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ARTICLE

On the viability of Mg extraction in MgMoN_2 : a combined experimental and theoretical approachR. Verrelli^a, M.E. Arroyo-de-Dompablo^b, D. Tchitchevova^a, A.P. Black^a, C. Frontera^a, A. Fuertes^a, M.R. Palacin^{a*}Received 00th January 20xx,
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Layered MgMoN_2 was prepared by solid state reaction at high temperature between Mo and Mg_3N_2 in N_2 which represents a simple synthetic pathway compared to the previously reported method that used NaN_3 as nitrogen source. The crystal structure of MgMoN_2 was studied by synchrotron X-ray and neutron powder diffraction. The feasibility of oxidizing this compound and concomitantly extracting magnesium from the structure was assessed by both chemical and electrochemical approaches, using different protocols. The X-ray diffraction patterns of oxidized samples do not exhibit any relevant difference with respect to that of the as prepared MgMoN_2 and no differences in the cell parameters are deduced from Rietveld refinements. No hints pointing at the presence of any amorphous phase are observed either. These results are rationalized through DFT calculated energy barriers for Mg^{2+} ion migration in MgMoN_2 .

Introduction

The evolution of the global energy market towards ever-increasing energy and power density demanding applications has brought about a renewed interest in battery technologies based on light multivalent metal anodes and multivalent ion host cathodes, which hold the promise for a real breakthrough in achievable energy density when compared to lithium based systems.^{1,2} Indeed, for divalent charge carriers, the number of ions that must react to achieve a certain electrochemical capacity should diminish by a factor of two when compared to monovalent ions such as lithium or sodium, or, for the same number of reacted ions there would be a concomitant two-fold increase in the energy density of the cells. Furthermore, the exploitation of naturally abundant elements, such as Ca, Mg and Al in replacement of conventional Li-ion battery chemistry would bear substantial environmental and cost benefits.² Among the multivalent metals, Mg is a compelling choice since it couples the advantages of very high theoretical volumetric capacity (i.e. 3830 mAh/L versus 700 mAh/L of conventional graphite based Li-ion batteries) with high natural abundance, low cost and environmental sustainability.^{3,4} These unique features make Mg batteries one of the most attractive candidates for the

development of a sustainable “post-lithium” energy landscape.

The main caveat in multivalent ion based concepts is their slow diffusion, that has been successfully addressed in the case of Mg^{2+} by using more covalent hosts for insertion, as coulombic interactions with the anionic framework diminish if electrons are less localized. This allowed proof of concept for a secondary magnesium metal based battery with $\text{Mo}_6\text{S}_{8-y}\text{Se}_y$ ($y=1,2$) Chevrel phase cathode and a complex electrolyte solution⁵, yielding a cell potential < 2 V vs. Mg^{2+}/Mg . The extension of this approach has proved fast and reversible Mg^{2+} migration also in layered MS_2 ($\text{M}=\text{Mo}, \text{Ti}$) compounds^{6,7} and MgTi_2S_4 ⁸ thiospinel, delivering a stable capacity of 150 mAh g^{-1} at 60°C. However, the low average potential of these electrodes (i.e. < 1.8 V vs Mg^{2+}/Mg) limits the achievable energy density and hence their practical application scope. The development of alternative high redox potential cathodes with practical Mg^{2+} remains a presently unaddressed target^{2,9,10} in spite of the progresses in electrolytes exhibiting a larger electrochemical stability window and allowing reversible Mg stripping/deposition.^{4,9,11–13} In contrast, the feasibility of calcium metal plating and stripping in conventional alkylcarbonate electrolytes¹⁴ exhibiting a large operation voltage window even at high temperature recently opened the quest for high potential cathodes in multivalent systems, with oxides as the first target. Indeed, CaMoO_3 , CaMn_2O_4 have been investigated which unfortunately exhibited too large energy barriers for calcium ion diffusion even at high temperature.^{15,16} Alternatively, $\text{Mg}_2\text{Mo}_3\text{O}_8$ was also found to exhibit high activation barriers for bulk Mg^{2+} diffusion and deemed to be too ionic for effective divalent ion diffusion.¹⁷

