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Authors
Rong, Z
Xiao, P
Liu, M
et al.

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Fast Mg$^{2+}$ diffusion in Mo$_3$(PO$_4$)$_3$O for Mg batteries$^\dagger$

Ziqin Rong, $^{b, a}$ Penghao Xiao, $^{b}$ Miao Liu, $^{b}$ Wenzuan Huang, $^{b}$
Daniel C. Hannah, $^{b}$ William Scullin, $^{c}$ Kristin A. Persson$^{b, d}$ and Gerbrand Ceder$^{a, d}$

In this work, we identify a new potential Mg battery cathode structure Mo$_3$(PO$_4$)$_3$O, which is predicted to exhibit ultra-fast Mg$^{2+}$ diffusion and relatively high voltage based on first-principles density functional theory calculations. Nudged elastic band calculations reveal that the migration barrier of the percolation channel is only $\sim 80$ meV, which is remarkably low, and comparable to the best Li-ion conductors. This low barrier is verified by ab initio molecular dynamics and kinetic Monte Carlo simulations. The voltage and specific energy are predicted to be $\sim 1.98$ V and $\sim 173$ W h kg$^{-1}$, respectively. If confirmed by experiments, this material would have the highest known Mg mobility among inorganic compounds.

A promising strategy to increase the energy density of rechargeable batteries is to transition from monovalent to multivalent batteries, such as Mg batteries, in which Mg$^{2+}$ is reversibly exchanged for Li$^+$ or Na$^+$ as ions. However, Mg$^{2+}$ diffusion in cathode structures has only yielded a few materials that exhibit reasonably fast reversible electrochemical Mg$^{2+}$ intercalation, i.e., Chevrel Mo$_6$S$_8$ ($\sim 135$ mA h g$^{-1}$ at $\sim 1.0$–$1.3$ V),$^2$ orthorhombic V$_2$O$_5$ ($\sim 150$ mA h g$^{-1}$ at $\sim 2.3$–$2.6$ V),$^5$ MoO3 ($\sim 220$ mA h g$^{-1}$ at $\sim 1.7$–$2.8$ V)$^3$ and spinel TiS$_2$ ($\sim 200$ mA h g$^{-1}$ at $\sim 1.5$ V).$^{10,11}$ However, the low voltages limit the power densities of sulfides. Oxides and phosphates generally have higher voltages but at the cost of poorer Mg$^{2+}$ diffusivity.

In this work, we identify a new possible phosphate compound Mo$_3$(PO$_4$)$_3$O which is shown to exhibit ultra-fast Mg$^{2+}$ diffusion and relatively high voltage based on first-principles density functional theory (DFT) calculations. First-principles calculations have proven to be accurate and effective in studying the voltage and mobility of Li-ion$^{12–19}$ and multivalent electrode materials.$^6,7,20$ Our first-principles nudged elastic band (NEB) calculations$^{21–23}$ predict that Mo$_3$(PO$_4$)$_3$O has an unusually low Mg migration barrier of $\sim 80$ meV, which is lower than the values previously reported for spinel TiS$_2$ ($\sim 550$ meV)$^{10}$ and Chevrel phases ($\sim 360$ meV)$^{11}$ suggesting that this structure may enable very high Mg$^{2+}$ diffusivity.

The crystal structure of MgMo$_3$(PO$_4$)$_3$O is shown in Fig. 1. MgMo$_3$(PO$_4$)$_3$O is derived from known compounds such as CaFe$_3$(PO$_4$)$_3$O, SrFe$_3$(PO$_4$)$_3$O and Bi$_{4}$Fe$_4$(PO$_4$)$_3$O by substituting Fe by Mo and the other metal ion (Ca, Sr, Bi) by Mg. The structure is relaxed in both lattice parameters and atomic positions after direct substitutions. Apart from placing Mg in the Ca site in CaFe$_3$(PO$_4$)$_3$O (site B in Fig. 1), we also investigated other possible sites for Mg to reside in the empty host structure Mo$_3$(PO$_4$)$_3$O. One site (site A in Fig. 1) is 9.8 meV lower in energy than site B. As shown in Fig. 1, there are one A site and two B sites in the unit cell, and site A and site B are too close to accommodate Mg cations simultaneously. Hence our calculations predicted that Mg resides in site A at Mg$_{60}$Mo$_3$(PO$_4$)$_3$O composition and in site B in MgMo$_3$(PO$_4$)$_3$O. Chains composed of edge-sharing Mo$_6$ octahedra along the [010] direction form the backbone of the structure and are interconnected by predominantly corner-sharing Mo$_2$ trigonal bipyramids, MoO$_4$ tetrahedra, and PO$_4$ tetrahedra.
Except for the \([\text{MoO}_3]\) chains, there are only two edge-sharing links in the unit cell, which are between \(\text{PO}_4\) tetrahedra and MoO\(_6\) octahedra. All the other links between polyhedra are corner-sharing links, which enables the polyhedra to rotate slightly, creating an adaptive tunnel to facilitate \(\text{Mg}^{2+}\) diffusion. Similar to \(\text{LiFePO}_4\), a 1D diffusion channel exists along the \(b\)-axis for \(\text{Mg}^{2+}\).

**Fig. 1** Crystal structure of \(\text{MgMo}_3(\text{PO}_4)_2\text{O}\) in (a) \(b\)-c and (b) \(a\)-c planes. The structure is built on \([\text{MoO}_2]_3\) chains interconnected by predominantly corner-sharing polyhedra. Similar to \(\text{LiFePO}_4\), a 1D diffusion channel exists along the \(b\)-axis for \(\text{Mg}^{2+}\).

