Supplementary Information

Voltage, Stability and Layer spacing calculations:

We use the Density Functional Theory (DFT)[1] as implemented in the Vienna Ab initio Simulation Package (VASP)[2,3] for our calculations. The Perdew-Burke-Ernzerhof (PBE) implementation of the Generalized Gradient Approximation (GGA) functional[4] is used to describe the exchange-correlation interactions. The wave functions are described using the Projector Augmented Wave (PAW) theory[5] with a well converged energy cut-off of 520 eV and are sampled on a Γ-centered 4x4x4 *k*-point mesh, and all structures are converged within 0.25 meV/f.u. A Hubbard *U* extension is added to the GGA Hamiltonian (GGA+*U*) to remove the spurious self-interaction errors on the *d*-electrons of vanadium.[6,7] The *U* value is set to 3.1 eV, as obtained by Jain *et al.*[8]

The V_2O_5 layers in the fully deintercalated α and δ polymorphs are bound by van der Waals interactions, which are not well described by standard DFT.[9–11] Hence, in order to obtain a better estimate of the spacing between the layers in α and δ-V_2O_5, we used the vdW-DF2 (+*U*) functional[12,13] to describe the van der Waals forces instead of the PBE (+*U*) functional. Though including the van der Waals interactions in DFT gives better agreement with experimental layer spacing values, it leads to higher errors in the calculated average voltages as pointed out by Carrasco.[14]

Migration barrier calculations:

The Nudged Elastic Band (NEB)[15] method is used to estimate the activation barriers for ionic diffusion in α and δ-V_2O_5. In order to minimize the fictitious interactions between periodic images, a distance of at least 9 Å is introduced between the diffusing species and a total of nine images are used between the endpoints to capture the diffusion trajectory. The endpoint energies are converged to 0.01 meV/supercell while the forces in the NEB are considered converged within 0.1 eV/Å. Standard GGA is used for the NEB calculations since the convergence of GGA+*U* NEB calculations is problematic.[16]

Mechanical Instability:

In a few thermodynamically unstable structures (see **Fig. 2c** in the manuscript), such as Li, Mg and Zn (in the intercalated α-V_2O_5), Al (in both intercalated and deintercalated α) and Ca (in the intercalated δ-V_2O_5) the energies of the initial and final states for the NEB could not be converged. At first glance, all these structures undergo a shear-like transformation (mechanical instability), which involves the sliding of alternating V_2O_5 layers along the *a*-direction, leading to an artificial change in the layer stacking from α to δ (and vice-versa in the case of Ca in δ-V_2O_5).

Mg migration barrier in the "ε" phase:

In order to estimate the change in the migration barriers with increasing Mg concentration, we performed NEB calculations on a specific Mg ordering at half Mg insertion in α-V_2O_5, referred to as the "ε" phase. Consisting of alternate Mg sites occupied in the *a* direction, the ε phase has also been observed in the Li-V_2O_5 system.[17] The NEB calculations on the ε phase require a vacancy in the supercell, and two

symmetrically equivalent hops to account for the specific Mg ordering of this phase. The migration energies displayed in **Fig. 3a** in the manuscript (dashed red lines) correspond to half of the total path explaining the difference in energies between the NEB endpoints.

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