

Supporting Information: Phase stability of intercalated V_2O_5 battery cathodes elucidated through the Goldschmidt tolerance factor

Kit McColl¹ and Furio Corà¹

¹Department of Chemistry, University College London, 20 Gordon Street,
London, WC1H 0AJ, United Kingdom

February 7, 2019

Contents

1	Constrained geometry optimisations	2
2	Magnetic ordering of V^{4+} ions in MV_2O_5	4
3	Structural properties of MV_2O_5 phases	6

1 Constrained geometry optimisations

Our calculations on ionic migration and layer translation have been performed using constrained geometry optimisations. Constrained optimisations may over-estimate activation barriers compared to techniques such as nudged elastic-band (NEB) calculations in some cases where reaction steps involve a change of more than one geometric coordinate. However, this is not expected to be an issue for ionic migration in α - and δ - V_2O_5 , in both of which the migration pathway consists of an elementary reaction step, with a highly symmetric profile.¹⁻³

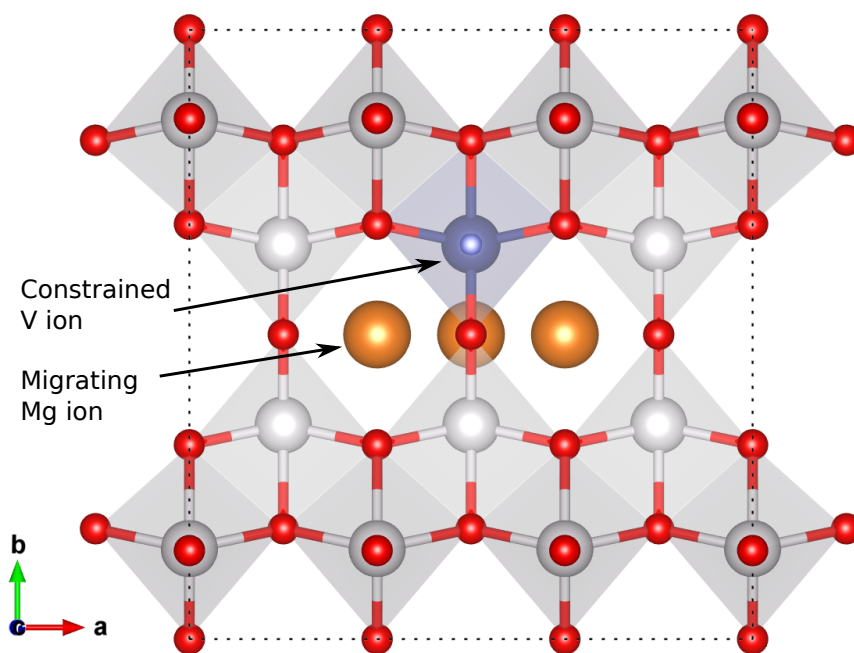


Figure S1: Details of constrained geometry optimisations to determine Mg migration barrier in α - V_2O_5 . The V ion indicated in blue was constrained during the optimisation, along with the a coordinate of the migrating Mg ion.

