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# Phase stability of intercalated V<sub>2</sub>O<sub>5</sub> battery cathodes elucidated through the Goldschmidt tolerance factor

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Orthorhombic V<sub>2</sub>O<sub>5</sub> is a promising Mg battery cathode material, and reversible intercalation in the layered  $\alpha$ -phase has been claimed experimentally. However, these results, based on electrochemistry and XRD, are controversial. Previous computational studies have predicted high activation barriers (~1 eV) for ionic migration in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, although improved Mg<sup>2+</sup> mobility is expected in the  $\delta$ -phase. Here, hybrid-exchange density functional theory is used to discuss structure, stability and intercalation in the  $\alpha$  and  $\delta$  phases, beginning with a model system with MV<sub>2</sub>O<sub>5</sub> stoichiometry, and varying ionic radius of the M cations. The relative stability of the two phases upon intercalation of M is rationalised through a tolerance factor-like behavioural trend, providing a framework for phase selection using intercalants of different ionic size. This tolerance factor behaviour is due to the presence of ferroelectrically distorted  $(2 \times 2 \times 2)$  perovskite blocks within the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure. The  $\delta$ -phase is found to undergo a barrierless phase change to  $\alpha$  in fully charged (de-intercalated) Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> (x=0), indicating that stabilisation of  $\delta$ -Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> is required at low x if the  $\delta$  phase is to be retained for higher Mg mobility. By employing dispersion interactions to accurately reproduce the interlayer distance, activation barriers for ion migration are found to be higher than reported in previous studies, clarifying questions regarding the extent of Mg intercalation that can be achieved experimentally. Interlayer ions are found to lower activation barriers for Mg<sup>2+</sup> mobility by up to  $\sim$ 330 meV in the  $\alpha$  phase by expanding the interlayer space. The results address open questions about the electrochemical performance of orthorhombic  $V_2O_5$  as Mg battery cathode material, and indicate atomic level mechanisms that activate ionic mobility in layered V<sub>2</sub>O<sub>5</sub>.

# 1 Introduction

Multivalent batteries based on Mg<sup>2+</sup> intercalation chemistry provide a route to surpassing the volumetric and specific energy density of current Li-ion battery technology.<sup>1</sup> In a Li-ion battery, an intercalation host is required at the anode, to avoid dendritic growth of Li metal upon cycling, leading to battery shortcircuiting and failure.<sup>2</sup> In a Mg battery, metallic Mg may be used at the anode.<sup>3</sup> Dendritic growths have been observed for Mg anodes under some conditions.<sup>4</sup> However, metallic Mg plates more uniformly than Li, making Mg metal anode viable if electrolyte conditions are controlled.<sup>1,5,6</sup> By removing the intercalation host at the anode, significant savings in volumetric and specific energy density are made, meaning magnesium batteries can surpass energy densities of current Li-ion technology.<sup>1,7</sup>

One of the main challenges in developing Mg batteries is find-

ing a suitable cathode material with sufficient voltage, theoretical capacity and Mg ion mobility. At present, the choice of materials is narrow. Many compounds that can intercalate Li<sup>+</sup> ions cannot be used in Mg batteries, since they either undergo conversion reactions, exhibit such limited Mg kinetics that they are impractical, or have low voltage and limited energy density.<sup>7</sup> The prototypical Mg battery demonstrated by Aurbach *et al.* employed a Mo<sub>6</sub>S<sub>8</sub> Chevrel phase cathode which provided reasonable kinetics, but the low operating voltage of ~1.1 eV vs. Mg metal resulted in limited energy density of ~70 mA h g<sup>-1</sup>.<sup>3</sup> Many subsequent works demonstrating reversible Mg kinetics in cathode materials have also used sulphide based materials, and all have had limited energy densities, due to their low voltages.<sup>8–10</sup>

One fundamental route to improving energy density is to move from sulphide to oxide based materials which have higher ionic character, thus providing higher voltages vs. Mg metal, whilst the lower atomic mass of O relative to S reduces weight.<sup>7</sup> However the very feature that enhances intercalation voltage, *i.e.* the stronger electrostatic interaction between the Mg ion and the anionic framework of the oxide cathode host, also increases acti-



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vation barriers for ionic migration, leading to reduced mobility and poor kinetics.<sup>7</sup> Improving the limited kinetics of oxide based  $Mg^{2+}$  cathode materials is therefore a key challenge for Mg batteries that can provide competitive energy density to Li-ion batteries.

Orthorhombic V<sub>2</sub>O<sub>5</sub> is considered one of the most promising oxide cathode materials for Mg batteries.<sup>7</sup> The accessible reversible redox between V<sup>5+</sup> and V<sup>4+</sup> allows relatively easy distribution of the electrons that are co-introduced by the divalent Mg<sup>2+</sup> ions, mitigating conversion reactions. V<sub>2</sub>O<sub>5</sub> has an average operating voltage of ~2.5 V, and its layered structure can accommodate 1 Mg per formula unit (MgV<sub>2</sub>O<sub>5</sub>) providing a theoretical capacity of ~300 mA g<sup>-1</sup>.

Despite these attractive properties, critical issues remain that have limited progress in applying V<sub>2</sub>O<sub>5</sub> as a Mg cathode material. Experimentally, it has often been reported that Mg is insertable only up to a stoichiometry of Mg<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub>, limiting the capacity to ~150 mA g<sup>-1</sup>.<sup>11,12</sup> Theoretical results have predicted the existence of a stable ordering of Mg ions in  $\alpha$ -Mg<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub> (denoted  $\varepsilon$ -Mg<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub>),<sup>13</sup> which has subsequently been reported experimentally, based on local STEM images.<sup>12</sup> Such an ordering is predicted to limit further Mg insertion.

Furthermore, questions have been raised about the extent of Mg intercalation into  $V_2O_5$  in numerous reports, based on a critical evaluation of electrochemical results and structural characterisation.<sup>14</sup> The incorporation of water, or electrolyte degradation and concurrent proton intercalation rather than the desired Mg intercalation have been shown to give similar structural and electrochemical signals to those previously reported for Mg intercalation.<sup>14,15</sup> These observations highlight both the difficulties of achieving Mg intercalation electrochemically and the extent of subsequent chemical and structural analysis required to confirm Mg intercalation.

The challenge of achieving Mg intercalation into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> is apparent from the predicted ionic mobility of Mg. Activation barriers for mobility are calculated to be ~1000 meV or higher, <sup>13,16–18</sup> far greater than the maximum estimated for a reasonable ionic mobility in a battery cathode material. <sup>19</sup> Mobility in the  $\delta$ -phase is predicted to be improved by several orders of magnitude over  $\alpha$ , due to lower activation barriers of ~600-700 meV yet these still translate to low ionic mobility at room temperature. <sup>13,17,19</sup>

Orthorhombic V<sub>2</sub>O<sub>5</sub> has also attracted attention as a proposed cathode materials in Ca-ion batteries and intercalation has been claimed experimentally.<sup>20,21</sup> However activation barriers for Ca mobility in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> are thought to exceed 1500 meV, indicating that Ca insertion into the structure is extremely challenging.<sup>17,22</sup> Low barriers of ~200 meV are predicted in the  $\delta$ -phase,<sup>17</sup> yet  $\delta$ -CaV<sub>2</sub>O<sub>5</sub> is not known to exist. Indeed,  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub> is predicted to be stable over  $\delta$ -CaV<sub>2</sub>O<sub>5</sub>,<sup>22</sup> and  $\alpha$ -phase CaV<sub>2</sub>O<sub>5</sub> is observed experimentally as a spin-ladder system.<sup>23,24</sup> Electronic conductivity and formation of stable localised lattice distortions (polarons) are additional factors proposed to affect mobility of intercalated ions in V<sub>2</sub>O<sub>5</sub>.<sup>25–29</sup>

One key factor affecting intercalation in  $Mg_xV_2O_5$  is the crystal structure at varying *x* compositions. The structure of  $V_2O_5$  has been investigated as a Li-ion battery cathode, and it is known to



**Fig. 1** a)  $2 \times 1 \times 2$  expansion of the primitive unit cell of  $\alpha$ -V<sub>2</sub>O<sub>5</sub>. b)  $2 \times 1 \times 1$  expansion of the crystallographic unit cell of  $\delta$ -V<sub>2</sub>O<sub>5</sub>. The structures are viewed along the *a* and *b* directions and in a 3D projection (left - right). Interatomic and bond distance are indicated.

undergo multiple phase changes upon lithiation. These phases are well characterised and are relevant to Mg battery chemistry, so we outline them here.

