Supporting Information

Role of structural H_2O in intercalation electrodes: the case of Mg in nano-crystalline Xerogel-V_2O_5

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1 Grand-potential phase diagrams

Each graph in Figure S1 plots the relative stability of the Xerogel structures as function of Mg composition, with green triangles, red diamonds and blue dots representing structures with $n_{H_2O} = 0,\ 0.5,$ and 1, respectively. The formation energy is plotted with respect to the lowest energy states at $x_{Mg} = 0$ and $x_{Mg} = 0.5$ so that the relative stability of the states at $x_{Mg} = 0.25$ can be assessed. Finally, the dashed purple lines indicate the stable phases at 0 K under the given electrolyte conditions.

For a wet electrolyte ($a_{H_2O} \sim 1$), the ground state structures in Figure S1a consist of the fully magnesiated − fully hydrated structure (x_{Mg} =0.5, $n_{H_2O} = 1$ per V_2O_5), the 'half' magnesiated − half hydrated structure (x_{Mg} =0.25, $n_{H_2O} = 0.5$), and the fully demagnesiated − dehydrated structure (x_{Mg} =0, $n_{H_2O} = 0$).

When a dry electrolyte is employed (Figure S1b), set by $a_{H_2O} \sim 10^{-4}$, the ground state phases are: x_{Mg} =0.5, $n_{H_2O} = 0.5$ (fully magnesiated − half hydrated), x_{Mg} =0.25, $n_{H_2O} = 0.5$ (half magnesiated − half hydrated), and x_{Mg} =0, $n_{H_2O} = 0$ (fully demagnesiated − dehydrated).

Figure S1c displays the stability values for a superdry electrolyte ($a_{H_2O} \sim 10^{-8}$) consisting of the fully dehydrated structures, both at $x_{Mg} = 0.5$ (fully magnesiated) and $x_{Mg} = 0$ (fully demagnesiated).

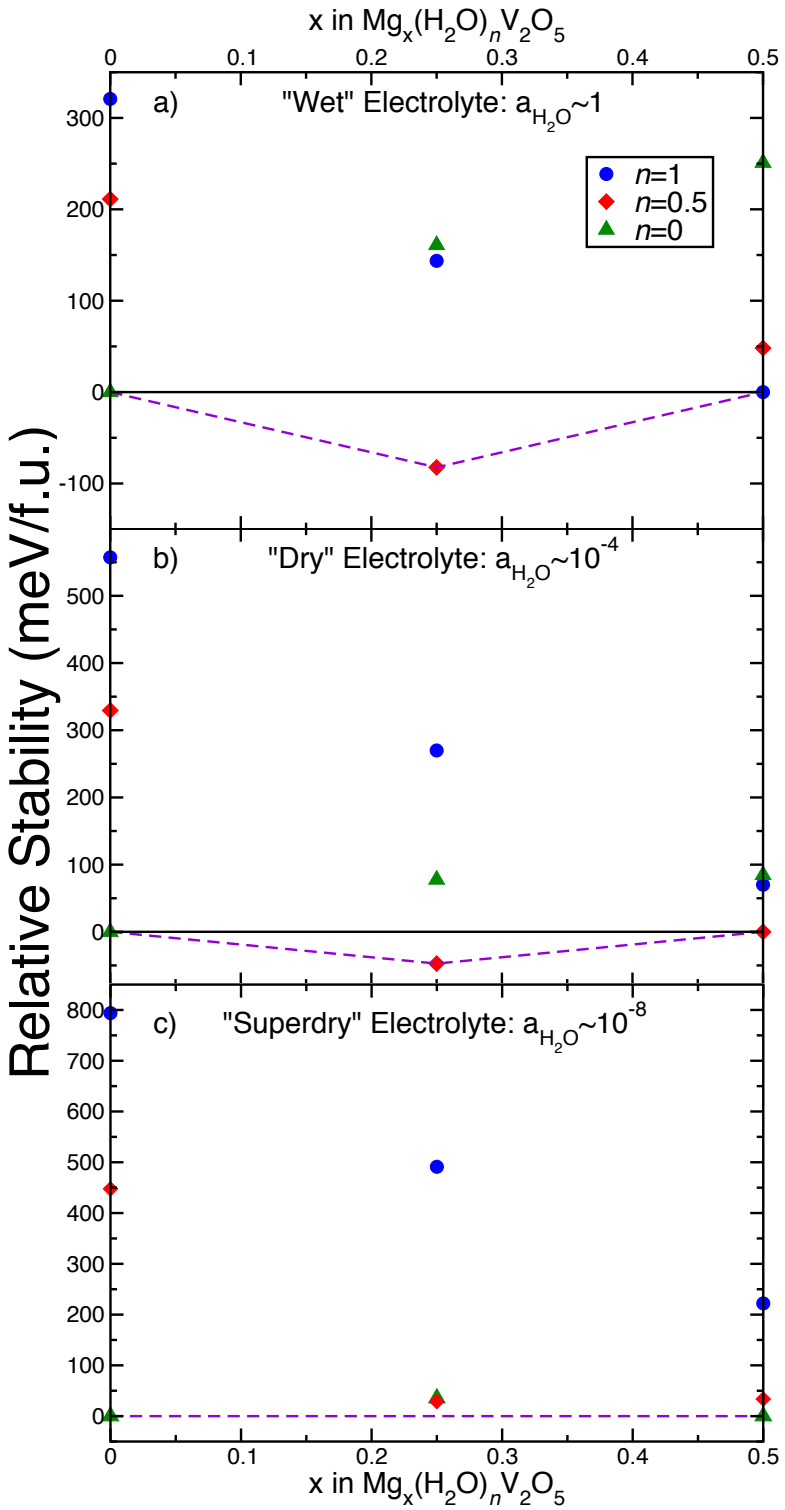

Figure S1: The Grand-potential phase diagram at 0 K of the Mg-Xerogel V_2O_5 system in a (a) wet, (b) dry, and (c) superdry electrolytes. Blue dots, red diamonds and green triangles respectively indicate structures with $n_{H_2O} = 1$, 0.5, and 0 at different x_{Mg}.

2 Structures and lattice parameters of ground states

Figure S2 shows the structures of the ground state configurations at different Mg and H_2O concentrations, as described in Figure 2 of the manuscript and Figure S1, including the fully magnesiated − half hydrated ($x_{Mg} = 0.5$, n_{H_2O}=0.5; Figure S2a), the half magnesiated − half hydrated ($x_{Mg} = 0.25$, n_{H_2O}=0.5; Figure S2b), the fully magnesiated − dehydrated ($x_{Mg} = 0.5$, n_{H_2O}=0; Figure S2c) and the fully demagnesiated − dehydrated states ($x_{Mg} = 0$, n_{H_2O}=0.5; Figure S2d). Mg can be found in a 5- and 4-coordinated environment in Figure S2a and c respectively, with the ground state configuration in Figure S2a being in a $2 \times 1 \times 1$ supercell configuration. The bilayered-V_2O_5 framework is retained while calculating the fully dehydrated configurations of Figure S2c and d. The lattice parameters of all ground state configurations (including those displayed in Figure 1 of the manuscript), resulting from GGA ($+U$) and vdW-DF2 ($+U$) calculations are given in Table S1. The atomic coordinates of all ground states have been indicated in Section 9.

