

# Identification of new Mg2+ solid ionic conductors through the exploration of the Mg(BH4)2-Mg(NH2)2 phases diagram

Ronan Le Ruyet

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# Thèse de Doctorat

### Mention : Chimie Spécialité : Chimie des Solides et Sciences des Matériaux

présentée à l'Ecole Doctorale en Sciences Technologie et Santé (ED 585)

# de l'Université de Picardie Jules Verne

par

# **Ronan LE RUYET**

pour obtenir le grade de Docteur de l'Université de Picardie Jules Verne

Identification of new  $Mg^{2+}$  solid ionic conductors through the exploration of the  $Mg(BH_4)_2$ - $Mg(NH_2)_2$  phases diagram

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A ma famille,

A Laura

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# **General introduction**

In a world consuming more and more electricity (*cf.* Figure 1a),<sup>1</sup> rechargeable batteries are playing a key role.<sup>2</sup> They are used in many applications such as: electrical vehicles (EVs), mobile electronics and stationary energy storage. Rechargeable batteries have been mainly used until now for portable electronics but a growing demand is coming from other applications such as electrical vehicles (*cf.* Figure 1b).<sup>3</sup> EVs are expected to replace the majority of the vehicles using internal combustion engines in the coming years. The production of stationary batteries could also start to grow in the context of renewable energies. Indeed, renewable energies are intermittent and need to be stored to ensure a continuous electricity supply.



Figure 1. a) World electricity consumptions per year for the different regions of the world. b) Li-ion batteries sales per year for different applications.<sup>1,3</sup>

Nowadays, the most common rechargeable batteries are based on Li-ion technology. This leadership is mainly due to their energy density that is the highest of all existing technologies (up to 200 Wh.kg<sup>-1</sup>, *cf.* Figure 2).<sup>4</sup> Their large impact on the society has been rewarded with the Nobel Prize of Chemistry 2019 to John B. Goodenough, Stanley Whittingham and Akira Yoshino for the development of rechargeable Li-ion batteries. This technology is so versatile that its massive utilization starts to create problem of sustainability. Elements such as Co, which is used in the cathode material of most of the commercial Li-ion batteries, are rare and present in only few regions of the world. For these reasons, their price and availability are unstable.<sup>5</sup> Solutions are studied to substitute these elements by more abundant ones or to replace them totally by using post Li-ion technologies such as Li-S batteries. Beyond Li-based batteries, other technologies are studied. For instance, systems based on Na or K ions, two elements which are much more abundant than lithium, are developed. Then, systems based on multivalent Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup> or Al<sup>3+</sup> ions are studied to try to increase the energy density of the batteries.<sup>6</sup> Among these multivalent ions, Mg<sup>2+</sup> has been the one attracting the more interest during the last two decades.



Figure 2. Comparison of different battery technologies in terms of volumetric and gravimetric energy densities.<sup>4</sup>

Rechargeable Mg batteries have been studied since the early 90's but it is only in 2000 that a functional cell has been assembled by Aurbach *et al.*. Nevertheless, this first cell could not deliver

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large energy amounts. Thus, important efforts have been put by the scientific community to design better cells but none of them can deliver high capacity and/or high voltage for many cycles. The main problems lay in finding cathode materials allowing fast insertion of Mg ions and electrolytes with good ionic conductivities and wide electrochemical stability windows. To improve rechargeable Mg batteries, our approach was to study the possibility of using solid-state electrolytes. Indeed, they could offer benefits such as better chemical and electrochemical stabilities and better safety. The candidates as solid electrolyte materials were selected among the existing inorganic solid Mg<sup>2+</sup> ionic conductors (*i.e.* no mixed electronic/ionic conductors such as electrode materials). Few materials are reported as Mg<sup>2+</sup> is a strongly polarizing cation and, thus, it has a sluggish mobility in solids. Most of the inorganic solid state Mg<sup>2+</sup> ionic conductors are listed in **Chapter I**. Three families can be found: the phosphates, the sulphides and the complex hydrides. The phosphates, based on Mg-Zr-PO<sub>4</sub>, have high ionic conductivities but only at high temperatures, typically ~10<sup>-3</sup> S.cm<sup>-1</sup> at 800°C. Then, the sulphides, based on MgS-P<sub>2</sub>S<sub>5</sub> glasses or glass/ceramics, have too low ionic conductivities (~10<sup>-7</sup> S.cm<sup>-1</sup> at 200°C) to be interesting as solid electrolytes. Finally, the complex hydrides, based on  $Mg(BH_4)_2$ , have the best ionic conductivities at low temperatures (~10<sup>-5</sup>-10<sup>-6</sup> S.cm<sup>-1</sup> below 150°C). Furthermore, they are the only ones that have been characterized regarding possible applications in Mg batteries (e.q. Mg deposition/stripping, electrochemical stability, etc.). It was decided to start our study with  $Mg(BH_4)(NH_2)$  that was previously reported as a promising  $Mg^{2+}$  solid ionic conductor.<sup>7</sup> Mg(BH<sub>4</sub>)(NH<sub>2</sub>) was described for the first time by Noritake *et al.* in 2013.<sup>8,9</sup> They synthesized it from the reaction of  $Mg(BH_4)_2$  with  $Mg(NH_2)_2$ . Unfortunately, the synthesis parameters were not reported (ball-milling speed, annealing time or temperature, etc.).

The first part of this thesis is dedicated to the determination of the appropriate synthesis parameters needed to obtain Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (*cf.* **Chapter II**). After several attempts with different synthesis parameters, crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>) could be obtained. It appeared however by <sup>11</sup>B MAS-NMR spectroscopy that none of our samples was completely pure as they all contain an additional phase. Interestingly, this additional phase had an important effect on the ionic conductivity values.

The next part of the thesis was the exploration of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram (*cf.* **Chapter III**). A series of syntheses with different stoichiometries has been performed: it revealed the existence of three other crystalline phases. Two rich in amide that we labeled  $\alpha$  and  $\beta$ -phase, and one rich in borohydride labeled the  $\gamma$ -phase. These phases were studied for the first time as no other reported work describes these compounds. Their crystal structures and ionic

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conductivities were especially studied. It appeared that the ionic conductivity follows a trend as a function of the composition and that new compounds with a high Mg<sup>2+</sup> mobility can be obtained. Once it was demonstrated that good inorganic solid Mg<sup>2+</sup> ionic conductors could be obtained, these materials had to be further characterized to assess their potential use as solid electrolytes.

The final part of this PhD thesis is dedicated to the characterization of the chemical and electrochemical stability of the newly discovered  $Mg^{2+}$  ionic conductors (*cf.* **Chapter IV**). The chemical stability was characterized by annealing a mixture of our solid electrolytes with electrode materials that can be used in rechargeable Mg batteries (*e.g.* Mg metal as the anode electrode and the Chevrel phase  $Mo_6S_8$  as the cathode). Then, the electrochemical stability was characterized by polarization and cyclic voltammetry experiments.

### References

- World power consumption, electricity consumption. Available at: https://yearbook.enerdata.net/electricity/electricity-domestic-consumption-data.html. (Accessed: 21<sup>st</sup> November 2019)
- 2. Battery 2030. *Manifesto European scientific leadership*. (2019).
- 3. European Commission. *Li-ion batteries for mobility and stationary storage applications Scenarios for costs and market growth*. (2018).
- Tarascon, J.-M. & Armand, M. Issues and challenges facing rechargeable lithium batteries. Nature 414, 359–367 (2001).
- 5. European Commission. *List of Critical Raw Materials for the EU*. (2017).
- Larcher, D. & Tarascon, J.-M. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* 7, 19–29 (2015).
- 7. Higashi, S., Miwa, K., Aoki, M. & Takechi, K. A novel inorganic solid state ion conductor for rechargeable Mg batteries. *Chem. Commun.* **50**, 1320–1322 (2014).
- Noritake, T. *et al.* Synthesis and crystal structure analysis of complex hydride Mg(BH<sub>4</sub>)(NH<sub>2</sub>). *Int. J. Hydrogen Energy* 38, 6730–6735 (2013).
- Noritake, T. et al. Dehydrogenation properties and crystal structure analysis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>). J. Alloys Compd. 580, S85–S89 (2013).
- 10. Borgschulte, A. *et al.* Surface and bulk reactions in borohydrides and amides. *Energy Environ. Sci.* **5**, 6823–6832 (2012).

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# <u>Chapter I -</u> State-of-the-art: Rechargeable Mg batteries and Mg<sup>2+</sup> inorganic solid electrolytes

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Chapter I - State-of-the-art: Rechargeable Mg batteries and Mg<sup>2+</sup> inorganic solid electrolytes

### I-1. Batteries: short reminder of their principle and main characteristics

A battery is the assembly of one or several cells used to store electrical energy under chemical one through electrochemical reactions. Each cell is made of two electrodes separated by an electrolyte (*cf.* Figure I. 1). Batteries can be separated into two categories: the primary cells and the secondary cells. The primary cells are not rechargeable and secondary cells can be recharged. If a cell is charged, connecting the two electrodes will allow the electrical current to pass from one electrode to the other and the battery will discharge. Once a cell is discharged, it can be charged by applying a reverse current.



Figure I. 1. Scheme of the principle of a battery upon discharge (a) and charge (b).

Redox reactions are occurring simultaneously at both electrodes: at the anode and at the cathode. In electrochemistry, the oxidation happens at the anode (negative electrode) while the reduction happens at the cathode (positive electrode). In batteries, it is commonly admitted to call "anode" the electrode with the lower redox potential and "cathode" the one with the higher redox potential. The cells are characterized by their working potential  $V_{cell}$  and their capacity  $Q_{cell}$ . The working potential  $V_{cell}$  is the difference between the potential of each electrode. The capacity Q is the quantity of charges that can be released or stored by the electrodes and it can be calculated by the Faraday's law:

$$Q = n. n_e. F$$
 Equation I. 1

with

n: the number of exchange species (mol)  $n_{e}$ : the number of electrons exchanged

F: the Faraday's constant (96500 C.mol<sup>-1</sup>, and 1 C = 1 A.s)

Equation I.1 gives the capacity Q in Coulomb but the unit commonly used for batteries is the Ah. The specific and volumetric capacity can be calculated modifying Equation I. 1. The specific capacity is:

$$Q_{spe} = \frac{1}{M} \cdot n_{e} \cdot F$$
 Equation I. 2

with M: the molar mass of the electrode

The volumetric capacity is obtained in a similar way with the equation II.3:

$$Q_{vol} = \frac{\rho}{M} \cdot n_{e^-} \cdot F$$
 Equation I. 3

with p: the density of the electrode

In a full cell, the capacity is limited by the electrode having the lowest capacity. To avoid dead weight of electrode materials, the battery must be balanced to have the same capacity at both cathode and anode. The specific and volumetric capacities are expressed as:

$$\begin{array}{cccc}
Q_{spe\ cell} & Q_{vol\ cell} & Equation 1. 4 \\
= \frac{Q_{spe\ cathode} \cdot Q_{spe\ anode}}{Q_{spe\ cathode} + Q_{spe\ anode}} & \text{and} & = \frac{Q_{vol\ cathode} \cdot Q_{vol\ anode}}{Q_{vol\ cathode} + Q_{vol\ anode}} & Equation 1. 5
\end{array}$$

From  $V_{cell}$  and  $Q_{cell}$  it is possible to determine the energy  $E_{cell}$  (usually in Wh) that can be delivered by the cell:

$$E_{cell} = V_{cell}.Q_{cell}$$
 Equation I. 6

The power P<sub>cell</sub> (in W) of the cell is calculated by dividing the energy by the time:

$$P_{cell} = \frac{E_{cell}}{t}$$
 Equation I. 7

with t: the time of charge/discharge

To ensure the charge balance of the redox reactions, it is necessary to have an electrolyte between the two electrodes. The electrolyte is an ionic conductive medium that allows ions to pass from an electrode to the other; whereas it is an electronic insulator avoiding short-circuits between the electrodes. It is characterized by different intrinsic properties:

- the transference number,
- the viscosity,
- the ionic conductivity,
- the electrochemical stability window.