In its fully charged state (V2O5) the stable polymorph under ambient conditions is the orthorhombic  $\alpha$ -phase, shown in Figure 1a. In the Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> system, the following phases are observed at increasing values of *x*;  $\alpha$  (*x* < 0.1),  $\varepsilon$  (0.3 < *x* < 0.7),  $\delta$  (0.9 < *x* < 1.0),  $\gamma$  (1.0 < *x* < 2.0) and  $\omega$  (*x* > 2.0).<sup>30,31</sup> The phases are linked as follows:  $\varepsilon$  constitutes a low energy ordering of intercalant ions arranged in the structure of the  $\alpha$  phase, with ions separated to minimise Coulombic repulsion. The  $\delta$  phase (Figure 1b) is formed by a translation of adjacent layers in the  $\alpha$ polymorph, by a/2, and a simultaneous 'puckering' of the layers to form a different coordination environment around each intercalated ion. The  $\gamma$  phase constitutes a flipping of half the VO<sub>5</sub> pyramids and a significant buckling of the layers. The  $\omega$ -phase is a disordered rocksalt structure.<sup>32</sup> In the Mg<sub>r</sub>V<sub>2</sub>O<sub>5</sub> system, the  $\gamma$  and  $\omega$  phases are not observed, <sup>33</sup> and the predicted state of a fully discharged cathode (*i.e.* x=1 in Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub>), is the  $\delta$  phase.<sup>13</sup>

Since mobility of Mg is predicted to be higher by several orders of magnitude in the  $\delta$ -phase than  $\alpha$ , it has been proposed that starting in the  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> and removing Mg could be a route to improved electrochemical performance.<sup>13</sup> However an attempt to electrochemically extract Mg from  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> at ambient and elevated temperatures was unsuccessful,<sup>14</sup> suggesting that Mg mobility in the  $\delta$ -phase is more limited than predicted.

An additional consideration that arises with this strategy is the stability of the  $\delta$ -Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase at low *x*. In the Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase diagram, the  $\delta$ -phase is observed only between 0.9 < *x* < 1.<sup>30</sup> In the Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> system, the  $\delta$ -phase has not been observed for *x* < 1, and calculations predict the instability of  $\delta$ -Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> to transformation into  $\alpha$ -Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> for some arrangements of Mg in the structure.<sup>13</sup>

De-intercalated  $\delta$ -V<sub>2</sub>O<sub>5</sub> has been suggested to be metastable, <sup>13</sup> yet it has not been observed experimentally. A density functional

theory (DFT) investigation by Zhou *et al.* on the initial stages of Mg-insertion into V<sub>2</sub>O<sub>5</sub> identified that there was a barrierless and downhill energy pathway for a phase change from  $\delta$  to  $\alpha$ .<sup>16</sup> The instability of the  $\delta$ -phase of Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> at low *x* would have significant implications for the cycling of Mg starting with the fully discharged  $\delta$ -MgV<sub>2</sub>O<sub>5</sub>.

One possibility is that removal of Mg would result in transformation of the structure to the  $\alpha$ -phase, whereby Mg reinsertion would be limited by the poor kinetics in that phase. <sup>13,16,17,19</sup> Removal of only some fraction of the Mg to prevent a transformation to the  $\alpha$ -phase would lead to reduced capacity, compared to fully cycling to x=0. This type of behaviour would mirror the phase changes of Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> spinel. <sup>34</sup>

It is therefore important to understand the factors affecting phase stability of the  $\alpha$  and  $\delta$ -V<sub>2</sub>O<sub>5</sub> polymorphs, ionic mobility in each phase and how mobility can be improved in a systematic way. Of particular interest is a strategy to stabilise the  $\delta$ -Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase at low *x*, retaining the improved ionic mobility of this phase over a broad range of *x*.

A number of experimental studies have shown that the incorporation of aliovalent cations into the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure, into either substitutional or interlayer sites can improve electrochemical performance for Li-ion cathode materials, <sup>35–61</sup> and such strategies may also be applicable for Mg battery cathode materials. <sup>62</sup> The location and effect of dopants however, is challenging to determine experimentally, and an understanding of where dopants are located in the structure is only recently emerging from computational investigations. <sup>62,63</sup>

Here we examine the structure of  $V_2O_5$  with a range of different intercalated ions, using hybrid-exchange DFT. We investigate the effect of the intercalated ions on the stability of  $\alpha$  and  $\delta$ -V<sub>2</sub>O<sub>5</sub> phases using a model MV<sub>2</sub>O<sub>5</sub> system. We demonstrate that the relative stability of the  $\alpha$  and  $\delta$  phases of V<sub>2</sub>O<sub>5</sub> can be modified by varying the size of intercalant or dopant ions M, with behaviour that mirrors the tolerance factor of perovskites, and can be rationalised with the presence of  $(2 \times 2 \times 2)$  perovskite-like structural units in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>. We therefore provide a theoretical framework for modifying the stability of the  $\alpha$  and  $\delta$  polymorphs of V<sub>2</sub>O<sub>5</sub> through doping or interlayer ion incorporation. We then extend the work to examine the energetics of the  $\alpha$  to  $\delta$  phase transition, and the effect of different interlayer ions on the migration barriers of Mg<sup>2+</sup> ions in the  $\alpha$  and  $\delta$  phases. We conclude by discussing modifications that could be used to affect the electrochemical properties of V<sub>2</sub>O<sub>5</sub> for Mg and Li-ion batteries.

# 1.1 Structure of $\alpha$ and $\delta$ -V<sub>2</sub>O<sub>5</sub> and similarities to perovskite units in the $\alpha$ -phase.

The stable polymorph of  $V_2O_5$  under ambient conditions is the orthorhombic  $\alpha$ -phase which crystallises in space group *Pmmn* (no. 59) with lattice constants a=3.564, b=11.512 and c=4.368 Å.<sup>64</sup> The structure is generally considered to be layered (Figure 1a), and is formed of distorted square VO<sub>5</sub> pyramids, arranged such that each shares three corners and two edges with neighbouring pyramids in the [001] plane. Layers are stacked in an AA regime, with each VO<sub>5</sub> pyramid pointing towards an image of itself in the next layer. There are two V<sub>2</sub>O<sub>5</sub> formula units in the crystallographic unit cell, which contains four symmetry unique atoms: one vanadium and three oxygens, conventionally denoted O1, O2 and O3<sup>65</sup>. O1 is the oxygen at the end of the short (1.585 Å) V-O1 'vanadyl' bond. Two-fold coordinate O2 atoms link between corner sharing VO<sub>5</sub> pyramids along the *b* axis, and three fold coordinate O3 atoms link corner-sharing pyramids in the *a* direction. The interatomic V-O1 interlayer distance of ~2.79 Å is considered too long to be a conventional ionic or covalent interaction<sup>66</sup> which leads to the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure being interpreted as layered in the [001] plane, with the interlayer forces predominantly of weak van-der Waals (vdW) type. The distortions of the  $\delta$ -phase, discussed above, leave the general structure of the layers similar to those of  $\alpha$ , without undergoing atomic rearrangement. However, the layers in  $\delta$  are stacked in an AB regime.