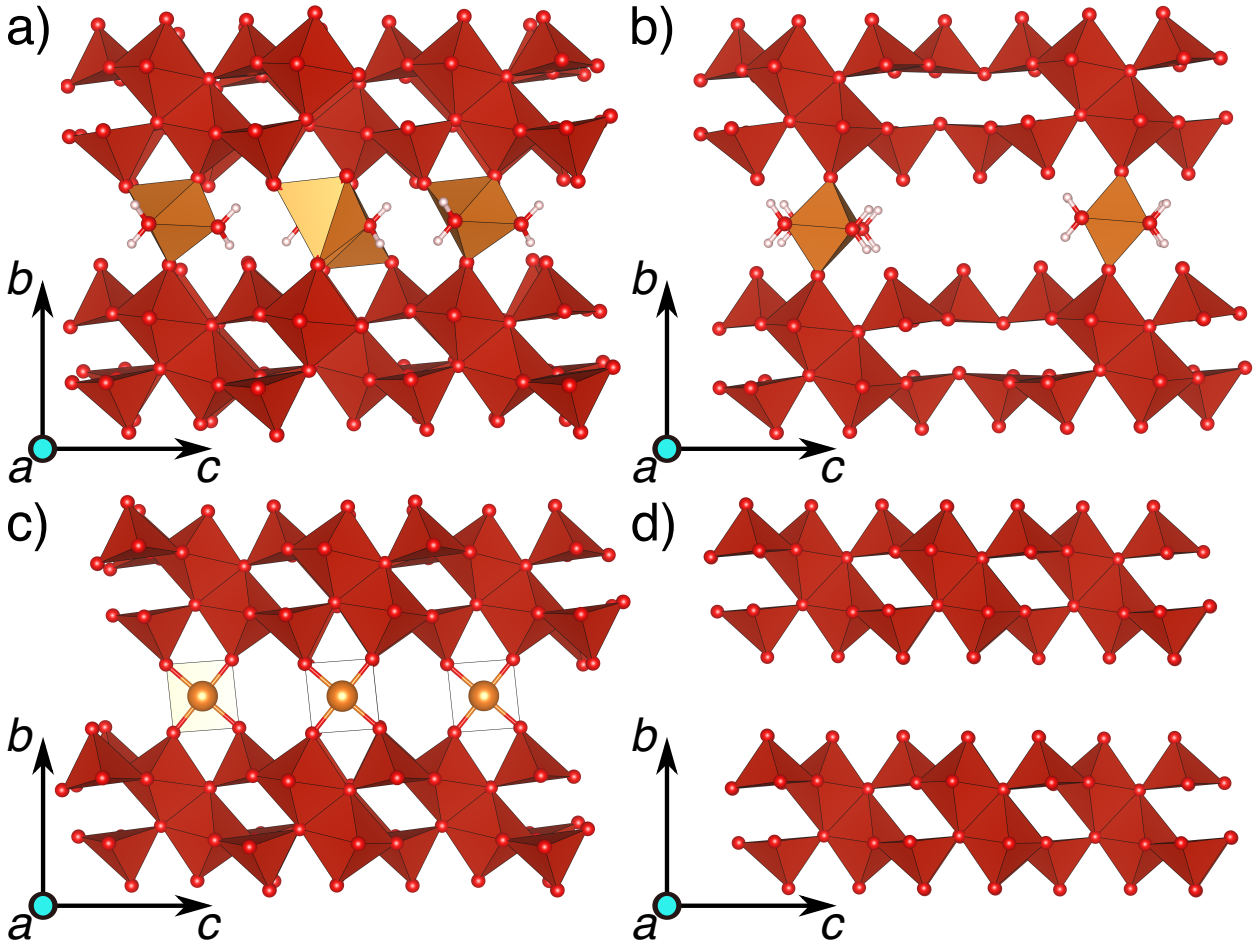

Figure S2: The ground state configurations at different Mg and H_2O contents within the Xerogel structure are displayed. Sub-panels (a), (b), (c), and (d) indicate the stable states at (x_{Mg} = 0.5, n_{H_2O}=0.5), (x_{Mg} = 0.25, n_{H_2O}=0.5), (x_{Mg} = 0.5, n_{H_2O}=0), and (x_{Mg} = 0, n_{H_2O}=0), respectively. The notation used for the crystallographic axes is the same as that used in Figure 1 of the manuscript, while the orange and red polyhedra correspond to the Mg and V atoms (at the center) coordinated by oxygen atoms.

Table S1: The lattice parameters of all ground state configurations of the Mg-Xerogel V_2O_5 system. The Hubbard $+U$ correction was added to both GGA and vdW-DF2 calculations with the cell symmetry broken.

Phase	Functional	Lattice parameters					
		a	b	c	α	β	γ
		Å			o		
$Mg_{0.5}(H_2O)V_2O_5$	GGA	3.73	10.18	11.86	94.60	90.06	89.86
	vdW-DF2	3.72	10.22	12.19	93.69	89.91	90.19
$Mg_{0.5}(H_2O)_{0.5}V_2O_5$	GGA	7.6	9.64	11.70	90.09	90.01	90.03
	vdW-DF2	7.66	9.76	11.85	90.12	90.01	90.00
$Mg_{0.25}(H_2O)_{0.5}V_2O_5$	GGA	3.70	10.30	11.70	93.16	90.00	90.00
	vdW-DF2	3.71	10.79	11.97	94.46	90.00	90.00
$Mg_{0.5}V_2O_5$	GGA	3.80	9.30	11.66	81.06	90.00	90.00
	vdW-DF2	3.84	9.42	11.81	81.25	90.00	90.00
V_2O_5	GGA	3.66	10.01	11.74	95.52	90.00	90.00
	vdW-DF2	3.69	9.30	11.90	95.85	90.00	90.00
$(H_2O)V_2O_5$	GGA	3.69	12.76	11.69	96.73	90.00	87.30
	vdW-DF2	3.69	11.28	11.91	94.37	90.06	91.21

3 Calculating voltages

Consider an electrochemical reaction, where Mg intercalates into a V_2O_5 host and compensating electrons are absorbed into the cathode host from the external circuit.

$$Mg_xV_2O_5 + \Delta x\ Mg \rightleftharpoons Mg_{x+\Delta x}V_2O_5 \tag{1}$$

Starting from the Nernst equation and using thermodynamic arguments, the voltage for reaction 1 can be written as a function of the Mg chemical potential in the cathode ($Mg_xV_2O_5$) and the anode (Mg metal), as in Eq. 2, with z and F being the number of electrons transferred (2 per Mg) and the Faraday constant, respectively.

$$V(x) = -\frac{\mu^{cathode}_{Mg_xV_2O_5} - \mu^{anode}_{Mg\ metal}}{zF} \tag{2}$$

The average voltage ($\langle V \rangle$) between 2 given compositions of Mg (x_1 and x_2) in V_2O_5 are

obtained by integrating Eq. 2. Usually, average voltages are computed across the Mg compositions under consideration, which in this study is $x_1 = 0$ and $x_2 = 0.5$. Neglecting the entropic ($T\Delta S$) and volumetric ($P\Delta V$) components, the chemical potential (or Gibbs energy per unit composition) can be approximated as the internal energy calculated by Density Functional Theory (DFT) at 0 K, i.e., $G_{\mathrm{Mg}_x\mathrm{V_2O_5}} \approx E^{DFT}_{\mathrm{Mg}_x\mathrm{V_2O_5}}$, thus allowing the average voltage to be computed directly from DFT energies.[1,2]

$$\langle V \rangle = -\frac{E(\mathrm{Mg}_{x_2}\mathrm{V_2O_5}) - E(\mathrm{Mg}_{x_1}\mathrm{V_2O_5}) - (x_2 - x_1)E(\text{Mg metal})}{(x_2 - x_1)zF} \tag{3}$$

Eq. 3 is applicable for electrochemical systems where the cathode framework ($\mathrm{V_2O_5}$) remains constant as the Mg concentration is changed.

However, in the case of Xerogel-$\mathrm{V_2O_5}$, as Mg is (de)intercalated the cathodic composition changes due to $\mathrm{H_2O}$ shuttling along with the $\mathrm{Mg^{2+}}$ (see Figure 2 in the manuscript). In order to account for changes in the Xerogel composition on (de)magnesiation, the grand-potential energies (Φ, as described in the Methods section of the manuscript) must be used in calculating the average voltage, with Eq. 3 being re-written as Eq. 4.

$$\langle V \rangle = -\frac{\Phi[\mathrm{Mg}_{x_2}(\mathrm{H_2O})_{n_2}\mathrm{V_2O_5}] - \Phi[\mathrm{Mg}_{x_1}(\mathrm{H_2O})_{n_1}\mathrm{V_2O_5}] - (x_2 - x_1)E(\text{Mg metal})}{(x_2 - x_1)zF} \tag{4}$$

where, $\Phi[\mathrm{Mg}_{x_2}(\mathrm{H_2O})_{n_2}\mathrm{V_2O_5}] = E[\mathrm{Mg}_{x_2}(\mathrm{H_2O})_{n_2}\mathrm{V_2O_5}] - n_2.\mu_{\mathrm{H_2O}}$, with E calculated using DFT and the value of μ obtained through the procedure described in Section 5.