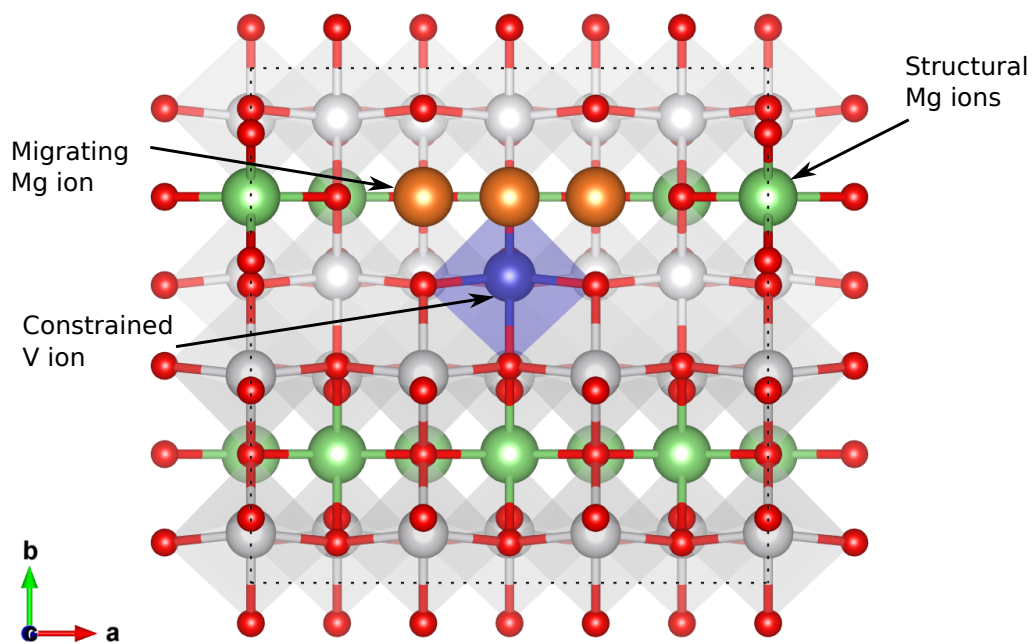


Figure S2: Details of constrained geometry optimisations to determine Mg migration barrier in δ - MgV_2O_5 . The V ion indicated in blue was constrained during the optimisation, along with the a coordinate of the migrating Mg ion. The structural Mg ions are shown here in green, with the migrating Mg ion shown in orange.

2 Magnetic ordering of V^{4+} ions in MV_2O_5

The d^1 electrons on V^{4+} ions in MV_2O_5 may be aligned in either a ferromagnetic (FM) or antiferromagnetic (AFM) order. Here we consider 3 possible AFM configurations, identified previously as being the lowest energy orderings.⁴ The energy difference between magnetic orderings is always <50 meV/f.u., and will not contribute significantly to the relative stability of α vs. δ for each MV_2O_5 phase. For computational ease, we therefore selected FM orderings for all cases in systems containing d^1 electrons.

Table S1: Energetics and structural properties of different magnetic orderings of α - MgV_2O_5 . Values in brackets indicate the difference respect to the calculated lattice parameters for the FM case

α - MgV_2O_5	ΔE (eV/f.u.)	a (Å)	b (Å)	c (Å)
FM	0.000	3.4313	11.1978	4.7093
AFM1	-0.034	3.4391 (0.2 %)	11.2045 (0.1 %)	4.7030 (-0.1 %)
AFM2	-0.015	3.4363 (0.1 %)	11.1900 (-0.1 %)	4.7003 (-0.2 %)
AFM3	-0.011	3.4312 (0.0 %)	11.2086 (0.1 %)	4.7078 (0.0 %)

Table S2: Energetics and structural properties of different magnetic orderings of δ - MgV_2O_5 . Values in brackets indicate the difference respect to the calculated lattice parameters for the FM case

δ - MgV_2O_5	ΔE (eV/f.u.)	a (Å)	b (Å)	c (Å)
FM	0.000	3.6673	9.9088	10.9417
AFM1	-0.021	3.6658 (0.0 %)	9.8933 (-0.2 %)	10.9531 (0.1 %)
AFM2	-0.005	3.6715 (0.1 %)	9.8976 (-0.1 %)	10.9375 (0.0 %)
AFM3	-0.016	3.6656 (0.0 %)	9.8996 (-0.1 %)	10.9484 (0.1 %)

Table S3: Energetics and structural properties of different magnetic orderings of α - CaV_2O_5 . Values in brackets indicate the difference respect to the calculated lattice parameters for the FM case

α - CaV_2O_5	ΔE (eV/f.u.)	a (Å)	b (Å)	c (Å)
FM	0.000	3.6029	11.2193	4.7800
AFM1	-0.047	3.6026 (0.0 %)	11.2304 (0.1 %)	4.7667 (-0.3 %)
AFM2	-0.030	3.6059 (0.1 %)	11.2188 (0.0 %)	4.7686 (-0.2 %)
AFM3	-0.013	3.6008 (-0.1 %)	11.2320 (0.1 %)	4.7795 (0.0 %)

Table S4: Energetics and structural properties of different magnetic orderings of δ -CaV₂O₅. Values in brackets indicate the difference respect to the calculated lattice parameters for the FM case

δ -CaV ₂ O ₅	ΔE (eV/f.u.)	a (Å)	b (Å)	c (Å)
FM	0.000	3.7265	10.9595	11.1558
AFM1	-0.022	3.7275 (0.0 %)	10.9664 (0.1 %)	11.1467 (-0.1 %)
AFM2	-0.004	3.7288 (0.1 %)	10.9546 (0.0 %)	11.1399 (-0.1 %)
AFM3	-0.012	3.7291 (0.1 %)	10.9533 (-0.1 %)	11.1567 (0.0 %)