For solid electrolytes, the important parameters are the ionic conductivity and the electrochemical stability window. The transference number in inorganic solid electrolytes is usually 1 as only one ion is the charge carrier, the counter anions/cations are fixed in the structure and the electronic conductivity must be close to zero.

### I-2. Rechargeable Mg batteries

### I-2a. From Li-ion to post Li-ion batteries

Nowadays, the most commonly used rechargeable batteries are Li-ion batteries (LIBs). They have many advantages in terms of energy density, lifetime and can be used at different scales: portable electronics, vehicles and stationary energy storage systems. Nevertheless, the massive production of LIBs needed to meet the ever-growing demand in electricity has arisen new problematics such as the shortage of raw materials because of their low relative abundance and geopolitical issues. For instance, there is a mismatch between some of the most abundant element on earth which are the constituents of the biomass (H, O, S, P, Na, K, Ca, Mg, Mn, Fe, Ti) and main constituents of LIBs (for example, Li, Co, Ni, Cu, F). In 2017, the European Commission has classified Li and Co as critical raw materials for the European Union (EU) because of risks of supply shortage.<sup>1</sup> To anticipate this situation, researchers are looking for post Li-ion technologies based on more abundant elements like Na, K, Mg, Ca, Zn or Al. Among these new technologies Na-ion batteries (NIBs) are the most advanced one, achieving high voltage (>3 V) and good capacity retention. <sup>2</sup>

Mg batteries are another option to replace LIBs. On the contrary to NIBs for which the knowledge transfer from LIBs helped their development, the rechargeable Mg batteries need specific electrolytes and electrode materials. The particular chemistry of Mg open the way for new advantages but also new challenges that will be described in the following subsections.<sup>3</sup>

### I-2b. Magnesium metal anode

The intrinsic properties of magnesium present many advantages that make it an excellent candidate as anode material for batteries. First of all, it has a highly negative standard potential of -2.356 V *vs.* NHE close to the one of lithium (-3.040 V vs NHE, *cf.* Figure I. 2b). The second interesting feature of magnesium as anode material is its divalency as a cation. Its redox reaction involves two electrons and its theoretical gravimetric capacity is 2205 mAh.g<sup>-1</sup>. This value is lower than the one of lithium (3829 mAh.g<sup>-1</sup>) but taking into account the higher density of magnesium (1.74 g.cm<sup>-3</sup>), its volumetric capacity overpasses the one of lithium (3833 mAh.cm<sup>-3</sup> *vs.* 2046 mAh.cm<sup>-3</sup>, *cf.* Figure I. 2c).



Figure I. 2. Illustration of some intrinsic advantages of Magnesium. a) Magnesium is a solid metal in ambient conditions. b) Standard redox potentials and c) gravimetric and volumetric capacities of different anode materials: Li, Na and Mg.

Magnesium has also interesting technical properties. It is solid at room temperature ( $T_{melting} = 650$ °C). It can be manipulated in ambient atmosphere. It has a large abundance in the Earth crust of 21,100 ppm (*vs.* 10 ppm for Lithium)<sup>4</sup> but it is considered as a critical raw materials by the European Comission as Li and Co because of geopolitical issues. Actually, 94 % of Mg consumed in the EU comes from China. In terms of electrochemistry, its deposition has been considered for many years to be dendrites free.<sup>5–7</sup> In fact, many studies have proved that the electrodeposition of magnesium leads to the formation of smooth films (*cf.* Figure I. 3a).<sup>8</sup> Nevertheless, this consideration has been questioned and a recent paper from Davidson *et al.* warns on the possibility of dendrites formation on magnesium electrodes<sup>9</sup>. They show that magnesium, as any other electrodeposited metals, can form dendrites under certain conditions. They concluded that local inhomogeneities can result in an electrochemical reaction rate that overpasses self-diffusion rate and thus leads to the formation of dendrites (*cf.* Figure I. 3b). So the dendrite free characteristic of Mg electrodeposition has to be considered with caution because it depends on the studied system.

a)





Figure I. 3. a) Smooth electrodeposited Mg film using an electrolyte made of 0.25 M of EtMgCl-2Me<sub>2</sub>AlCl (Et = ethyl and Me = methyl) in THF (THF = tetrahydrofuran) applying 1.0 mA cm<sup>-2</sup> in a cell made of a polished Pt working electrode and a Mg foil counter electrode.<sup>8</sup> b) Magnesium dendrites formed in a cell using 0.5 M of MeMgCl in THF and operating at a constant current of 0.921 mA.cm<sup>-2</sup> in a Mg-Mg symmetrical cell.<sup>9</sup>

### I-2c. Prototypes of rechargeable Mg batteries

Here, we describe how the rechargeable Mg batteries have evolved during the past 30 years and give a non-exhaustive list of examples of rechargeable prototypes. Thomas D. Gregory *et al.* were the first to consider the feasibility of rechargeable Mg batteries in 1990.<sup>10</sup> Trying different intercalation materials as cathode and different electrolytes, they assembled the first rechargeable Mg battery. Their cell was made of Mg for the anode and Co<sub>3</sub>O<sub>4</sub> for the cathode with an electrolyte made of 0.25 M of Mg[B(Bu<sub>2</sub>Ph<sub>2</sub>)]<sub>2</sub> (Bu = butyl and Ph = phenyl) in THF/DME (DME = dimethoxyethane) solvent (*cf.* Figure I. 4). It was a preliminary study on materials that could be used for rechargeable Mg batteries. Only few cycles were performed and the electrolyte might have decomposed because of the high potential of cobalt oxide (2.28 V *vs.* Mg<sup>2+</sup>/Mg).



Figure I. 4. a) Cycling behavior of a cell Mg/0.25M Mg[B(Bu<sub>2</sub>Ph<sub>2</sub>)]<sub>2</sub>,THF/DME/Co<sub>3</sub>O<sub>4</sub>.<sup>10</sup>

Ten years later, in 2000, Aurbach et al. published a study on the first prototype of rechargeable Mg battery able to handle hundreds of cycles.<sup>11</sup> There were two breakthroughs in their study. First, the development of a new family of liquid electrolytes based on Mg organo-haloaluminate salts such as Mg(AlCl<sub>3</sub>R)<sub>2</sub> and Mg(AlCl<sub>2</sub>RR')<sub>2</sub>, where R and R' are alkyl groups, in THF or polyethers of the glyme family. These electrolytes have a good ionic conductivity (~10<sup>-3</sup> S.cm<sup>-1</sup> at room temperature) and allow a deposition/stripping of magnesium with a coulombic efficiency close to 100%. The other advantage of these electrolytes is their electrochemical stability that reaches 2.5 V vs Mg<sup>2+</sup>/Mg using a Pt working electrode. The second breakthrough is the use of the Chevrel phase Mo<sub>6</sub>S<sub>8</sub> as cathode material. Indeed, usual cathode materials for Mg batteries suffer from slow kinetics and/or too high working potentials compared to the electrolyte electrochemical stability. This Mo<sub>6</sub>S<sub>8</sub> cathode allows Mg to be reversibly intercalated electrochemically, at relatively fast kinetics and at moderate potential ( $\sim$ 1.2 V vs. Mg<sup>2+</sup>/Mg). Thus they assembled a cell made of Mg/0.25 M Mg(AlCl<sub>2</sub>BuEt)<sub>2</sub> in THF/Mo<sub>6</sub>S<sub>8</sub> that could perform hundreds of cycles with a high coulombic efficiency at both cathode and anode sides (cf. Figure I. 5). Still, this battery cannot compete with any type of Li-ion battery in terms of energy density because its working potential is too low and the maximum theoretical capacity of Mo<sub>6</sub>S<sub>8</sub> is only 122 mAh.g<sup>-1</sup>. However, with its theoretical energy density (~60 Wh.kg<sup>-1</sup>, considering that only 50 % of the mass is active), it could be a substitute to Ni-Cd and lead-acid batteries (about 40 Wh.kg<sup>-1</sup>).<sup>12</sup>



 Figure I. 5. a) Typical electrochemical behavior and the basic structure of the Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> cathodes, 0 < x < 2, corresponding to a maximal charge capacity of 122 mAh.g<sup>-1</sup>. b) Performance of rechargeable Mg–Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> coin-cell batteries during cycling at constant currents
 (0.2-0.3 mA.cm<sup>-2</sup>). The electrolyte was 0.25 M Mg(AlCl<sub>2</sub>BuEt)<sub>2</sub> in THF. The specific capacity of the active mass is plotted against cycle number for three cells, at different optimization levels, together with voltage profiles of representative charge–discharge cycles.<sup>11</sup>

It has been demonstrated that other  $MX_n$  electrodes (M = transition metal and X = S, Se) can allow reversible Mg intercalation.<sup>13</sup> Among them,  $TiS_2$  has been reported as an interesting insertion electrode for rechargeable magnesium batteries. Sun *et al.* showed that at 60°C and at C/10 it was possible to obtain a stable capacity of 115 mAh.g<sup>-1</sup> (*cf.* Figure I. 6).<sup>14</sup> This capacity is lower than the one obtained for the first discharge (250 mAh.g<sup>-1</sup>). The authors explain this capacity

drop as a consequence of  $Mg^{2+}$  entrapment in the crystalline structure owing to complex ordering and kinetic effects that were not studied in that paper. Furthermore, the working potential is quite low (~1 V vs.  $Mg^{2+}/Mg$ ), so TiS<sub>2</sub> as cathode material is limited in terms of energy density. Still, it is an interesting material to study the Mg diffusion in solid phases. This can provide guidance in the search for new Mg positive electrode materials. It can also be considered as a standard intercalation material for evaluating new electrolytes.



