Li-ion batteries. In particular, early work on the Li_xFePO_4 material demonstrated its potential to reversibly cycle Li at 3.4–3.5 V.¹ It has a theoretical capacity of 170 mAh/g, much of which can be realized in the optimized material, and can yield practical gravimetric (volumetric) energy densities somewhat greater (less than) those of Li_xCoO_2 .² The olivines represent a whole class of potential cathode materials, and in addition to Fe, Li cycling has been demonstrated in Co,³ Mn,⁴ and Mn-substituted materials.^{1,5–7} Low cost, good stability, flexibility, and competitive electrochemical properties make the olivine family an exciting area for cathode development.

In this article we use first-principles techniques to study the diffusion of Li through the olivine structure for a range of cations. We focus on the *intrinsic ionic diffusivity*, which is determined by the activation barrier along the Li hopping paths, and is the ionic diffusivity assuming a high concentration of highly mobile electrons. In case of very low electrical conductivity the barriers to electron motion, not ionic motion, determine the macroscopic chemical Li diffusivity. For example, this seems to be the case for particles of undoped Li_xFePO_4 material, where electrical conductivity is very low and greatly inhibits high-rate applications.⁸ However, recent efforts to increase conductivity through such methods as particle size minimization,² intimate carbon coating,⁹ and doping⁸ have dramatically improved early rate problems in the Fe material, so intrinsic ionic diffusivity may become quite relevant. In addition, the role of electrical vs. ionic conductivity is not clear in the many other olivine materials presently being developed. Intrinsic ionic diffusivities therefore either directly determine the Li motion, or provide useful bounds to suggest when electrical conduction plays an important role.

We find that Li motion in the olivine crystal structure occurs through one-dimensional (1D) channels. This intrinsic ionic diffusion is rapid, but the 1D paths are particularly susceptible to blockage by defects and impurities.

Calculation Methods

We use first-principles electronic structure techniques, working with the generalized gradient approximation (GGA) to density functional theory. Ultrasoft pseudopotentials and the Perdew-Wang exchange correlation functional are used, as implemented in the Vienna *Ab Initio* Simulation Package (VASP).¹⁰ All activation barrier calculations are done in supercells containing eight formula units to reduce interactions between images of the Li being moved. The Li images are ≈ 6 Å or more apart. Activation barriers are determined in the dilute Li limit ($x \approx 0$) by including 1 Li in an otherwise

delithiated cell with eight formula units, and in the dilute vacancy limit ($x \approx 1$) with 7 Li and 1 vacancy site in the cell. All lattice parameters are fixed at the $x = 0$ or 1 values for the activation barrier calculations and all internal degrees of freedom are relaxed. We estimate the activation barriers to be converged with respect to plane wave cutoff and Brillouin zone integration (k -points) to within ≈ 20 meV. All calculations have been done with ferromagnetic spin-polarization. The true magnetic ground state of these materials is generally antiferromagnetic, but with a transition to paramagnetic well below room temperature.^{11–14} We do not expect the magnetic ordering to have any significant impact on the activation barriers.

Olivine Structure

We treat all the alloys studied here as being isostructural with the LiFePO_4 material, allowing for system specific relaxations of lattice parameters and atom positions. The LiFePO_4 olivine structure (also known as triphylite) consists of a distorted hexagonal close-packed (hcp) framework containing Li and Fe in octahedral sites and P in tetrahedral sites (Fig. 1). It is an orthorhombic structure, space group $Pnma$, with lattice parameters of $a = 10.3290(10.330)$ Å, $b = 6.0065(6.053)$ Å, and $c = 4.6908(4.736)$ Å (the GGA calculated parameters are given in parentheses).¹⁴ During battery cycling the Li ions are removed topotactically to yield heterosite, which maintains the topology of the FePO_4 framework.¹⁵ The a and b axes lie in the hexagonal planes of the hcp oxygen host, while the c axis is along the canonical c axis of the oxygen hcp lattice. There are two distinct octahedral sites in this material: M1 is occupied by Li, and M2 is occupied by Fe. The M1 sites form linear chains of edge sharing octahedra along the b axis, while the M2 sites form staggered lines of corner sharing octahedra along the b axis. The metal atoms can be viewed as occupying b - c metal planes, where the planes are alternatively occupied by each type of metal, *i.e.*, there is a Li-Fe-Li-Fe ordering along the a axis.