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Following the study of more covalent M-X frameworks for divalent ion insertion, we decided to investigate nitrides as a new family of potential cathodes. In this case, the decrease in operating voltage induced by the enhanced degree of covalence within the host framework can be counterbalanced through the selection of suitable transition metal redox centers exhibiting high operating potentials. Furthermore, enhanced Mg^{2+} transport properties may be achieved by using low dimensionality (2D or 1D), open host structures characterized by short diffusion distances as well as by low energy diffusion topologies. In this work layered MgMoN_2 ternary nitride is explored as a potential cathode for Mg batteries through a combined experimental and modeling approach.

Ternary transition metal nitrides have been investigated for several applications including superconductivity¹⁸, as high permittivity dielectrics¹⁹ and as catalysts²⁰. They also have been already proved to allow faster Li^+ intercalation kinetics^{21–24}, which encourages the exploration of nitride phases as viable hosts for multi-valent charge carriers attempted in this work.

MgMoN_2 is isostructural to MnMoN_2 ²⁵ and exhibits a crystal structure built up by alternating layers along c of edge-sharing MgN_6 octahedra and MoN_6 trigonal prisms. This framework seems an interesting choice as it combines the advantages of delocalized electron distribution of the Mo-N framework with the expected high operating voltage of the Mo^{IV} redox centers while at the same time exhibiting an open, layered structure. Ternary MgMoN_2 nanosheets and micromeshes were previously synthesized by solid state reaction of a Mo source (Mo for nanosheets and MoO_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4\cdot 4\text{H}_2\text{O}$ for micromeshes), Mg and NaN_3 in autoclave at 700°C.²⁶ In this study highly crystalline MgMoN_2 is prepared by solid state reaction at high temperature between Mo and Mg_3N_2 in N_2 which represents a simple synthetic pathway avoiding the use of hazardous, thermally sensitive NaN_3 precursor which could violently explode when heated close to its decomposition temperature. Mg^{2+} (de-)intercalation is investigated both chemically and electrochemically, under various cell operative conditions and energy barriers to Mg^{2+} ion migration are estimated by DFT simulations. A computational study of the physical properties of the MgMoN_2 and fully de-magnesiased MoN_2 phase is also originally reported.

Experimental

Synthesis

Mg_3N_2 (Sigma Aldrich, > 99.5%) and Mo (Alfa Aesar, 99.9%) either in stoichiometric ratio or using a 38.5% or 85% (w/w) excess of Mg_3N_2 were mixed, grounded and pressed into pellets (10 Ton) under inert atmosphere. The pellets, placed in Mo (Alfa Aesar, 99.95%) crucibles inside a silica tube, were annealed at 1080°C for 20 hours under flowing N_2 (Air Products, Alphagaz, >99.9999%). A 300°C/hour rate was used for the heating step while the samples were naturally cooled after the thermal treatment. Zr foil (Goodfellow, 99.2%) was employed as sample holder caps and tube inlet traps in order to scavenge any adventitious oxygen or water around the pellets. A large expansion of the pellet volume was

observed after the thermal treatment and a black powder product was obtained. Batches of 300 and 500 mg of precursors' powder mixtures pressed into pellets were used for the synthesis.

The residual Mo in the obtained products was removed by two washing treatments with 3.5 M HNO_3 . The powders were stirred in HNO_3 solution (50 ml HNO_3 /g product) for three hours, vacuum filtered and then dried in vacuum oven at 75°C. N contents were determined by combustion analysis in oxygen in a Thermo Fisher Scientific instrument, heating the samples up to 1060 °C and using MgO, WO_3 and Sn as additives and atropine as a reference standard. Energy-Dispersive X-Ray Spectroscopy (EDS) analyses of cation contents were performed in a FEI Quanta 200 FEG scanning electron microscope equipped with a EDAX detector with an energy resolution of 132 eV.