3 Structural properties of MV_2O_5 phases

Table S5: Structural properties of α - MV_2O_5 . Values in brackets indicate the expansion or contraction with respect to the calculated lattice parameters for the undoped V_2O_5 phase

M	r (Å)	a (Å)	b (Å)	c (Å)	Vol (Å ³)
No dopant		3.544	11.490	4.378	178.27
Li ⁺	0.76	3.598 (+1.5%)	11.091 (-3.5%)	4.567 (+4.3 %)	182.20 (+2.2 %)
Be	0.45	3.584 (+1.1%)	10.432 (-9.2%)	4.707 (+7.5 %)	175.98 (-1.3%)
Fe (ls)	0.61	3.526 (-0.5%)	11.099 (-3.4%)	4.668 (+6.6 %)	182.65 (+2.5 %)
Mg	0.72	3.431 (-3.2%)	11.198 (-2.5%)	4.709 (+7.6 %)	180.95 (+1.5 %)
Zn	0.74	3.493 (-1.4%)	11.255 (-2.0%)	4.709 (+7.6 %)	185.11 (+3.8 %)
Fe (hs)	0.78	3.509 (-1.0%)	11.156 (-2.9%)	4.668 (+6.6 %)	182.74 (+2.5 %)
Cd	0.95	3.572 (+0.8%)	11.303 (-1.6%)	4.805 (+9.8 %)	194.02 (+8.8 %)
Ca	1.00	3.603 (+1.7%)	11.219 (-2.4%)	4.780 (+9.2 %)	193.21 (+8.4 %)
Sr	1.18	3.728 (+5.2%)	11.175 (-2.7%)	4.921 (+12.4%)	204.99 (+15.0%)
Ba	1.35	3.876 (+9.4%)	10.850 (-5.6%)	5.349 (+22.2%)	224.94 (+26.2%)

Table S6: Structural properties of δ - MV_2O_5 . Values in brackets indicate the expansion or contraction with respect to the calculated lattice parameters for the undoped V_2O_5 phase

M	r (Å)	a (Å)	b (Å)	c (Å)	Vol (Å ³)
No dopant		3.559	11.356	9.375	378.940
Li ⁺	0.76	3.615 (+1.6%)	11.113 (-2.1%)	9.669 (+3.1%)	388.441 (+2.5%)
Be	0.45	3.296 (-7.4%)	11.781 (+3.7%)	9.251 (-1.3%)	359.220 (-5.2%)
Fe (ls)	0.61	3.703 (+4.0%)	10.769 (-5.2%)	10.010 (+6.8%)	399.224 (+5.4%)
Mg	0.72	3.667 (+3.0%)	10.942 (-3.6%)	9.909 (+5.7%)	397.602 (+4.9%)
Zn	0.74	3.617 (+1.6%)	11.193 (-1.4%)	10.013 (+6.8%)	405.363 (+7.0%)
Fe (hs)	0.78	3.678 (+3.3%)	11.098 (-2.3%)	10.065 (+7.4%)	410.856 (+8.4%)
Cd	0.95	3.679 (+3.4%)	11.311 (-0.4%)	10.866 (+15.9%)	452.172 (+19.3%)
Ca	1.00	3.727 (+4.7%)	11.156 (-1.8%)	10.960 (+16.9%)	455.616 (+20.2%)
Sr	1.18	3.782 (+6.2%)	11.053 (-2.7%)	11.794 (+25.8%)	492.939 (+30.1%)
Ba	1.35	3.872 (+8.8%)	10.642 (-6.3%)	12.771 (+36.2%)	526.198 (+38.9%)

References

- [1] G. S. Gautam, P. Canepa, R. Malik, M. Liu, K. Persson and G. Ceder, *Chem. Commun.*, 2015, **51**, 13619–13622.
- [2] G. S. Gautam, P. Canepa, A. Abdellahi, A. Urban, R. Malik and G. Ceder, *Chem. Mater.*, 2015, **27**, 3733–3742.

- [3] Z. Rong, R. Malik, P. Canepa, G. S. Gautam, M. Liu, A. Jain, K. Persson and G. Ceder, *Chem. Mater.*, 2015, **27**, 6016–6021.
- [4] M. A. Korotin, V. I. Anisimov, T. Saha-Dasgupta and I. Dasgupta, *J. Phys. Condens. Matter*, 2000, **12**, 113–124.