Figure I. 6. a) Discharge and charge profile of TiS<sub>2</sub> vs. Mg at 60°C and b) its capacity and coulombic efficiency upon cycling.<sup>14</sup>

There is a need to find high capacity cathode materials for magnesium batteries to achieve high energy densities. A promising cathode for rechargeable Mg batteries is sulphur. Using S as the cathode allows to reach very high capacities and to develop batteries with high energy density. With a theoretical voltage of 1.77 V vs  $Mg^{2+}/Mg$ , Mg-S batteries would surpass the volumetric energy of Li-S batteries, 3221 Wh.L<sup>-1</sup> and 2856 Wh.L<sup>-1</sup> respectivley.<sup>15</sup> Zhao-Karger *et al.* did a comprehensive study of Mg-S batteries. They used an electrolyte based on Mg-HMDS (HMDS =  $N(SiMe_3)_2^-$  = hexamethyldisilazide) and have obtained a high capacity of 800 mAh.g<sub>s</sub><sup>-1</sup> during the first discharge.<sup>16</sup> They could also demonstrated that the reaction pathway of Mg with S is similar to the one of Li-S batteries forming different MgS<sub>x</sub> species (8 > x > 1, *cf.* Figure I. 7). More works have been done to improve Mg-S batteries but, as Li-S batteries, suffer from fast capacity fading due to side reactions as the dissolution of polysulphides in the electrolyte.<sup>17</sup> CuS has also been reported as high capacity cathode (560 mAh.g<sup>-1</sup> in theory). This conversion electrode suffers however from poor cyclability because of important volume changes during the magnesiation and demagnesiation. Kravchyk *et al.* reported the possibility to maintain a good capacity during cycling by downsizing the CuS particles to 20 nm. Hence, they obtained a stable capacity of approximately 300 mAh.g<sup>-1</sup> at a working potential of about 1.2 V vs Mg<sup>2+</sup>/Mg with a rate of 1C for more than 100 cycles.<sup>18</sup>



Figure I. 7. a) The discharge profile of a Mg-S cell. b) Cycling performance of S/CMK400PEG(mesoporous carbon impregnated with S) cathode in different electrolytes: diglyme/PP14TFSI (denoted as DEGIL in blue), in tetraglyme/PP14TFSI (denoted as TEGIL in green), in tetraglyme (denoted as TEG in red) using CMC or PVDF as binder.<sup>16</sup>

To reach high energy densities, the working potential of cathode materials for Mg batteries has to be increased. In this way, an interesting material as cathode is  $V_2O_5$  because of its large interstitial vacancies able to accommodate Mg cations and its working potential of about 2.4 V vs Mg<sup>2+</sup>/Mg. However, the electrolytes stable at this potential are scarce and generally very corrosive, thus, leading to corrosion issues with the steal of the cells and aluminum of the current collectors. To study V<sub>2</sub>O<sub>5</sub>, Gershinsky *et al.* used an electrolyte made of 0.1 M of MgTFSI<sub>2</sub> in acetonitrile but Mg metal cannot be used with this electrolyte as a passivation layer would be formed at its surface. To solve this problem, they used activated carbon as the negative electrode on which Mg ions are reversibly adsorbed and desorbed. They could cycle a thin film of  $V_2O_5$  and get a relatively stable capacity of 150 mAh g<sup>-1</sup> with a good coulombic efficiency (*cf.* Figure I. 8b).<sup>19</sup> Fu *et al.* used a similar approach to cycle  $V_2O_5$  nano-tubes, but instead of activated carbon as the negative electrode, they used Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub>. They did in-situ measurements on their  $V_2O_5$  electrode and observed the reversible magnesiation/demagnesiation. Nevertheless, their electrode had a poor cyclability with an important capacity fading.<sup>20</sup>



Figure I. 8. a) Discharge and charge profile of V<sub>2</sub>O<sub>5</sub> thin film b) its capacity and coulombic efficiency upon cycling.<sup>19</sup>

These studies show that electrodes enabling reversible magnesiation/demagnesiation exist. They also show that for some materials the downsizing is important to promote the magnesium diffusion. Nevertheless, there are few systems with high voltage, high capacity and high cycling capability. The next section describes the main limitation of these systems focusing on the problems of the electrolytes.

### I-2d. Limitations of rechargeable Mg batteries

In the paper of Gregory *et al.* of 1990 cited previously, it was said: "Over the past 25 years, a considerable amount of attention has been paid to the use of alkali metals, particularly Li, in

Chapter I

non-aqueous secondary batteries, but comparatively little work has been done with the alkaline earth metals".<sup>10</sup> At that time, the first commercial rechargeable Li-ion battery was arriving on the market. In the case of rechargeable Mg batteries, after more than 25 years of work on this topic, no commercial device exists. There are two main reasons explaining why the scientific community is still struggling to find a viable system for rechargeable Mg batteries. The first one is the difficulty to find electrodes enabling reversible magnesiation/demagnesiation with good performances. This is due to the sluggish diffusion of Mg<sup>2+</sup> into solids: the double charge of the cation increases the electrostatic interaction with the surrounding ions. The other reason is the difficulty to find a good electrolyte for Mg-based systems.<sup>13</sup>

Contrarily to Li-ion batteries, there is no standard liquid electrolyte working for Mg batteries yet. For instance, the electrolytes using carbonate-based solvents, which are the best for LIBs, cannot be used with the Mg metal anode. The carbonates are reduced at the surface of the Mg metal forming the well-known solid electrolyte interface (SEI). This interface is, in the Mg case, very detrimental because it blocks the Mg ions migration.<sup>6</sup>

To replace carbonate-based electrolytes, liquid electrolytes compatible with Mg metal were needed. Grignard reagents-based electrolytes are stable versus Mg metal and allow a very good Mg deposition/stripping. They are known since the beginning of 20<sup>th</sup> century as electrolyte for Mg electrodeposition. It is only in the 90's that they started to be used as electrolytes for Mg batteries.<sup>21</sup> The best ones have a good oxidative stability: typically 3.7 V vs Mg<sup>2+</sup>/Mg using a Pt working electrode for (Mg<sub>2</sub>( $\mu$ Cl)<sub>3</sub>·6THF)(B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>Ph).<sup>22</sup> Nevertheless, they are very air sensitive and strongly corrosive because of the presence of chlorine. Indeed, they cannot be used at potentials higher than 2.2 V vs. Mg<sup>2+</sup>/Mg if the cell contains stainless steel as a consequence of corrosion.

Then, non-corrosive electrolytes are needed to work at high potential. Mohtadi *et al.* developed borohydride-based electrolytes. They used Mg(BH<sub>4</sub>)<sub>2</sub> as a salt in THF or DME. This electrolytes suffer from high overpotential during Mg deposition/stripping and have a low electrochemical stability (1.7 V *vs.* Mg<sup>2+</sup>/Mg).<sup>23</sup> Later, Tutusaus *et al.* used MgCB<sub>11</sub>H<sub>12</sub> in tetraglyme. This halide-free electrolyte is compatible with Mg metal and allows deposition and stripping with an excellent coulombic efficiency (> 99%). It has also a high electrochemical stability (~3.8 V *vs.* Mg<sup>2+</sup>/Mg using a stainless steel working electrode). Nevertheless, these salts have a low solubility so the conduction properties of these liquid electrolytes are still limited.<sup>24</sup> More recent studies from Zhao-Karger *et al.* show the good properties of Cl-free electrolytes using Mg(B(hfip)<sub>4</sub>)<sub>2</sub> (hfip = hexafluoroisopropyloxy) dissolved in DME.<sup>25,26</sup> These electrolytes have high ionic conductivities (~10<sup>-3</sup> mS.cm<sup>-1</sup>). They also have a large electrochemical stability window of 3.5

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V vs.  $Mg^{2+}/Mg$  (using a Pt working electrode). They are used in Mg-S batteries for which the dissolution of polysulphides in the electrolyte remains problematic.

Consequently, there is a real need of new electrolytes for rechargeable Mg batteries. These new electrolytes should:

- be compatible with Mg anode and cathode materials,
- be non-corrosive,
- have good transport properties,
- have a large electrochemical stability window.

Beside the liquid electrolytes, some groups have been working on gels, polymers, ionic liquid electrolytes or MOF-based electrolytes (MOF = metal-organic framework)<sup>27</sup> but these works are out of this thesis scope. Our approach was to look for inorganic solid electrolytes and to know if they can fulfill the criteria described above.

### I-3. Interest for solid electrolytes

To improve existing rechargeable magnesium batteries, it would be interesting to use a solid electrolyte. Two main possibilities exist to use solid electrolytes in batteries:

- as bulk electrolyte in an all-solid-state battery (cf. Figure I. 9a and b)
- as coating for the electrode materials (cf. figure 9b and c)

The all-solid-state battery is an old concept developed at the beginning of the 20<sup>th</sup> century with the work of Tubandt and Lorentz on  $\alpha$ -Agl as solid-state electrolyte. The interest for solid electrolytes grew in the 60's with the discovery of the superionic conduction of Na<sup>+</sup> in  $\beta$ -Al<sub>2</sub>O<sub>3</sub>. This solid electrolyte enabled the development of efficient Na-S batteries working between 270°C and 350°C. Nowadays, a new hype is growing around all-solid-state batteries as many private and academic groups are focused on the discovery of functional solid electrolytes at room temperature. This interest comes from the advantages that all-solid-state batteries could offer. They are expected to be safer as no liquid electrolyte is used, avoiding problems of thermal decomposition that can lead to the release of toxic and flammable gases. Then, without liquid electrolyte, an increase of the range of workable temperatures is expected. The assembly of an all-solid-state battery could also be simpler than the one of a battery using a liquid electrolyte. Instead of assembling several cells, an all-solid-state battery could be made simply by successive stacks of all-solid-state cells as the one on Figure I. 9a or b.<sup>28</sup>

We have to bear in mind that solid electrolytes can be used as bulk electrolytes but also as coating materials for electrodes. Actually, some solid electrolytes have a poor ionic conductivity but have really good electrochemical and chemical stabilities. These stable materials can be used as interface between the electrodes and the electrolyte. Of course, their thickness has to be minimized (typically few nanometers) to ensure a good ionic diffusion. The coating of electrodes with solid electrolytes can be done with a solution of dissolved solid electrolyte in which the electrode is dipped before subsequent evaporation of the solvent and recrystallisation of the solid electrolyte.<sup>29,30</sup> More sophisticated techniques can also be used as physical vapor deposition.<sup>31</sup> The following section reviews the main families of inorganic solid state Mg<sup>2+</sup> conductors known at the time of this PhD thesis.



Figure I. 9. Illustration of Mg batteries with different uses of solid electrolytes. a) Bulk solid electrolyte. b) Solid electrolyte used as protective layer between the electrode active materials and another solid electrolyte. c) Solid electrolyte used as protective layer between the electrode active materials and a liquid electrolyte.

### I-4. Mg<sup>2+</sup> inorganic solid electrolytes

### I-4a. Phosphates

The first solid Mg<sup>2+</sup> inorganic electrolytes were reported in 1987. That year, the team of Kaname Ito from the Nagoya Technological Institute was the first one to propose the use of solid electrolytes in Mg batteries.<sup>32</sup> As explained in their work, the research in monovalent solid ionic conductors was progressing fast but in the meantime almost nothing was done on multivalent ion

conductors. They foresaw that the discovery of Mg<sup>2+</sup> solid electrolytes would "not only be academically interesting but also be highly expected to compose higher energy density electrochemical devices using such materials". They studied different NASICON-like (NASICON = Na super ionic conductor) Mg<sup>2+</sup> conductors in the system Mg-Zr-PO<sub>4</sub>. A standard ceramic synthesis route at high temperature (1200°C) was used to synthesize materials with different Mg:Zr:PO4 molar ratio. Then, they made pellets from the as-obtained materials by sintering at 1200°C for 24h. It is known that oxides are hard to compact and in their study, the pellets have an important porosity, even after sintering (about 20-30%). The pellets are used to measure the ionic conductivity by AC (alternative current) impedance spectroscopy. The ionic conductivity of these materials follows an Arrhenius law (cf. Figure I. 10a). The best ionic conductor was MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> with a conductivity of 6.1x10<sup>-3</sup> S.cm<sup>-1</sup> at 800°C and an activation energy E<sub>a</sub> of 84.18 kJ.mol<sup>-1</sup> (**0.88 eV**). They described its crystallographic structure as the same as the NASICON material  $NaZr_2(PO_4)_3$ . Later, Nomura *et al.* demonstrated that the structure is actually monoclinic of the  $\beta$ -Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>-type with cell parameters a = 8.863 Å, b = 8.888 Å, c = 12.408 Å,  $\beta$  = 90.64 Å, Z = 4 and d = 3.265 g.cm<sup>-3</sup>.<sup>33</sup> Magnesium ions randomly occupy 50% of the tetrahedral interstitial sites within the structure creating vacancies. These vacancies enable Mg<sup>2+</sup> conduction. Ikeda et al. performed the polarization of  $MgZr_4(PO_4)_6$  between two platinum electrodes at 800°C and could electro-deposit Mg through a solid for the first time. To prove this, they performed Electron Probe Microanalysis (EPMA) along the electrolyte and revealed that Mg metal was deposited on the cathodic part which also confirmed the mobility of Mg<sup>2+</sup> in the material (cf. Figure I. 10b). A more recent study was published by Adamu et al. In their work, MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> was synthesized via a sol-gel method.<sup>34</sup> They could obtain pellets with better compactness after sintering at 1300°C for 24 h (99 % of the theoretical density). This improvement of compactness leads to a slight increase of the conductivity value reaching 7.23x10<sup>-3</sup> S.cm<sup>-1</sup> at 725°C. They determined an activation energy of 0.84 eV which is in agreement with the value previously reported by Ikeda et al. (0.88 eV).