Table 1  Average voltages of \(\text{MgMo}_3(\text{PO}_4)_2\text{O}\) calculated using different levels of theory

<table>
<thead>
<tr>
<th>Functionals</th>
<th>Average voltage (V)</th>
<th>Specific energy (W h kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA(^+)U (Mo (U = 4.38) eV)(^{29,30})</td>
<td>1.98</td>
<td>173</td>
</tr>
<tr>
<td>SCAN(^{31})</td>
<td>1.52</td>
<td>133</td>
</tr>
<tr>
<td>HSE06(^{32})</td>
<td>1.69</td>
<td>148</td>
</tr>
</tbody>
</table>

60 meV in the migration barrier corresponds to a decrease of one order of magnitude in the diffusivity at room temperature.\(^2\) The percolation channel for \(\text{Mg}^{2+}\) intercalation is therefore along the inner-channel path. The inner-channel path is divided into two segments, as shown in Fig. 2(a1) and (a2), with migration lengths and activation energies of 5.32 and 7.00 Å and \(\sim 80\) and \(\sim 70\) meV, respectively. Multiple minima exist along both paths because the \(\text{PO}_4\) groups can easily rotate to accommodate the Mg at different positions. The flexibility of the \(\text{PO}_4\) groups is a result of the corner-sharing connection between polyhedrons in the structure.

**Fig. 2** The minimum energy paths for \(\text{Mg}^{2+}\) migration in \(\text{MgO}_2(\text{PO}_4)_2\text{O}\). (a1) Migration path and (a2) minimum energy path for inner-channel diffusion. (b1) Migration path and (b2) minimum energy path for inter-channel diffusion. A–D in (a2) are markers for the migration processes. A and B corresponds to site A and B in Fig. 1. The inner-channel diffusion in (a1) and (a2) is the percolation channel for \(\text{Mg}^{2+}\) intercalation.
number for Mg$^{2+}$ in every image of the two paths. Mg$^{2+}$ almost always maintains 4-fold coordination along the inner-channel path, which differs greatly from its behavior along the inter-channel path, where Mg$^{2+}$ experiences a coordination number change of 4 → 2 → 4. A larger coordination number change has been previously shown to lead to larger site energy differences along the migration path and ultimately to a larger activation barrier.7 Moreover, the corner-sharing connections of most of the polyhedra in the structure facilitate Mg$^{2+}$ migration by enabling rotation to accommodate the presence of a local Mg ion. From this perspective, the inner-channel along the $b$-axis is more advantageous than the inter-channel along the $c$-axis because rotation of the MoO$_6$ octahedra along the edge-sharing [010] [Mo$_6$O$_{28}$] chains is much easier around the $b$-axis than the $c$-axis. In addition, the void in the middle of the inter-channel path is too open, and moderate polyhedral rotations cannot mediate the coordination number decrease.

To verify the migration barriers obtained from zero-K NEB calculations, we performed $ab$ initio molecular dynamics (AIMD) simulations.36,37 The mean square displacement (MSD) at 650 K is plotted in Fig. 3. The main contribution of the displacement is along the $b$-axis, which further confirms the 1D diffusion channel, as indicated by the inner-channel path. The diffusivity calculated using AIMD is $2.82 \times 10^{-5}$ cm$^2$ s$^{-1}$.

For comparison, a kinetic Monte Carlo (kMC)38,39 simulation was conducted based on the inner-channel path in Fig. 2(a2). Hopping rates between local minima were calculated using harmonic transition state theory:40

$$ k = \frac{3N}{\sum_{i=1}^{3N} v_i} \exp \left( -\frac{\Delta E}{k_B T} \right) \prod_{i=1}^{3N} v_i^* $$

Table 3. The other half of the path is symmetrically equivalent to ABCD.

The diffusivity at 650 K determined using kMC is $13.70 \times 10^{-5}$ cm$^2$ s$^{-1}$. The fact that the diffusivities from AIMD and kMC are within one order of magnitude confirms that the effective barrier of diffusion is low. The room temperature (300 K) Mg diffusivity estimated using kMC is $4.68 \times 10^{-5}$ cm$^2$ s$^{-1}$.

In summary, the key property for developing Mg battery cathode materials is the Mg$^{2+}$ cation mobility in the host structure. In this work, we show that Mo$_3$(PO$_4$)$_3$O exhibits extraordinarily fast Mg$^{2+}$ cation mobility based on NEB (activation barrier ~80 meV), AIMD (diffusivity ~$2.82 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 650 K), and kMC (diffusivity ~$13.70 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 650 K, ~$4.68 \times 10^{-5}$ cm$^2$ s$^{-1}$ at 300 K) simulations. This is to our knowledge the lowest migration barrier ever predicted for Mg$^{2+}$ in an oxide. Its voltage is slightly higher than previously reported sulfides based on GGA+U (1.98 V), SCAN (1.52 V), and HSE06 (1.69 V) calculations, but the capacity of 91 mA h g$^{-1}$ is relatively low. Our systematic first-principles studies indicate that Mo$_3$(PO$_4$)$_3$O may be a promising 1D cathode material for Mg batteries and is worthy of possible experimental investigation. In addition, the unusually high predicted mobility indicates that while Mg$^{2+}$ diffusion generally is slow in inorganic compounds, there may be notable exceptions.

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Notes and references