3.1 Feature on the voltage profile

The kink in the blue voltage curve of Figure 3 in the manuscript, at $a_{\mathrm{H_2O}} \sim 10^{-7}$, together with the red curve, indicates a scenario where the ground state hull is comprised of the $\mathrm{x_{Mg}} = 0$, $n_{\mathrm{H_2O}} = 0$ (fully demagnesiated − dehydrated), $\mathrm{x_{Mg}} = 0.25$, $n_{\mathrm{H_2O}} = 0.5$ (half magnesiated − half hydrated), and $\mathrm{x_{Mg}} = 0.5$, $n_{\mathrm{H_2O}} = 0$ (fully magnesiated − dehydrated) states, implying that Mg co-intercalates with $\mathrm{H_2O}$ into the empty Xerogel up to $\mathrm{x_{Mg}} = 0.25$

beyond which the H_2O exits the structure upon more Mg insertion.

4 Strategy for resolving H-positions

We use a 3-step strategy to resolve the H-positions in both Mg-intercalated and empty Xerogel structures. Firstly, we obtain Voronoi positions ~ 1 Å away from the O^w atoms (see Figure 1 in the manuscript), since the O−H bonds in water are ~ 1 Å long.[3,4] Secondly, we order the H-sites obtained from the Voronoi positions,[5] based on Ewald summation energies[6,7] to minimize electrostatic repulsion between the H-atoms by assigning formal charges of +2, +5, −2 and +1 to Mg, V, O, and H atoms, respectively. In order to ensure a diverse set of H-positions to initialize our first-principles calculations, we also assign sets of unphysical charges to the Mg, V, and O atoms, such as Mg^{2-}, V^{5-}, and O^{2+}. Each permutation of the charges assigned to the Mg, V and O atoms give rise to $\sim 40 - 50$ distinct H-orderings. The pymatgen library[8] is used to obtain both the Voronoi positions and enumerate the H-orderings. Finally, each structure stemming from the ordering procedure is subjected to a two-step structure relaxation calculation. In the first step the H-atoms are allowed to rotate about the O^w atoms while the positions of all other atoms in the structure are fixed. In the second step we perform the full structure relaxation allowing all ions in the structure to relax. The fully relaxed H-ordering with the lowest energy among those calculated is considered to be the 'ground state' configuration for the given Mg and H_2O content in the Xerogel (and plotted in Figure S1). The above procedure is then repeated for other Mg and H_2O concentrations in the Xerogel structure.

5 Obtaining μ_{H_2O} for calculating the Grand-potential

In order to calculate the Grand-potential, Φ, described in the manuscript, reliable first-principles values for the chemical potential of H_2O, μ_{H_2O}, need to be obtained. With $\mu^0_{H_2O}$, a_{H_2O}, R and T defined as the chemical potential of H_2O in its standard state, activity of H_2O

in the electrolyte (external to the Xerogel cathode), universal gas constant and temperature, respectively. μ_{H_2O} can be expanded as,

$$\mu_{H_2O} = \mu^0_{H_2O} - RT \ln a_{H_2O} \tag{5}$$

By assigning various values to a_{H_2O}, different electrolyte conditions can be simulated, such as the wet ($a_{H_2O} \sim 1$), dry ($a_{H_2O} \sim 10^{-4}$), and superdry ($a_{H_2O} \sim 10^{-8}$) electrolytes. Hence, to obtain reliable values of μ_{H_2O}, an accurate value of $\mu^0_{H_2O}$ needs to be calculated.

To obtain a reliable value of $\mu^0_{H_2O}$ from DFT, we consider two approaches in this work, namely using the "Ice" and "Vapor" references. In the case of the "Ice" reference, $\mu^0_{H_2O}$ is obtained by adding to the DFT energy of ice (E_{Ice}) the experimental enthalpy of melting of ice ($\Delta H^{melting}_{\text{Ice}}$, at 298 K) and the entropy of liquid H_2O at 298 K (S_{Water}).

$$\mu^0_{H_2O} = E_{\text{Ice}}(calc.) + \Delta H^{melting}_{\text{Ice}}(exp.) - T.S_{\text{Water}}(exp.) \tag{6}$$

The ice-XI structure reported by Leadbetter *et al.*[9] is used for calculating the DFT ice energy in Eq. 6, with a k-point mesh of 6×4×4. Similarly, for the "Vapor" reference, $\mu^0_{H_2O}$ is given by starting from the DFT total energy of water vapor (E_{Vapor}), which is obtained by calculating the energy of a single molecule of H_2O in a 15×15×15 Å^3 box, and subtracting the experimental enthalpy of evaporation of water ($\Delta H^{evaporation}_{\text{Water}}$, at 298 K) and S_{Water} at 298 K. Both the Ice and the Vapor calculations were done with the Generalized Gradient Approximation as elaborated in the Methods section in the manuscript.

$$\mu^0_{H_2O} = E_{\text{Vapor}}(calc.) - \Delta H^{evaporation}_{\text{Water}}(exp.) - T.S_{\text{Water}}(exp.) \tag{7}$$

Using both the Ice and the Vapor references, the formation energies of a few alkali and alkaline earth hydroxides (from their corresponding oxides) are calculated from DFT and compared with the experimental enthalpies of formation (ΔH_{r}) in order to determine which

of the two reference states describes a realistic value for $\mu^0_{H_2O}$. For example, consider the reaction MgO + $H_2O \rightarrow Mg(OH)_2$. The experimental enthalpy of formation of $Mg(OH)_2$ from MgO can be computed as,

$$\Delta H_{r,Mg(OH)_2} = H^0_{Mg(OH)_2} - H^0_{MgO} - H^0_{H_2O} \tag{8}$$

where H^0 of a species is the standard enthalpy of formation of that species at 298 K, obtained from the Kubaschewski[10] and Wagman[11] tables. Similarly, the enthalpy of formation of $Mg(OH)_2$ from MgO can be calculated from the DFT total energies as in Eq. 9, while disregarding the negligible volumetric (PV), the zero point energy and the temperature contributions to the enthalpy at 298 K. The E_{H_2O} in Eq. 9 will either correspond to the Ice reference ($E_{Ice} + \Delta H^{melting}_{Ice}$, Eq. 6) or the Vapor reference ($E_{Vapor} - \Delta H^{evaporation}_{Water}$, Eq. 7). Thus, the Ice- or Vapor-based $\Delta H_{r,Mg(OH)_2}$ that benchmarks best with the experimental $\Delta H_{r,Mg(OH)_2}$ will be used further in our grand-potential phase diagram calculations.

$$\Delta H_{r,Mg(OH)_2} = E_{Mg(OH)_2} - E_{MgO} - E_{H_2O} \tag{9}$$

In order to benchmark a wide range of experimental and calculated ΔH_r, we considered a set of alkali and alkaline earth hydroxides and oxides that satisfied few conditions:

- The valence state of the metal or oxygen should not change during hydroxide formation from the oxide. For example, NaOH formation from a conventional Na_2O will be considered instead of a Na_2O_2 peroxide.

- The existence of reliable experimental structures for both oxides and hydroxides with known positions of all atoms in the structure, including the H-atoms. The Inorganic Crystal Structure Database[12] database was used for the structure search.