In the late 90's, another Japanese team from the Osaka University continued the work started by Ikeda *et al.* and tried to improve the ionic conductivity of MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>. First, Imanaka *et al.* added excess of Zr<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>.<sup>35,36</sup> They obtained composite materials made of Mg<sub>1+x</sub>Zr<sub>4</sub>P<sub>6</sub>O<sub>1+x</sub> + x Zr<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>. They found an optimum composition in terms of ionic conductivity for x = 0.4 reaching 6.92x10<sup>-3</sup> S.cm<sup>-1</sup> at 800°C and Ea = 135.8 kJ.mol<sup>-1</sup> (1.41 eV). This value is the same than the one obtained by Ikeda *et al.* for pure MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> but it is one order of magnitude higher than the one they obtained in the same study for MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> (*cf.* Figure I. 10a). They explained this result by the improvement of the compactness due to the presence of Zr<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>. It increased from 93.1 % of the theoretical compactness for x = 0 to 99.3 % for x = 0.4. Nevertheless, the presence of a too large excess of  $Zr_2O(PO_4)_2$  would be detrimental for the ionic conductivity as this material is an insulator. The  $Zr_2O(PO_4)_2$  presence also explains the increase in term of activation energy as compared to pure  $MgZr_4(PO_4)_6$ . As Ikeda *et al.*, they demonstrated the deposition of Mg metal by EPMA after polarization of their composite material. Imanaka et al. worked also on the substitution of Zr by Nb in MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>.<sup>37</sup> They could synthesize a Mg<sub>1-2x</sub>(Zr<sub>1-x</sub>Nb<sub>x</sub>)<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> solid solution and observed the shrinkage of the cell as the radius of Nb<sup>5+</sup> (0.78 Å) is smaller than the radius of  $Zr^{4+}$  (0.86 Å). The optimum composition in terms of conductivity was for **x** = 0.15 with a conductivity of **3.7x10<sup>-3</sup> S.cm<sup>-1</sup> at 750°C** and Ea ~ 80 kJ.mol<sup>-1</sup> (**0.83 eV**). Whithout any information about the compactness, it remains difficult to know if the slight improvement of conductivity compared to  $MgZr_4(PO_4)_6$  is due to a lower porosity or to the formation of Mg vacancies. Later, they synthesized composite materials  $Mg_{0.7+x}(Zr_{0.85}Nb_{0.15})_4(PO_4)_{6+x} + xZr_2O(PO_4)_2$  and got a maximum conductivity of  $9.53 \times 10^{-3}$  S.cm<sup>-1</sup> at 800°C for x = 0.4.<sup>38</sup> To better understand the Mg<sup>2+</sup> conduction process in the materials described above, Kawamura et al. performed <sup>31</sup>P solid state NMR spectroscopy. They proved that, in these materials, the hopping of Mg<sup>2+</sup> from one site to another was related to a large deformation of the coordinating PO<sub>4</sub> tetrahedra. Thus, they could link the  $E_a$  determined from the relaxation time measured by <sup>31</sup>P NMR spectroscopy to the  $E_a$ determined by impedance spectroscopy and confirmed the fast motion of Mg<sup>2+</sup>.<sup>39</sup> So, MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>based materials allow to reach high ionic conductivities (~10<sup>-3</sup> S.cm<sup>-1</sup>) but only at high temperatures (~800°C). The only application reported for these solid electrolytes is as Mg<sup>2+</sup> conductor in Cl<sub>2</sub> gas sensors.<sup>40</sup> The very high operating temperatures make the application of these materials in solid-state batteries difficult.

It has been demonstrated recently by Su *et al.* that **magnesium phosphates**, Mg<sub>x</sub>P<sub>y</sub>O<sub>z</sub> thin films (~100 nm) can be deposited by ALD.<sup>41</sup> These films are glasses and can have different networks depending on the deposition parameters. Such films have really low ionic conductivities, **1.6x10<sup>-7</sup> S.cm**<sup>-1</sup> **at 500°C** and an activation energy of **1.37 eV**. The ionic conductivity should be improved for use in batteries. The authors proposed that further work on the nitridation of the films could be done to increase the ionic conductivity, equivalently to what has already be done with LiPON solid electrolytes.<sup>42</sup> We can give the example of a patent from Panasonic describing **nitridated magnesium silicate glasses**, Mg<sub>x</sub>SiO<sub>y</sub>N<sub>z</sub>, thin films (< 20 µm) but their ionic conductivities are also low, around **1x10<sup>-8</sup> S.cm**<sup>-1</sup> **at 800°C**.<sup>43</sup>

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- ••  $Mg_{1,1}(Zr_{0.85}Nb_{0.15})_4(PO_4)_{6,4} + 0.4Zr_2O(PO_4)_2$
- --- Mg<sub>0.7</sub>(Zr<sub>0.85</sub>Nb<sub>0.15</sub>)<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>
- ---  $Mg_{1.4}Zr_4P_6O_{1.4} + 0.4Zr_2O(PO_4)_2$
- ----- MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>

Figure I. 10. a) Thermal evolution of the ionic conductivity for  $Mg_{1.1}(Zr_{0.85}Nb_{0.15})_4(PO_4)_{6.4} + 0.4$  $Zr_2O(PO_4)_2$ ,  $Mg_{0.7}(Zr_{0.85}Nb_{0.15})_4(PO_4)_6$ ,  $Mg_{1.4}Zr_4P_6O_{1.4} + 0.4 Zr_2O(PO_4)_2$  and  $MgZr_4(PO_4)_6$ .<sup>38</sup> b) EPMA elementary analysis patterns along a  $MgZr_4(PO_4)_6$  pellet after polarization at 800°C.<sup>32</sup>

#### I-4b. Sulphides

The group of Masahiro Tatsumisago from Osaka Prefecture Univeristy has a great experience in the synthesis of sulphide-based glasses (e.g. Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> and Na<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub>) and their application as solid electrolytes.<sup>44</sup> They discovered that after annealing of these glasses, they could obtain glass-ceramic materials. These materials are interesting solid electrolytes as the coexistence of a crystalline and an amorphous phase results in superionic conductivity at room temperature.<sup>45,46</sup> In 2014, they studied new glasses based on **MgS-P<sub>2</sub>S<sub>5</sub>**.<sup>47</sup> They synthesized first the mother glass 60MgS-40P<sub>2</sub>S<sub>5</sub>. After annealing of the glass at 450°C for 1h, they could observe some diffraction peaks indexed as Mg<sub>2</sub>P<sub>2</sub>S<sub>6</sub> crystallizing in the space group C2/m (*cf.* Figure I. 11a and b). They confirmed this result by Raman spectroscopy as only the vibration bands of the P<sub>2</sub>S<sub>6</sub><sup>4-</sup> groups remained after annealing. Hence, they claimed that they synthesized a glass-ceramic material. **The conductivity at 200°C** of the **60MgS-40P<sub>2</sub>S<sub>5</sub>** solid electrolyte jumps from **2x10**<sup>-10</sup> **S.cm**<sup>-1</sup> **for the glass to 1x10<sup>-7</sup> S.cm**<sup>-1</sup> **for the glass-ceramic** (*cf.* Figure I. 11c). They also added Mgl<sub>2</sub> to the material with different (100-x)(60MgS-40P<sub>2</sub>S<sub>5</sub>)-xMgl<sub>2</sub> compositions to increase the number of charge carriers. For various compositions, new unexplained weak peaks appeared by X-ray diffraction while the ones of Mg<sub>2</sub>P<sub>2</sub>S<sub>6</sub> remained. The effect of Mgl<sub>2</sub> on the ionic conductivity is

negligible for the glass-ceramic but clearly improves the one of the glass (*i.e.* by two orders of magnitude, *cf.* Figure I. 11c). For the glass-ceramic samples, the ionic conductivity at 200°C increases from 1x10<sup>-7</sup> S.cm<sup>-1</sup> to 2x10<sup>-7</sup> S.cm<sup>-1</sup> for x=0 and x=20, respectively. The ionic conductivity of these sulphides is too low and needs to be improved for solid electrolyte application.



Figure I. 11. a) XRD patterns of the (100-x)(0.6MgS-0.4P<sub>2</sub>S<sub>5</sub>)-xMgI<sub>2</sub> samples after 1 h of ball-milling and b) after annealing. c) Composition dependence of the conductivities at 200 °C for (100-x)(0.6MgS-0.4P<sub>2</sub>S<sub>5</sub>)-xMgI<sub>2</sub> solid electrolytes.<sup>47</sup>

#### I-4c. Complex hydrides

Another class of materials has been studied as solid state electrolyte for Mg batteries: the complex hydrides. This thesis is exclusively based on the study of complex hydrides as Mg<sup>2+</sup> ionic conductors. Hence, extra details will be given in this subsection to understand better why these materials are interesting as solid electrolytes.

In 2006, the group of Shinichi Orimo at the Tohoku University in Japan revealed for the first time the possibility to use complex hydrides as solid state ionic conductor. While studying **LiBH**<sub>4</sub> as hydrogen storage material, they measured how the material behaves when it is heated up by

microwaves.<sup>48</sup> They observed that the behavior of LiBH<sub>4</sub> is similar to other complex hydrides at low temperature but drastically change around 110°C (cf. Figure I. 12a). This is due to the phase transition that undergoes LiBH<sub>4</sub> with a reorganization of the  $(BH_4)^-$  anions in the structure (cf. Figure I. 12c). The crystal structure changes from a low temperature (LT) orthorhombic phase (space group: Pnma) to a high temperature (HT) hexagonal phase (space group: P6<sub>3</sub>mc). They actually discovered that this structural transition affects the electrical properties of the material. Performing dielectric constant measurements, they could determine that LiBH<sub>4</sub> was passing from an insulator to a conductor behavior (cf. Figure I. 12b). They predicted that the charge carrier would be Li<sup>+</sup> cation as B and H are strongly covalently bonded in the BH<sub>4</sub> units. They measured the ionic conductivity by AC impedance spectroscopy and as predicted, the conductivity exceptionally increases with the structural transition at 110°C from ~10<sup>-7</sup> S.cm<sup>-1</sup> to ~10<sup>-3</sup> S.cm<sup>-1</sup> (cf. Figure I. 12d).<sup>49</sup> Thus, they demonstrated the superionic conductivity of the hexagonal HT-LiBH<sub>4</sub> phase. The activation energies were found by the Arrhenius law to be 0.69 eV and 0.53 eV for the orthorhombic LT and hexagonal HT LiBH<sub>4</sub> phases, respectively. They confirmed that Li<sup>+</sup> was the mobile specie by <sup>7</sup>Li solid state MAS-NMR spectroscopy. A great narrowing of the NMR peak can be observed after the phase transition from LT- to HT-phase, indicating the increased Li<sup>+</sup> mobility (cf. Figure I. 12e). Then, they measured the spin-lattice relaxation time (T1) as a function of the temperature from which they could extract an activation energy of 0.56 eV which is in agreement with the one determined by impedance spectroscopy (0.53 eV).



