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 ~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 ~1.98 V and ~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 inserted into/extracted from the cathode. Because dendrites are less likely to grow on Mg metal than Li metal during charging, Mg metal can be directly used as the anode, resulting in a substantial improvement of the electrochemical performance of interesting cathode candidates. As a result, the search for Mg cathode structures has only yielded a few materials that exhibit reasonably fast reversible electrochemical Mg$^{2+}$ intercalation, i.e., Chevrel Mo$_6$S$_8$ (~135 mA h g$^{-1}$ at ~1.0–1.3 V), orthorhombic V$_2$O$_5$ (~150 mA h g$^{-1}$ at ~2.3–2.6 V), MoO$_3$ (~220 mA h g$^{-1}$ at ~1.7–2.8 V) and spinel TiS$_2$ (~200 mA h g$^{-1}$ at ~1.1–1.5 V). 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 ~80 meV, which is lower than the values previously reported for spinel TiS$_2$ (~550 meV)$^{10}$ and Chevrel phases (~360 meV), 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 was derived from known compounds such as CaFe$_3$(PO$_4$)$_3$O$^{24}$ SrFe$_3$(PO$_4$)$_3$O$^{25}$ and Bi$_6$Fe$_4$(PO$_4$)$_3$O$^{26}$ 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 A site in CaFe$_3$(PO$_4$)$_3$O, there is 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$_6$ trigonal bipyramids, Mo$_6$ tetrahedra, and PO$_4$ tetrahedra.
Except for the \([\text{Mo}_6\text{O}_{28}]\) chains, there are only two edge-sharing links in the unit cell, which are between \(\text{PO}_4\) tetrahedra and \(\text{MoO}_6\) 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 shows the minimum energy paths for \(\text{Mg}^{2+}\) migration in \(\text{Mg}_3(\text{PO}_4)_2\). The \(\text{PO}_4\) groups can easily rotate to accommodate the \(\text{Mg}^{2+}\) in the \(b\)-direction with \(\sim 10^{18}\) times less diffusivity at room temperature. The diffusion of \(\text{Mg}^{2+}\) is expected to occur along the \(b\)-axis, with a very low activation barrier of \(\sim 80\) meV. Because diffusion scales as the inverse exponential of the activation barrier, the activation energy for \(\text{Mg}^{2+}\) diffusion is expected to occur.

Fig. 2 shows the minimum energy paths for \(\text{Mg}^{2+}\) migration in \(\text{Mg}_3(\text{PO}_4)_2\), as calculated using the NEB method. \(\text{Mg}^{2+}\) can follow two paths for migration from one stable site to the nearest equivalent site, an inner- or inter-channel path. The inner-channel path involves migration along the \(b\)-axis and across the unit cell boundary (the unit cell is shown in Fig. 1), with a very low activation barrier of \(\sim 80\) meV. The inter-channel path involves migration along the \(c\)-axis with a much higher activation barrier of \(\sim 1200\) meV.

Because diffusivity scales as the inverse exponential of the activation barrier, migration along the inter-channel path is unlikely at room temperature hopping along the \(c\)-direction should be approximately \(\sim 10^{18}\) times less frequent than along the inner-channel path (an increase of 60 meV in the migration barrier corresponds to a decrease of one order of magnitude in the diffusivity at room temperature). 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 \(\text{Mg}^{2+}\) at different positions. The flexibility of the \(\text{PO}_4\) groups is a result of the corner-sharing connection between polyhedrons in the structure.

Table 1 shows the calculated thermodynamic electrochemical properties of \(\text{Mg}_3(\text{PO}_4)_2\). The 

<table>
<thead>
<tr>
<th>Functional</th>
<th>Average voltage (V)</th>
<th>Specific energy (Wh kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGA+U (Mo U = 4.38 eV)</td>
<td>1.98</td>
<td>173</td>
</tr>
<tr>
<td>SCAN</td>
<td>1.52</td>
<td>133</td>
</tr>
<tr>
<td>HSE06</td>
<td>1.69</td>
<td>148</td>
</tr>
</tbody>
</table>

Table 1: Average voltages of \(\text{Mg}_3(\text{PO}_4)_2\) calculated using different levels of theory.
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 $\rightarrow$ 2 $\rightarrow$ 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.6,37 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) 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

$$
    k = \frac{3N}{3N-1} \frac{1}{\prod_{i=1}^{N} v_i} \frac{1}{\prod_{i=1}^{N} v_i^*} e^{-\Delta E/k_B T}
$$

where $N$ is the number of atoms; $v_i$ and $v_i^*$ are the positive normal mode frequencies at the local minimum and transition state, respectively; and $\Delta E$ is the energy barrier, as determined from NEB calculations. The pre-factors $\frac{3N}{3N-1}$ and barriers $\frac{1}{\prod_{i=1}^{N} v_i}$ and $\frac{1}{\prod_{i=1}^{N} v_i^*}$ between minima A, B, C, and D in Fig. 2(a2) are listed in 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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**Table 2** Thermodynamic electrochemical properties of MgMo$_3$(PO$_4$)$_3$O

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo$_3$(PO$_4$)$_3$O energy above hull</td>
<td>42 meV per atom</td>
</tr>
<tr>
<td>MgMo$_3$(PO$_4$)$_3$O energy above hull</td>
<td>36 meV per atom</td>
</tr>
<tr>
<td>Volumetric capacity</td>
<td>330 A h L$^{-1}$</td>
</tr>
<tr>
<td>Energy density</td>
<td>651 Wh L$^{-1}$</td>
</tr>
<tr>
<td>Gravimetric capacity</td>
<td>87 mA h g$^{-1}$</td>
</tr>
</tbody>
</table>

**Table 3** Summary of hopping processes

<table>
<thead>
<tr>
<th>Process</th>
<th>Calculated prefactor (THz)</th>
<th>Barrier (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A $\rightarrow$ B</td>
<td>1.59</td>
<td>70.4</td>
</tr>
<tr>
<td>B $\rightarrow$ A</td>
<td>0.58</td>
<td>60.6</td>
</tr>
<tr>
<td>B $\rightarrow$ C</td>
<td>0.46</td>
<td>66.5</td>
</tr>
<tr>
<td>C $\rightarrow$ B</td>
<td>2.75</td>
<td>16.5</td>
</tr>
<tr>
<td>C $\rightarrow$ D</td>
<td>8.18</td>
<td>29.5</td>
</tr>
<tr>
<td>D $\rightarrow$ C</td>
<td>2.24</td>
<td>46.3</td>
</tr>
</tbody>
</table>

---

Fig. 3 MSD of Mg$^{2+}$ at 650 K from AIMD simulations. The main contribution of the displacement is along the $b$-axis, which shows a one-dimensional diffusion channel, as indicated by the inner-channel path in Fig. 2(a1) and (a2).

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Notes and references