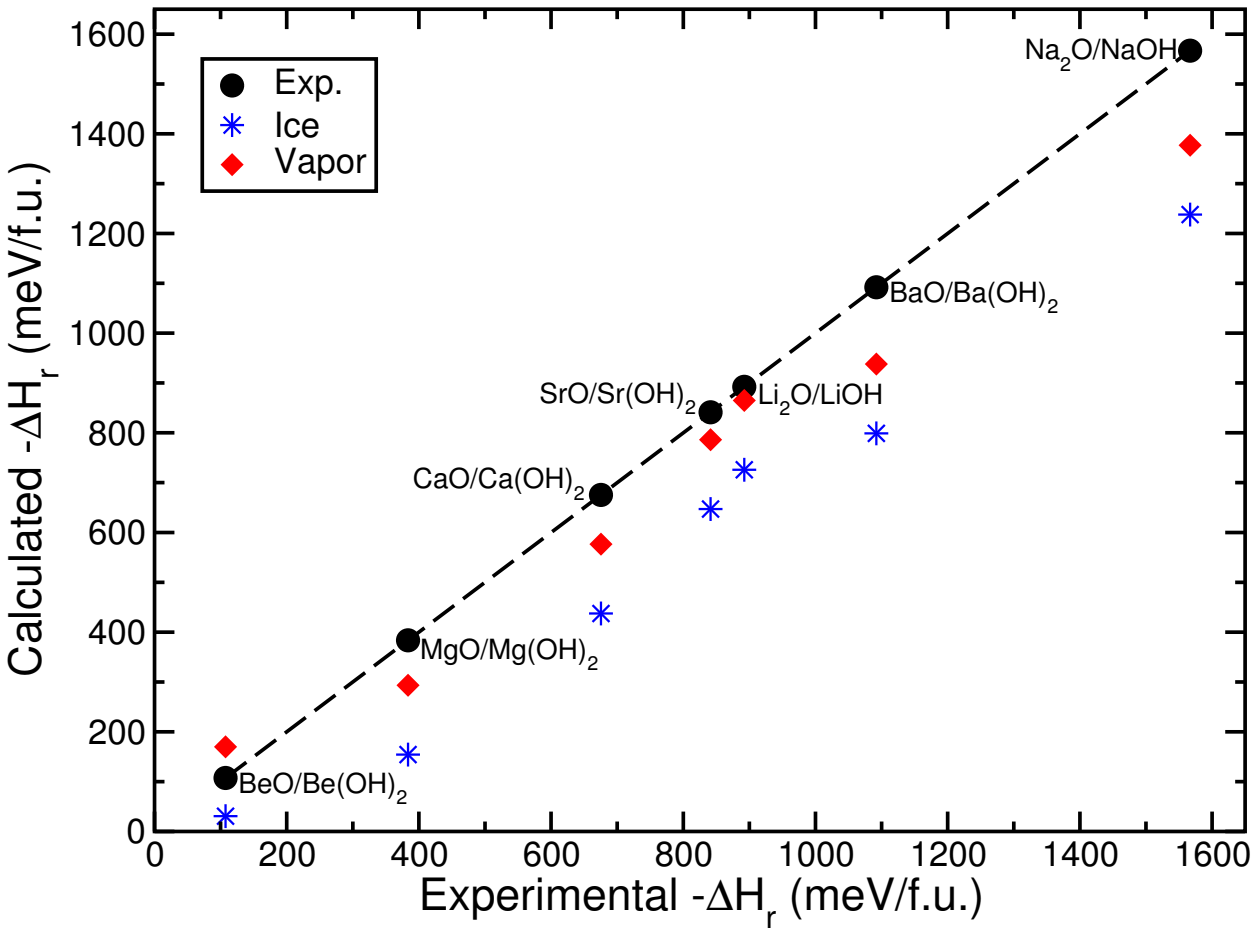

Figure S3: Benchmarking the DFT "Ice"- and "Vapor"-referenced formation enthalpies of alkali and alkaline earth hydroxides from their corresponding oxides, with respect to the analogous experimental values.

5.1 Benchmarking $\mu^0_{H_2O}$

Figure S3 displays the benchmarking of the DFT and experimental formation enthalpies of a few alkali (Li, Na) and alkaline earth (Be, Mg, Ca, Sr and Ba) hydroxides from the corresponding oxides. The black dots indicate the experimental values obtained from the literature,[10,11] while the theoretical calculations using the Ice and Vapor references are marked by the blue stars and the red diamonds respectively. The absolute distances between the black dot and the DFT points denote the errors encountered in predicting the experimental enthalpy values. The text annotations in the graph correspond to the respective systems for which the experimental and computed values are displayed. For example, the notation

$CaO/Ca(OH)_2$ is equivalent to the reaction $CaO + H_2O \rightarrow Ca(OH)_2$.

While the Vapor-referenced calculations predict the experimental formation enthalpies of the hydroxide from the oxide with an average error of $\sim 16\%$, the Ice-referenced calculations predict the same enthalpies with almost twice the error ($\sim 32\%$). Also, the Vapor-referenced calculations have lower errors consistently than the Ice-referenced calculations for all the oxide/hydroxide systems considered. Thus, it can be concluded that the Vapor-referenced calculations capture the energetics of H_2O better than the Ice-referenced calculations, specifically for obtaining a reliable $\mu^0_{H_2O}$. The results described in the manuscript are based on the Vapor-referenced calculations.

6 Obtaining μ_{Mg}

Similar to μ_{H_2O}, the chemical potential of Mg (μ^{ref}_{Mg}) can be referenced to the Mg chemical potential in its standard state (μ^0_{Mg}).

$$\mu^{ref}_{Mg} = \mu^0_{Mg} + \Delta\mu_{Mg} \tag{10}$$

μ^0_{Mg} is obtained from DFT calculations of pure Mg metal, in its Hexagonal Close-packed form, and by neglecting the entropic and volumetric contributions.

$$\mu^0_{Mg} \approx E^{DFT}_{Mg} \tag{11}$$

The Mg chemical potential scale is then re-normalized, such that $\mu_{Mg} = 0$ corresponds to the DFT-computed value of μ^0_{Mg}, and the grand-potential energies (Φ) are adjusted (as in Eq. 13) to reflect this normalization.

$$\mu_{Mg} = \mu^{ref}_{Mg} - \mu^0_{Mg} \equiv \Delta\mu_{Mg} \tag{12}$$

$$\Phi'[\mathrm{Mg}_x(\mathrm{H_2O})_n\mathrm{V_2O_5}] = \Phi[\mathrm{Mg}_x(\mathrm{H_2O})_n\mathrm{V_2O_5}] - x \cdot \mu^0_{\mathrm{Mg}} \tag{13}$$

The normalized Φ' thus obtained is minimized as a function of both $a_{\mathrm{H_2O}}$ and the shift in the Mg chemical potential (μ_{Mg}) as in Eq. 14. The phases that have the lowest Φ' are subsequently plotted in Figure 2 of the manuscript.

$$\min_{\Phi'}\{\Phi'[\mathrm{Mg}_x(\mathrm{H_2O})_n\mathrm{V_2O_5}] - x \cdot \mu_{\mathrm{Mg}} - n \cdot (\mu^0_{\mathrm{H_2O}} - RT \ln a_{\mathrm{H_2O}})\};\ \forall\ \mu_{\mathrm{Mg}} \leq 0, a_{\mathrm{H_2O}} \leq 1 \tag{14}$$

Note that with Eq. 12 as the definition of the Mg chemical potential, μ_{Mg} is related to the voltage as ($\langle V \rangle \approx \frac{\mu_{\mathrm{Mg}}}{2}$).

7 k-point convergence

Figure S4 displays the energy per atom as a function of the k-point grid density for the Mg-Xerogel V_2O_5 system, indicating rapid convergence of the energy with increase in k-points. A fully magnesiated − hydrated ($\mathrm{x_{Mg}} = 0.5$, $n_{\mathrm{H_2O}} = 1$) unit cell, as illustrated in Figure 1a in the manuscript with lattice parameters provided in Table S1, was used for performing the convergence study. As indicated by the text in Figure S4, a k-point density of ~ 1000 per atom corresponds to a mesh of $6 \times 2 \times 2$, with energy per atom converged to within < 0.1 meV/atom compared to a denser k-point meshes. Hence, a $6 \times 2 \times 2$ mesh was used in all our energy calculations.

