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

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1 Computational Methodology

We utilize density functional theory (DFT)[1] as implemented in the Vienna *ab initio* Simulation Package (VASP).[2,3] The exchange-correlation functional were approximated by the Perdew-Burke-Ernzerhoff (PBE) implementation of the Generalized Gradient Approximation (GGA) functional.[4] The wavefunctions were described by the Projector Augmented Wave (PAW)[5] 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.[6,7] The U values obtained by Jain *et al.* were used.[8] Ionic migration barriers were calculated using the Nudged Elastic Band (NEB) method[9] 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.[10]

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

Based on phase diagrams constructed using the Materials Project database,[11] we display below the predicted decomposition reactions for the metastable $MgV_{2-x}Ti_xO_4$ (x = 0, 0.75, 2) materials:

$$MgV_2O_4\,(CaFe_2O_4\text{−type}) \rightarrow MgV_2O_4\,(\text{spinel}) \tag{1}$$

$$MgV_{1.25}Ti_{0.75}O_4 \rightarrow MgTiO_3 + TiVO_3 + MgV_2O_4 + V \tag{2}$$

$$MgTi_2O_4 \rightarrow Ti_2O_3 + MgO \tag{3}$$

3 Voltage curves for V/Ti post-spinel compounds

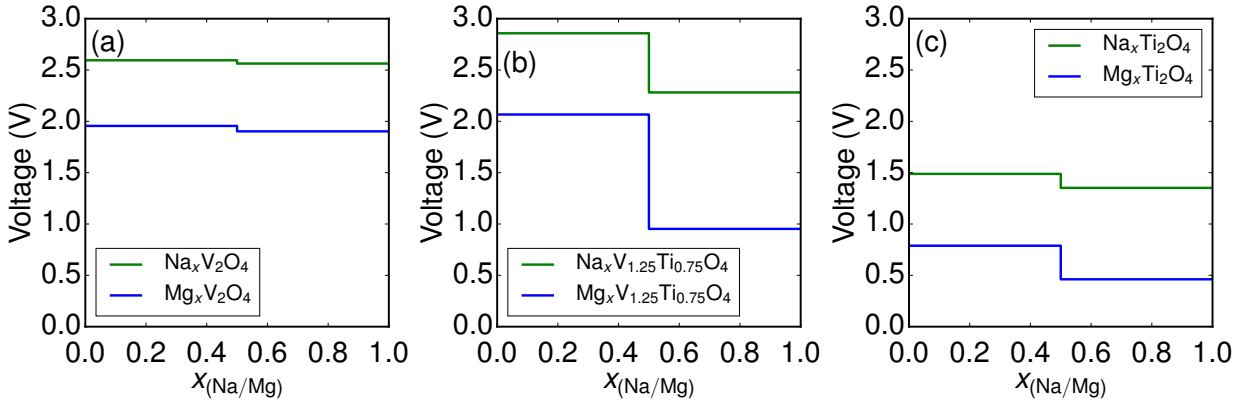

Figure 1: Voltage as a function of the extent of sodiation/magnesiation for (a) V_2O_4, (b) $V_{1.25}Ti_{0.75}O_4$, (c) Ti_2O_4. The structures at $x = 0.5$ were taken to be the lowest energy structures among possible working ion/vacancy orderings at this concentration.

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 3×1×1 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 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

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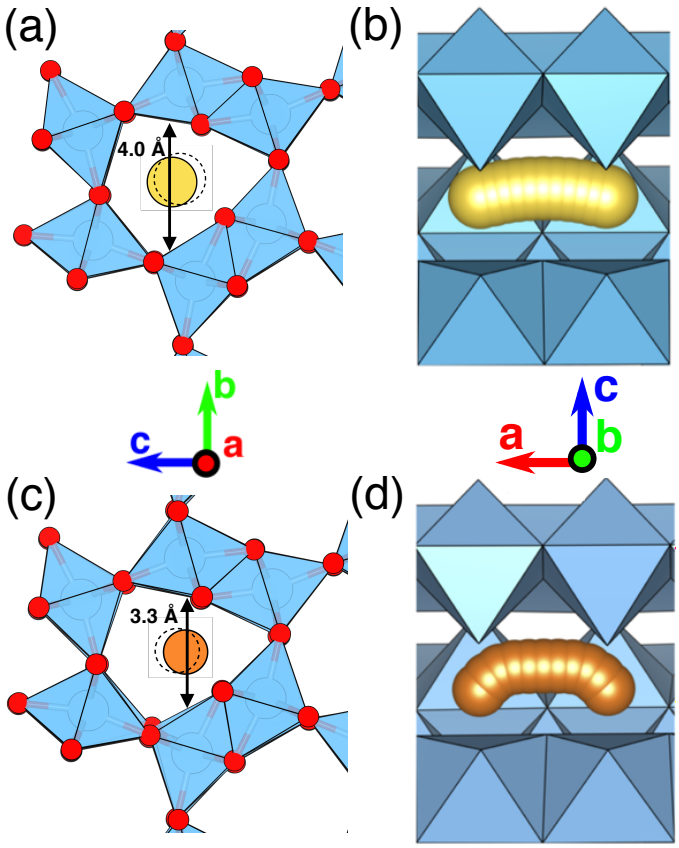

Figure 2: (a) Na ion position obtained following DFT relaxation of the charged state structure of Na in Ti_2O_4. The concentric circle represents the channel "center" defined here as the geometric centroid of the 8 coordinating oxygen atoms. The black arrow and label indicate the distance between channel walls in the b direction. (b) Minimum energy migration path for Na in Ti_2O_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_2O_4. The labels on the figure have the same meaning as in (a). (d) Minimum energy migration path for Mg in Ti_2O_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).