Structural characterization

X-ray powder diffraction data were collected on a Siemens - model D-5000 diffractometer using $\text{CuK}\alpha$ radiation. High resolution synchrotron X-ray powder diffraction data at room temperature for MgMoN_2 were measured from a rotating capillary (0.5 mm diameter) samples in the angular range $3.2^\circ \leq 2\theta \leq 49.5^\circ$ at the MSPD beamline²⁷ of the ALBA Synchrotron Light Source (Cerdanyola del Vallès, Spain). Using a double Si (111) and monochromator, a short wavelength was selected and calibrated with Si NIST ($\lambda = 0.41269 \text{ \AA}$). Ultra-high resolution was achieved by using MAD bank of detectors equipped with Si (111) analyzer crystals. Room temperature neutron powder diffraction data for MgMoN_2 were collected on the D2B diffractometer at the Institut Laue-Langevin (ILL), Grenoble using 1 g of sample placed in a 5 mm diameter vanadium can. The neutron wavelength was 1.594 Å. Rietveld analysis was carried out using the program Fullprof.²⁸

Chemical and electrochemical oxidation reactions

Two chemical oxidation tests were performed by stirring under reflux for 6 hours or 1 day a 1:4 mol:mol mixture of MgMoN_2 and NO_2BF_4 powders (Alfa Aesar, 96%) in 50 ml of anhydrous acetonitrile, under continuous Ar bubbling. Evolution of NO_2 gas was immediately observed. Ar bubbling within the solution was maintained to avoid eventual passivation of the nitride particles through undesired reactions with the NO_2 gas, as reported for the LiMoN_2 phase.²⁹ Once the reaction finished, the mixtures were vacuum filtered and the obtained powders were rinsed with anhydrous acetonitrile and dried under vacuum before being analyzed.

First electrochemical tests were done using two- and three-electrode Swagelok cells with Li metal foil counter electrode. The reason for this stems from the lack of available large potential window electrolytes enabling magnesium plating, which would be the process taking place at the counter electrode if MgMoN_2 was oxidized at the working electrode. Lithium was also used as reference electrode, as it has proved to be much more reliable than other mono valent and divalent metals.³⁰ The working electrode consisted of either powder mixtures of 85% wt MgMoN_2 and 15% wt Super P carbon (Timcal) or tape casted electrodes (MgMoN_2

(85% wt), Super P carbon (7% wt) and polyvinylidene difluoride (PVdF, Kynar) binder (8% wt). The latter were punched from doctor-blade casted tapes on Al foil (Goodfellow, 99%) from N-methyl pyrrolidinone (NMP, Sigma-Aldrich) slurries. These were prepared by a 1 hour mechanical milling treatment of the prepared dispersion at 500 Hz with a RETSCH PM100 instrument before tape casting.

1M LiPF_6 salt in a 1:1 v mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) solvents (Solvionic, 99.9%) was used as electrolyte solution for room temperature and 55°C electrochemical tests, soaked in a glass fiber Whatman separator. Alternatively, 1M Lithium bis-oxalate borate (LiBOB, Sigma-Aldrich) in a mixture of ethylene carbonate (EC, Sigma-Aldrich, 99%) and propylene carbonate (PC, Sigma-Aldrich, 99.7%) (EC:PC 1:1 v) was used for high temperature tests (120°C and 100°C).

Electrochemical oxidation tests at 100°C were also performed in three electrode cells with Ca metal counter and reference electrodes, using 0.45 M $\text{Ca}(\text{BF}_4)_2$ in EC:PC (1:1 v) mixture as electrolyte.

The Li and Ca electrolytes used are stable in the electrochemical window explored and they enable, respectively, Li and Ca metal plating under the conditions employed, thus ensuring reliable electrochemical tests. (Note that metal plating would take place at the counterelectrode if the working electrode is oxidized).

All the electrochemical cells were Swagelok type and assembled in Ar-filled dry box. Al and stainless steel current collectors were used for the working and reference/counter electrodes, respectively. Polished Li-metal and Ca metal discs (obtained by pressing Ca pieces under inert atmosphere) were used as counter/reference electrodes. Whatman separators soaked in 0.6 ml of electrolyte solution were employed. The amount of active material in the powder and tape electrodes used was of about 5 mg and 2 mg, respectively.