 $\alpha$ -V<sub>2</sub>O<sub>5</sub> is generally depicted as layered, however a representation that introduces the  $\sim$ 2.79 Å interlayer V-O1 bonds to the picture (Figure 2a) reveals that the interlayer interstices in which dopant and intercalant ions reside, 62 enclosed by the V-O1 'vanadyl', V-O2, V-O3 and V-O1 interlayer bonds (Figure 2b) are structurally related to the (2×2×2)  $BO_6$  octahedral cornersharing unit in which the A site-cation resides (Figure 2c) in an ABO<sub>3</sub> perovskite. An alternative understanding of 'layered'  $\alpha$ -V2O5 is thus as a 3D structure formed by highly ferroelectric (FE)-like distorted VO<sub>6</sub> octahedra, which are linked through their axial V-O bonds along the (interlayer) c-direction, and 4 octahedral neighbours are linked through their equatorial O-bonds to form empty perovskite-like units. Rather than being linked only through octahedral corners as in a true perovskite, the V<sub>2</sub>O<sub>5</sub> perovskite-like units are linked along the [001] plane across shared edges to neighbouring units. The ferroelectric distortion of d<sup>0</sup> B cations in perovskites is a well-known phenomenon,<sup>67</sup> and the units of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> can be considered an extreme version of this effect, where the interlayer forces are reduced to a vdWtype interaction only,<sup>66</sup> but the octahedral coordination of the vanadium ions is essentially retained. The layer translation phase change from  $\alpha \rightarrow \delta$  constitutes a breaking of the weak V-O1 interlayer vdW-type bonds, thus the  $\delta$  phase no longer exhibits the perovskite-like structural units.

The distortions of  $ABO_3$  perovskites from the cubic phase can be rationalised using the concept of tolerance factor. <sup>68</sup> The Goldschmidt tolerance *Z* is a dimensionless parameter characterised by the expression:

$$Z = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \tag{1}$$

where  $r_A$ ,  $r_B$  and  $r_O$  are the radii of the A and B site cations and oxygen respectively. Typically the following behaviour is seen: if Z > 1 the B cation 'rattles' in an expanded octahedron, giving rise to stable FE-like distortions for d<sup>0</sup> transition metal ions. At Z=1 the ions are of perfect size, allowing the formation of cubic perovskites. Generally between 0.9 < Z < 1.0 perovskites with cubic symmetry can still form. Between 0.8 < Z < 0.9 the A site cations become too small to fit perfectly into the octahedral holes between the BO<sub>6</sub> framework, and thus tilting of the BO<sub>6</sub> octahedra is observed, which reduces the size of the A site and stabilises the structure. This produces perovskites with orthorhombic or



**Fig. 2** a) Representation of the structure of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> including and omitting the V-O1 interlayer (vdW) bonds, highlighting the perovskite-like units that are apparent when the interlayer bonds are illustrated. b) A model of  $\alpha$ -Mg<sub>0.5</sub>Ba<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub>, indicating the approximate location that Mg and Ba dopant or intercalant ions occupy in the structure, residing in the perovskite-like units. c) A prototypical ABO<sub>3</sub> perovskite for comparison, cubic BaTiO<sub>3</sub>.

rhombohedral symmetry. Below Z=0.8 the A and B cations approach similar sizes and non-perovskite structures form. Since  $\alpha$ -V<sub>2</sub>O<sub>5</sub> contains (2×2×2) perovskite blocks enclosing the interlayer interstitial sites, we explore whether the Goldschmidt tolerance factor *Z* can be employed to rationalise the phase stability trends in intercalated V<sub>2</sub>O<sub>5</sub>.

We begin with a model of  $\alpha$ -MV<sub>2</sub>O<sub>5</sub>, with full occupation of M ions into the V<sub>2</sub>O<sub>5</sub> interstices. In this model, the M cation is equivalent to the A site in a perovskite, and the V ion occupies a site equivalent to the B cation. We then construct the stoichiometrically equivalent  $\delta$ -MV<sub>2</sub>O<sub>5</sub> structure, which no longer exhibits perovskite-like units, and assess the relative stability of the  $\alpha$  and  $\delta$  phases as the size of the M ions is varied.

#### 2 Computational methods

First-principles calculations were performed using the periodic density functional theory (DFT) code CRYSTAL17.<sup>69,70</sup> Electronic exchange and correlation were approximated using the hybrid-exchange functional B3LYP, which is known to give accurate estimates of the band structure of transition metal oxides which exhibit highly correlated electrons.<sup>71</sup> Atom-centred Gaussian basis sets were used for all atoms, available from the CRYSTAL online database (www.crystal.unito.it). All electron basis sets were used for the following atoms, indicated by the associated labels online: V (V-86-411d31G-harrison-1993), O (O-8-411d1-cora-2005), Li (Li-5-11(1d)G-baranek-2013), Be (Be-6-211d1G-2012), Mg (Mg-8-511d1G-valenzano-2006), Zn

(Zn-86-411d31G-jaffe-1993), Fe (Fe-s86411p6411d411-Heifets-2013), Cd (Cd-dou-1998), Ca (Ca-86-511d21G-valenzano-2006). Effective core pseudopotential basis sets were used for the following atoms: Sr (Sr-ECP28MDF-s411p411d11-Heifets-2013) and Ba (Ba-m-S-RSC-Heyd-2005). The Coulomb and exchange series were truncated with thresholds of  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$ ,  $10^{-7}$  and  $10^{-14}$ . Reciprocal space was sampled using a Pack-Monkhorst net,<sup>72</sup> with a shrinking factor of IS=8 along each periodic direction. The self-consistent field (SCF) procedure was performed up to a convergence threshold of  $\Delta E = 10^{-8}$  Hartree per unit cell. Full geometry optimisations (lattice parameters and atomic positions) were performed using the default convergence criteria in CRYS-TAL17.69 Activation barriers were determined by running constrained geometry optimisations, by fixing the motion of the ion in question along the direction of migration, and performing a set of calculations at fixed intervals along the pathway. To ensure the entire structure does not move along with the ion, a single additional atom in the structure was also constrained. The location of these constrained structural V atoms are indicated for the  $\alpha$  and  $\delta$  phases in Figures S1 and S2.  $3 \times 1 \times 2$  expansions of the primitive unit cell of  $\alpha$  and  $3 \times 1 \times 1$  expansions of the crystallographic unit cell of  $\delta$ -V<sub>2</sub>O<sub>5</sub> were chosen, allowing a minimum distance of 7 Å between each migrating ion. Similar constrained geometry optimisations were conducted to examine the energetics of phase transition between  $\alpha$  and  $\delta$  phases.  $1 \times 1 \times 2$  and  $1 \times 1 \times 1$ expansions of the primitive and crystallographic unit cells of  $\alpha$ and  $\delta$  phases respectively were chosen to give a match between cell sizes. A linear interpolation of atomic positions between the two structures was performed, creating a set of images. In each of these images an atom in each layer was constrained in the direction of translation, and geometry optimisations were performed, allowing all other parameters to relax, determining the energy at selected points along the translation distance of a/2. The interlayer interactions in  $V_2O_5$  are an important contribution, <sup>73,74</sup> affecting the structure and the relative energy of different phases. We discuss the effects of dispersion interactions in the following section, however unless explicitly discussed in the text, the results presented here were obtained using Grimme's semi-empirical D3 correction to B3LYP. 75-77

### 3 Results and Discussion

# 3.1 Structure and relative stability of $\alpha$ and $\delta$ -V<sub>2</sub>O<sub>5</sub>: effect of dispersion interactions.

Table 1 reports the calculated lattice parameters for the  $\alpha$  and  $\delta$  phases of V<sub>2</sub>O<sub>5</sub>, using different approximations for the dispersion forces. The *c* direction defines the layer orientation in  $\alpha$  and  $\delta$ -V<sub>2</sub>O<sub>5</sub> and is the direction in which dispersion interactions are most important, and thus the comparison of the *c* lattice parameter for these two phases with experiment gives an indication of the quality of the representation of the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> *c* parameter by +13.2%. This is improved on by B3LYP-D2<sup>78</sup> to +3.5% and further by B3LYP-D3 to an expansion of +0.2%, representing an excellent agreement with experiment. The *a* and *b* lattice parameters are also in good agreement with experiment, <sup>64</sup> indicating

**Table 1** Structural properties and interlayer cohesive energy ( $E_{coh}$ ) of  $\alpha$  and  $\delta$  phases of V<sub>2</sub>O<sub>5</sub> calculated using B3LYP and the D2 and D3 dispersion schemes. For the  $\alpha$ -phase, results are compared with experimental values, and the numbers in brackets give errors with respect to the experimental results.

