Supporting Information for Magnesium Ion Mobility in Post-Spinels Accessible at Ambient Pressure

Daniel C. Hannah,† Gopalakrishnan Sai Gautam,‡,†,¶ Pieremanuele Canepa,†,‡
Ziqin Rong,‡ and Gerbrand Ceder*,¶,†,‡

† Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
‡ Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
¶ Department of Materials Science and Engineering, University of California Berkeley, CA 94720, USA

E-mail: gceder@berkeley.edu, gceder@lbl.gov
1 Computational Methodology

We utilize density functional theory (DFT)\cite{Hohenberg1964} as implemented in the Vienna \textit{ab initio} Simulation Package (VASP)\cite{Kresse1993}. The exchange-correlation functional were approximated by the Perdew-Burke-Ernzerhoff (PBE) implementation of the Generalized Gradient Approximation (GGA) functional\footnote{Perdew, J. P.; Burke, K.; Ernzerhoff, M. \textit{Phys. Rev. B} \textbf{1996}, \textit{54}, 11259.}. The wavefunctions were described by the Projector Augmented Wave (PAW)\footnote{Kresse, G.; Joubert, D. \textit{Phys. Rev. B} \textbf{1999}, \textit{59}, 1758.} theory combined with a kinetic energy cutoff of 520 eV and were sampled on a Monkhorst-Pack mesh with a $k$-point density of 1000/(number of atoms in the unit cell). For voltage and stability calculations, spurious self-interaction errors on $d$-electrons were accounted for by adding a Hubbard-$U$ correction\footnote{Jain, H.; Politis, A.; Onida, G.; Reining, A.; Römer, W.; Van Audekerke, J.; Van der Marel, P. \textit{Phys. Rev. B} \textbf{2002}, \textit{65}, 245105.}. The $U$ values obtained by Jain \textit{et al.} were used\footnote{Jain, H.; Politis, A.; Onida, G.; Reining, A.; Römer, W.; Van Audekerke, J.; Van der Marel, P. \textit{Phys. Rev. B} \textbf{2002}, \textit{65}, 245105.}. Ionic migration barriers were calculated using the Nudged Elastic Band (NEB) method\footnote{Jain, H.; Politis, A.; Onida, G.; Reining, A.; Römer, W.; Van Audekerke, J.; Van der Marel, P. \textit{Phys. Rev. B} \textbf{2002}, \textit{65}, 245105.} with a total of 9 images between the endpoints. Standard GGA is used in the NEB calculations owing to the problematic convergence of GGA+$U$ NEB calculations\footnote{Jain, H.; Politis, A.; Onida, G.; Reining, A.; Römer, W.; Van Audekerke, J.; Van der Marel, P. \textit{Phys. Rev. B} \textbf{2002}, \textit{65}, 245105.}.

2 Decomposition reactions for magnesiated V/Ti post-spinel compounds

Based on phase diagrams constructed using the Materials Project database\footnote{The Materials Project is a database for materials science.}, we display below the predicted decomposition reactions for the metastable MgV$_{2−x}$Ti$_x$O$_4$ ($x = 0, 0.75, 2$) materials:

\begin{equation}
\text{MgV}_2\text{O}_4 \text{ (CaFe}_2\text{O}_4\text{−type)} \rightarrow \text{MgV}_2\text{O}_4 \text{ (spinel)}
\end{equation}

\begin{equation}
\text{MgV}_{1.25}\text{Ti}_{0.75}\text{O}_4 \rightarrow \text{MgTiO}_3 + \text{TiVO}_3 + \text{MgV}_2\text{O}_4 + \text{V}
\end{equation}

\begin{equation}
\text{MgTi}_2\text{O}_4 \rightarrow \text{Ti}_2\text{O}_3 + \text{MgO}
\end{equation}
3 Voltage curves for V/Ti post-spinel compounds

Figure 1: Voltage as a function of the extent of sodiation/magnesiation for (a) V$_2$O$_4$, (b) V$_{1.25}$Ti$_{0.75}$O$_4$, (c) Ti$_2$O$_4$. The structures at $x = 0.5$ were taken to be the lowest energy structures among possible working ion/vacancy orderings at this concentration.

Figure 1 displays the voltages for V and Ti-containing post-spinel compounds at 0, 50, and 100% sodiation (magnesiation). The structures at 50% discharge ($x = 0.5$) were taken to be the lowest-energy structures among all possible working ion/vacancy orderings in a $3 \times 1 \times 1$ supercell with 50% A-site occupancy. As with the voltage data presented in the main manuscript, voltages were calculated using the free energy change of the intercalation reaction to a particular concentration (i.e. 50 or 100 %).

4 Comparison of stable sites and migration paths for Na and Mg ions

The stable sites for Na and Mg differ in displacement from the channel centroid, which is indicated by a dashed circle in Figures 2a and 2c. The stable site for Na (Fig. 2a) is in a part of the channel which is 17.5% larger in the $b$ direction compared to the stable site for Mg (Fig. 2c). The absolute distances between channel walls in the $b$ direction are indicated by black double-sided arrows on Figs. 2a and 2c. The differences in stable site result in a
slightly different migration path for Na and Mg. The paths are compared in Figures 2b and 2d. The Mg ion first moves along the $c$ direction into a more central part of the channel before migrating along a roughly linear trajectory followed by a move back to the stable Mg site. During movement along the $c$ axis the Mg ion passes through a distorted square plane of oxygen atoms, creating a local activated state which manifests as the multi-peaked energy profile for migration (Fig. 3b, d, f in the main manuscript). In contrast, the motion of the Na ion is predominantly in the $a$ direction and only a single maximum is observed (Fig. 3a, c, e in the main manuscript). In the discharged limit, the Mg site more closely resembles the Na site, resulting in a migration energy profile similar to the one observed for Na ions (Fig. 3 in the main manuscript).

References


Figure 2: (a) Na ion position obtained following DFT relaxation of the charged state structure of Na in Ti$_2$O$_4$. The concentric circle represents the channel "center" defined here as the geometric centroid of the 8 coordinating oxygen atoms. The black arrow and label indicate the distance between channel walls in the $b$ direction. (b) Minimum energy migration path for Na in Ti$_2$O$_4$ derived from NEB calculations in the charged limit. (c) Mg ion position obtained following DFT relaxation of the charged state structure of Mg in Ti$_2$O$_4$. The labels on the figure have the same meaning as in (a). (d) Minimum energy migration path for Mg in Ti$_2$O$_4$ derived from NEB calculations in the charged limit. The compass on the left applies to (a) and (c), while the compass on the right applies to (b) and (d).