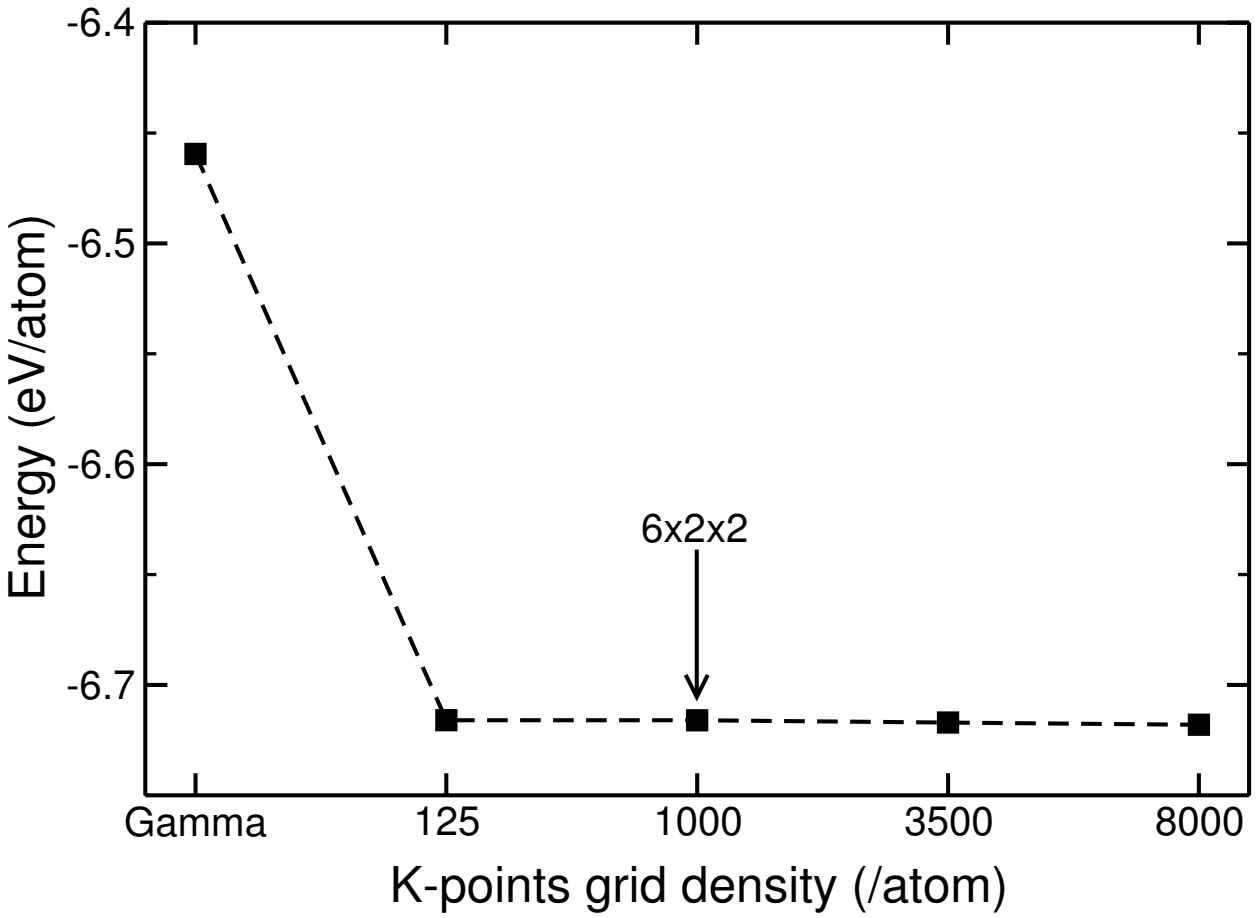

Figure S4: Convergence of energy per atom with respect to k-point grid size for the calculations done on the Mg-Xerogel system.

8 Impact of H_2O on the electronic structure of Mg-V_2O_5

The presence of excess electrons from H_2O partially shielding the divalent Mg^{2+} ion can be observed from the difference in charge densities between hydrated and dehydrated structures of a fully magnesiated xerogel-V_2O_5 ($x_{Mg} = 0.5$) in Figure S5. To this end, we analyze variations of the electronic charge density and the density of states (DOS) when Mg intercalates with and without water in the xerogel Mg-V_2O_5 system.

In order to perform a valid comparison of charge densities (and the DOS), the ground

state configuration at $x_{Mg} = 0.5$, $n_{H_2O} = 1$ (Figure 1a in the manuscript) is chosen and electronic relaxation is done with and without water molecules. The blue regions indicate zones of excess electrons in the hydrated structure as compared to the dehydrated version, with the iso-surface displayed in Figure S5 being ~ 0.0133 electrons. The presence of H_2O thus significantly alters the electronic structure of the Mg-Xerogel V_2O_5 system, influencing both the ground state configurations observed and the Mg-intercalation kinetics.

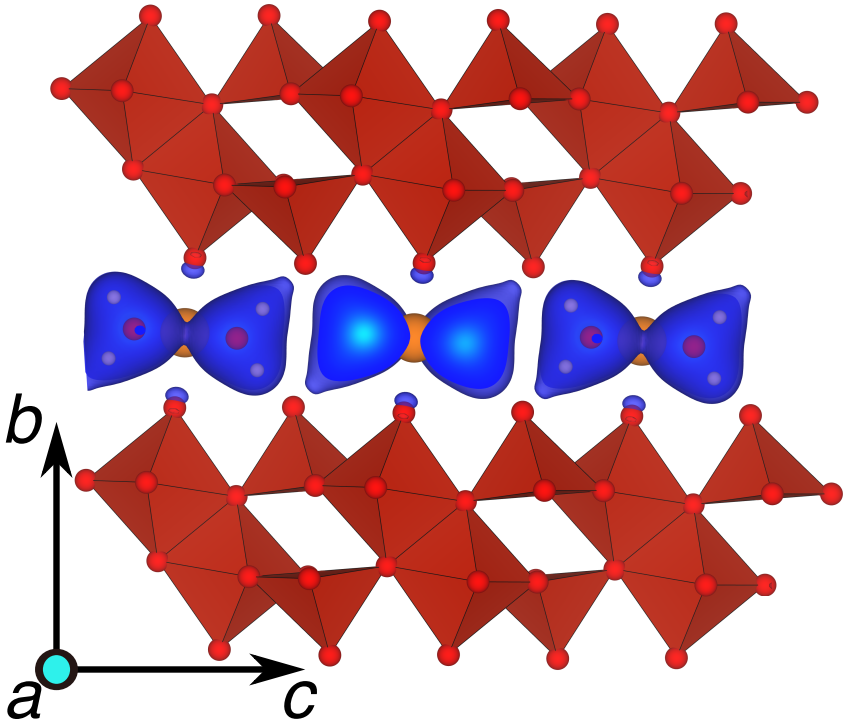

Figure S5: The red polyhedra contain the V atoms at the center and the orange spheres indicate Mg atoms in Mg-Xerogel V_2O_5. The difference between the electronic charge densities of the fully magnesiated, fully hydrated structure ($x_{Mg} = 0.5$, $n_{H_2O} = 1$) and the fully magnesiated, dehydrated structure ($x_{Mg} = 0.5$, $n_{H_2O} = 0$) is displayed. The ground state configuration of Figure 1a in the manuscript is chosen for comparing the charge densities. The blue regions show the excess of electrons in the hydrated structure in comparison to the dehydrated version.

The projected DOS of the dehydrated ($x_{Mg} = 0.5$, $n_{H_2O} = 0$) and fully hydrated ($x_{Mg} = 0.5$, $n_{H_2O} = 1$) Mg-Xerogel V_2O_5 are compared in Figure S6. From the DOS an increase of the band-gap from the dehydrated (~ 0.6 eV, Figure S6a) to hydrated (~ 0.8 eV, Figure S6b) Mg-Xerogel structure is observed, indicating the importance of nano-crystallinity

in ensuring reasonable electrical conductivity of the cathode.