Method	a (Å)	b (Å)	c (Å)	Vol (Å <sup>3</sup> )	$ ho$ (g cm $^{-3}$ )	$E_{coh}$ (meV Å <sup>-2</sup> )
Expt. <sup>64</sup>	3.563	11.51	4.369	179.173	3.37	
B3LYP-D3	3.544 (-0.5%)	11.490 (-0.2%)	4.378 (+0.2%)	178.27 (-0.5%)	3.39	-20
B3LYP-D2	3.536 (-0.8%)	11.512 (+0.0%)	4.521 (+3.5 %)	184.04 (+2.7 %)	3.28	-13
<b>B3LYP</b>	3.582 (+0.5%)	11.448 (-0.5%)	4.944 (+13.2%)	202.79 (+13.2%)	2.98	-3
B3LYP-D3	3.559	11.356	9.375	378.94	3.19	-13
B3LYP-D2	3.535	11.491	9.728	395.20	3.06	-7
B3LYP 3.58	3.587	11.359	13.013	530.21	2.28	0
	Method Expt. <sup>64</sup> B3LYP-D3 B3LYP-D2 B3LYP B3LYP-D3 B3LYP-D2 B3LYP	Method         a (Å)           Expt. <sup>64</sup> 3.563           B3LYP-D3         3.544 (-0.5%)           B3LYP-D2         3.536 (-0.8%)           B3LYP         3.582 (+0.5%)           B3LYP-D3         3.559           B3LYP-D2         3.535           B3LYP-D3         3.559	Method $a$ (Å) $b$ (Å)Expt. $^{64}$ 3.56311.51B3LYP-D33.544 (-0.5%)11.490 (-0.2%)B3LYP-D23.536 (-0.8%)11.512 (+0.0%)B3LYP3.582 (+0.5%)11.448 (-0.5%)B3LYP-D33.55911.356B3LYP-D23.53511.491B3LYP3.58711.359	Method $a$ (Å) $b$ (Å) $c$ (Å)Expt. 643.56311.514.369B3LYP-D33.544 (-0.5%)11.490 (-0.2%)4.378 (+0.2%)B3LYP-D23.536 (-0.8%)11.512 (+0.0%)4.521 (+3.5%)B3LYP3.582 (+0.5%)11.448 (-0.5%)4.944 (+13.2%)B3LYP-D33.55911.3569.375B3LYP-D23.53511.4919.728B3LYP3.58711.35913.013	Method $a$ (Å) $b$ (Å) $c$ (Å)Vol (ų)Expt. 643.56311.514.369179.173B3LYP-D33.544 (-0.5%)11.490 (-0.2%)4.378 (+0.2%)178.27 (-0.5%)B3LYP-D23.536 (-0.8%)11.512 (+0.0%)4.521 (+3.5%)184.04 (+2.7%)B3LYP3.582 (+0.5%)11.448 (-0.5%)4.944 (+13.2%)202.79 (+13.2%)B3LYP-D33.55911.3569.375378.94B3LYP-D23.53511.4919.728395.20B3LYP3.58711.35913.013530.21	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

that B3LYP-D3 reproduced the structure of  $\alpha$ -V<sub>2</sub>O<sub>5</sub> with good accuracy.

No experimental lattice parameters exist for  $\delta$ -V<sub>2</sub>O<sub>5</sub>. However, the calculated parameters using B3LYP and the D2 and D3 schemes, show the same trends as for the calculated parameters for  $\alpha$ -V<sub>2</sub>O<sub>5</sub>. When dispersion forces are omitted, the *c* lattice parameter is significantly expanded. The expansion of the *c* axis is greater for  $\delta$  than for  $\alpha$  when dispersion interactions are omitted. Interlayer interactions in the  $\alpha$  phase are relatively strong due to the highly polar linear V-O1-V-O1 chains extending along the *c* direction. During the transition from  $\alpha$  to  $\delta$ , the V-O1 interlayer interactions are broken. In  $\delta$ , the polarised V-O1 bonds are oriented linearly towards the O-ions in the adjacent layers, weakening the interlayer binding. The expansions observed in the calculated lattice parameters for the  $\delta$  phase relative to  $\alpha$  are therefore reasonable.

We have calculated the interlayer cohesive energy ( $E_{coh}$ ) for both V<sub>2</sub>O<sub>5</sub> phases, according to

$$E_{coh} = \frac{E_{layer} - E_{bulk}}{2 \cdot A} \tag{2}$$

where A is the area of the unit cell, with the results reported in Table 1. The cohesive energy of 20 meV Å<sup>-2</sup> for the (001) face of the  $\alpha$ -phase calculated with B3LYP-D3 is in good agreement with the results of Björkman *et al.*, who report that most layered systems, irrespective of chemical composition, show an interlayer cohesive energy of ~20 meV Å<sup>-2</sup>.<sup>79</sup> The interlayer cohesive energy of the  $\alpha$ -phase calculated with D2 and uncorrected B3LYP is less than this value, consistent with a weaker binding giving rise to the over-estimation of the *c* parameter. The cohesive energy is reduced in the  $\delta$ -phase. From this analysis, we conclude that the D3 correction to B3LYP reproduces the layered structure of V<sub>2</sub>O<sub>5</sub> well, and accurately captures the interactions that define the interlayer distance.

The formation energy of  $\delta$ -V<sub>2</sub>O<sub>5</sub> relative to  $\alpha$ -V<sub>2</sub>O<sub>5</sub> was calculated using the three dispersion corrected functionals. For each functional,  $\alpha$ -V<sub>2</sub>O<sub>5</sub> is found to be the stable phase, as is understood experimentally. The energy difference between  $\alpha$  and  $\delta$  is +91 meV/f.u. for B3LYP, +258 meV/f.u. for D2 and +298 meV/f.u. with D3. The difference in stability between the  $\alpha$  and  $\delta$  phases of V<sub>2</sub>O<sub>5</sub> found here using the dispersion-uncorrected B3LYP functional (91 meV/f.u.) is in close agreement with the value of 100 meV/f.u. found by Sai Gautam *et al.* using PBE+U, also omitting dispersion interactions.<sup>13</sup>

#### 3.2 Relative stability of M-incorporated $\alpha$ and $\delta$ -V<sub>2</sub>O<sub>5</sub>

To understand how interlayer ions affect the stability of each phase, calculations were performed on  $MV_2O_5$  models of the  $\alpha$ and  $\delta$  phases (where M=Be<sup>2+</sup>, Mg<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>2+</sup> (high and low spin),  $Ca^{2+}$ ,  $Cd^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ). The relative stability of the two phases ( $\Delta E[\alpha - \delta]$ ) upon incorporation of each ion *M*, was compared. Divalent ions were chosen to give a model system containing only  $V^{4+}$ . The spins on the  $(d^1)$  V ions were aligned in a ferromagnetic ordering, a justification for which is provided in the ESI<sup>†</sup>. The specific M<sup>2+</sup> ions were selected predominantly to give a range of ionic radii within which to explore trends in behaviour. However, certain ions are of practical interest as dopants incorporated between the layers, or intercalants in a battery system. In addition to  ${\rm Mg}^{20,80}$  it is claimed that  ${\rm Zn}^{81}$  and  ${\rm Ca}^{20}$  can be electrochemically inserted into  $V_2O_5$ , and are thus of interest to examine. Ba<sup>44</sup> and Fe<sup>46,47,82</sup> have been used as dopants in the V<sub>2</sub>O<sub>5</sub> system for Li-ion batteries in the literature. Be and Cd are not of experimental interest as dopants or intercalants due to their toxicity, but were selected to give additional data points to demonstrate the stability-radius trend. Figure 3 shows the relative stability of the two phases, plotted as a function of the Shannon ionic radius of the incorporated ion<sup>83</sup> and the tolerance factor *Z* of the system.