Li Mobility

It has been suggested that the planes of Li chains in the olivine structure may form ion conducting 2D layers, analogous to those found in layered cathode materials with the NaFeO_2 structure.¹ However, based on the experimental atom positions in Ref. 14 the Li within the chains are only 3.0 Å apart, while the chains in a given b - c plane are 4.7 Å apart and the chains in different b - c planes are 5.7 Å apart. The large interchain distances, combined with the complex energy landscape between chains, makes it plausible that interchain Li hopping is difficult compared to intrachain motion. The basic geometry of the olivine structure therefore favors transport of Li along 1D tunnels.

The above qualitative observation on the influence of the olivine structure on Li diffusion can be made more quantitative by first-principles calculation. The intrinsic Li diffusion constant can be cal-

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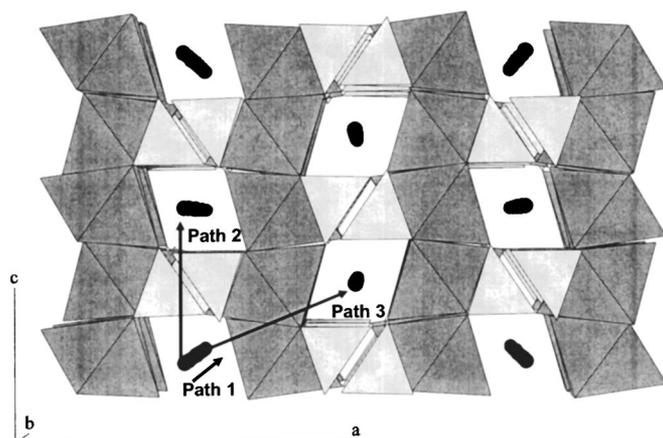


Figure 1. The olivine structure. The Fe octahedra are dark gray, the P tetrahedra are light gray, and the Li atoms are black. Black lines show candidate diffusion paths for the Li ions.

culated from the atomic scale behavior of the Li. Under the assumption of only nearest-neighbor hops among equivalent sites, noninteracting particles, and excluded volume (no two Li can occupy the same site), the diffusion constant for a 1D chain takes the particularly simple form of $D = \Gamma a^2$,¹⁶ where Γ is the hopping frequency from a filled to a vacant site and a is the hopping length. Transition state theory¹⁷ can be used to show that $\Gamma \approx \nu^* \exp(-E_{\text{act}}/k_B T)$, where ν^* is the attempt frequency and E_{act} is the activation barrier for the hop. Putting these together we get the following estimate for the diffusion constant

$$D = a^2 \nu^* \exp(-E_{\text{act}}/k_B T) \quad [1]$$

Li interactions alter Eq. 1 by changing the thermodynamic factor and correlated motion, as well as introducing configurational dependence for E_{act} .^{18,19} However, in the very low and high concentration limits ($x \approx 0$ and 1), Eq. 1 again becomes exact, because the Li (vacancies) are too far apart to interact significantly. Therefore, we only calculate D in these limits. These limits are particularly appropriate for Li_xFePO_4 , because it is strongly phase separating into a Li-rich and Li-poor material at room temperature. Generally, we believe these limits provide a useful estimate for the range of Li diffusivities for all the olivines studied. To apply Eq. 1 we must determine the activation barriers for the possible hopping paths for Li.

There are three obvious paths for Li hopping that must be considered, corresponding to motion along chains along the b axis (path 1), motion between chains in the same b - c layer (path 2), and motion between chains in neighboring b - c layers (path 3). These paths are labeled in Fig. 1.

Path 1 requires hopping between two neighboring octahedral M1 sites along the Li chain. We used the nudged elastic band method²⁰ to determine the maximum energy along the lowest energy path between two neighboring M1 sites. These activation barriers are given in Table I for $M = \text{Mn}, \text{Fe}, \text{Co},$ and Ni and for $x \approx 0$ and 1. The transition state for path 1 is the approximately tetrahedral site between the two octahedral sites. This is consistent with the transition state found in layered Li_xCoO_2 for Li transport.¹⁸ Values of D in Table I were calculated from the activation barriers using Eq. 1 with $a = 3 \text{ \AA}$ (approximately the distance of a hop along path 1) and $\nu^* = 10^{12} \text{ Hz}$ (ν^* is generally in the range of phonon frequencies).¹⁷

Path 2 requires hopping along the c axis, with the initial and final octahedra of the hop sharing faces with an intermediate octahedron. Nudged elastic band calculations in the Fe olivine give a barrier for path 2 of over 2.5 eV for both $x \approx 0$ and 1. This gives

Table I. Calculated activation barriers and diffusion constants for Li hopping along 1D chains in Li_xMPO_4 for different choices of M.