Galvanostatic Cycling with Potential Limitations (GCPL) and Extended Potentiostatic Steps (EPS) tests at different rates, ranging between C/10 and C/400, were performed using VMP3 and MPG (Bio-logic) potentiostats. After the electrochemical tests the working electrodes were washed with DMC and dried in Ar-filled dry box and active material recovered and sealed inside 0.5 mm diameter borosilicate glass capillaries.

Computational Study

First principles calculations have been performed using the ab-initio total-energy and molecular dynamics program VASP (Vienna ab-initio simulation program) developed at the Universität Wien.³¹ Total energy calculations based on Density Functional Theory (DFT) were performed for MgMoN_2 within the General Gradient Approximation (GGA), with the exchange and correlation functional form developed by Perdew, Burke, and Ernzerhof (PBE).³² For a better description of the van der Waals interactions, the calculations were also performed using the optB86b-vdW exchange-correlation functional.³³ The interaction of core electrons with the nuclei is described by the Projector Augmented Wave (PAW) method.³⁴ The pseudopotentials used were Mg_{pv} ($2p^6 3s^2$),

Mo_{sv} ($4p^6 5s^2 4d^4$), and N ($2s^2 p^3$). The energy cut off for the plane wave basis set was kept fix at a constant value of 650 eV throughout the calculations. The reciprocal space sampling was done in a $8 \times 8 \times 6$ k-point grid. A convergence of the total energy close to 10 meV per formula unit is achieved with such parameters. All crystal structures were fully relaxed (atomic positions, cell parameters and volume). The final energies of the optimized geometries were recalculated so as to correct the changes in the basis set of wave functions during relaxation. Spin polarized calculations were performed in all cases. Migration barriers for Mg hops between adjacent octahedral sites in MgMoN_2 were calculated using the Nudged Elastic Band method (NEB) as implemented in VASP considering a $\text{Mg}_{17}\text{Mo}_{18}\text{N}_{36}$ supercell, where one Mg atom is removed leaving a vacant octahedral site. Constant volume calculations were performed for three and six intermediate images. To calculate the energy at the saddle point, cubic splines were fit through the images along each hop.

Results and discussion

Synthesis and characterization

MgMoN_2 was prepared at 1080 °C according to the reaction:

The samples with lowest impurities were obtained by using a Mg_3N_2 excess, as significant Mg loss was observed above 1000 °C. **Figure 1** shows the X-ray powder diffraction patterns of samples obtained by using stoichiometric Mo/ Mg_3N_2 ratio (light blue) and 38.5 % and 85% weight excess of Mg_3N_2 (blue and grey line, respectively).

All samples exhibit the diffraction peaks of MgMoN_2 ²⁶ together with those of Mo (Powder Diffraction File PDF 42-1120) appearing at 2 theta values of 40.5, 58.6 and 73.7 degrees with the MgMoN_2/Mo ratio enhanced by increasing the amount of Mg_3N_2 . Residual Mo in the samples was removed by two washing treatments with diluted HNO_3 . This compound proved to be stable in ambient air over prolonged time.

A combined Rietveld analysis of synchrotron X ray and neutron powder diffraction data was performed using the reported structural model from X-ray diffraction²⁶ as initial crystal parameters. Results of the refinements are shown in **Figures 2a** and **2b** and in Table 1. The crystal structure of the MgMoN_2 is depicted in the inset of **Figure 2a**. The thermal factor of Mg ($\sim 0.3 \text{\AA}^2$) is considerable smaller than that previously reported for LiMoN_2 ($\sim 6 \text{\AA}^2$)²⁹ which is consistent with lower Mg mobility. Refinement of occupation factors results in a stoichiometric N/Mo ratio, and a slight Mg deficiency [$\text{Mg}/\text{Mo}=0.94(2)$].