Figure I. 12. a) Temperature and pressure changes as a function of microwave irradiation time for MBH<sub>4</sub> M=Li, Na, or K. b) Temperature dependence of the dielectric constants εr' and εr" of LiBH<sub>4</sub> at a frequency of 2.16 GHz.<sup>48</sup> c) Crystal structures of low temperature (LT) and high temperature (HT) phases of LiBH<sub>4</sub>. d) Thermal evolution of the ionic conductivity of LiBH<sub>4</sub>. d) <sup>7</sup>Li solid state NMR spectra of LiBH<sub>4</sub> at different temperatures.<sup>49</sup>

Later, the electrochemical stability of LiBH<sub>4</sub> was determined by cyclic voltammetry done on HT-LiBH<sub>4</sub> at 120°C.<sup>50</sup> A pellet was sandwiched between a lithium and a molybdenum electrode and the potential scanned at a speed of 5 mV.s<sup>-1</sup>. Only the lithium deposition/stripping (around 0 V vs Li<sup>+</sup>/Li) and no oxidation of the electrolyte were observed (*cf.* Figure I. 13a). **The electrochemical stability window of LiBH<sub>4</sub> was estimated between 0 and 5 V vs Li<sup>+</sup>/Li** which is really interesting for all-solid-state batteries. Nowadays, we know that the characterization of solid electrolyte with

planar counter electrodes (here molybdenum) can hinder the decomposition process.<sup>51</sup> This electrochemical stability window was overestimated. Recent studies have demonstrated that the actual stability of LiBH<sub>4</sub> is about 2.1 V vs Li<sup>+</sup>/Li.<sup>52,53</sup> Nevertheless, in 2014, Takahashi et al. assembled the first all-solid-state Li battery using LiBH<sub>4</sub> as solid electrolyte and working at 120°C.<sup>31</sup> They used Li as anode and LiCoO<sub>2</sub> as cathode. When bare LiCoO<sub>2</sub> was used an important interface resistance was observed after cycling. By Raman spectroscopy, they showed that this interfacial resistance was due to the reaction of LiBH<sub>4</sub> with charged Li<sub>1-x</sub>CoO<sub>2</sub>. Species as Co<sub>3</sub>O<sub>4</sub> and CoO(OH) were formed. To prevent the reaction of the borohydride with the high potential cathode, a  $LiCoO_2$ cathode thin-film coated with Li<sub>3</sub>PO<sub>4</sub> solid electrolyte was prepared (cf. Figure I. 13b). Li<sub>3</sub>PO<sub>4</sub> is used here as a protective layer. This strategy worked as no degradation of the electrode was observed after cycling and the interfacial resistance with the electrolyte remained stable (cf. Figure I. 13c). This first all-solid-state battery using a borohydride showed the feasibility of such systems but also shed the light on the reactivity of these materials with high potential cathodes. Another study made by Unemoto et al. was done on a full-cell using a low potential cathode material, TiS<sub>2</sub> (cf. Figure I. 13d).<sup>54</sup> This time, no coating of the cathode was necessary to achieve good capacity retention. They observed that a stable interface was formed between  $TiS_2$  and LiBH<sub>4</sub>. This interface could be made of closo-borane as Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and appeared to be stable, ensuring a good capacity retention after 300 cycles (cf. Figure I. 13f). Their study also demonstrated that borohydrides can have good physical interfaces with the electrodes even by simple cold-pressing assembly and reach very high compactness (close to 100 % of the theoretical density, cf. Figure I. 13e). These mechanical characteristics are of major interest for the assembling of all solid-state batteries. The low density of borohydride ( $< 1 \text{ g.cm}^{-3}$ ) is also an advantage as, for the same volume, these solid electrolytes would represent less mass than other solid electrolytes (e.g. sulphides or oxides) so the energy density of the cell would increase.

Other all-solid-state batteries have been assembled using LiBH<sub>4</sub> as solid electrolyte<sup>55,56</sup> but an important issue remained: the high conductivity of LiBH<sub>4</sub> can only be reached at elevated temperatures (> 120°C). Different approaches were developed to obtain good conductivity at room temperature with LiBH<sub>4</sub>-based materials. Among these approaches, the mixture of the lithium borohydride with lithium halides can be cited. It has been proved that a mixture with LiX (X = Cl, Br and I) can form a solid solution where HT-LiBH<sub>4</sub> is stabilized at lower temperatures.<sup>57</sup> The best mixture with LiI resulted in superionic conductivity at room temperature (cf Figure I. 14a). The HT-LiBH<sub>4</sub> polymorph can also be stabilized by nano-confinement into mesoporous silica scaffolds (*cf.* Figure I. 14b).<sup>58</sup>

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Figure I. 13. a) Cyclic voltammogram of HT-LiBH<sub>4</sub> sandwiched between lithium and molybdenum electrodes at 120°C with a voltage scan rate of 5 mV.s<sup>-1.50</sup> b) A cross-sectional SEM image of a thin-film LiCoO<sub>2</sub> cathode coated with a thin layer of amorphous Li<sub>3</sub>PO<sub>4</sub>.<sup>31</sup> c) Charge-discharge curves at 120°C of a cell using LiBH<sub>4</sub> solid electrolyte and LiCoO<sub>2</sub> cathode coated with Li<sub>3</sub>PO<sub>4</sub>. d) Photograph of a bulk-type all-solid-state cell Li/LiBH<sub>4</sub>/TiS<sub>2</sub> and e) cross-sectional FIB-SEM image of the TiS<sub>2</sub>+LiBH<sub>4</sub> composite cathode.<sup>55</sup> f) Charge-discharge curves at 120°C of a bulk-type all-solid-state cell Li/LiBH<sub>4</sub>/TiS<sub>2</sub>.<sup>54</sup>



Figure I. 14. a) Thermal evolution of the ionic conductivity of LiBH<sub>4</sub>-LiX composites (X = Cl, Br and I) compared to LiBH<sub>4</sub> and Lil. <sup>57</sup> b) Ionic conductivities of bulk (red) and nanoconfined LiBH<sub>4</sub> (black).<sup>59</sup>

Another approach was to use compounds from the LiBH<sub>4</sub>-LiNH<sub>2</sub> binary system that have already been studied as hydrogen storage materials. LiNH<sub>2</sub> was also known as a fast Li<sup>+</sup> ionic conductor since 1979.<sup>60</sup> Its ionic conductivity is **3x10<sup>-4</sup> S.cm<sup>-1</sup> at 25°C** but its poor electrochemical stability (**0.7 V vs Li<sup>+</sup>/Li**) does not allow a practical use as solid electrolyte. Two crystalline defined compounds have been reported in the LiBH<sub>4</sub>-LiNH<sub>2</sub> binary phases diagram: Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>) (space group: R-3) and Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> (space group: I2<sub>1</sub>3) (*cf.* Figure I. 15a).<sup>61</sup> Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>) has an ionic conductivity of **1×10<sup>-4</sup> S.cm<sup>-1</sup> at room temperature** with **Ea = 0.56 eV**. Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> has a conductivity of about **2×10<sup>-4</sup> S.cm<sup>-1</sup> at room temperature** and its activation energy is two times lower (**0.26 eV**).<sup>62</sup> These materials melt at elevated temperatures which induces a decrease of the activation energy and an increase of the ionic conductivity (*cf.* Figure I. 15b). Their conductivities

reach  $6 \times 10^{-2}$  S.cm<sup>-1</sup> at 105°C for Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>) and  $2 \times 10^{-1}$  S.cm<sup>-1</sup> at 240°C for Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub>. Later, it was also shown that the ionic conductivity of Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> can be enhanced by changing the stoichiometry. With a 2:3 Li(BH<sub>4</sub>):Li(NH<sub>2</sub>) ratio, the conductivity reaches  $6.4 \times 10^{-3}$  S cm<sup>-1</sup> at 40°C.<sup>63</sup> Yan *et al.* even demonstrated that this material could be used as solid electrolyte. A cell with Li as the negative electrode and LTO (LTO = Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>) as the positive was assembled and showed excellent rate and stable cycling capability (140 mAh.g<sup>-1</sup> for 400 cycles at 1C at 40°C).



Figure I. 15. a) Binary LiBH<sub>4</sub>-LiNH<sub>2</sub> phases diagram.<sup>61</sup> b) Thermal evolution of the ionic conductivity of Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>) and Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> compared to LiBH<sub>4</sub> and LiNH<sub>2</sub>.<sup>62</sup>

An analogous strategy was used to find solid-state Na<sup>+</sup> ionic conductors. The NaBH<sub>4</sub>-NaNH<sub>2</sub>-Nal ternary system was explored (*cf.* Figure I. 16a).<sup>64</sup> On the NaBH<sub>4</sub>-NaI side, a solid solution is formed with different (1-x)NaBH<sub>4</sub>-xNaI compositions. This solid solution has a slightly better ionic conductivity than the raw materials. Then, on the NaNH<sub>2</sub>-NaI side, a defined compound is obtained with the composition Na(NH<sub>2</sub>)<sub>0.5</sub>I<sub>0.5</sub> with also an improved ionic conductivity. Finally, on the NaBH<sub>4</sub>-NaNH<sub>2</sub> side, the compound **Na(BH<sub>4</sub>)**<sub>0.5</sub>(**NH<sub>2</sub>**)<sub>0.5</sub> was synthesized. This compound has the best ionic conductivity from all the phases described previously: **2x10<sup>-6</sup> S.cm**<sup>-1</sup> **at room temperature**. The better ionic conductivity is assumed to come from its anti-perovskite structure where Na ions can migrate through vacancies. This material is known to have two crystalline allotropes with a structural transition at 100°C. In this study, they declared to observe only the high temperature one. They have also characterized the electrochemical stability of Na<sub>2</sub>(BH<sub>4</sub>)<sub>0.5</sub>(NH<sub>2</sub>)<sub>0.5</sub> by sandwiching this compound between Na and Mo electrodes and applying a scan rate of 1 mV.s<sup>-1</sup> (*cf.* Figure I. 16b). They concluded that the **electrochemical stability of the material was up to 6 V vs Na<sup>+</sup>/Na** but as it was mentioned previously, this technique might highly overestimate the electrochemical stability.



Figure I. 16. a) Thermal evolution of the ionic conductivity of different materials in the NaBH<sub>4</sub>-NaNH<sub>2</sub>-NaI system. b) Cyclic voltammogram measured at 333 K for Na(BH<sub>4</sub>)<sub>0.5</sub>(NH<sub>2</sub>)<sub>0.5</sub> sandwiched between sodium and molybdenum electrodes.<sup>64</sup>

Now, coming back to the case of Mg<sup>2+</sup> ionic conductors, a material inspired from the discoveries introduced previously was studied as solid electrolyte for Mg batteries. This material is Mg(BH<sub>4</sub>)(NH<sub>2</sub>). As the above complex hydrides, it was first synthesized and studied as hydrogen storage material.<sup>65</sup> Its structure was solved by Noritake et al. in a tetragonal crystal system (space group: I4<sub>1</sub>) with a= 5.814(1) Å, c = 20.450(4) Å, V = 691.3(2) Å and Z = 8. The material has a **low** density of 0.9966 g.cm<sup>-3</sup>.<sup>66</sup> This low density is very interesting for a solid-state electrolyte as it allows obtaining good ionic percolation in composite electrodes with a relatively low weight of electrolyte, ensuring reasonable electrochemical gravimetric capacities for the composite electrodes. In 2014, a team from the Toyota research center in Japan studied Mg(BH<sub>4</sub>)(NH<sub>2</sub>) as solid electrolyte.<sup>67</sup> A **band gap of 4.9 eV** was determined by first principle calculations so this material is an electronic insulator. It was also calculated that the bonds between Mg and the anions are ionic while the B-H and N-H bonds are covalent. From this first theoretical work, it appeared that this material could be an ionic conductor. They measured an ionic conductivity of 1x10<sup>-6</sup> S.cm<sup>-1</sup> at 150°C by AC impedance spectroscopy and an activation energy of 1.31 eV (cf. Figure I. 17a). This conductivity was the highest ever reported for a Mg<sup>2+</sup> inorganic ionic conductor at low temperatures so far. It is three orders of magnitude higher than one measured for  $Mg(BH_4)_2$ (~10<sup>-9</sup> S.cm<sup>-1</sup> at 150°C). This improved ionic conductivity might be due to the shortest distance between the nearest Mg atoms in Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (3.59 Å) than in Mg(BH<sub>4</sub>)<sub>2</sub> (4.32 Å), indicating that Mg hopping diffusion may be favored in this structure. The electrochemical stability window was also estimated up to 3 V vs Mg<sup>2+</sup>/Mg using cyclic voltammetry with a cell made of Mg/Mg(BH<sub>4</sub>)(NH<sub>2</sub>)/Pt (cf. Figure I. 17b). This stability is interesting for a solid electrolyte application in batteries but needs to be confirmed with proper measurements. Finally, Higashi et al. tried for the first time to assemble an all-solid-state Mg battery using Mg(BH<sub>4</sub>)(NH<sub>2</sub>) as solid electrolyte, a Mg anode and different sulfur-based cathodes (S, FeS and Ag<sub>2</sub>S, cf. Figure I. 17c). Unfortunately, they were unable to cycle these cells and only observed a potential decay while applying current. Even so, the stack was done well enough to have the expected OCV for each cathode tried. It was the most advanced work reported so far on all-solid-state magnesium batteries.