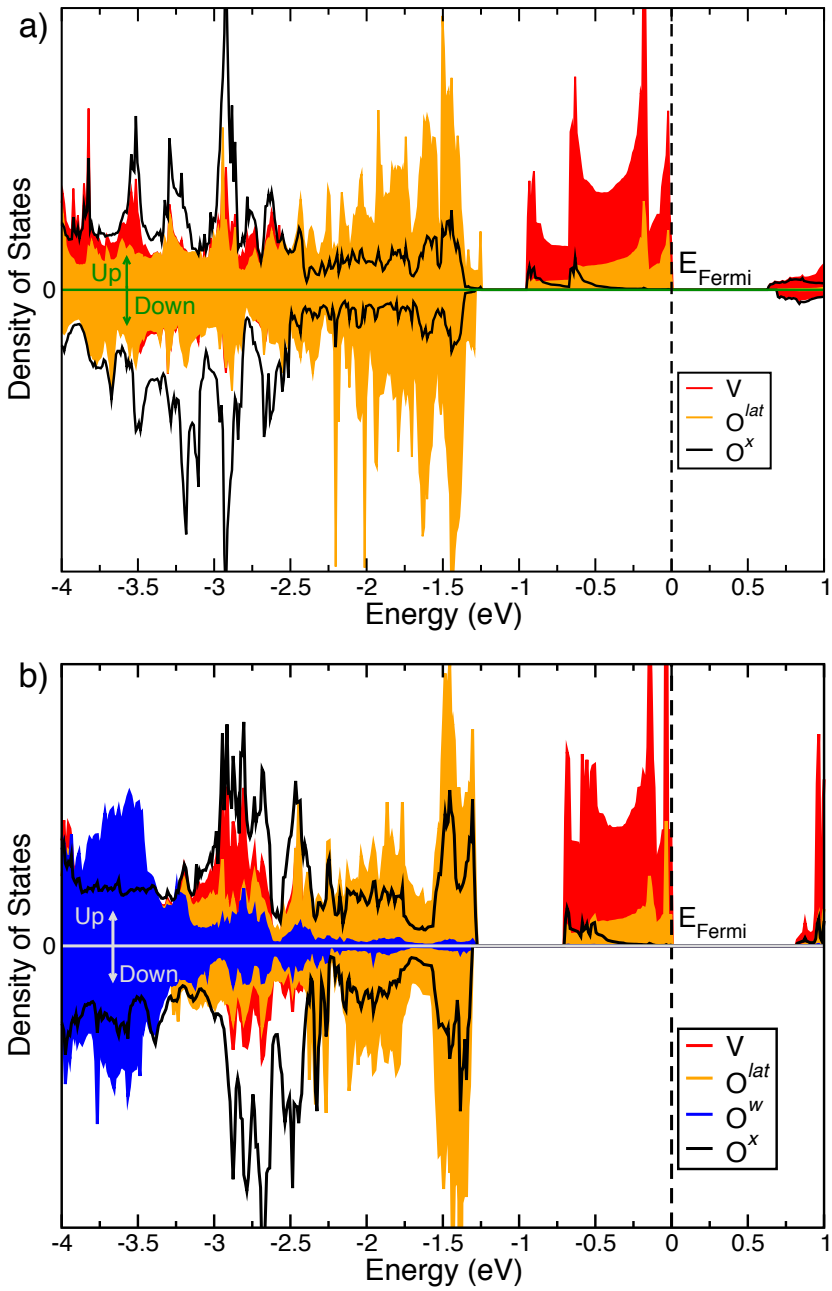

Figure S6: Projected Density of States on vanadium (V, red), lattice oxygen away from Mg (O^{lat}, orange), lattice oxygen bonded to the Mg (O^{x}, black) and the oxygen of the water molecules (O^{w}, blue) in the a) dehydrated ($x_{Mg} = 0.5$, $n_{H_2O} = 0$) and b) fully hydrated ($x_{Mg} = 0.5$, $n_{H_2O} = 1$) Mg-Xerogel V_2O_5 are displayed. The Fermi energy, indicated by dashed lines is arbitrarily set at the top of the valence band. Positive and negative DOS indicate spin-up and spin-down electrons, respectively.

In the DOS of Figure S6a and b, the valence band is dominated by localized V (*3d*) spin-up orbitals, a sign that the electrons have been transferred from Mg to V during the intercalation. Close to the Fermi energy, the V (*3d*) states are slightly hybridized with the O (*2p*) of the V_2O_5 bilayers. However, most of the O (*2p*) are found at lower energies and are well separated from the valence band (V (*3d*)), with an increase in separation on hydration. The O (*2p*) orbitals from the water molecules (O^w in Figure S6b) are found at lower energies (between -4.0 and -3.0 eV) and hybridize with V (*3p*) orbitals, screening the Mg. Finally, the Mg levels, which are not shown for simplicity in Figure S6b, overlap with O^w states attesting the stabilizing coordination effect exerted by H_2O molecules on the intercalated Mg ions.

9 Atomic coordinates of ground states

All atomic positions are given in fractional coordinates defined by the lattice parameters given for each structure.

A $Mg_{0.5}(H_2O)V_2O_5$

A.1 GGA

a 3.73 b 10.18 c 11.86
α 94.60 β 90.06 γ 89.86

O 0.012741 0.685121 0.772431
O 0.996311 0.691940 0.032341
O 0.005753 0.916003 0.909949
O 0.500740 0.881778 0.105826
O 0.507347 0.882021 0.736529
O 0.506992 0.684734 0.272438
O 0.504150 0.692174 0.532540
O 0.502892 0.915983 0.409790
O 0.005794 0.881941 0.605782
O 0.002163 0.881533 0.236513
O 0.003770 0.315284 0.227768
O 0.000847 0.307941 0.967704
O 0.001214 0.084065 0.090391
O 0.504260 0.118147 0.894441
O 0.501295 0.118477 0.263664
O 0.505284 0.314924 0.727794
O 0.496361 0.308144 0.467798
O 0.504048 0.084055 0.590242
O 0.000777 0.118266 0.394366
O 0.004914 0.118057 0.763686
O 0.980774 0.509829 0.388255
O 0.002314 0.490694 0.612062

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O  0.478350 0.490240 0.112034
O  0.497419 0.509440 0.888185
H  0.957836 0.590161 0.348090
H  0.985121 0.433442 0.328167
H  0.999495 0.409953 0.652031
H  0.003234 0.566975 0.672361
H  0.458546 0.409822 0.152177
H  0.483315 0.566576 0.172157
H  0.482770 0.590129 0.848280
H  0.498729 0.433171 0.827902
V  0.008563 0.847983 0.766599
V  0.000919 0.856790 0.064621
V  0.502736 0.847673 0.266588
V  0.505559 0.857079 0.564624
V  0.001274 0.152356 0.233599
V  0.003845 0.143029 0.935581
V  0.505188 0.152073 0.733610
V  0.500746 0.143277 0.435551
Mg 0.488434 0.500215 0.500143
Mg 0.983866 0.499907 0.000156
```

A.2 vdW-DF2

a 3.72 b 10.22 c 12.19
α 93.69 β 89.91 γ 90.19

```
O  0.985590 0.687118 0.767826
O  0.003369 0.690150 0.035154
O  0.002620 0.909338 0.919301
O  0.503622 0.876048 0.093399
O  0.496784 0.900056 0.726562
O  0.511624 0.687080 0.267712
O  0.492339 0.690060 0.535127
O  0.497624 0.909245 0.419292
O  0.996329 0.876029 0.593378
O  0.003345 0.900057 0.226580
O  0.999094 0.312634 0.231720
O  0.008138 0.309638 0.964306
O  0.003699 0.090491 0.080425
O  0.504850 0.123628 0.906342
O  0.499736 0.099706 0.273162
O  0.515909 0.312656 0.731734
O  0.494389 0.309718 0.464442
O  0.498892 0.090515 0.580447
O  0.997808 0.123691 0.406389
O  0.004466 0.099693 0.773130
O  0.974060 0.512746 0.387550
O  0.985072 0.487196 0.610682
O  0.502309 0.487284 0.110671
O  0.517725 0.512627 0.887803
H  0.949708 0.591914 0.346092
H  0.979333 0.436849 0.330406
H  0.961980 0.407761 0.651867
H  0.986901 0.562935 0.667905
H  0.501127 0.407643 0.151958
H  0.503372 0.563056 0.167932
H  0.540363 0.591848 0.846264
H  0.515140 0.436615 0.830729
V  0.995922 0.852257 0.758923
V  0.003683 0.856082 0.054840
V  0.503195 0.852203 0.258929
V  0.495908 0.856023 0.554842
V  0.000216 0.147583 0.240799
V  0.005312 0.143649 0.944856
V  0.505357 0.147541 0.740802
```

```
V  0.497214 0.143746 0.444904
Mg 0.470949 0.500035 0.498874
Mg 0.014872 0.500070 0.998956
```

B $Mg_{0.5}(H_2O)_{0.5}V_2O_5$

B.1 GGA

a 7.6 b 9.64 c 11.70
α 90.09 β 90.01 γ 90.03