Figure 1: X ray diffraction patterns of the MgMoN_2 samples obtained by solid state reaction of Mg_3N_2 and Mo under N_2 gas, with stoichiometric Mo/ Mg_3N_2 ratio (light blue) and with 38.5% (dark blue) and 85% weight excess (grey) of Mg_3N_2 . Mo reflections are indicated by asterisks.)

Figure 2: (a) Observed and calculated synchrotron X ray diffraction patterns of MgMoN_2 ($\lambda = 0.41269 \text{ \AA}$). Inset: crystal structure of MgMoN_2 . Color code: Mg in yellow, Mo in purple and N in blue.. (b) Observed and calculated neutron diffraction patterns of MgMoN_2 ($\lambda = 1.594 \text{ \AA}$).

Table 1. Atomic coordinates in hexagonal space group $P6_3/mmc$ (no. 194) with cell parameters $a = 2.91059(3)$, $c = 10.5484(1) \text{ \AA}$ and isotropic temperature factors for MgMoN_2 from the combined refinement to synchrotron ($\lambda = 0.41269 \text{ \AA}$) and neutron ($\lambda = 1.594 \text{ \AA}$) powder diffraction data at room temperature.^a

Atom	Wyckoff Site	x	y	z	B($\text{\AA}^2$)
Mg	2a	0	0	0	0.28(6)
Mo	2d	0.3333	0.6667	0.75	0.06(2)
N	4f	0.3333	0.6667	0.1292 (2)	0.26 (3)

Interatomic distances ($\text{\AA}$):

Mo-N 2.109(1) Mg-N 2.164(1)

Mo-Mo 2.91059(3) Mg-Mg 2.91059(3)

^aOccupation factors were fixed to the ideal stoichiometry. Agreement factors for synchrotron data: $\chi^2 = 1.05$; Rwp = 10.5 %; RBragg = 2.50 %. Agreement factors for neutron data: $\chi^2 = 3.64$; Rwp = 3.52 %; RBragg = 2.52 %.

The Mg/Mo molar ratio determined by EDX spectroscopy was 1.1 while the N content (% weight) determined by elemental analysis was 19.3 %, which is, within experimental error, close to 18.9 % expected for MgMoN_2 .

The Scanning Electron Microscopy (SEM) micrographs in **Figures 3a** and **3b** show the morphology of the synthesized MgMoN_2 sample, which is composed by micrometric aggregates of homogeneous particles. As noticeable in **Figure 3b**, each aggregate is formed by layers of sub-micrometric and nanometric nitride particles. The high chemical homogeneity degree of the sample was assessed through combined SEM-EDX analysis.

Figure 3: SEM micrographs of the MgMoN₂ sample.

Attempts to de-intercalate Mg²⁺

Mg²⁺ de-intercalation in MgMoN₂ was attempted both chemically and electrochemically using different types of electrodes (powdered or tape casted) and under very different conditions (*i.e.* temperature, electrolyte, rate, etc.).

Figure 4(a) displays representative voltage vs. capacity profiles for the MgMoN₂ tape electrode in lithium three electrode cell upon oxidation at room temperature and 120°C (*i.e.* the lowest and highest temperature investigated in this study) using, respectively, 1M LiPF₆, EC:DMC 1:1 vol and 1M LiBOB, EC:PC 1:1 vol electrolytes. The inset depicts further cycling for a MgMoN₂ powder electrode (with 15% weight of super P Carbon) at room temperature, in lithium two electrode cell.

A sloping increase of the potential is observed at room temperature, with very low capacity (< 50 mA h g⁻¹) delivered between 4 and 4.5 V vs Li⁺/Li, regardless the use of tape casted or powder electrodes, which is not recovered upon subsequent reduction. In contrast, a plateau between 4 and 4.25 V vs Li⁺/Li is observed at 120°C (the charge test was capacity limited up to the complete de-magnesiumation of MgMoN₂). Similar results were obtained in cells using calcium metal counter electrodes and 0.45M CaBF₄ in EC:PC(1:1v) electrolyte(100°C).

