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 MgVxOy-type phases (δ-MgV2O5, spinel MgV2O4, and MgVO3) containing V3+ or V4+ 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 magnesiumation and local charge distributions. Rotor-Assisted Population Transfer is used as a much needed signal-to-noise enhancement technique. The use of oxide precursors with different stoichiometries of single crystalline MgV2O5 samples synthesized under different partial pressures of H2 in Ar,[15–13] This problem is exacerbated for vanadium oxides with mixed valences such as V2O3, 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 δ-MgV2O5 and spinel MgV2O4, which are potential candidate materials for Mg-ion battery cathodes,[5,17,18–20] via controlled stoichiometric carbothermal reduction (CTR) of the V4+ 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 low-dimensional 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 illustrated for other Mg-cathode materials,[7,18,27–30] now with assistance from advanced—and much needed—signal-to-noise enhancement methods.

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 Mg-battery technologies, a field of much active research,[1,3,4] spinel-type MgV2O4 phases and various polymorphic phases of MgV2O4 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 MgV2O4, 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 high-temperature superconducting materials.[8–11] The wide-ranging applicability of these vanadate compounds partly arises from the multiple oxidation states available to vanadium: values from +2 (3d2) to +5 (3d3) 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 AVxOy (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 MgV2O5 samples synthesized under different partial pressures of H2 in Ar.[15–13]
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 CO$_2$) are possible depending on the reaction temperature:

\[
\begin{align*}
\text{C(s)} + \text{O}_2(g) &\rightarrow \text{CO}_2(g), <973 \text{ K} \quad (1) \\
2\text{C(s)} + \text{O}_2(g) &\rightarrow 2\text{CO}(g), >973 \text{ K} \quad (2)
\end{align*}
\]

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 °C).\[31,32\]

These reactions, which forms the basis of modern metallurgical extraction using blast furnaces, have previously been applied to prepare advanced lithium-ion battery materials in reduced transition metal oxidation states such as Li$_x$V$_2$O$_5$ and LiFePO$_4$ starting from the more accessible V$^{5+}$ and Fe$^{3+}$ 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), 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-MgV$_2$O$_5$, MgV$_2$O$_4$, and MgVO$_3$ through CTR method (Figure 1a). We first discuss the synthesis approach for MgV$_2$O$_4$ and MgV$_2$O$_5$ 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 MgV$_2$O$_6$, the product of a synthesis reaction performed in air, the free energy change $\Delta G$ 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 ($\Delta G$) 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$_2$O$_4$ reduction reactions, carbothermal reduction of the MgV$_2$O$_6$ precursor to both MgV$_2$O$_4$, a V$^{3+}$ compound (purple line, Figure 2) and δ-MgV$_2$O$_5$, a V$^{4+}$ compound (green line, Figure 2) is thermodynamically allowed under standard conditions.
To control which of the two possible products, MgV$_2$O$_5$ or δ-MgV$_2$O$_6$, 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 CO$_2$ 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$_2$O$_5$ and MgV$_2$O$_4$ are also favored under $<$1 atm partial pressures of CO$_2$. But crucially, the reduction leading to MgV$_2$O$_5$ has a more negative free energy change at low CO$_2$ partial pressures. Intuitively, this result could be simply understood as the lower vanadium oxidation state ($V^{3+}$, as in MgV$_2$O$_5$) is favored relative to the higher oxidation state $V^{4+}$ (as in δ-MgV$_2$O$_6$) under strongly reducing conditions. Thus, the reaction to produce bulk MgV$_2$O$_4$ is straightforward: MgV$_2$O$_5$ 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.

\[
\text{MgV}_2\text{O}_5(s) + C(s) \rightarrow \text{MgV}_2\text{O}_4(s) + 2\text{CO}(g) \tag{3}
\]

In practice the kinetic considerations dictate that an elevated temperature is necessary. Thus, spinel-type MgV$_2$O$_4$ phase was simply produced in this work by heating the carbon-MgV$_2$O$_5$ 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 $V^{3+}$.

In contrast, the reaction needs to be arrested at $V^{4+}$ to produce δ-MgV$_2$O$_6$, as MgV$_2$O$_4$ is the more favored $V^{3+}$ reduction product under standard conditions. This requires a stoichiometric reduction involving carbon; in practice this could only be achieved by carbon oxidation to CO$_2$ below 923 K: oxidation to CO, which is thermodynamically favored above this temperature, inevitably involves some CO$_2$ as the oxidized product during the initial heating step 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 MgV$_2$O$_4$ is exposed to a stoichiometric amount of carbon under these conditions, the ‘intermediate’ reaction mixture is expected to comprise of primarily unreacted MgV$_2$O$_5$ and the full reduction product MgV$_2$O$_4$, with a small amount of comproportionated MgV$_2$O$_6$. 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 $V^{4+}$. 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-MgV$_2$O$_6$. 1173 K was chosen as the calcination temperature as δ-MgV$_2$O$_6$ is known to decompose above 1223 K. Overall, the reaction would proceed according to the stoichiometry outlined in Equation 4.

\[
\text{MgV}_2\text{O}_4(s) + 0.5\text{C} \rightarrow \text{MgV}_2\text{O}_5(s) + 0.5\text{CO}_2(g) \tag{4}
\]

