Synthesis and Characterization of Magnesium Vanadates as potential Mg-ion Cathode Materials through an *Ab Initio* Guided Carbothermal Reduction Approach

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Abstract: Many technologically relevant transition metal oxides for advanced energy storage and catalysis feature reduced transition metal (TM) oxides and are often nontrivial to prepare because of the need to control the reducing nature of the atmosphere in which they are synthesized. In this work, we show that an ab initio predictive synthesis strategy can be used to produce multiple gram-scale products of various MgV_xO_y -type phases (δ -MgV₂O₅, spinel MgV₂O₄, and MgVO₃) containing V^{3+} or V^{4+} relevant for Mg-ion battery cathodes. Characterization of these phases using ²⁵Mg solid-state NMR spectroscopy illustrates the potential of ²⁵Mg NMR for studying reversible magnesiation and local charge distributions. Rotor-Assisted Population Transfer is used as a much needed signal-tonoise enhancement technique. The ab initio guided synthesis approach is seen as a step forward towards a predictive synthesis strategy for targeting specific complex TM oxides with variable oxidation states of technological importance beyond Mg-ion (and indeed Li-ion) chemistry.

Introduction

Many alkali and alkaline earth vanadium oxides and phosphates find applications as technologically-important electrode materials in energy storage and photocatalysis.[1-3] Specifically, for Mgbattery technologies, a field of much active research,^[1,3,4] spineltype MgV₂O₄ phases and various polymorphic phases of MgV₂O₅ have been computationally predicted and/or experimentally shown to exhibit reversible Mg-ion insertion with fast kinetics, making them potentially suitable as cathodes in advanced energy storage systems.^[1,5-8] δ-phase MgV₂O₅, for example, was previously predicted to be a promising Mg-ion battery material with a relatively small solid-state Mg migration barrier.^[5] In addition, many of these compounds show interesting magnetism and electronic effects such as charge ordering, low dimensional magnetism, large spin gap energies, and metal-insulator transitions, which are not only of academic interest, but may also find technological use in advanced memory devices and hightemperature superconducting materials.[9-11] The wide-ranging applicability of these vanadate compounds partly arises from the multiple oxidation states available to vanadium: values from +2 $(3d^3)$ to +5 $(3d^0)$ are reported in the literature, with the +3 and +5 oxidation states widely known in nature.

Despite many previous reports on the preparation and characterization of complex vanadium oxides with chemical formulae AV_xO_y (A=Li, Na, Ca, Mg...), it is not, in general, straightforward to prepare stoichiometric compounds of alkali and alkaline earth vanadium oxides with reduced V3+ and V4+ oxidation states. This is evidenced by the subtle difference in stoichiometries of single crystalline MgV₂O₄ samples synthesized under different partial pressures of H₂ in Ar.^[12,13] This problem is exacerbated for vanadium oxides with mixed valences such as V₆O₁₃, a material which requires a careful optimization of the synthetic conditions.[14-16] In addition, many conventional syntheses of these compounds (especially δ -MgV₂O₅) rely on heating the precursors in evacuated and sealed quartz ampoules, which puts limits on the scalability of synthesis for large-scale applications. Clearly, more reliable ways of preparing these complex oxides are needed.

In this work, we present a novel method of preparing $\delta\text{-MgV}_2O_5$ and spinel MgV₂O₄, which are potential candidate materials for Mg-ion battery cathodes,[5,17,7,18-20] via controlled stoichiometric carbothermal reduction (CTR) of the V5+ precursors. These preparations do not require sealing of an evacuated quartz ampoule. Most importantly, a rational design approach using ab initio computation of phase free energies allows us to prepare the δ -phase MgV₂O₅ in a straightforward manner, illustrating the key concept of 'predictive solid-state synthesis' as recently highlighted.^[21] The use of oxide precursors with different stoichiometries allows us to prepare other V4+ oxides with different Mg-V stoichiometries such as MgVO₃ and VO₂. Although these materials have not yet been explored in terms of Mg-battery applications, MgVO₃ has been studied in terms of its potential lowdimensional magnetism with linear S=1/2 V4+ chains, [22,23] where it was prepared through a solid-state reaction of MgO and VO2 precursors. VO₂ is a phase which has potential applications in 'smart' windows, transistors, and memory devices.^[24,25] Finally, the work highlights the role of ²⁵Mg solid-state Nuclear Magnetic Resonance (ssNMR), a powerful technique for probing the local structure, defects and ionic motion in many advanced battery materials, [26] as a practical characterization tool as recently



Figure 1. (a) Reaction scheme to prepare δ -MgV₂O₅, MgV₂O₄, and MgVO₃ via the carbothermal approach. Crystal structures of (b) MgVO₃, (c) spinel MgV₂O₄, and (d) δ -MgV₂O₅. Coordination polyhedra for Mg and V are also shown.

illustrated for other Mg-cathode materials,^[7,18,27–30] now with assistance from advanced—and much needed—signal-to-noise enhancement methods.