Figure 4: (a) Potential vs. capacity profiles for the MgMoN₂ tape electrodes in three electrode cells using lithium counter electrodes at room temperature and 120°C. Electrolyte solutions: 1M LiPF₆ in EC:DMC 1:1 v (RT) and 1M LiBOB in EC:PC 1:1 v (120°C). Inset: Potential vs. capacity profile for a Li/1M LiPF₆, EC:DMC 1:1/MgMoN₂-Carbon (85:15 %w) cell at RT. (b) Ex-situ XRD patterns of the MgMoN₂ sample as prepared (black), after 1 day reaction with NO₂BF₄ (green), after galvanostatic charge at room T (light blue), 100°C (blue) and 120°C (dark blue).

Figure 4(b) depicts the XRD patterns of as prepared MgMoN₂ and those corresponding to the powders recovered after electrochemical oxidation in different conditions and chemical oxidation with NO₂BF₄.

The X-Ray Diffraction (XRD) patterns of electrochemically oxidized samples (see **Fig. 4(b)**), do not exhibit any relevant difference with respect to the one corresponding to prepared MgMoN₂ and no significant differences in the cell parameters are deduced from Rietveld refinements (listed in **Table 2**). No hints are observed either which would point at the presence of an amorphous phase, as observed, for example, after oxidation of Mg₂Mo₃O₈.¹⁷ Electrochemical experiments aiming at reducing MgMoN₂ through additional ion intercalation were also attempted down to 0.5 V vs Li⁺/Li but the XRD pattern of the electrochemically reduced sample did not reveal any appreciable lithiation of the MgMoN₂ phase either.

Chemical oxidation with NO_2BF_4 , following the reaction:

was also attempted but no appreciable de-magnesiation of the MgMoN_2 phase was achieved, even using large excess of NO_2BF_4 (i.e. 100% excess) and extending the reaction time from 6 to 24 hours, as deduced by the absence of significant peak shift or additional phase formation in the XRD pattern of the MgMoN_2 sample after reaction with NO_2BF_4 (shown in Fig. 4b).

The NO_2 evolution observed at the beginning of the chemical oxidation tests may be reasonably ascribed to several, concomitant processes, including: i) the reaction of NO_2BF_4 with some water contained in the solvent employed (even if dry acetonitrile was used and Ar was continuously fluxed in the reaction vessel); ii) the oxidation of residual traces of Mo metal in the sample; iii) possible superficial oxidation MgMoN_2 , which is dissolved/decomposed in acetonitrile and not recovered upon filtration.

Table 2. Cell parameters of pristine and samples after attempts of chemical oxidation determined by Rietveld refinement of data depicted in Figure 4.^a

	Pristine	Chem.	Electroch. RT	Electroch. 120°C
$a(\text{\AA})$	2.91059(3)	2.9092(13)	2.9085(13)	2.9077(13)
$c(\text{\AA})$	10.5484(1)	10.551(5)	10.550(5)	10.546(5)

Aiming to shed light on the factors hampering the reversible migration of Mg^{2+} ions, a theoretical study of the MgMoN_2 host phase in terms of Mg^{2+} diffusion barrier and topology was performed by DFT simulations.

Table 3 summarizes the cell parameters estimated through the BPE and the optB86 approximations. The experimental lattice parameters and cell volume of MgMoN_2 are well reproduced within the two approximations. As shown in **Figure 5** the calculated DOS corresponds to a diamagnetic material with a band gap of 0.7 eV. The strong hybridization between d-Mo and p-N orbitals indicates a highly covalent Mo-N bond. However, we should note that diamagnetic properties are consistent with Mo^{4+} (d^2 configuration) ions in a prismatic coordination. This is comparable to the simplest picture of the ligand field splitting in MoS_2 , where the two d electrons fill the band formed by the lowest dz^2 orbitals.^{35,36} As for MoS_2 ^{37,38}, the utilization of hybrid functionals in the calculation will provide a better description of the electronic structure of Mg_xMoN_2 phases, which is out of the scope of this paper.