**Experimental validation of synthesis predictions via CTR:** Figure 3 presents the powder X-ray diffraction (XRD) data of δ-MgV$_2$O$_6$ and MgV$_2$O$_4$ (5 g batches) prepared by the CTR approach developed above. Rietveld refinement results are also shown in Tables S1 and S2. Apart from a minor VO$_2$ impurity (1.05±0.05 wt%) in the MgV$_2$O$_5$ sample, XRD unambiguously identifies the products as desired δ-MgV$_2$O$_6$ and spinel-type MgV$_2$O$_4$ with lattice parameters consistent with previous literature reports. Excess VO$_2$ phase in δ-MgV$_2$O$_6$ 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 a under-stoichiometry of Mg in the mixture. For MgV$_2$O$_4$, a composition of Mg$_{0.98}$V$_2$O$_4$ 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-MgV$_2$O$_6$ and MgV$_2$O$_4$ 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$_2$O$_5$ and (b) MgV$_2$O$_4$ samples prepared via CTR route. Allowed reflections for each phase are shown above as tick marks.](image-url)
We also highlight that this approach could be applied to different $V^{4+}$ oxides with varying Mg:V stoichiometries by choosing a precursor with the required stoichiometry. This is illustrated by successful preparation of two additional compounds, MgVO$_3$ and VO$_3$, 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 Mg$_2$V$_2$O$_7$/MgV$_2$O$_6$. A $V^{5+}$ precursor compound with Mg:V stoichiometry of 1:1 is necessary for MgVO$_3$, and Mg$_2$V$_2$O$_7$ is the only known such compound. Hence, the synthetic approach detailed in Section S1 starts by preparing this compound, which is subsequently reduced to $V^{4+}$ by the CTR approach using a stoichiometric CO$_2$ reduction at 873 K followed by annealing at 1173 K. For the case of VO$_3$, the reduction can simply use commercial V$_2$O$_5$ 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 $^{25}$Mg NMR, of these phases.

$^{25}$Mg NMR characterization: Having obtained samples of δ-MgV$_2$O$_5$ and Mg$_2$V$_2$O$_7$ through the CTR method, we now turn our attention to characterization of these compounds by means of $^{25}$Mg solid-state NMR. Figure 4a shows the $^{25}$Mg spectrum of as-synthesized δ-MgV$_2$O$_5$. Fitting the distinct MAS second-order quadrupolar lineshape of this spectrum gives $\delta_{iso}$=1783 ppm, together with the quadrupolar coupling constant $C_Q$=5.3 MHz and asymmetry parameter $\eta_{Q}$=0, in good agreement to previously reported results for this compound ($\delta_{iso}$=1799 ppm, $C_Q$=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 $C_Q$ recorded in paramagnetic Mg environments, as expected from a distorted 6-fold Mg coordination environment of the Mg sites in MgV$_2$O$_5$ (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-MgV$_2$O$_5$ as predicted computationally,[39] 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 $^{25}$Mg 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 $^{25}$Mg spectra.[39] In brief, RAPT pulse sequence works by saturating the satellite transitions (STs) in quadrupolar $^{25}$Mg, whereas one typically observes the central transition (CT) in quadrupolar NMR spectroscopy.[39] 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 $^{25}$Mg (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 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 ball-milled MgV$_2$O$_5$ sample (SEM and XRD of ball-milled sample are shown in 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. 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 $^{25}$Mg 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 LiMn$_2$O$_4$ and MgAl$_2$O$_4$. Along this line, the $^{25}$Mg NMR spectrum of the CTR synthesized MgV$_2$O$_5$ spinel sample was also acquired and is shown in the SI (Figure S7), with the detailed discussion on the spectrum on Section S7. The spectrum broadly agrees with our previously reported data on solid-state synthesized MgV$_2$O$_5$ with the existence of mixed V$^{2+}$/V$^{4+}$ (3d$^2$/3d$^1$) ions giving slightly lower shifts (1783, 1713 ppm) in comparison to the shift observed in solid-state synthesized MgV$_2$O$_5$ (1845 ppm). This mixed valence likely arises from the Mg deficiency in the MgV$_2$O$_5$ precursor as discussed above, where the expected stoichiometry of the final spinel compound is Mg$_{0.65}$V$_2$O$_5$ with mixed valence vanadium ions. We also note that this multi-peak spectrum resembles the $^{25}$Mg spectrum of a MgCr$_{0.65}$V$_2$O$_5$ spinel with a mixed d-electron count Cr$^{3+}$/V$^{4+}$ (3d$^2$/3d$^3$) thus, our method of $^{25}$Mg NMR allows to detect the individual local Mg environments as defined by different vanadium oxidation states.

Many of the potential high-voltage cathode materials for Mg-ion batteries, for instance Mg$_9$Nb$_2$O$_{11}$ and Mg$_5$Mo$_2$O$_{12}$ 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 H$_2$/Ar. The comproportionation route often requires a crucible inside an evacuated quartz ampoule (MgO reacts with SiO$_2$ at elevated temperatures), which poses a moderate experimental difficulty. The reduction route under H$_2$ 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 H$_2$, a strong reducing agent, so the reaction typically proceeds to yield products with lower oxidation states (i.e. in our case, H$_2$ reduction of MgV$_2$O$_5$ would yield MgV$_2$O$_4$ and not MgV$_2$O$_3$); moreover, it is difficult to stoichiometrically reduce the reaction mixture with a controlled quantity of gaseous flowing H$_2$. Our method of stoichiometric CTR using carbon as a reductant is thus a promising alternative to the widely used H$_2$ 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 V$^{5+}$. 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 quartz 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 vanadates and niobates 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$_2$O$_4$, MgV$_2$O$_5$, 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. $^{25}$Mg 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 alkaline or alkaline earth containing metal oxide positive or negative electrode as the source of the mobile ions.

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Keywords: Solid-phase synthesis • Synthesis design • Ab initio calculations • NMR spectroscopy • Vanadates

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

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