Results and Discussion

DFT-based optimization of synthesis temperatures: Carbothermal reduction (CTR) synthesis relies on the fact that elemental carbon is readily oxidized upon heating with oxygen sources, thereby being potentially able to reduce the other species present in the mixture. Two oxidation products (CO and CO₂) are possible depending on the reaction temperature:

$$\begin{array}{ll} C(s) + O_2(g) \to CO_2(g), <973 \ \ (1) \\ 2C(s) + O_2(g) \to 2CO(g), >973 \ \ (2) \end{array}$$

Due to the strong dependence of entropic contributions to the Gibbs free energy, Equation 1 with the same number of gaseous species on both sides is favored at low temperatures, whereas Equation 2 with an extra gaseous CO molecule on the product side becomes thermodynamically favored at elevated temperatures. For carbon, the well-established crossover between the two oxidation reactions takes place at 973 K (700 $^{\circ}$ C).^[31,32]

These reactions, which form the basis of modern metallurgical extraction using blast furnaces,^[32] have previously been applied to prepare advanced lithium-ion battery materials in reduced transition metal oxidation states such as LiV₂O₅ and LiFePO₄ starting from the more accessible V5+ and Fe3+ precursor compounds.^[33,34] However, synthesis of Mg-containing compounds with varying vanadium oxidation states using this method has not been reported before. The principal issue here is that while experimental thermodynamic parameters are available for conventional (binary) oxides (e.g. the Ellingham diagram),^[31,35] these are often nonexistent for ternary and higher compounds which are technologically relevant for e.g. battery electrodes. As the thermodynamic parameters of these compounds depend critically on the redox states and the crystal structure, our method of ab initio guided CTR reaction exploits the ability of computational methods to predict the relevant thermodynamic parameters, therefore providing guidance for choosing the optimum reaction conditions.

Above, we present the reaction scheme for preparing δ -MgV₂O₅, MgV₂O₄, and MgVO₃ through CTR method (Figure 1a).

We first discuss the synthesis approach for MgV₂O₄ and MgV₂O₅, as these species have found uses as Mg-ion battery cathodes and share the same Mg:V=1:2 stoichiometry. For successful syntheses of the desired solid phases from MgV₂O₆, the product of a synthesis reaction performed in air, the free energy change ΔG needs to be negative under the given thermodynamic condition. As a first approximation, we consider the free energy changes under standard 1 atm gaseous partial pressures. Figure 2 shows the free energy changes (ΔG) of the relevant redox reactions plotted versus reaction temperature. As the carbon oxidation reactions have more negative free energy changes than both the reactions to form MgV_2O_6 reduction reactions, carbothermal reduction of the MgV₂O₆ precursor to both MgV₂O₄, a V³⁺ compound (purple line, Figure 2) and δ -MgV₂O₅, a V⁴⁺ compound (green line, Figure 2) is thermodynamically allowed under standard conditions.



Figure 2. Free energy ΔG vs temperature *T* plot, commonly known as an Ellingham diagram, for the various oxidation reactions involved in the syntheses of MgV₂O₅ and MgV₂O₄ phases, calculated from Density Functional Theory (DFT). All values are under standard 1 atm partial pressures. The two carbon oxidation lines cross at *T*=973 K (700 °C). To allow a direct calculation of ΔG , the values are normalized with respect to 1 molecule of O₂.

To control which of the two possible products, MgV_2O_4 or δ -MgV₂O₅, is thermodynamically favored, the chemical potentials and thus the free energy changes under varying gaseous partial pressures needs to be considered. This is required because gaseous CO and CO₂ species are continuously removed from the reaction tube by means of a flowing Ar environment, and are not necessarily present at 1 atm. As seen in the SI Section S4, both reduction reactions leading to MgV_2O_4 and MgV_2O_5 are also favored under <<1 atm partial pressures of CO₂, but crucially the reduction leading to MgV₂O₄ has a more negative free energy change at low CO₂ partial pressures. Intuitively, this result could be simply understood as the lower vanadium oxidation state (V³⁺, as in MgV₂O₄) is favored relative to the higher oxidation state V⁴⁺ (as in δ -MgV₂O₅) under strongly reducing conditions. Thus, the reaction to produce bulk MgV₂O₄ is straightforward: MgV₂O₄ can simply be produced under the strongly reducing conditions that result by mixing the starting materials in the stoichiometry given in Equation 3 at any temperature.