**Fig. 3** Relative stability of  $\alpha$  and  $\delta$  phases of MV<sub>2</sub>O<sub>5</sub> as a function of the ionic radius of the incorporated cation M. The trend line is a guide for the eye only.

The trend is evident, and it indicates an increasing stabilisation of the  $\alpha$  polymorph *vs*  $\delta$  as the ionic radius of M (and tolerance factor *Z*) are increased. Below *Z*=0.87, the  $\alpha$  polymorph is destabilised relative to  $\delta$ , whilst above *Z*=0.87, the  $\alpha$  polymorph is stabilised with respect to  $\delta$ .

The trend line indicates three distinct regions of behaviour; Z < 0.8, 0.8 < Z < 1.0 and Z > 1.0. In each region, the energy difference varies linearly with tolerance factor (and ionic radius), but at different rates for each section. The linear relationship indicates that the ionic radius of the cation M influences directly the relative stability of the polymorphs. The region between 0.8 < Z < 1.0 shows a total change in relative stability between the two phases of 1600 meV/f.u. as the tolerance factor varies, and has a steeper gradient than the regions of Z < 0.8 and Z > 1.0. Thus in this central region varying the ionic radius has the greatest influence on the relative stability of the two polymorphs. A maximum stability of  $\alpha$  vs  $\delta$  is achieved at  $Z \sim 1.0$ , where  $\Delta E[\alpha - \Delta E]$  $\delta$ ]=1200 meV/f.u. Above this point, the incorporation of a larger ion into the interstice begins to slightly destabilise the  $\alpha$  polymorph and the stability no longer increases relative to  $\delta$ . The distinct behaviour in the three regions noted above, and the maximum stability at Z=1, correlates with the stability dependence of perovskite on the Goldschmidt tolerance factor, <sup>68</sup> justifying its relevance for the intercalation chemistry of V<sub>2</sub>O<sub>5</sub>.

 $\mathrm{Sr}^{2+}$  ions offer a maximum stabilising effect on the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure of 1200 meV/f.u. The plot also indicates that upon complete  $Fe^{2+}$  incorporation, the  $\alpha$  and  $\delta$  polymorphs become near-isoenergetic, with the  $\delta$ -phase stabilised by 40 meV/f.u. Full Li<sup>+</sup> incorporation (LiV<sub>2</sub>O<sub>5</sub>) is included for comparison with the results for the  $M^{2+}$  ions, and it results in stabilisation of the  $\delta$ phase by 100 meV/f.u. Notably the relative stability of the two phases for LiV<sub>2</sub>O<sub>5</sub> falls approximately on the same trend line as for the divalent MV2O5 systems, suggesting that the tolerance factor-like relationship is independent of the charge of the cation M, and is instead most strongly dependent on its ionic radius.  $Mg^{2+}$  intercalation results in the greatest stabilisation of the  $\delta$ phase (373 meV/f.u.) over  $\alpha$  for an ion in the central tolerance factor region 0.8 < Z < 1.0, consistent with the prediction of the  $\delta$  phase for fully discharged MgV<sub>2</sub>O<sub>5</sub><sup>17</sup>, and experimental synthesis of  $\delta$ -MgV<sub>2</sub>O<sub>5</sub>.<sup>33</sup>

The driving force for the change in relative stability of the two phases originates from the coordination environment of the incorporated ions, as illustrated in Figure 4. In the  $\alpha$ -phase, the ions in the perovskite-like units are offset from the centre of the interstices, in the *c* direction, towards one of the layers, and have four bonds to O1 ions, and two pairs of bonds to O2 and O3 ions in the adjacent layer, and are thus 8-coordinated (Figure 4a).<sup>19</sup> This off-centre coordination is dictated by the large c/a ratio in the (2×2×2) perovskite block in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, in turn caused by the extreme ferroelectric off-centring of V in the VO<sub>6</sub> octahedra, and contrasts with the 12 coordinate A site cation environment in a cubic perovskite. In the  $\delta$  phase, the shifting of the layers means that the ions have a similar coordination to two pairs of O2 and O3 ions in one layer, but are coordinated to only two O1 ions from the adjacent layer, leaving a 4+2, or 6-coordinate environment (Figure 4b).



Fig. 4 Coordination environment of M cations in a)  $\alpha$  and b)  $\delta$ -MV<sub>2</sub>O<sub>5</sub>.

The coordination in the  $\delta$  phase has also been described as 'tetrahedral', with the distances to the O3 ions considered too long to be real coordination lengths, leaving coordination to two O2 ions in one layer and two O1 ions in the adjacent layer.<sup>28,33</sup> The relative stability of the  $\alpha$  and  $\delta$ -phases is clearly linked with the size of the interlayer ion M: smaller M ions have a preference for the lower (4+2) coordination in the  $\delta$  phase, and stabilise it, whilst larger M ions favour the higher coordination number (8) in the  $\alpha$  phase.

In ABO<sub>3</sub> perovskites, as the size of the A site cation is reduced, the BO<sub>6</sub> octahedra experience tilting distortions that accommodate and stabilise the structure around the small A cations. In the  $\alpha$ -V<sub>2</sub>O<sub>5</sub> structure, tilting of the distorted VO<sub>6</sub> octahedra is constrained by the edge-sharing of VO<sub>6</sub> octahedra in the [001] plane between neighbouring perovskite-like units. As the size of the M cation is reduced, the increasing preference for lower coordination is accommodated in V<sub>2</sub>O<sub>5</sub> by shearing of the layers, which breaks the V-O1 interlayer vdW bonds, and forms the  $\delta$  phase.

# 3.3 Stabilisation of $\delta$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> as a function of composition (x)

Figure 5 shows the  $\alpha$  and  $\delta M_x V_2 O_5$  phase stability diagram, where M = Mg, Zn and Li and x=0, 0.5 and 1. We have omitted results for Fe<sup>2+</sup> (hs) and larger ions since they only stabilise the  $\alpha$ -phase, and Fe<sup>2+</sup> (ls) and Be<sup>2+</sup> since they have ionic radii <0.7 Å.

The energetics at all points on the diagram are calculated relative to  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\alpha$ -MV<sub>2</sub>O<sub>5</sub> for each cation M. The thick solid lines show the hull energy for the  $\alpha$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> system. Within this  $\alpha$ -phase, each ion shows a stable ordering in the  $\alpha$ -phase at *x*=0.5, denoted previously as  $\varepsilon$ -M<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub>.<sup>13</sup> The stability of the ' $\varepsilon$ ' phase is greatest for Li, followed by Mg and Zn.

No orderings of the Li, Mg or Zn ions are found to be stable in  $\delta$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> at *x*=0.5, relative to the respective  $\delta$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> endmembers. Thus the hull for the  $\delta$ -phase (indicated by the thin lines) connecting *x*=0 and *x*=1 is linear. The  $\delta$ -phase hull therefore gives the relative stability of  $\delta$ - *vs*  $\alpha$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub>. At *x*=0, the  $\delta$ -phase is unstable by 298 meV/f.u. The points at which the  $\alpha$  and  $\delta$  lines intersect gives the crossing point for stability between the two phases as a function of composition. The  $\delta$  phase is stabilised at *x*>0.58 for Mg (in contrast to previous work which found *x*>0.35 omitting dispersion interactions), *x*>0.62 for Zn and *x*>0.83 for Li. We note that the stabilisation of the  $\delta$ -Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub>



Fig. 5 Formation energy for the  $\alpha$  and  $\delta$  phases of MgV<sub>2</sub>O<sub>5</sub>, ZnV<sub>2</sub>O<sub>5</sub> and LiV<sub>2</sub>O<sub>5</sub>. Stability is plotted relative to the  $\alpha$ -endmembers.

phase is in good agreement with the appearance of the  $\delta$ -phase in the Li<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase diagram at *x*≈0.9.<sup>30</sup>

The dotted lines link the overall ground state phases for each cation. For Mg and Zn ions, the ground state hull connects  $\alpha$ - $\delta$ . This indicates that for Mg ions, the system exhibits a preference for phase segregation into  $\alpha$ -V<sub>2</sub>O<sub>5</sub> and  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> at intermediate Mg<sub>x</sub>V<sub>2</sub>O<sub>5</sub> compositions, in agreement with previous results.<sup>13</sup> We predict similar behaviour in the ZnV<sub>2</sub>O<sub>5</sub> system. For the Li system, we predict phase segregation into  $\epsilon$ -Li<sub>0.5</sub>V<sub>2</sub>O<sub>5</sub> and  $\delta$ -LiV<sub>2</sub>O<sub>5</sub> between 0.5<*x*<1.