Cation M	$x \approx$	E_{Act} (meV)	D (cm^2/s)
Mn	0	330	10^{-9}
Mn	1	250	10^{-7}
Fe	0	200	10^{-7}
Fe	1	270	10^{-8}
Co	0	110	10^{-5}
Co	1	360	10^{-9}
Ni	0	120	10^{-5}
Ni	1	130	10^{-5}

The approximate Li concentration at which the barrier is calculated is denoted by x . D is calculated from Eq. 1 with $a = 3 \text{ (\AA)}$ and $\nu^* = 10^{12} \text{ (Hz)}$.

$D(\text{path } 2)/D(\text{path } 1) \approx 10^{-37}$ for the Fe olivine at room temperature, showing that path 2 makes no significant contribution to the Li motion. We believe that the large barrier is due to the octahedral transition state in path 2 being face-sharing with two P tetrahedra. Therefore, the topological similarity between the Li_xMPO_4 olivines suggests that this path is inactive for all choices of M.

Path 3 involves chains that are quite far apart and is difficult to study directly with the elastic band method. However, the shortest path involves migration through two tetrahedral sites and one octahedral site that shares faces with two Fe ions and a P ion. The nudged elastic band calculation for path 2 has established the high energetic penalty associated with sites that share faces with P ions and hence the barrier through the face sharing octahedra along path 3 is expected to be large. With a lower-bound estimate for this barrier of 1 eV, the room-temperature ratio for diffusion along the highest path 1 barrier (Co, $x \approx 1$) and path 3 is $D(\text{path } 3)/D(\text{path } 1) \approx 10^{-11}$. In practice, this means that path 3 does not contribute significantly to Li transport.

In summary, only path 1 allows significant Li motion. This result likely applies for other cations, and cation mixtures, in the olivine structure, because the barriers are due to gross features of the structure, rather than material specific interactions.

The picture emerging from these calculations is one of dominant 1D diffusion with little crossover between the 1D channels. Although the estimates for D are approximate, the largest barrier we found gives $D \approx 10^{-9} \text{ cm}^2/\text{s}$, which is well within the range 10^{-13} to $10^{-7} \text{ cm}^2/\text{s}$ of D that has been found for Li_xCoO_2 , (see Ref. 21 and references cited therein) one of the most common cathode material used today in rechargeable batteries. Hence, the olivine materials examined here have adequate intrinsic Li mobility for use as rechargeable cathodes.

However, the relevant quantity for Li intercalation and deintercalation is the total diffusivity, which in Li_xFePO_4 may be limited by electrical conductivity. Even for materials with good electronic conductivity, rate problems could occur due to defects blocking the 1D channels. Blockages in 1D diffusion are fundamentally different from blockages in 2D and 3D diffusion, where ions can move around blocked sites. Diffusion through olivine structures with a large fraction of blocked channels likely are dominated by the mobility of other species in the material (e.g., the blocking ion, or defects that allow crossover between different 1D channels). As an example, blocking of 1D channels by Fe on Li sites is likely to be the cause of reduced Li mobility in hydrothermally synthesized LiFePO_4 , as discussed by Yang *et al.*²²

Conclusions

We have used first-principles methods to study Li transport in olivine structures with compositions Li_xMPO_4 ($M = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$). We demonstrate that in Li_xMPO_4 Li moves

rapidly through 1D channels with little possibility for crossing between channels. This is consistent with the conventional belief that rate problems in Li_xFePO_4 materials are due to electron conductivity limitations. These mobility results are also expected to apply to other olivine materials, because the transport properties are largely determined by the topology of the olivine structure. If other olivines avoid defects blocking the 1D channels and the electrical conductivity problems of Fe, the high intrinsic ionic conductivity of the olivine structure could make for very good rate capability.

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