$$MgV_2O_6(s) + C(s) \rightarrow MgV_2O_4(s) + 2CO(g)$$
 (3)

In practice the kinetic considerations dictate that an elevated temperature is necessary. Thus, spinel-type MgV_2O_4 phase was simply produced in this work by heating the carbon- MgV_2O_6 mixture to 1173 K (900 °C). In this case, an excess of carbon in the starting mixture can also be added to enhance the electric conductivity of final product, if required (e.g., for use in a battery electrode) since the reduction reaction does not proceed beyond V³⁺.

In contrast, the reaction needs to be arrested at V⁴⁺ to produce δ - MgV_2O_5 , as MgV_2O_4 is the more favored V³⁺ reduction product under standard conditions. This requires a stoichiometric reduction involving carbon; in practice this could only be achieved by carbon oxidation to CO₂ below 923 K: oxidation to CO, which is thermodynamically favored above this temperature, inevitably involves some CO₂ as the oxidized product during the initial heating step. This would lead to over-reduction and wrong oxygen stoichiometry of the final product. Hence, a judicious choice of 873 K is taken for this initial reduction step, a temperature lower than 923 K but still high enough to allow overcome the kinetic barrier for reaction. When the precursor MgV₂O₆ is exposed to a stoichiometric amount of carbon under these conditions, the 'intermediate' reaction mixture is expected to comprise of primarily unreacted MgV_2O_6 and the full reduction product MgV_2O_4 , with a small amount of comproportionated MgV_2O_5 . However, as the averaged oxidation state over the whole mixture is controlled by the amount of reducing carbon in the starting mixture, this mixture would exhibit an overall oxidation state of V⁴⁺. The sample is then further calcined in the same reaction tube by simply ramping the temperature to 1173 K to kinetically facilitate the comproportionation reaction to yield δ -MgV₂O₅. 1173 K was chosen as the calcination temperature as δ -MgV₂O₅ is known to decompose above 1223 K. Overall, the reaction would proceed according to the stoichiometry outlined in Equation 4.

$$MgV_2O_6(s) + 0.5C(s) \rightarrow MgV_2O_5(s) + 0.5CO_2(g)$$
 (4)

Experimental validation of synthesis predictions via CTR: Figure 3 presents the powder X-ray diffraction (XRD) data of δ -MgV₂O₅ and MgV₂O₄ (5 g batches) prepared by the CTR approach developed above. Rietveld refinement^[36] results are also shown

in Tables S1 and S2. Apart from a minor VO₂ impurity (1.05±0.05 wt%) in the MgV₂O₅ sample, XRD unambiguously identifies the products as desired δ -MgV₂O₅ and spinel-type MgV₂O₄ with lattice parameters consistent with previous literature reports.[37,12] Excess VO₂ phase in δ -MgV₂O₅ is likely to be present due to the hydrated magnesium acetate precursor (nominally tetrahydrate but slightly excess in water in the reagent used here; see SI Section S2 for details) which would result in an understoichiometry of Mg in the mixture. For MgV₂O₄, a composition of Mg_{0.98}V₂O₄ is expected from this off-stoichiometry of the precursor; however, refinements of site occupancies were not performed due to the insensitivity of laboratory X-ray diffraction to these parameters. However, the successful synthesis of both δ-MgV₂O₅ and MgV₂O₄ clearly shows the success of our rational design strategy; it also highlights the scalable nature of CTR method.



Figure 3. Powder X-ray diffraction data and Rietveld refinements for the (a) MgV_2O_5 and (b) MgV_2O_4 samples prepared via CTR route. Allowed reflections for each phase are shown above as tick marks.

We also highlight that this approach could be applied to different V⁴⁺ oxides with varying Mg:V stoichiometries by choosing a precursor with the required stoichiometry. This is illustrated by successful preparation of two additional compounds, MgVO3 and VO₂, through the controlled CTR method. The syntheses of these compounds are different in a sense that the Mg:V ratio is now 1:1 or 0:1, different from the 1:2 ratio used for MgV₂O₄/MgV₂O₅. A V⁵⁺ precursor compound with Mg:V stoichiometry of 1:1 is necessary for MgVO₃, and Mg₂V₂O₇ is the only known such compound. Hence, the synthetic approach detailed in Section S1 starts by preparing this compound, which is subsequently reduced to V4+ by the CTR approach using a stoichiometric CO₂ reduction at 873 K followed by annealing at 1173 K. For the case of VO₂, the reduction can simply use commercial V2O5 as the precursor since Mg is absent from this system; see SI Sections S8 and S9 for details on the preparation and characterization, including XRD and ²⁵Mg NMR (of MgVO₃), of these phases.