These results indicate that the  $\delta$ -phase is only stable at high concentrations of interlayer ions (x>0.5), thus there is no practical route to stabilising the  $\delta$ -phase over  $\alpha$  at low concentrations of interlayer ion.

#### 3.4 Structural properties of $\alpha$ and $\delta$ -MV<sub>2</sub>O<sub>5</sub>

Tables S5 and S6 report the calculated lattice parameters and cell volumes of the  $\alpha$  and  $\delta$ -MV<sub>2</sub>O<sub>5</sub> structures respectively, compared with the calculated parameters for the undoped phases.

The most prominent result from the data is the expansion of the interlayer space upon ion incorporation, that for both phases increases as the size of the interlayer ion increases (Figure 6). The expansion occurs for all ions in both phases, with the exception of  $\delta$ -BeV<sub>2</sub>O<sub>5</sub> where there is a small lattice contraction along the *c* direction. The expansion of the *c* parameter with respect to the undoped V<sub>2</sub>O<sub>5</sub> material has implications for ionic migration, which we discuss later.

The expansion of the interlayer separation is much more pronounced in the  $\delta$  than the  $\alpha$  phase, due to the different stacking of planes and larger interstices in the  $\alpha$ -phase.

An evaluation of the volume change upon incorporation of Mg<sup>2+</sup> ions is of value for battery applications. It is well known that large lattice expansions are unfavourable in practical applications, since they cause mechanical stress, leading to structural failure. The volume change from the undoped  $\alpha$ -V<sub>2</sub>O<sub>5</sub> phase to a fully intercalated  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> phase is 11.3%, which is approximately in line with what is observed for graphite anodes in cur-



**Fig. 6** Change in *c* lattice parameter of the  $\alpha$  and  $\delta$ -MV<sub>2</sub>O<sub>5</sub> model systems as a function of ionic radius of cation M. The dotted lines represent the *c* lattice parameter for the undoped  $\alpha$  and  $\delta$ -V<sub>2</sub>O<sub>5</sub> systems.

rent Li-ion batteries.<sup>84</sup> However the expansion from a hypothetical de-intercalated  $\delta$ -V<sub>2</sub>O<sub>5</sub> phase to a  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> phase is +4.8%, which is a smaller and more favourable volume change. We note here also for interest, that the expansion from an empty  $\alpha$ -V<sub>2</sub>O<sub>5</sub> to fully intercalated  $\delta$ -LiV<sub>2</sub>O<sub>5</sub> in a Li-ion battery is a +8.8% volume change.

Figure 7 shows the evolution of two key structural features in the  $\alpha$ -MV<sub>2</sub>O<sub>5</sub> systems as ionic radius of the M cation varies. The first is the 'puckering angle'  $\theta$ , defined as the angle made between lines drawn linking O1-O2-O1 atoms of adjacent VO5 pyramids (Figure 8), when the structure is viewed along the b direction.<sup>13</sup> As the extent of 'puckering' increases, and the pyramids tilt towards each other, the angle  $\theta$  decreases. In the undoped phase of  $\alpha$ -V<sub>2</sub>O<sub>5</sub>,  $\theta$ =78°. These pyramids tilt upon incorporation of any ions, with the most substantial puckering ( $\theta$ =51°) upon incorporation of the smallest ion, Be, as the O1 ions are drawn in to form short Be-O bonds. As the size of the M ion increases, the puckering angle increases to a maximum of  $\theta = 67^{\circ}$  at an ionic radius of  $\sim 1.2$  Å, or a tolerance factor of Z=1 (for Sr<sup>2+</sup>). For incorporation of ions greater than this size, the 'puckering' begins to increase again, *i.e.* the puckering angle  $\theta$  decreases. This reverse of the behaviour indicates the radius of M ions that yields a maximum stabilising effect on the lattice, defining the upper limit of the linear 'tolerance factor' region.

The second structural feature of note is the angle  $\phi$  between the O1-V-O1 atoms, along the interlayer distance (Figure 8). In the undoped pristine material, the angle is 180°, whilst in all doped systems the angle is reduced, in line with the puckering of the pyramids. Starting with the ions M of the largest size, as the size of the ion is reduced, the  $\phi$  decreases. A minimum is found at  $Z=\sim0.8$ , defining the lower limit of the 'tolerance factor' region. Below this *Z* value,  $\phi$  begins to increase again.

#### 3.5 Energy of the phase change from $\alpha$ to $\delta$ -V<sub>2</sub>O<sub>5</sub>

Having established how the relative stability of the  $\alpha$  and  $\delta$  phases is affected by interlayer ions, it is now of interest to ex-



**Fig.** 7 Evolution of a) the 'puckering angle'  $\theta$  and b) O1-V-O1 angle  $\phi$  in the  $\alpha$ -MV<sub>2</sub>O<sub>5</sub> system, as a function of the radius of ion M. Dotted lines indicate that upper and lower limits of the 'tolerance factor region'.



**Fig. 8** Structural properties ( $\theta$  and  $\phi$ ) of the  $\alpha$ -MV<sub>2</sub>O<sub>5</sub> system that determine the upper and lower bounds of the 'tolerance factor region', illustrated on the optimised structures of a)  $\alpha$ -MgV<sub>2</sub>O<sub>5</sub> and b)  $\alpha$ -SrV<sub>2</sub>O<sub>5</sub>

amine the effects on the phase transition from  $\alpha \rightarrow \delta$  (or  $\delta \rightarrow \alpha$ ). As discussed earlier, the transition between the two phases can be understood as a translation of one layer relative to its neighbours by a distance of a/2 in the *a* direction, illustrated in Figure 9.

Computational investigations of fully de-intercalated  $\delta$ -V<sub>2</sub>O<sub>5</sub> have rarely considered its structural stability, whilst some have speculated that the  $\delta$ -phase is metastable.<sup>13</sup> However a  $\Gamma$  point phonon calculation of the crystallographic unit cell (with symmetry constraints removed, *i.e.* in *P*1 space group), using the B3LYP-D3 functional reveals a negative mode at -42.7 cm<sup>-1</sup> corresponding to the shearing of the layers along the *a* direction, demonstrating that the  $\delta$  phase is unstable and relaxes to  $\alpha$  with a barrierless transition. An equivalent calculation for  $\alpha$ -V<sub>2</sub>O<sub>5</sub> results in no negative modes.

Due to this layer shearing mode, we assume that the phase change does occur via a mutual translation of the layers. The rotation about a point in one of the layers has been suggested as a possible alternative route for the phase transition<sup>16</sup>, however this would involve a more complex restructuring of the bulk material over different length scales, which is less likely than a layer shearing. In the translation for the  $MV_2O_5$  systems that we have considered, the M ions remain coordinated to two O2 and two O3 oxygens on the layer adjacent to them, and it is the layer which binds through the O1 ions to M that moves relative to the first.



**Fig. 9** Illustration of the transition between the  $\alpha$  and  $\delta$  phases, occurring via a translation of layer 1 relative to layer 2, by a distance of a/2.

Figure 10 shows the relative energy of the  $\alpha$  and  $\delta$  phases in the V<sub>2</sub>O<sub>5</sub> and MV<sub>2</sub>O<sub>5</sub> systems, and the energetics of the transition between the two phases.