The last ionic conductor mentioned in this state of the art chapter is not a fully inorganic material but rather a hybrid material combining  $Mg(BH_4)_2$  with organic molecules. Indeed, Roedern *et al.* discovered that it was possible to coordinate ethylene diamine molecules with  $Mg(BH_4)_2$ .<sup>68</sup> They studied two different mixtures prepared by ball-milling:  $Mg(en)_3(BH_4)_2$  and  $Mg(en)_1(BH_4)_2$  (en = ethylene diamine).The best conductivity was obtained for  $Mg(en)_1(BH_4)_2$  with  $6 \times 10^{-5}$  Scm<sup>-1</sup> at 70°C (*cf.* Figure I. 18a). It is a crystalline compound but the structure remains

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unknown yet. Infrared and Raman spectroscopy measurements unveil that the chelating *cis* configuration is favored. This material as a thermal stability up to 75°C before to undergo an endothermic phase transition then it starts to decompose above 100°C. They proved that reversible Mg deposition/stripping was possible at 60°C by cyclic voltammetry with this material as solid electrolyte (*cf.* Figure I. 18b). Despite its good ionic conductivity, it suffers from a **low electrochemical stability of 1.2 V vs Mg<sup>2+</sup>/Mg**.



Figure I. 17. a) Thermal evolution of the ionic conductivity of Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)(NH<sub>2</sub>) compared to MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> and Mg<sub>1.4</sub>Zr<sub>4</sub>P<sub>6</sub>O<sub>24.4</sub>+0.4Zr<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub>. b) Cyclic voltammogram measured at 150°C of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) sandwiched between magnesium and platinum electrodes.
c) Discharge curves at 150°C of Mg-S, Mg-FeS and Mg-Ag<sub>2</sub>S cells using Mg(BH<sub>4</sub>)(NH<sub>2</sub>) as solid electrolyte. Inset shows the photo of a cell.<sup>67</sup>



Figure I. 18.a) Thermal evolution of the ionic conductivity of Mg(BH<sub>4</sub>)<sub>2</sub>, Mg(en)<sub>3</sub>(BH<sub>4</sub>)<sub>2</sub> and Mg(en)<sub>1</sub>(BH<sub>4</sub>)<sub>2</sub>, compared with MgZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub>, Mg<sub>1.4</sub>Zr<sub>4</sub>P<sub>6</sub>O<sub>24.4</sub> + 0.4Zr<sub>2</sub>O(PO<sub>4</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)(NH<sub>2</sub>). b) Cyclic voltammogram of Mg(en)<sub>1</sub>(BH<sub>4</sub>)<sub>2</sub> sandwiched between magnesium and platinum electrodes measured at 60°C with a scan rate of 10mV.s<sup>-1</sup>.Inset: Mg stripping charge vs. cycle number.<sup>68</sup>

### I-5. Aims of the PhD thesis

Reviewing the state-of-the-art of rechargeable Mg batteries shows that some systems are very interesting in terms of energy density but suffer from limitations. One of the main limitations is the difficulty to find viable liquid electrolytes. Hence, our approach is to study the possibility of using a solid-electrolyte in Mg rechargeable batteries and to determine if it would be beneficial or not. The second part of the state-of-the-art chapter was on inorganic solid-state Mg<sup>2+</sup> ionic conductors and it appears that few of them exist. This can be explained by the important electrostatic interaction of the double positive charge of Mg<sup>2+</sup> with its surrounding atoms making its diffusion in solids very sluggish. Each of the three families of materials reported as solid electrolytes has different range of ionic conductivities. The phosphates have high ionic conductivities but only at high temperatures, typically ~10<sup>-3</sup> S.cm<sup>-1</sup> at 800°C. This temperature is too high for using these materials in practical energy storage devices. Then, sulphides have too low ionic conductivities ( $^{-10^{-7}}$  S.cm<sup>-1</sup> at 200°C) to be interesting as solid electrolytes. The third and most recent family of materials is the one of complex hydrides. These materials have the best ionic conductivities at low temperatures (~10<sup>-5</sup>-10<sup>-6</sup> S.cm<sup>-1</sup> below 150°C). Furthermore, they are the only ones that have been really characterized regarding possible applications in Mg batteries (e.g. Mg deposition/stripping, electrochemical stability, etc.). Figure I. 19 compares the different magnesium solid electrolytes in terms of ionic conductivity.

To assemble a magnesium all-solid-state battery, it is paramount to have a good solid electrolyte in terms of ionic conductivity, electrochemical stability and ease of implementation (*i.e.* good electrode/electrolyte interface, chemical stability with the electrode components, *etc.*). Nevertheless, to be used as a solid electrolyte in batteries, an ionic conductor must have an ionic conductivity higher than 10<sup>-4</sup> S.cm<sup>-1</sup> as close as possible to room temperature. Diffusion of Mg<sup>2+</sup> is sluggish in solids at low temperatures so we first target materials having good ionic conductivities below 200°C. Few Mg<sup>2+</sup> inorganic solid electrolytes exist and none of them present an ionic conductivity reaching our target. So the goals of this PhD thesis was:

- I. the synthesis and, when possible, improvement of existing Mg<sup>2+</sup> inorganic conductors,
- II. the identification of new Mg<sup>2+</sup> inorganic conductors,
- III. the characterization of the possible use of the obtained ionic conductors as solid electrolytes.

To achieve these goals, the most promising **starting material was Mg(BH<sub>4</sub>)(NH<sub>2</sub>)**. Indeed, it was the best Mg<sup>2+</sup> inorganic conductor reported in the literature at the beginning of this thesis and it was demonstrated that it allows reversible Mg deposition/stripping at 150°C. Then, we extended the **study to the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phase diagram** to identify new ionic-conducting phases as what has been done with LiBH<sub>4</sub> and LiNH<sub>2</sub> for instance. Finally, we characterized the ionic conductors as solid electrolytes using proper techniques.



T (°C)

Figure I. 19. Thermal evolution of the ionic conductivity of the different Mg<sup>2+</sup> inorganic conductors reported in the literature. The different families of reported materials are highlighted. The range of ionic conductivity targeted for a suitable solid electrolyte in a magnesium all-solid-state battery is also displayed.

## References

- 1. European Commission. List of Critical Raw Materials for the EU. (2017).
- 2. Larcher, D. & Tarascon, J.-M. Towards greener and more sustainable batteries for electrical energy storage. *Nat. Chem.* **7**, 19–29 (2015).
- 3. Fichtner, M. Chapter 1. Motivation for a magnesium battery. in *Magnesium batteries:* research and applications 1–16 (2019).
- 4. Anderson, D. L. *Theory of the Earth*. (Blackwell Scientific Publications, 1998).
- 5. Yoo, H. D. *et al.* Mg rechargeable batteries: an on-going challenge. *Energy Environ. Sci.* **6**, 2265–2279 (2013).
- 6. Mohtadi, R. & Mizuno, F. Magnesium batteries: Current state of the art, issues and future perspectives. *Beilstein J. Nanotechnol.* **5**, 1291–1311 (2014).
- 7. Muldoon, J., Bucur, C. B. & Gregory, T. Quest for nonaqueous multivalent secondary batteries: Magnesium and beyond. *Chem. Rev.* **114**, 11683–11720 (2014).
- 8. Matsui, M. Study on electrochemically deposited Mg metal. *J. Power Sources* **196**, 7048–7055 (2011).
- 9. Davidson, R. *et al.* Formation of magnesium dendrites during electrodeposition. *ACS Energy Lett.* **4**, 375–376 (2019).
- 10. Gregory, T. D. Nonaqueous electrochemistry of magnesium. *J. Electrochem. Soc.* **137**, 775-780 (1990).
- 11. Aurbach, D. *et al.* Prototype systems for rechargeable magnesium batteries. *Nature* **407**, 724–727 (2000).
- 12. Aurbach, D. *et al.* A short review on the comparison between Li battery systems and rechargeable magnesium battery technology. *J. Power Sources* **97–98**, 28–32 (2001).
- 13. Canepa, P. *et al.* Odyssey of multivalent cathode materials: open questions and future challenges. *Chem. Rev.* **117**, 4287–4341 (2017).
- 14. Sun, X., Bonnick, P. & Nazar, L. F. Layered TiS<sub>2</sub> positive electrode for Mg batteries. *ACS Energy Lett.* **1**, 297–301 (2016).
- 15. Kong, L. *et al.* A review of advanced energy materials for magnesium-sulfur batteries. *Energy Environ. Mater.* **1**, 100–112 (2018).
- 16. Zhao-Karger, Z. *et al.* Performance improvement of magnesium sulfur batteries with modified non-nucleophilic electrolytes. *Adv. Energy Mater.* **5**, 1401155 (2015).
- 17. Zhao-Karger, Z. & Fichtner, M. Beyond intercalation chemistry for rechargeable Mg batteries: A short review and perspective. *Front. Chem.* **6**, (2019).
- 18. Kravchyk, K. V *et al.* Copper sulfide nanoparticles as high-performance cathode materials for Mg-ion batteries. *Sci. Rep.* **9**, 7988 (2019).