²⁵Mg NMR characterization: Having obtained samples of δ- MqV_2O_5 and MqV_2O_4 through the CTR method, we now turn our attention to characterization of these compounds by means of ²⁵Mg solid-state NMR. Figure 4a shows the ²⁵Mg spectrum of assynthesized δ -MqV₂O₅. Fitting the distinct MAS second-order quadrupolar lineshape of this spectrum gives δ_{iso} =1763 ppm, together with the guadrupolar coupling constant $C_0=5.3$ MHz and asymmetry parameter, $\eta_{0}=0$, in good agreements to previously reported results for this compound (δ_{iso} =1799 ppm. Co=5.67 MHz and asymmetry $\eta_Q = 0.3$, ^[29,30] although the use of lower field in the previous study (11.7 T versus 16.4 T used in this study) precluded accurate fitting of the NMR lineshape. This is by far the largest C_{0} recorded in paramagnetic Mg environments, as expected from a distorted 6-fold Mg coordination environment of the Mg sites in MgV₂O₅ (Figure 4a, inset). Values of C_Q are often regarded as a measure of the local site distortions away from spherical symmetry,^[38] and also a measure of the distortion away from the energetically stable 6-fold octahedral coordination (e.g. Mg in rocksalt MgO). As fast diffusion of Mg would likely require the ions to be in a higher energy coordination environment, [39] it is tempting to suggest that the large value of C_Q may be a signature of the potential for fast Mg diffusion in δ -MgV₂O₅ as predicted computationally;^[5] however, we note that in addition to site energies, vacancies for the ions to hop into are also required for rapid motion.

While materials with large C_{Q} values may be technologically important, the large values of C_Q additionally reduces the NMR sensitivity and resolution due to the severe (second-order) quadrupolar broadening. Considering the already challenging nature of ²⁵Mg NMR measurements due to the low gyromagnetic ratio and low natural abundance, signal enhancement techniques are beneficial for reducing the experimental time and increasing the spectrum sensitivity, especially for potential Mg-ion cathode materials. Thus, we have opted to demonstrate the signal enhancing ability of Rotor Assisted Population Transfer (RAPT) pulse sequence, as used in the previous studies for signal enhancements in paramagnetic ²⁵Mg spectra.^[28] In brief, RAPT pulse sequence works by saturating the satellite transitions (STs) in quadrupolar ²⁵Mg, whereas one typically observes the central transition (CT) in quadrupolar NMR spectroscopy.[40] The saturation is performed with a train of Gaussian pulses at a given offset frequency which matches with the ST frequency, which results in a theoretical enhancement in CT polarization by 3 for ²⁵Mg (a spin-5/2 nucleus).^[41] In terms of the experiment, the large quadrupolar coupling observed in this material poses a significant challenge in saturating the STs, as discussed on the SI (Section S5). Despite these challenges, Figure 4b demonstrates a maximum enhancement of around 1.6 using the RAPT pulse sequence, which would result in approximately 60% reduction in experimental time required to achieve the same signal-to-noise ratio. It is also seen that the lineshape distortion is minimal upon



Figure 4. ²⁵Mg solid-state NMR spectra of CTR-prepared MgV₂O₅ samples. (a) Hahn echo spectrum of as-prepared pristine MgV₂O₅. (b) RAPT signal enhancement of pristine MgV₂O₅. (c) RAPT signal enhancement of ball-milled MgV₂O₅. The local coordination polyhedron around the Mg site is illustrated in (a) with orange (Mg) and teal (O) atoms.

RAPT enhancement, which further confirms the applicability of RAPT in quadrupolar NMR of paramagnetic species. This could also be useful for studying materials extracted from batteries, as the small amount of available sample and large quadrupolar coupling typically requires long (>12 h) measurement times. Finally, we show that this technique is equally applicable to ballmilled MgV₂O₅ sample (SEM and XRD of ball-milled sample are shown on SI Section S6). The spectrum shows a similar shift to the pristine sample at 1763 ppm, supporting the XRD data that also showed that the long-range structure of the sample has not been altered. The characteristic (central transition) lineshape, however, has now completely disappeared, possibly due to the reduced crystalline sizes and/or presence of defects as created by the milling.^[42,43] As the quadrupolar coupling interaction is specific to each Mg local environment, which results from a local coordination environment and not the overall crystallinity, the RAPT pulse sequence is still expected to enhance the ²⁵Mg signals regardless of the milling. Under these conditions, application of the RAPT pulse sequence to this material still displays an overall enhancement factor of about 1.5.