In the undoped  $V_2O_5$  system, the  $\delta$  phase is higher in energy than the  $\alpha$  phase by 298 meV/f.u. The transition pathway from the  $\delta$  phase to  $\alpha$  is downhill in energy for the entire translation, although the gradient flattens off near the  $\alpha$  phase. The downhill energy pathway across the entire translation and the negative phonon mode in the vibrational frequency analysis confirm that the  $\delta$  phase of  $V_2O_5$  will spontaneously relax to the  $\alpha$  phase without activation barriers.

For comparison, we have also calculated the  $\alpha \rightarrow \delta$  transition without the use of dispersion interactions (B3LYP). Here the stability difference between the two phases is smaller (91 meV/f.u.). Figure 10 shows that the energy of the phase change is downhill overall, however the gradient near the  $\delta$  phase is very small and becomes numerically appreciable only for a translation of the layers by at least a/8 from the  $\delta$ -phase. This can be attributed to the dramatic expansion of the interlayer space with respect to experiment when dispersion interactions are omitted, to the point where there is negligible interaction between neighbouring layers, and the translation of the layers relative to each other causes little change of energy. These results further support the importance of dispersion interactions in describing the behaviour of V<sub>2</sub>O<sub>5</sub>.

We next considered the phase translation energetics for three



**Fig. 10** Energetics of the phase transition between  $\alpha$  and  $\delta$  for the V<sub>2</sub>O<sub>5</sub> and selected MV<sub>2</sub>O<sub>5</sub> systems as a function of the layer translation, expressed as a percentage of *a*/2.

cation intercalated  $MV_2O_5$  systems.  $Sr^{2+}$  and  $Mg^{2+}$  were chosen because they correspond to the greatest stabilisation of the  $\alpha$  and  $\delta$  phases within the 'tolerance factor' region, and high spin Fe<sup>2+</sup> was chosen because the two phases ( $\alpha$  and  $\delta$ ) are near isoenergetic. For the  $Sr^{2+}$  system, there is no barrier for conversion between  $\delta$  and  $\alpha$ , and only the  $\alpha$  phase is a minimum on the potential energy surface (PES). The  $\delta$  phase corresponds to a transition state between two  $\alpha$ -phases. Conversely for  $Mg^{2+}$  there is no barrier for conversion from the  $\alpha$  to  $\delta$  phase, and the  $\delta$  phase is the only minimum on the PES. In the FeV<sub>2</sub>O<sub>5</sub> system, the energy difference between the two phases is small, with  $\delta$  lower in energy than  $\alpha$  by ~30 meV/f.u., and there is a minimum energy at ~55% path length, making the ground state an intermediate between the  $\alpha$  and  $\delta$  phases. Only in the case of Fe<sup>2+</sup> does a small barrier exist in the  $\alpha \rightarrow \delta$  pathway.

These results have implications for the use of orthorhombic V<sub>2</sub>O<sub>5</sub> as a Ca battery cathode. Mobility of Ca is extremely limited in the  $\alpha$ -phase with activation barriers >1.5 eV, which we can rationalise here as being a result of the stable coordination of the large Ca ions in the interstices of  $\alpha$ -V<sub>2</sub>O<sub>5</sub>. Mobility is predicted to be high in the  $\delta$ -phase, with activation barriers of  $\sim 0.2$ eV,<sup>17</sup> which can be attributed to a highly frustrated tetrahedral (or 4+2) coordination between the layers in  $\delta$ .<sup>19</sup> However since incorporation of Ca will only increase the stability of the  $\alpha$ -phase, and the translation to  $\alpha$ -CaV<sub>2</sub>O<sub>5</sub> from  $\delta$ -CaV<sub>2</sub>O<sub>5</sub> will be barrierless, intercalation of Ca ions into  $\delta\text{-}V_2O_5$  will not be possible. Since mobility of Ca is extremely low in the  $\alpha$ -phase, these results support the limited direct experimental evidence for Ca intercalation into orthorhombic V<sub>2</sub>O<sub>5</sub>.<sup>14</sup> We note however that Ca intercalation may be possible into other topochemically de-intercalated phases of  $V_2O_5$ , as predicted by computational studies.<sup>18</sup>

# 3.6 Ionic migration barriers of Mg<sup>2+</sup> ions in $\alpha$ and $\delta$ phases and the effect of interlayer ions.

The results to this point have indicated that interlayer ions may be used to stabilise the  $\alpha$  and  $\delta$  phases of V<sub>2</sub>O<sub>5</sub>. However, we do not know what effects the dopants may have on the activation barriers for Mg<sup>2+</sup> migration in the structure. Previous computational investigations using forcefield methods have indicated that dopants can affect the mobility of  $Mg^{2+}$  ions in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> by expanding the interlayer space.<sup>62</sup> We have therefore considered the migration of Mg<sup>2+</sup> in the  $\alpha$ -phase, and in the  $\alpha$ -phase where the size of interlayer space is modified by the incorporation of ions of varying radius. Migration of Mg in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> is predicted to be highly anisotropic, with the low energy pathways running along the a direction.<sup>17</sup> The 1-dimensional nature of the pathways further justifies considering  $\alpha$ -V<sub>2</sub>O<sub>5</sub> as a tunnel structure, rather than layered. Figure 11 shows the pathway that Mg can take in the [100] direction, and the location of the M cations relative to the Mg ion. The calculations for ionic migration used a  $(3 \times 1 \times 2)$  expansion of the unit cell, which corresponds to a stoichiometry of  $\sim M_{0.08}V_2O_5$  for the cells with incorporated M cations.

Figure 12 shows the energy profile for migration in the undoped  $\alpha$  phase. The single maximum, corresponding to the 3 coordinated activated site has a barrier of 1440 meV. This is  $\sim$ 150-300 meV higher than most previous investigations, <sup>13,16,17,19</sup> however many of these have omitted dispersion interactions. Interestingly, Carrasco reported barriers for Mg ion migration in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> of 770 meV using PBE, but 970 meV using optPBE-vdW (with a Hubbard U parameter applied).<sup>73</sup> In the work, the author concluded that the effects of dispersion make an important contribution to activation barriers in V<sub>2</sub>O<sub>5</sub>, and should not be omitted. Clearly, the magnitude of activation barriers are highly sensitive to the exchange-correlation functional and dispersioninclusive method used. A recent study by Barnes et al. determined that PBE and PBE+U were inadequate for finding migration barriers for Mg ions in  $\alpha$ -MoO<sub>3</sub>, underestimating energies compared to hybrid functionals.

The accurate representation of interlayer distances using the D3 dispersion scheme, and application of the hybrid-exchange functional B3LYP in our work are expected to give reliable estimations of activation barriers. Previous results finding  $\sim$ 1100 meV barriers have underestimated their magnitude by omitting dispersion interactions and expanding the interlayer separation, or failing to account for electron correlation.

Figure 12 also indicates the energy profile for  $Mg^{2+}$  migration when Ba dopants are included in the structure relative to the  $Mg^{2+}$  ion, as indicated in Figure 11. The activation barrier is reduced by 335 meV, which corresponds to ~5 orders of magnitude improvement in diffusivity at room temperature.We should note however that is it estimated that activation barriers must be >580 meV for the material to be practical in a battery, <sup>19</sup> and the barrier for the Ba-doped  $V_2O_5$  structure is still significantly higher than this limit.

To assess the effect of different dopants on the activation barrier, we conducted equivalent migration calculations for doped



**Fig. 11** Migration pathway for a  $Mg^{2+}$  ion in the *a* direction in  $\alpha$ -V<sub>2</sub>O<sub>5</sub>, between two stable 8-coordinated insertion sites, through the activated 3-coordinate site. The model also indicates the pathway for the  $Mg^{2+}$  ion that has been considered relative to the selected modifying M cation. The model is shown as a) a 3D projection and b) viewed along the *c* axis.



Fig. 12 Activation barriers for the migration of an Mg ion in undoped and Ba-doped  $V_2O_5$  at the dilute limit of Mg incorporation.