- 19. Gershinsky, G., Yoo, H. D., Gofer, Y. & Aurbach, D. Electrochemical and spectroscopic analysis of  $Mg^{2+}$  intercalation into thin film electrodes of layered oxides:  $V_2O_5$  and  $MoO_3$ . Langmuir **29**, 10964–10972 (2013).
- 20. Fu, Q. *et al.* In operando synchrotron diffraction and in operando X-ray absorption spectroscopy investigations of orthorhombic V<sub>2</sub>O<sub>5</sub> nanowires as cathode materials for Mg-ion batteries. *J. Am. Chem. Soc.* **141**, 2305–2315 (2019).
- 21. Muldoon, J., Bucur, C. B. & Gregory, T. Fervent hype behind magnesium batteries: An open call to synthetic chemists-electrolytes and cathodes needed. *Angew. Chemie Int. Ed.* **56**, 12064–12084 (2017).
- 22. Muldoon, J. *et al.* Electrolyte roadblocks to a magnesium rechargeable battery. *Energy Environ. Sci.* **5**, 5941–5950 (2012).
- 23. Mohtadi, R., Matsui, M., Arthur, T. S. & Hwang, S. J. Magnesium borohydride: From hydrogen storage to magnesium battery. *Angew. Chemie Int. Ed.* **51**, 9780–9783 (2012).
- 24. Tutusaus, O. *et al.* An efficient halogen-free electrolyte for use in rechargeable magnesium batteries. *Angew. Chemie Int. Ed.* **54**, 7900–7904 (2015).
- 25. Zhao-Karger, Z., Gil Bardaji, M. E., Fuhr, O. & Fichtner, M. A new class of non-corrosive, highly efficient electrolytes for rechargeable magnesium batteries. *J. Mater. Chem. A* **5**, 10815–10820 (2017).
- 26. Zhao-Karger, Z. *et al.* Toward highly reversible magnesium–sulfur batteries with efficient and practical Mg[B(hfip)<sub>4</sub>]<sub>2</sub> electrolyte. *ACS Energy Lett.* **3**, 2005–2013 (2018).
- 27. Deivanayagam, R., Ingram, B. J. & Shahbazian-Yassar, R. Progress in development of electrolytes for magnesium batteries. *Energy Storage Mater.* **21**, 136–153 (2019).
- 28. Viallet, V. & Fleutot, B. Introduction. in *Inorganic massive batteries* VII-XX5 (John Wiley & Sons, Inc., 2018).
- Yubuchi, S., Uematsu, M., Deguchi, M., Hayashi, A. & Tatsumisago, M. Lithium-ionconducting argyrodite-type Li<sub>6</sub>PS<sub>5</sub>X (X = Cl, Br, I) solid electrolytes prepared by a liquidphase technique using ethanol as a solvent. ACS Appl. Energy Mater. 1, 3622–3629 (2018).
- 30. Duchêne, L. *et al.* A stable 3 V all-solid-state sodium-ion battery based on a closo-borate electrolyte. *Energy Environ. Sci.* **10**, 2609–2615 (2017).
- 31. Takahashi, K. *et al.* All-solid-state lithium battery with LiBH<sub>4</sub> solid electrolyte. *J. Power Sources* **226**, 61–64 (2013).
- Ikeda, S., Takahashi, M., Ishikawa, J. & Ito, K. Solid electrolytes with multivalent cation conduction. 1. Conducting species in Mg-Zr-PO<sub>4</sub> system. *Solid State Ionics* 23, 125–129 (1987).
- Nomura, K., Ikeda, S., Ito, K. & Einaga, H. Framework structure, phase transition, and transport properties in M<sup>II</sup>Zr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> compounds (M<sup>II</sup> = Mg, Ca, Sr, Ba, Mn, Co, Ni, Zn, Cd, and Pb). *Bull. Chem. Soc. Jpn.* 65, 3221–3227 (1992).

- Adamu, M. & Kale, G. M. Novel sol–gel synthesis of MgZr<sub>4</sub>P<sub>6</sub>O<sub>24</sub> composite solid electrolyte and newer insight into the Mg<sup>2+</sup>-ion conducting properties using impedance spectroscopy. *J. Phys. Chem. C* **120**, 17909–17915 (2016).
- 35. Imanaka, N., Okazaki, Y. & Adachi, G. Divalent magnesium ionic conduction in the magnesium phosphate based composites. *Chem. Lett.* **28**, 939–940 (1999).
- 36. Imanaka, N., Okazaki, Y. & Adachi, G. Divalent magnesium ion conducting characteristics in phosphate based solid electrolyte composites. *J. Mater. Chem.* **10**, 1431–1435 (2000).
- 37. Imanaka, N. Divalent magnesium ionic conduction in Mg<sub>1-2x</sub>(Zr<sub>1-x</sub>Nb<sub>x</sub>)<sub>4</sub>P<sub>6</sub>O<sub>24</sub> (x=0–0.4) solid solutions. *Electrochem. Solid-State Lett.* **3**, 327 (1999).
- 38. Imanaka, N., Okazaki, Y. & Adachi, G. Optimization of divalent magnesium ion conduction in phosphate based polycrystalline solid electrolytes. *Ionics (Kiel)*. **7**, 440–446 (2001).
- 39. Kawamura, J. *et al.* High temperature <sup>31</sup>P NMR study on Mg<sup>2+</sup> ion conductors. *Solid State Commun.* **120**, 295–298 (2001).
- 40. Imanaka, N., Okamoto, K. & Adachi, G. ya. A chlorine gas sensor based on the combination of Mg<sup>2+</sup> cation conducting and O<sup>2-</sup> anion conducting solid electrolytes with lanthanum oxychloride as an auxiliary electrode. *Electrochem. commun.* **3**, 49–51 (2001).
- 41. Su, J. *et al.* Atomic layer deposition of a magnesium phosphate solid electrolyte. *Chem. Mater.* **31**, 5566–5575 (2019).
- 42. Kozen, A. C., Pearse, A. J., Lin, C.-F., Noked, M. & Rubloff, G. W. Atomic layer deposition of the solid electrolyte LiPON. *Chem. Mater.* **27**, 5324–5331 (2015).
- 43. Fujinoki, N., Tsujita, T., Nishitani, Y. & Tomiyama, M. Solid electrolyte having magnesium ion conductivity and magnesium secondary battery using the same. (Patent, 2017).
- 44. Hayashi, A., Sakuda, A. & Tatsumisago, M. Development of sulfide solid electrolytes and interface formation processes for bulk-type all-solid-state Li and Na batteries. *Front. Energy Res.* **4**, 1–13 (2016).
- 45. Mizuno, F., Hayashi, A., Tadanaga, K. & Tatsumisago, M. New, highly ion-conductive crystals precipitated from Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glasses. *Adv. Mater.* **17**, 918–921 (2005).
- 46. Tsukasaki, H., Mori, S., Morimoto, H., Hayashi, A. & Tatsumisago, M. Direct observation of a non-crystalline state of Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> solid electrolytes. *Sci. Rep.* **7**, 1–7 (2017).
- Yamanaka, T., Hayashi, A., Yamauchi, A. & Tatsumisago, M. Preparation of magnesium ion conducting MgS–P<sub>2</sub>S<sub>5</sub>–Mgl<sub>2</sub> glasses by a mechanochemical technique. *Solid State Ionics* 262, 601–603 (2014).
- 48. Nakamori, Y., Orimo, S. & Tsutaoka, T. Dehydriding reaction of metal hydrides and alkali borohydrides enhanced by microwave irradiation. *Appl. Phys. Lett.* **88**, 112104 (2006).
- Matsuo, M., Nakamori, Y., Orimo, S., Maekawa, H. & Takamura, H. Lithium superionic conduction in lithium borohydride accompanied by structural transition. *Appl. Phys. Lett.* 91, 224103 (2007).
- 50. Matsuo, M. & Orimo, S. I. Lithium fast-ionic conduction in complex hydrides: Review and prospects. *Adv. Energy Mater.* **1**, 161–172 (2011).

- 51. Tian, Y. *et al.* Compatibility issues between electrodes and electrolytes in solid-state batteries. *Energy Environ. Sci.* **10**, 1150–1166 (2017).
- 52. Gulino, V. *et al.* Phase stability and fast ion conductivity in the hexagonal LiBH<sub>4</sub>–LiBr–LiCl solid solution. *Chem. Mater.* **31**, 5133–5144 (2019).
- 53. Asakura, R. *et al.* Electrochemical oxidative stability of hydroborate-based solid-state electrolytes. *ACS Appl. Energy Mater.* **2**, 6924–6930 (2019).
- 54. Unemoto, A. *et al.* Stable interface formation between TiS<sub>2</sub> and LiBH<sub>4</sub> in bulk-type all-solidstate lithium batteries. *Chem. Mater.* **27**, 5407–5416 (2015).
- 55. Unemoto, A., Matsuo, M. & Orimo, S. I. Complex hydrides for electrochemical energy storage. *Adv. Funct. Mater.* **24**, 2267–2279 (2014).
- 56. Guzik, M. N., Mohtadi, R. & Sartori, S. Lightweight complex metal hydrides for Li-, Na-, and Mg-based batteries. *J. Mater. Res.* **34**, 877–904 (2019).
- 57. Maekawa, H. *et al.* Halide-stabilized LiBH<sub>4</sub>, a room-temperature lithium fast-ion conductor. *J. Am. Chem. Soc.* **131**, 894–895 (2009).
- 58. Blanchard, D. *et al.* Nanoconfined LiBH₄ as a fast lithium ion conductor. *Adv. Funct. Mater.*25, 184–192 (2015).
- De Jongh, P. E., Blanchard, D., Matsuo, M., Udovic, T. J. & Orimo, S. Complex hydrides as room-temperature solid electrolytes for rechargeable batteries. *Appl. Phys. A Mater. Sci. Process.* **122**, 1–6 (2016).
- 60. Boukamp, B. A. & Huggins, R. A. Ionic conductivity in lithium imide. *Phys. Lett. A* **72**, 464–466 (1979).
- 61. Borgschulte, A. *et al.* Surface and bulk reactions in borohydrides and amides. *Energy Environ. Sci.* **5**, 6823–6832 (2012).
- 62. Matsuo, M. *et al.* Complex hydrides with (BH<sub>4</sub>)<sup>-</sup> and (NH<sub>2</sub>)<sup>-</sup> anions as new lithium fast-ion conductors. *J. Am. Chem. Soc.* **131**, 16389–16391 (2009).
- 63. Yan, Y. *et al.* A lithium amide-borohydride solid-state electrolyte with lithium-ion conductivities comparable to liquid electrolytes. *Adv. Energy Mater.* **1700294**, 1–7 (2017).
- 64. Matsuo, M. *et al.* Sodium ionic conduction in complex hydrides with [BH<sub>4</sub>]<sup>-</sup> and [NH<sub>2</sub>]<sup>-</sup> anions. *Appl. Phys. Lett.* **100**, 2–6 (2012).
- 65. Noritake, T. *et al.* Dehydrogenation properties and crystal structure analysis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>). *J. Alloys Compd.* **580**, S85–S89 (2013).
- 66. Noritake, T. *et al.* Synthesis and crystal structure analysis of complex hydride Mg(BH<sub>4</sub>)(NH<sub>2</sub>). *Int. J. Hydrogen Energy* **38**, 6730–6735 (2013).
- 67. Higashi, S., Miwa, K., Aoki, M. & Takechi, K. A novel inorganic solid state ion conductor for rechargeable Mg batteries. *Chem. Commun.* **50**, 1320–1322 (2014).
- 68. Roedern, E., Kühnel, R.-S., Remhof, A. & Battaglia, C. Magnesium ethylenediamine borohydride as solid-state electrolyte for magnesium batteries. *Sci. Rep.* **7**, 46189 (2017).

Chapter I - State-of-the-art: Rechargeable Mg batteries and Mg<sup>2+</sup> inorganic solid electrolytes

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Chapter II

#### II-1. Introduction

My PhD work started with the study of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) that was previously reported as a promising Mg<sup>2+</sup> solid ionic conductor.<sup>1</sup> It has been described for the first time by Noritake *et al.* in 2013.<sup>2,3</sup> They synthesized this compound in the scope of finding new solid state hydrogen storage materials. Through a series of synchrotron X-ray diffraction measurements at different temperatures, they could obtain this phase pure and solve its crystal structure. The synthesis was done from the reaction of Mg(BH<sub>4</sub>)<sub>2</sub> with Mg(NH<sub>2</sub>)<sub>2</sub> (*cf.* Equation II. 1):

$$Mg(BH_4)_2 + Mg(NH_2)_2 \rightarrow 2 Mg(BH_4)(NH_2) \qquad Equation II. 1$$

Magnesium borohydride has been extensively studied as hydrogen storage material because of its high gravimetric hydrogen density (14.5 wt%) and its capability of dehydrogenation at moderate temperatures (250-400°C).<sup>4</sup> It can also be used as salt in liquid electrolytes for Mg batteries,<sup>5</sup> as described in chapter I, but its ionic conductivity as solid electrolyte is very low (~10<sup>-12</sup> S.cm<sup>-1</sup> at 70°C and ~10<sup>-9</sup> S.cm<sup>-1</sup> at 150°C).<sup>1,6</sup> Mg(BH<sub>4</sub>)<sub>2</sub> is known to have several crystal structures which will be described in the following section.