Utilizing this potential of ssNMR as a technique sensitive to local structural features, previous application of ssNMR to spinel oxides allowed the probing of local defects in these structures such as LiMn₂O₄ and MgAl₂O₄.^[44,45] Along this line, the ²⁵Mg NMR spectrum of the CTR synthesized MqV₂O₄ spinel sample (CTR- MqV_2O_4) was also acquired and is shown in Figure 5. The spectrum broadly agrees with our previously reported data on solid-state synthesized MgV₂O₄,^[28] but with three ²⁵Mg resonances (1861, 1783, and 1713 ppm) in comparison to the single resonance observed in solid-state synthesized SS-MaV₂O₄ (at 1845 ppm). The additional tetrahedral Mg environments are likely to arise from the existence of mixed V^{3+}/V^{4+} ($3a^2/3a^1$) ions, which are expected to originate from the Mg deficiency in the MgV₂O₆ precursor as discussed above. The stoichiometry of the CTR spinel compound (determined from the starting Mg/V ratio of the precursor; see SI Section 2) is given by [Mg_{0.98}]_{tet} $[V^{3+}_{1.96}V^{4+}_{0.04}]_{oct} O_4$ with mixed valence vanadium ions (V^{3+}/V^{4+}) and assuming no inverse spinel behavior, a reasonable assumption given the crystal field stabilization energy arguments.^[46,47]

Whereas a full ab initio calculation of the individual site shifts to assign these resonances is beyond the scope of this work, approximate insights into the nature of these resonance can be gained by considering the bond pathway contributions in the isostructural spinels MgCr2O4 and SS-MgV2O4. [28,48,18] Oxide spinel structures can in general be written in an AB2O4-type formula, where the A and B sites are tetrahedrally and octahedrally coordinated by the neighboring oxygen atoms, respectively. As each A-site (tetrahedral) Mg is neighboring twelve B-site TMs, the contribution of each Cr in MgCr₂O₄ (δ_{iso} =2862 ppm) approximates to 238.5 ppm per Cr³⁺ ion or 79.5 ppm per *d*-electron. ^{25}Mg in SS-MgV₂O₄, on the other hand, resonates at 1845 ppm, which gives 153.8 ppm per V3+ ion or 77 ppm per d-electron. This is in excellent agreement with the estimate derived from MgCr₂O₄, supporting the bond-pathway analysis approach for B-ions in octahedral sites. We also note that our multi-peak spectrum qualitatively resembles the ²⁵Mg spectrum of a MgCr_{0.4}V_{1.6}O₄ spinel with a mixed *d*-electron count Cr^{3+}/V^{3+} (3d³/3d²) where a broad resonance at 1760 ppm was observed.^[18]

As the V⁴⁺ cations have only one *d*-electron compared to the two of V³⁺, to a first approximation we can expect a smaller shift for the Mg ion neighboring V⁴⁺. Assuming that a single *d*-electron contributes 77 ppm to the total hyperfine shift of a tetrahedral Mg site, the hyperfine shifts of Mg atoms neighboring two and one V⁴⁺ ions are estimated as 1768 and 1691 ppm, respectively. These values are close to the observed shifts of 1783 and 1713 ppm, supporting our hypothesis that Mg deficiency leads to V⁴⁺ on the vanadium lattice (Table 1). Note that any octahedral Mg species (a product of potential spinel A/B-site inversion), if present, is expected to give hyperfine shifts much larger than those of the currently observed secondary resonances, as evidenced for ⁶Li shifts in spinel Li₄Mn₅O₁₂;^[44] such resonances are not detected in our spectrum.