```
O  0.018723 0.660442 0.801248
O  0.503369 0.674096 0.788641
O  0.502941 0.664674 0.058163
O  0.969969 0.689129 0.040815
O  0.008511 0.917888 0.909033
O  0.503137 0.911736 0.917501
O  0.242517 0.863398 0.112448
O  0.739369 0.881544 0.112763
O  0.256291 0.878434 0.743234
O  0.761000 0.863491 0.746959
O  0.231455 0.660276 0.301275
O  0.744994 0.673714 0.288714
O  0.278733 0.689638 0.540783
O  0.746211 0.664570 0.558194
O  0.240961 0.918159 0.408835
O  0.746336 0.911650 0.417446
O  0.006646 0.863617 0.612453
O  0.509978 0.881630 0.612688
O  0.993022 0.877452 0.243309
O  0.488365 0.863642 0.246922
O  0.973212 0.332049 0.209940
O  0.504986 0.335601 0.194503
O  0.000509 0.337457 0.942298
O  0.529790 0.309247 0.958492
O  0.996674 0.090521 0.082346
O  0.490246 0.080493 0.088904
O  0.256263 0.132039 0.887953
O  0.761536 0.122963 0.883375
O  0.240352 0.143033 0.251554
O  0.741219 0.120452 0.255069
O  0.276704 0.331699 0.710039
O  0.745291 0.335469 0.694649
O  0.249426 0.337591 0.442267
O  0.720593 0.309173 0.458611
O  0.253008 0.090630 0.582214
O  0.759481 0.080455 0.588877
O  0.993649 0.132042 0.387817
O  0.488324 0.123130 0.383328
O  0.009496 0.142630 0.751657
O  0.508629 0.120188 0.755101
O  0.939279 0.506173 0.392091
O  0.050977 0.490895 0.614560
O  0.199243 0.490921 0.114494
O  0.310305 0.505709 0.892037
H  0.865518 0.581007 0.352669
H  0.936054 0.428195 0.336070
H  0.130533 0.417589 0.649138
H  0.048340 0.565394 0.674053
H  0.119251 0.417830 0.149062
H  0.202596 0.565213 0.174149
H  0.383770 0.580620 0.852418
H  0.313242 0.427597 0.836121
```

V 0.009965 0.833402 0.776062
V 0.510216 0.843186 0.774743
V 0.989406 0.858967 0.073029
V 0.495052 0.839236 0.076889
V 0.239503 0.833244 0.276044
V 0.739063 0.842832 0.274780
V 0.259717 0.859492 0.572951
V 0.754159 0.839163 0.576905
V 0.987696 0.160759 0.224337
V 0.492120 0.166225 0.221608
V 0.004756 0.162952 0.921775
V 0.510663 0.139796 0.925840
V 0.262123 0.160385 0.724411
V 0.757830 0.166048 0.721638
V 0.245162 0.163088 0.421655
V 0.739313 0.139759 0.425795
Mg 0.189197 0.537391 0.448453
Mg 0.798486 0.462826 0.555600
Mg 0.451434 0.462743 0.055380
Mg 0.060563 0.537390 0.948429

B.2 vdW-DF2

a 7.66 b 9.76 c 11.85
α 90.12 β 90.01 γ 90.00

O 0.014473 0.657972 0.802591
O 0.510909 0.671329 0.788718
O 0.505969 0.663692 0.056456
O 0.968034 0.686047 0.041656
O 0.009176 0.916524 0.908590
O 0.503317 0.911704 0.917080
O 0.242412 0.860984 0.112216
O 0.738870 0.881482 0.113447
O 0.256603 0.872175 0.743826
O 0.761899 0.863384 0.746409
O 0.235408 0.658075 0.302608
O 0.738163 0.671472 0.288658
O 0.280993 0.686222 0.541692
O 0.743439 0.663609 0.556157
O 0.240501 0.916617 0.408607
O 0.746262 0.911614 0.417148
O 0.006929 0.861167 0.612273
O 0.510521 0.881401 0.613525
O 0.992871 0.872106 0.243802
O 0.487554 0.863855 0.246371
O 0.967967 0.333478 0.207158
O 0.508372 0.338487 0.195730
O 0.997231 0.338774 0.944937
O 0.531142 0.311986 0.958274
O 0.996860 0.089668 0.083147
O 0.489158 0.082754 0.089522
O 0.256092 0.134679 0.887719
O 0.761634 0.123074 0.883119
O 0.240138 0.148047 0.251955
O 0.741028 0.121672 0.255390
O 0.281584 0.333849 0.707176
O 0.741091 0.338753 0.695524
O 0.252222 0.338907 0.444913
O 0.718958 0.311914 0.458035
O 0.252607 0.089852 0.583205
O 0.760118 0.082726 0.589576
O 0.993581 0.134495 0.387777
O 0.487975 0.123083 0.383323
O 0.009414 0.148284 0.751860

O 0.508513 0.122208 0.755373
O 0.943190 0.506410 0.391926
O 0.045455 0.490378 0.613594
O 0.204164 0.490397 0.113687
O 0.306332 0.506231 0.892179
H 0.871224 0.579828 0.354743
H 0.936496 0.429911 0.336922
H 0.123204 0.417963 0.645926
H 0.044693 0.562794 0.672655
H 0.126710 0.417904 0.146126
H 0.205137 0.562899 0.172679
H 0.377937 0.579796 0.854922
H 0.313094 0.429828 0.837080
V 0.009855 0.830783 0.776979
V 0.511743 0.840259 0.775788
V 0.988789 0.856050 0.073238
V 0.495275 0.837935 0.075948
V 0.239734 0.830888 0.276983
V 0.737731 0.840407 0.275769
V 0.260535 0.856221 0.573283
V 0.754106 0.837792 0.575973
V 0.986211 0.163371 0.223164
V 0.492178 0.168727 0.221463
V 0.004428 0.164828 0.922514
V 0.510721 0.142307 0.926335
V 0.263278 0.163724 0.723170
V 0.757244 0.169004 0.721365
V 0.245166 0.164923 0.422588
V 0.739006 0.142152 0.426335
Mg 0.194209 0.536696 0.447626
Mg 0.791314 0.463610 0.556721
Mg 0.458309 0.463674 0.056893
Mg 0.055278 0.536561 0.947714

C $Mg_{0.25}(H_2O)_{0.5}V_2O_5$

C.1 GGA

a 3.70 b 10.30 c 11.70
α 93.16 β 90.00 γ 90.00

O 0.994055 0.681661 0.770223
O 0.992227 0.686517 0.041114
O 0.992967 0.901997 0.916043
O 0.492124 0.873440 0.098269
O 0.493862 0.878318 0.741277
O 0.489001 0.692938 0.282256
O 0.496694 0.691935 0.534809
O 0.493066 0.917585 0.410826
O 0.994258 0.880439 0.607630
O 0.991866 0.883823 0.231222
O 0.994030 0.318362 0.229775
O 0.992206 0.313498 0.958888
O 0.992961 0.098007 0.083961
O 0.492114 0.126564 0.901731
O 0.493855 0.121689 0.258723
O 0.488950 0.307084 0.717746
O 0.496679 0.308077 0.465193
O 0.493055 0.082423 0.589175
O 0.994254 0.119569 0.392369
O 0.991851 0.116183 0.768778
O 0.002581 0.487214 0.613306
O 0.002522 0.512798 0.386689

```
H  0.013649 0.408032 0.656137
H  0.000400 0.560394 0.673667
H  0.000357 0.439617 0.326333
H  0.013494 0.591973 0.343866
V  0.993986 0.839564 0.767550
V  0.992234 0.841754 0.060351
V  0.491515 0.849228 0.268792
V  0.494342 0.853962 0.565465
V  0.993975 0.160420 0.232452
V  0.992223 0.158238 0.939646
V  0.491495 0.150763 0.731211
V  0.494338 0.146045 0.434534
Mg 0.503726 0.500005 0.500001
```

C.2 vdW-DF2

a 3.71 b 10.79 c 11.97
α 94.46 β 90.00 γ 90.00

```
O  0.997991 0.678383 0.773927
O  0.995806 0.682138 0.041376
O  0.996779 0.900083 0.916920
O  0.496063 0.870813 0.098623
O  0.497815 0.875800 0.742287
O  0.494289 0.690090 0.285074
O  0.501527 0.689736 0.535341
O  0.496843 0.916831 0.410702
O  0.998296 0.878715 0.608636
O  0.995934 0.881097 0.231484
O  0.997979 0.321613 0.226060
O  0.995828 0.317854 0.958633
O  0.996775 0.099898 0.083059
O  0.496082 0.129182 0.901387
O  0.497795 0.124196 0.257725
O  0.494286 0.309919 0.714935
O  0.501523 0.310268 0.464666
O  0.496842 0.083166 0.589296
O  0.998288 0.121294 0.391373
O  0.995930 0.118897 0.768523
O  0.009286 0.485251 0.612706
O  0.009278 0.514753 0.387266
H  0.020759 0.405736 0.653895
H  0.007502 0.555484 0.672750
H  0.007502 0.444513 0.327233
H  0.020754 0.594265 0.346065
V  0.997963 0.836462 0.769721
V  0.995792 0.837818 0.059937
V  0.495613 0.846838 0.270429
V  0.498425 0.851811 0.565726
V  0.997928 0.163541 0.230303
V  0.995811 0.162174 0.940087
V  0.495622 0.153168 0.729606
V  0.498422 0.148215 0.434264
Mg 0.511816 0.500010 0.499988
```

D $Mg_{0.5}V_2O_5$

D.1 GGA

a 3.80 b 9.30 c 11.66
α 81.06 β 90.00 γ 90.00