 $V_2O_5$  systems with Ba replaced by Mg, Zn, Fe (hs), Ca and Sr. Figure 13 indicates how the activation barrier for Mg<sup>2+</sup> migration changes as a function of the radius of the dopant cation, and the expansion of the *c* axis. The barrier for Mg<sup>2+</sup> mobility with no dopant is 1447 meV, and is indicated by a dotted line. The introduction of any of the dopants considered, results in a reduction of the activation barrier. As the size of the dopant is increased, the activation barrier is reduced by a greater amount. Of the ions investigated, Ba offers the largest reduction in activation barrier. Figure 13b shows the change in activation barrier as a function of interlayer expansion within the range considered. The activation barrier is seen to decrease linearly with the expansion of the lattice, suggesting that increased expansion of the structure could offer further improvements in Mg<sup>2+</sup> mobility.

We note here that monolayer  $V_2O_5$  has been investigated as a Mg-ion cathode material, and it was established that the activation barrier for Mg migration across the surface of a single layer of  $V_2O_5$  (1360 meV) was higher than the activation barrier in bulk (1260 meV).<sup>85</sup> Factoring in our results, this implies that there is a maximum expansion for the interlayer space that will minimise the activation barrier for Mg migration, before the behaviour becomes akin to that of a  $V_2O_5$  monolayer. This expansion could be achieved by the intercalation of pillaring molecules of solvents, as has been demonstrated in layered TiS<sub>2</sub> for Mg battery cathodes.<sup>86</sup>

The presence of dopants also results in blocked migration pathways and insertion sites, which will limit capacity compared to



**Fig. 13** Change in activation barrier for Mg ionic migration in  $\alpha$ -V<sub>2</sub>O<sub>5</sub> as a function of a) radius of M<sup>2+</sup> dopant in M<sub>0.08</sub>V<sub>2</sub>O<sub>5</sub>, and b) extent of *c* lattice parameter expansion.



Fig. 14 Migration profile for mobility of Mg in the  $\delta$ -phase at the full lattice limit (Mg<sub>0.92</sub>V<sub>2</sub>O<sub>5</sub>).

undoped V<sub>2</sub>O<sub>5</sub>. Furthermore, the concentration of interlayer ions considered here is relatively high at  $M_{0.08}V_2O_5$ , which will result in an enhanced effect compared to lower doping concentrations that may be used experimentally. However the result clearly shows that interlayer modifiers can positively affect ionic migration barriers for Mg.

We now examine the mobility of Mg in the  $\delta$ -phase. Since the  $Mg_rV_2O_5$  structure is unstable at x=0, and cycling starting from  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> has been proposed as a strategy for improved battery performance, it is appropriate to examine mobility of Mg in the full lattice limit (*i.e.*  $x \approx 1$ ) rather than at x = 0. To allow Mg mobility via a vacancy-hopping mechanism, a single Mg vacancy must be created, giving a stoichiometry in a (3×1×1) unit cell of  $\delta$ -Mg<sub>0.92</sub>V<sub>2</sub>O<sub>5</sub>. The migration profile is reported in Figure 14. The activation barrier is found to be  $\sim$ 970 meV, which is  $\sim$ 200 meV higher than reported for Mg mobility in the full lattice limit in previous studies, omitting dispersion interactions. The barrier is  $\sim$ 400 meV higher than in the empty lattice limit from these previous studies. Notably the energy of the mid-point site at 50% path length is  $\sim$ 850 meV, which is  $\sim$ 500 meV higher than in previous studies. Our calculations find that this mid-path site is not metastable but represents a very small transition state with respect to the calculated points either side along the migration pathway at 40% and 60% path length. A barrier of  $\sim$ 970 meV is likely to be the origin of the limited mobility of Mg in the  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> phase, which restricts electrochemical extraction of Mg.<sup>14</sup> Clearly there is a large discrepancy in the energetics of migration found in our work and previous studies, both in terms of the barriers and energy of the metastable site. We attribute once more the higher activation barriers found in this study predominantly to the inclusion of dispersion interactions which results in a more accurate structural description of  $V_2O_5$ . However we also note that previous studies calculating activation barriers for ionic migration of Mg in  $V_2O_5$  have used GGA and GGA+U methods, which have been shown to find lower activation barriers for Mg mobility in  $\alpha$ -MoO<sub>3</sub> than when a hybrid functional is used.<sup>87</sup> Deconvoluting the effects of dispersion interactions and electronic localisation due to the use of hybrid functionals for Mg mobility in orthorhombic  $V_2O_5$  warrants further investigation, but is beyond the scope of this present work.

### 4 Conclusions

In this work we have investigated the properties of orthorhombic  $V_2O_5$  and how they change upon intercalation of different ions.

We demonstrate that the relative stability between the  $\alpha$  and  $\delta$  phases of V<sub>2</sub>O<sub>5</sub> can be understood and modified within the framework of the Goldschmidt tolerance factor, due to the existence of  $(2 \times 2 \times 2)$  octahedral corner-sharing perovskite-like units in the structure. Interlayer ions are accommodated in these interstices and the size of the ion affects the relative stability of the two phases, with large ions stabilising the  $\alpha$ -phase, and smaller ions preferring a lower coordination number in the  $\delta$ -phase, obtained through a shearing of the layers. This mechanism rationalises the phase transition from  $\alpha$  to  $\delta$  in the intercalation phase diagram for Mg (and small ions like Li and Zn) in orthorhombic V<sub>2</sub>O<sub>5</sub>. Similar structure-stability relationships may exist upon ion incorporation for other crystal phases that are not in the perovskite family, but show similar octahedral corner-sharing sub-units.

Regarding phase selection, among the ions of practical interest as intercalants, Mg has the strongest stabilising effect on the  $\delta$ -V<sub>2</sub>O<sub>5</sub> lattice. However, since the  $\delta$ -M<sub>x</sub>V<sub>2</sub>O<sub>5</sub> phase is highly unstable relative to  $\alpha$  at x=0 (+298 meV/f.u.), a high concentration of intercalant is required to stabilise the  $\delta$ -phase over  $\alpha$ . This result indicates that stabilising the  $\delta$ -phase through intercalation at low x, to take advantage of its improved Mg mobility properties, is impractical and will be ineffective.

We examined the energetics of the layer translation and find that the  $\delta$ -V<sub>2</sub>O<sub>5</sub> phase is unstable and the phase transition to  $\alpha$ -V<sub>2</sub>O<sub>5</sub> is barrierless. The  $\alpha \rightarrow \delta$  transition to the lowest energy phase is barrierless also for the fully intercalated MV<sub>2</sub>O<sub>5</sub> phases (where M=Sr, Mg).

Finally we examined the activation barriers for Mg mobility in the  $\alpha$  and  $\delta$  phases, with and without interlayer ion incorporation. In the undoped  $\alpha$  and  $\delta$  phases we find that activation barriers are ~300 meV higher than in some earlier studies, which we attributed to the interlayer space compression upon inclusion of dispersion forces. The barrier for migration in the full lattice limit of  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> is ~1 eV. Despite lower barriers than in the  $\alpha$ -phase (of ~1.4 eV), we expect the Mg mobility in the  $\delta$ -phase to be extremely limited. These results support the difficult electrochemical extraction of Mg from  $\delta$ -MgV<sub>2</sub>O<sub>5</sub> evidenced in the literature.<sup>14</sup> The mobility of Mg may be increased by interlayer ions in the  $\alpha$ -phase that expand the interlayer space, and that a greater expansion of the layers will provide further improvements to mobility. However the barriers are still too high in the modified phase at a concentration of  $M_{0.08}V_2O_5$  for the material to be of practical use as a battery cathode, and other activation strategies may be required.

In conclusion, our results clarify a number of issues regarding Mg intercalation into  $V_2O_5$ , highlight the usefulness of tolerance factor to rationalise behaviour, and demonstrate the importance of understanding the structural properties of materials at the atomic level to devise more effective activation strategies for future work.

## **Conflicts of interest**

There are no conflicts to declare.

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