This simple model is not however consistent with the relative intensities of these resonances by assuming a random distribution of the Mg vacancies and V4+ ions, thus approximating the Mg peak intensities as a binomial distribution. As each Mg site is bonded to twelve V sites, a composition of $Mg_{0.98}V^{3+}_{1.96}V^{4+}_{0.04}O_4$ should result in a relative intensity ratio of 78.6:19.2:2 for the resonances at 1861, 1783, and 1713 ppm, respectively. The experimental intensities, however, show a ratio of 9.4:80.2:10.4, clearly deviating from what is expected from a random distribution model of V⁴⁺ ions. While a random distribution model of V³⁺/V⁴⁺ ions in a spinel compound of chemical formula $Mg_{0.92}V^{3+}_{1.84}V^{4+}_{0.16}O_4$ would result in the 11V³⁺, 1V⁴⁺ peak at 1768 ppm having the highest intensity (38.4 %, Table 1, last row), this model a) still does not reproduce the large relative intensity of 80.2 % for this peak, and b) significantly overestimates the $12V^{3+}$ intensity. Thus a V⁴⁺ distribution random model does not appear to be valid for this sample and may point towards some degree of V³⁺/V⁴⁺ ion ordering in the B-sublattice, possibly coupled with the corresponding ordered Mg vacancies in the A-sublattice. Furthermore, V4+ octahedra are generally distorted, the V4+ ion moving off-center to form a shorter V-O bond, leaving the d electrons in either d_{x2-y2} or d_{xz} and d_{yz} orbitals depending on the nature of the distortion.[49] Thus a tentative assignment, which requires further analysis via ab initio calculations, is that the additional weaker peaks arise from distorted V4+ ions, the weaker peaks at higher and lower shifts resulting from interactions with dorbitals with half-filled and empty V⁴⁺ orbitals, respectively.



Figure 5. ^{25}Mg solid-state NMR spectra of CTR-prepared MgV₂O₄ sample. The local coordination polyhedron around the Mg site is illustrated with orange (Mg) and teal (O) atoms.

Table 1. Estimated hyperfine shifts and the intensity ratio for the Mg ions in the MgV₂O₄ spinel structure neighboring V³⁺ and V⁴⁺ ions. Integrated relative intensities are shown for the experimental spectrum and are also calculated assuming a random distribution of the V⁴⁺ ions (see text).

Coordination	12V ³⁺	11V ³⁺ , 1V ⁴⁺	10V ³⁺ , 2V ⁴⁺	Remarks
δ _{expt} / ppm	1861	1783	1713	Experimental
δ _{calc} / ppm	1845	1768	1691	Calculated from bond pathway contributions
I _{expt} / %	9.4	80.2	10.4	Experimental
I _{random} / %	78.6	19.2	2	Random distribution, $Mg_{0.98}V^{3*}_{1.96}V^{4+}_{0.04}O_4$
I _{random} / %	36.8	38.4	18.3	Random distribution, $Mg_{0.92}V^{3+}_{1.84}V^{4+}_{0.16}O_4$

Discussion: Many of the potential high-voltage cathode materials for Mg-ion batteries, for instance molybdates and vanadates,[1,27] have unconventional TM oxidation states and are not straightforward to prepare. The conventional way of preparing these compounds would be a comproportionation of precursors, or a (partial) reduction under a reducing gas such as H₂/Ar. The comproportionation route often requires a crucible inside an evacuated quartz ampoule (MgO reacts with SiO₂ at elevated temperatures), which poses a moderate experimental difficulty. The reduction route under H₂ cannot, in general, be used to easily control the final oxidation state of the product as the reduction potential is set by that of gaseous H₂, a strong reducing agent, so the reaction typically proceeds to yield products with lower oxidation states (i.e. in our case, H₂ reduction of MgV₂O₆ would yield MgV₂O₄ and not MgV₂O₅); moreover, it is difficult to stoichiometrically reduce the reaction mixture with a controlled quantity of gaseous flowing H₂. Our method of stoichiometric CTR using carbon as a reductant is thus a promising alternative to the widely used H₂ reduction method to produce various (magnesium) vanadates with these unusual oxidation states as it provides a way for stoichiometric reduction starting from a stable precursor such as those containing V5+. When combined with computational predictions of the thermodynamic parameters involved, the reaction scheme could be designed in a rational manner. This approach is, in principle, completely general and it could potentially be a powerful method to prepare many of these complex Li, Na, Mg, Ca, and Zn TM oxides which may have technological importance as advanced battery materials and/or photocatalysts. In addition, it could also be a valuable tool in exploring the complex magnetism in TM oxides, as many of these compounds exhibit unusual magnetic structures at low temperatures. The CTR method can be easily used to prepare large batches of samples for neutron diffraction to probe the magnetic order. This could be an advantage over the guartz ampoule route, where the amount of a single batch is determined by the size of ampoules used. We propose this ab-initio guided CTR method could readily be extended to other more complex TM oxides with reduced oxidation states.