```
O  0.000000 0.643397 0.852230
O  1.000000 0.665288 0.083636
O  0.000000 0.913845 0.923834
O  0.500000 0.865145 0.135109
O  0.500000 0.851165 0.767794
O  0.500000 0.643380 0.352247
O  0.500000 0.665274 0.583646
O  0.500001 0.913844 0.423826
O  0.000000 0.865153 0.635101
O  0.000000 0.851135 0.267800
O  0.000001 0.356612 0.147751
O  0.999999 0.334724 0.916351
O  0.000000 0.086154 0.076174
O  0.499999 0.134851 0.864902
O  0.500001 0.148864 0.232203
O  0.499998 0.356607 0.647762
O  0.500001 0.334728 0.416366
O  0.500000 0.086152 0.576167
O  0.000001 0.134859 0.364892
O  0.999999 0.148831 0.732208
V  0.000000 0.821104 0.802277
V  0.000000 0.843297 0.098352
V  0.500000 0.821088 0.302285
V  0.500000 0.843313 0.598345
V  0.000001 0.178922 0.197716
V  0.999999 0.156695 0.901656
V  0.499999 0.178874 0.697730
V  0.500000 0.156695 0.401647
Mg 0.500000 0.499993 0.500008
Mg 0.000000 0.500009 0.999985
```

D.2 vdW-DF2

a 3.84 b 9.42 c 11.81
α 81.25 β 90.00 γ 90.00

```
O  0.000000 0.641018 0.852240
O  1.000000 0.664284 0.082920
O  0.000000 0.913392 0.923015
O  0.500000 0.865008 0.135207
O  0.500000 0.848335 0.767933
O  0.500000 0.641020 0.352239
O  0.500000 0.664291 0.582919
O  0.500000 0.913394 0.423015
O  0.000000 0.865007 0.635210
O  1.000000 0.848339 0.267932
O  1.000000 0.358983 0.147761
O  0.000000 0.335711 0.917082
O  1.000000 0.086607 0.076987
O  0.500000 0.134991 0.864791
O  0.500000 0.151662 0.232068
O  0.500000 0.358978 0.647762
O  0.499999 0.335716 0.417081
O  0.500000 0.086609 0.576986
O  1.000000 0.134993 0.364793
O  0.000000 0.151663 0.732067
```

```
V  0.000000 0.818704 0.802898
V  1.000000 0.842020 0.097858
V  0.500000 0.818704 0.302898
V  0.500000 0.842012 0.597857
V  1.000000 0.181291 0.197104
V  0.000000 0.157986 0.902142
V  0.500000 0.181299 0.697099
V  0.500000 0.157983 0.402142
Mg 0.500000 0.500002 0.499997
Mg 1.000000 0.499998 1.000000
```

E V_2O_5

E.1 GGA

a 3.66 b 10.01 c 11.74
α 95.52 β 90.00 γ 90.00

```
O 0.000001 0.670473 0.763010
O 1.000000 0.674681 0.023638
O 1.000000 0.898770 0.911236
O 0.500000 0.865758 0.094277
O 0.500001 0.870801 0.728440
O 0.500005 0.670455 0.263025
O 0.500000 0.674705 0.523660
O 0.500000 0.898766 0.411224
O 1.000000 0.865786 0.594276
O 0.000001 0.870758 0.228435
O 0.999999 0.329548 0.236976
O 0.999999 0.325299 0.976336
O 0.000000 0.101241 0.088776
O 0.499999 0.134214 0.905724
O 0.500000 0.129249 0.271566
O 0.499998 0.329520 0.736989
O 0.499999 0.325316 0.476366
O 0.500000 0.101226 0.588764
O 0.000001 0.134244 0.405723
O 0.999999 0.129196 0.771561
V 1.000000 0.829570 0.760735
V 0.000000 0.833971 0.052166
V 0.500001 0.829532 0.260733
V 0.499999 0.833998 0.552168
V 0.000000 0.170476 0.239268
V 1.000000 0.165997 0.947830
V 0.499998 0.170427 0.739265
V 0.500001 0.166022 0.447833
```

E.2 vdW-DF2

a 3.69 b 9.30 c 11.90
α 95.85 β 90.00 γ 90.00

```
O 0.999999 0.638846 0.762683
O 0.999998 0.646554 0.020166
O 1.000000 0.890648 0.910330
O 0.499999 0.853980 0.093800
O 0.500000 0.857784 0.728221
O 0.499999 0.638839 0.262682
O 0.499999 0.646554 0.520159
O 0.500000 0.890650 0.410331
```

O 1.000000 0.853978 0.593800
O 0.999999 0.857788 0.228222
O 0.000001 0.361152 0.237321
O 0.000001 0.353443 0.979842
O 0.000000 0.109352 0.089671
O 0.500001 0.146022 0.906201
O 0.500000 0.142213 0.271778
O 0.500001 0.361161 0.737315
O 0.500001 0.353439 0.479831
O 0.500000 0.109349 0.589668
O 0.000001 0.146016 0.406198
O 0.000001 0.142214 0.771780
V 1.000000 0.812361 0.760578
V 0.999999 0.819929 0.050340
V 0.499999 0.812360 0.260579
V 0.499999 0.819931 0.550340
V 0.000001 0.187658 0.239422
V 0.000000 0.180075 0.949661
V 0.500001 0.187628 0.739423
V 0.500001 0.180074 0.449660

F $(H_2O)V_2O_5$

F.1 GGA

a 3.69 b 12.76 c 11.69
α 96.73 β 90.00 γ 87.30

O 0.009797 0.260547 0.241356
O 0.008987 0.257638 0.984181
O 0.036721 0.079652 0.090250
O 0.532557 0.107765 0.909180
O 0.533658 0.103184 0.272420
O 0.508475 0.261529 0.744906
O 0.508968 0.258083 0.478582
O 0.536864 0.081602 0.590319
O 0.032950 0.107157 0.407083
O 0.033223 0.103940 0.774440
O 0.092875 0.742053 0.755014
O 0.089037 0.744360 0.015786
O 0.062138 0.921049 0.907999
O 0.565481 0.894276 0.089884
O 0.566638 0.899559 0.725285
O 0.590146 0.741842 0.257383
O 0.593590 0.746359 0.516473
O 0.561977 0.922197 0.408504
O 0.067213 0.896728 0.590172
O 0.064944 0.898440 0.225283
O 0.938131 0.526170 0.409455
O 0.992064 0.429610 0.614666
O 0.461151 0.488863 0.247661
O 0.473544 0.506010 0.762279
H 0.745885 0.505394 0.349883
H 0.879355 0.600350 0.435758
H 0.781428 0.460138 0.663887
H 0.970158 0.459658 0.540744
H 0.431098 0.419899 0.204788
H 0.247443 0.502932 0.300604
H 0.275460 0.478624 0.708513
H 0.412135 0.580716 0.782872
V 0.028595 0.135001 0.242080
V 0.028583 0.132478 0.950440
V 0.528006 0.136677 0.742943

```
V 0.528735 0.132820 0.449921
V 0.071676 0.867829 0.756138
V 0.069323 0.869590 0.048540
V 0.569972 0.866815 0.255802
V 0.571199 0.872507 0.548528
```

F.2 vdW-DF2

a 3.69 b 11.28 c 11.91
α 94.37 β 90.06 γ 91.21

```
O 0.012689 0.296545 0.223760
O 0.015759 0.290131 0.963308
O 0.004596 0.090632 0.081978
O 0.507202 0.116921 0.898656
O 0.504587 0.116749 0.263977
O 0.525424 0.290447 0.727072
O 0.517718 0.294014 0.467973
O 0.504504 0.089659 0.579755
O 0.005868 0.121864 0.398199
O 0.007576 0.109599 0.763279
O 0.974437 0.705125 0.760126
O 0.977286 0.704064 0.023846
O 0.992493 0.907183 0.907888
O 0.490477 0.877415 0.090489
O 0.490733 0.886719 0.724869
O 0.483799 0.700736 0.260168
O 0.483035 0.705875 0.525380
O 0.492636 0.906159 0.405796
O 0.990883 0.879459 0.589638
O 0.991706 0.882445 0.224656
O 0.989996 0.530889 0.387412
O 0.130163 0.479850 0.621701
O 0.423683 0.482167 0.097812
O 0.451619 0.532257 0.862832
H 0.732571 0.517185 0.371174
H 0.011397 0.527705 0.469361
H 0.190828 0.517741 0.696257
H 0.341714 0.432329 0.601699
H 0.197092 0.439785 0.112329
H 0.438019 0.546724 0.157162
H 0.703964 0.514270 0.845757
H 0.426728 0.519955 0.943545
V 0.006031 0.153735 0.229921
V 0.008435 0.146662 0.940223
V 0.511250 0.147471 0.729940
V 0.508090 0.150879 0.440655
V 0.987462 0.848020 0.757902
V 0.988005 0.847303 0.047790
V 0.490010 0.844318 0.257984
V 0.489557 0.848998 0.547738
```

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