Mg_xMoN_2				
Method	a ($\text{\AA}$)	c ($\text{\AA}$)	v ($\text{\AA}^3$)	x
PBE	2.923	10.594	78.43	1
Opt_B86	2.909	10.549	77.35	
Experimental (this work)	2.91059(1)	10.54843(6)	77.389(1)	

Table 3: Calculated lattice parameters and volume of MgMoN_2 and. Experimental results are given for comparison.

Figure 5: Calculated density of states (DOS) of MgMoN_2 . The black lines denote the total DOS; the partial DOS of Mg, Mo and N are represented in yellow, blue and green lines, respectively. The zero of the energy has been set at the Fermi level.

The barrier for Mg^{2+} migration in MgMoN_2 is investigated assuming the simplest Mg^{2+} diffusion mechanism which implies the jump of a Mg^{2+} ion to an empty octahedral neighboring site. The two octahedral sites share a face with a tetrahedral site, providing a Oh-Th-Oh path for diffusion. The calculated energy barrier (PBE) is of 1.8 eV (see Figure 6a). Interestingly, in the low energy migration path (see figure 6b), the diffusing Mg^{2+} cation does not occupy the tetrahedral site, and a direct migration between octahedral sites is preferred. The tetrahedral site is also sharing a face with a Mo^{4+} -N octahedra, and it is likely that the strong Mo^{4+} - Mg^{2+} Coulombic repulsion penalizes the occupation of the tetrahedral site. Therefore, the diffusing Mg^{2+} ion passes through the N-N edge and at the saddle point the Mg^{2+} is coordinated by 2 N ions at a short distance of 1.86 $\text{\AA}$ (Mg-N distance is 2.16 $\text{\AA}$), resulting in a very high migration barrier. The high energy barrier to Mg^{2+} migration estimated by computational methods well rationalizes the absence of chemical and electrochemical activity of the MgMoN_2 phase observed experimentally.

Figure 6: Calculated energy barrier for Mg diffusion in MgMoN₂ (a) and corresponding migration path in the structure (b) with the diffusing Mg²⁺ ion in green.

These values are in agreement with the experimental observations that Mg²⁺ extraction from MgMoN₂ is not viable.

In line with the other computational studies on multivalent ions' mobility^{17,39}, this work underlines the importance of DFT calculations to assess energy migration barriers. Thus, the exploitation of highly covalent anionic framework, such as the nitride suggested in this work, may not represent a viable strategy to overcome the Mg²⁺ mobility issue if not coupled with a crystal chemistry guided design of phases with low energy Mg²⁺ diffusion pathway, i.e. with low energy intermediate state as well as with migration sites well matching with the preferred Mg²⁺ coordination.

Conclusions

MgMoN₂ phase was prepared by solid state reaction of Mg₃N₂ and Mo precursors followed by a washing treatment with diluted HNO₃. The structure of the obtained phase was investigated by XRD and neutron diffraction techniques. Despite the open layered structure and highly covalent anionic framework of MgMoN₂, attempts to de-intercalate Mg²⁺ ions both chemically, by oxidation reaction with NO₂BF₄, or electrochemically, by galvanostatic and potentiostatic tests under different conditions, were unsuccessful. As inferred from DFT simulations, the absence of electrochemical activity experimentally observed for the MgMoN₂ phase may be reasonably ascribed to the elevated migration barrier of Mg²⁺ ions within the host framework, estimated to be as high as 1.8 eV by computational methods. The high migration barrier is ascribed to the existence of N-N edges along the diffusion pathway that involve Mg-N interactions with a very short bond distance. Although unsuccessful from an application perspective, the results achieved in this study through combined experimental and computational approach contribute to the fundamental understanding of the Mg²⁺ mobility issue within layered hosts and are crucial to identify suitable cathode materials for magnesium batteries. The consideration of possible migration barriers will help in the design of new nitride-based magnesium networks (either fully nitrated or mixed anion compounds). These certainly deserve further investigation if we consider that they are much less explored than oxides, but with

analogous crystal chemistry and a larger covalent character of Mg-anion bond.

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