Conclusion

In this work, we demonstrate the potential of carbothermal reduction (CTR) method to prepare a series of (magnesium) vanadium oxides MgV_2O_4 , MgV_2O_5 , $MgVO_3$, and VO_2 in a straightforward manner. In particular, computational prediction of the thermodynamic parameters allows a rational design of reaction conditions leading to these compounds: an *ab initio*

guided predictive synthesis approach. ²⁵Mg NMR characterization of the resulting candidates as Mg-ion battery cathodes reveals the potential for utilizing solid-state NMR as a practical characterization tool for these series of compounds. Our method, which could easily be applied to other transition metal oxide systems, opens up a potential way for large-scale synthesis of battery materials whose synthesis requires reducing conditions. This has relevance to many Li-, Na-, Mg-, and Ca-ion chemistries, where it is often critical to produce an alkali or alkaline earth containing metal oxide positive or negative electrode as the source of the mobile ions.

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- [1] P. Canepa, G. Sai Gautam, D. C. Hannah, R. Malik, M. Liu, K. G. Gallagher, K. A. Persson, G. Ceder, *Chem. Rev.* 2017, *117*, 4287– 4341.
- [2] R. C. Ropp, Encyclopedia of the Alkaline Earth Compounds, Elsevier, 2013.
- [3] J. Muldoon, C. B. Bucur, T. Gregory, Chem. Rev. 2014, 114, 11683– 11720.
- [4] Z. Zhao-Karger, M. Fichtner, *Front. Chem.* **2019**, *6*, 656.
- [5] G. Sai Gautam, P. Canepa, A. Abdellahi, A. Urban, R. Malik, G. Ceder, Chem. Mater. 2015, 27, 3733–3742.
- [6] J. L. Andrews, A. Mukherjee, H. D. Yoo, A. Parija, P. M. Marley, S. Fakra, D. Prendergast, J. Cabana, R. F. Klie, S. Banerjee, *Chem* 2018, 4, 564–585.
- [7] A. Mukherjee, N. Sa, P. J. Phillips, A. Burrell, J. Vaughey, R. F. Klie, *Chem. Mater.* 2017, 29, 2218–2226.
- [8] S.-B. Son, T. Gao, S. P. Harvey, K. X. Steirer, A. Stokes, A. Norman, C. Wang, A. Cresce, K. Xu, C. Ban, *Nat. Chem.* **2018**, *10*, 532–539.
- [9] L. Balents, *Nature* **2010**, *464*, 199–208.
- [10] P. A. Lee, N. Nagaosa, X.-G. Wen, *Rev. Mod. Phys.* **2006**, *78*, 17–85.
- [11] T.-H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, Y. S. Lee, *Nature* **2012**, 492, 406–410.
- [12] A. T. M. N. Islam, E. M. Wheeler, M. Reehuis, K. Siemensmeyer, M. Tovar, B. Klemke, K. Kiefer, A. H. Hill, B. Lake, *Phys. Rev. B* 2012, 85, 024203.
- [13] E. M. Wheeler, B. Lake, A. T. M. N. Islam, M. Reehuis, P. Steffens, T. Guidi, A. H. Hill, *Phys. Rev. B* 2010, *82*, 140406.
- [14] H.-P. Liang, J. Du, T. G. J. Jones, N. S. Lawrence, A. W. Meredith, ACS Appl. Mater. Interfaces 2016, 8, 25674–25679.

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- Z. Huang, H. Zeng, L. Xue, X. Zhou, Y. Zhao, Q. Lai, J. Alloys Compd. 2011, 509, 10080–10085. [15]
- H. Li, P. He, Y. Wang, E. Hosono, H. Zhou, J. Mater. Chem. 2011, 21, [16] 10999-11009.
- J. P. Pereira-Ramos, R. Messina, J. Perichon, J. Electroanal. Chem. [17] Interfacial Electrochem. 1987, 218, 241–249.
- B. J. Kwon, K.-C. Lau, H. Park, Y. A. Wu, K. L. Hawthorne, H. Li, S. Kim, I. L. Bolotin, T. T. Fister, P. Zapol, R. F. Klie, J. Cabana, C. Liao, [18] S. H. Lapidus, B. Key, J. T. Vaughey, Chem. Mater. 2020, 32, 1162-1171.
- [19] L. Hu, J. R. Jokisaari, B. J. Kwon, L. Yin, S. Kim, H. Park, S. H. Lapidus, R. F. Klie, B. Key, P. Zapol, B. J. Ingram, J. T. Vaughey, J. Cabana, ACS Energy Lett. 2020, 5, 2721–2727.
- [20] N. Kuganathan, K. Davazoglou, A. Chroneos, J. Appl. Phys. 2020, 127. 035106.
- K. Kovnir, *Chem. Mater.* **2021**, *33*, 4835–4841. I. Chaplygin, R. Hayn, K. Koepernik, *Phys. Rev. B* **1999**, *60*, R12557– [21] [22] R12560.
- J. Choukroun, V. A. Pashchenko, Y. Ksari, J. Y. Henry, F. Mila, P. [23] Millet, P. Monod, A. Stepanov, J. Dumas, R. Buder, *Eur. Phys. J. B* 2000, *14*, 655–659.
- J. Jeong, N. Aetukuri, T. Graf, T. D. Schladt, M. G. Samant, S. S. P.
 Parkin, *Science* 2013, 339, 1402–1405.
 C. G. Granqvist, *Thin Solid Films* 1990, 193–194, 730–741. [24]
- [25] [26]
- O. Pecher, J. Carretero-González, K. J. Griffith, C. P. Grey, Chem. Mater. 2017, 29, 213-242.
- G. S. Gautam, X. Sun, V. Duffort, L. F. Nazar, G. Ceder, J. Mater. [27] [28]
- Chem. A 2016, 4, 17643–17648.
 J. Lee, I. D. Seymour, A. J. Pell, S. E. Dutton, C. P. Grey, *Phys. Chem. Chem. Phys.* 2017, *19*, 613–625.
 N. Sa, T. L. Kinnibrugh, H. Wang, G. Sai Gautam, K. W. Chapman, J. T. Vaughey, B. Key, T. T. Fister, J. W. Freeland, D. L. Proffit, P. J. [29] Chupas, G. Ceder, J. G. Bareno, I. D. Bloom, A. K. Burrell, Chem. Mater. 2016, 28, 2962-2969.
- H. Wang, P. Senguttuvan, D. L. Proffit, B. Pan, C. Liao, A. K. Burrell, [30] J. T. Vaughey, B. Key, ECS Electrochem. Lett. 2015, 4, A90-A93.
- [31] H. J. T. Ellingham, J. Soc. Chem. Ind. 1944, 63, 125-160.
- [32] A. Cottrell, An Introduction to Metallurgy, The Institute Of Materials, 1995. [33] J. Barker, M. Y. Saidi, J. L. Swoyer, J. Electrochem. Soc. 2003, 150,
- A1267-A1272. J. Barker, M. Y. Saidi, J. L. Swoyer, Electrochem. Solid-State Lett.
- [34] 2003, 6, A53-A55.
- I. Barin, G. Platzki, Thermochemical Data of Pure Substances, VCH, [35] Weinheim; New York, 1995.
- H. Rietveld, J. Appl. Crystallogr. 1969, 2, 65-71. [36]
- [37] J.-C. Bouloux, I. Milosevic, J. Galy, J. Solid State Chem. 1976, 16, 393-398.
- [38] A. P. M. Kentgens, Geoderma 1997, 80, 271-306.
- Z. Rong, R. Malik, P. Canepa, G. Sai Gautam, M. Liu, A. Jain, K. Persson, G. Ceder, *Chem. Mater.* **2015**, *27*, 6016–6021. [39]
- Z. Yao, H.-T. Kwak, D. Sakellariou, L. Emsley, P. J. Grandinetti, *Chem. Phys. Lett.* **2000**, 327, 85–90. S. Prasad, H.-T. Kwak, T. Clark, P. J. Grandinetti, *J. Am. Chem. Soc.* [40]
- [41] 2002, 124, 4964-4965.
- J. Cabana, J. Shirakawa, M. Nakayama, M. Wakihara, C. P. Grey, J. [42] Mater. Chem. 2011, 21, 10012.
- M. Morcrette, C. Wurm, C. Masquelier, Solid State Sci. 2002, 4, 239-[43] 246.
- Y. J. Lee, F. Wang, C. P. Grey, J. Am. Chem. Soc. 1998, 120, 12601-[44] 12613
- R. Dupree, M. H. Lewis, M. E. Smith, Philos. Mag. A 1986, 53, L17-[45] L20.
- H. S. C. O'Neill, A. Navrotsky, *Am. Mineral.* 1983, 68, 181–194.
 K. E. Sickafus, J. M. Wills, N. W. Grimes, *J. Am. Ceram. Soc.* 2004, [46] [47] 82. 3279-3292.
- D. S. Middlemiss, A. J. llott, R. J. Clément, F. C. Strobridge, C. P. Grey, *Chem. Mater.* 2013, 25, 1723–1734. [48]
- [49] C. J. Ballhausen, H. B. Gray, Inorg. Chem. 1962, 1, 111-122.

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Entry for the Table of Contents



Ab initio prediction of thermodynamic parameters leads to predictive synthesis strategy utilizing solid carbon for facile preparation of a series of magnesium vanadate compounds. ²⁵Mg solid-state NMR spectroscopy of these compounds are presented as a practical way for characterizing their local Mg structures.

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