Magnesium amide is also mainly known in the literature in the field of hydrogen storage materials, especially in the mixture  $Mg(NH_2)_2$ -2LiH, which can reversibly store 5.6 wt.% of hydrogen with suitable thermodynamics according to the following reaction:<sup>7–9</sup>

$$Mg(NH_2)_2 + 2 LiH \leftrightarrows Li_2Mg(NH)_2 + 2 H_2 \qquad Equation II. 2$$

This chapter will depict the precursors used for the synthesis of  $Mg(BH_4)(NH_2)$  *i.e.* commercial  $Mg(BH_4)_2$  and homemade  $Mg(NH_2)_2$ . Then, it will describe the optimization of the synthesis parameters of  $Mg(BH_4)(NH_2)$  and how its purity influences its ionic conductivity.

### II-2. Magnesium borohydride: Mg(BH<sub>4</sub>)<sub>2</sub>

#### II-2a. Polymorphs of Mg(BH<sub>4</sub>)<sub>2</sub>

The crystalline polymorphs of Mg(BH<sub>4</sub>)<sub>2</sub> that are described the most in the literature are the  $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -phase. Their structures and cell parameters are presented in Figure II. 1. In the literature, the existence of other phases is also discussed (*e.g.* amorphous phase,  $\beta'$ ,  $\varepsilon$ , etc.).<sup>4</sup> The  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub> polymorph is stable at room temperature and undergoes a phase transition at about 220°C forming the  $\beta$ -phase.<sup>10</sup> After cooling, the structure of  $\beta$ -Mg(BH<sub>4</sub>)<sub>2</sub> remains, it is considered

as a metastable phase at room temperature.  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> has an extremely porous structure and a very low density (0.5431 g.cm<sup>-3</sup>). The pores of its structure can accommodate gas molecules such as H<sub>2</sub> or N<sub>2</sub>.<sup>11</sup> It has two phase transitions: around 135-165°C to the  $\epsilon$ -phase and around 165-215°C to the  $\beta$ '-phase.<sup>12</sup> Finally,  $\delta$ -Mg(BH<sub>4</sub>)<sub>2</sub> is obtained under high pressures (> 2.1 GPa) from  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and it is stable at room temperature.<sup>11</sup>



Figure II. 1. Crystal structures of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -Mg(BH<sub>4</sub>)<sub>2</sub> polymorphs drawn with the software VESTA.<sup>13</sup>

#### II-2b. Commercially available Mg(BH<sub>4</sub>)<sub>2</sub> powders

The first magnesium borohydride used for the synthesis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) was the commercial  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> (> 95 %, Sigma-Aldrich). X-ray diffraction (XRD) measurement and Le Bail profile matching indicate that it is pure crystalline  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> (*cf.* Figure II. 2a) crystallizing in a cubic unit cell with space group Ia-3d with Z = 24 and the cell parameter a = 15.843(1) Å. Note that all the diffractograms measured with the Cobalt radiation present an important background due to the set-up of the diffractometer and to the beryllium window of the air-tight cell used for the measurements. As  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> stopped to be commercially available during this thesis, another precursor had to be used for the synthesis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>). This new precursor sold as "Mg(BH<sub>4</sub>)<sub>2</sub>" by Sigma-Aldrich (> 95 % pure) was, as a matter of fact, a mixture of  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>. The  $\gamma$  and  $\alpha$  phases are clearly detected by X-ray diffraction (*cf.* Figure II. 2b). Owing to a Rietveld refinement, it was determined that about 79% of the product was  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and 21 % was  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>.



Figure II. 2. XRD patterns of commercial a)  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and its profile matching and b) of  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub> and its Rietveld refinement.

Additionally, <sup>11</sup>B solid state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy was performed on  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub>. It shows one peak at about -39.6 ppm (*cf.* Figure II. 3a) which corresponds to the chemical shift of (BH<sub>4</sub>)<sup>-</sup>.<sup>12</sup> No peak is visible in the -10/-20 ppm region indicating that no boranes such as (B<sub>3</sub>H<sub>8</sub>)<sup>-</sup> or (B<sub>12</sub>H<sub>12</sub>)<sup>2-</sup> are present. Nevertheless, some borates are detected around 2 and 20 ppm, BO<sub>4</sub> (0.2 molar %) and BO<sub>3</sub> (2.7 molar %). For  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>, it shows as expected a peak around -40 ppm for the (BH<sub>4</sub>)<sup>-</sup> anion (*cf.* Figure II. 3b). The peak is made of two contributions: one at -39.2 ppm, which can be attributed to the  $\gamma$ -phase, and one at -38.7 ppm, due to the  $\alpha$ -phase.



Figure II. 3. <sup>11</sup>B MAS NMR spectra of commercial a)  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and b)  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>.

Infrared spectroscopy was also used to characterize these magnesium borohydrides. Only the characteristic vibrations bands of  $Mg(BH_4)_2$  appear on the infrared spectra of both products: the stretching bands around 2300 cm<sup>-1</sup> and the bending bands around 1200 cm<sup>-1</sup> (*cf.* Figure II. 4). No -OH impurities are visible (no bands around 3500 cm<sup>-1</sup>).<sup>14</sup>



Figure II. 4. Infrared spectra of commercial a)  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and b)  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>.

The differential scanning calorimetry (DSC) measurement shows the phase transition that undergoes  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> as described previously (*cf.* Figure II. 5a).<sup>12</sup> At 146°C, it starts to transform into the  $\varepsilon$ -phase and at 185°C into the  $\beta'$ -phase. For the product made of  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub> the result is different as the thermal phenomena linked to the two different phases are observed<sup>10,12</sup>:  $\gamma \rightarrow \varepsilon \rightarrow \beta'$  at 146°C and 185°C then  $\alpha \rightarrow \beta$  around 219°C (*cf.* Figure II. 5b). The borohydride starts to decompose around 280°C, forming first H<sub>2</sub> and amorphous species. Then at about 350°C, the amorphous species react exothermically with H<sub>2</sub> to form MgH<sub>2</sub>. Finally, the MgH<sub>2</sub> decomposes endothermically into Mg and H<sub>2</sub>. at about 365°C. The decomposition of Mg(BH<sub>4</sub>)<sub>2</sub> is still unclear and the steps given here are just one example among many described in the literature.<sup>4</sup>



Figure II. 5. DSC recorded at 5°C/min under argon flow of commercial a)  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and b)  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>.

### II-3. Magnesium amide: Mg(NH<sub>2</sub>)<sub>2</sub>

 $Mg(NH_2)_2$  is not commercially available and had to be synthesized during this thesis. This compound has been obtained from the reaction of magnesium hydride with gaseous ammonia as described in other studies.<sup>9,15</sup> The synthesis process is described on Figure II. 6 and the reaction is written in Equation II. 3:

$$MgH_{2(s)} + 2 NH_{3(g)} \rightarrow Mg(NH_2)_{2(s)} + 2 H_{2(g)}$$
Equation II. 3



Figure II. 6. Diagram summarizing the synthesis for  $Mg(NH_2)_2$ .

Commercial MgH<sub>2</sub> (> 98%, Alfa Aesar), is first ball-milled to increase its reactivity. In an argon-filled glovebox, 2 g of MgH<sub>2</sub> is introduced in a 50 cm<sup>3</sup> stainless steal jar with a balls to powder weight ratio of 53:1 and then ball-milled at 600 rpm using a Retsch PM100 miller for 2 h with a 2 min break every 30 min. By X-ray diffraction, MgH<sub>2</sub> appears well amorphized as all its reflections are much weaker and broader after ball-milling (*cf.* Figure II. 7b). A color change of the powder was noticed, before and after ball milling, from grey to brown. This is due to the partial transition from the  $\alpha$ -phase (s.g.: P4<sub>2</sub>/mnm, crystalline phase of MgH<sub>2</sub> at ambient conditions) to the  $\gamma$ -phase (s.g.: Pca2<sub>1</sub>) which is formed under high pressure (13.9 GPa).<sup>16</sup> Here, weak reflections of  $\gamma$ -MgH<sub>2</sub> appear at 30 and 36°.



Figure II. 7. XRD pattern after different steps of the Mg(NH<sub>2</sub>)<sub>2</sub> synthesis. a) As-received commercial MgH<sub>2</sub>. b) MgH<sub>2</sub> after ball-milling. c) Amorphous product after ball-milling of MgH<sub>2</sub> under NH<sub>3</sub> pressure. d) Crystalline Mg(NH<sub>2</sub>)<sub>2</sub> after annealing under NH<sub>3</sub> atmosphere.

Then, a jar with an inlet valve is used to perform the milling of  $MgH_2$  under  $NH_3$  pressure (99.9%, Messer). In an argon-filled glovebox, 600 mg of milled  $MgH_2$  is placed in a 25 cm<sup>3</sup> stainless steel jar equipped with a gas inlet. 23 stainless steel balls of 8 mm diameter are added (balls to powder weight ratio is 77:1). The jar is tightly closed and the following three steps are performed:

- step 1: vacuum at 1x10<sup>-5</sup> bar
- step 2: filling with 4 bar of  $NH_3$
- step 3: milling in a Spex miller for 1 h

After step 3, the process is repeated from step 1 twice to achieve a total of three cycles. The repetition allows to evacuate the formed  $H_2$  and to ensure that all of the MgH<sub>2</sub> has reacted with NH<sub>3</sub>. Once this ball milling is finished, the product is amorphous (*cf.* Figure II. 7c). The last step of the synthesis is an annealing at 290°C under 4 bar of NH<sub>3</sub> to crystallize Mg(NH<sub>2</sub>)<sub>2</sub> and to make sure that the reaction is completed. After annealing, pure crystalline Mg(NH<sub>2</sub>)<sub>2</sub> is obtained

(*cf.* Figure II. 7d). Figure II. 8 shows the diffractogram of as-synthesized Mg(NH<sub>2</sub>)<sub>2</sub> crystallizing in the space group I4<sub>1</sub>/acd with Z = 32 and the cell parameters a=10.393(1) Å, c = 20.089(3) Å and V = 2170.1(5)Å<sup>3</sup> which are close to the one of the literature (a = 10.37 Å, c = 20.15 Å and V = 2166.87 Å<sup>3</sup>).



Figure II. 8. a) XRD pattern of synthesized  $Mg(NH_2)_2$  and its profile matching. b) The crystalline structure of  $Mg(NH_2)_2$  drawn with VESTA.

The IR spectrum exhibits the typical vibration bands of  $Mg(NH_2)_2$ : sharp asymmetric and symmetric stretching bands at respectively ~3324 and ~3270 cm<sup>-1</sup> and bending bands at 1564 cm<sup>-1</sup> (*cf.* Figure II. 9).<sup>17,18</sup> Note that there is no trace of impurities as –OH groups around 3500 cm<sup>-1</sup>.



Figure II. 9. Infrared spectrum of as-synthesized  $Mg(NH_2)_2$ .

<sup>15</sup>N solid state MAS NMR spectroscopy features one peak at 4.8 ppm (*cf.* Figure II. 10). This peak is broad with a FWHM of 5.1 ppm. The existence of three distinct NH<sub>2</sub> in the crystalline structure might be causing this broadening. Even so, these NH<sub>2</sub> are very similar and that is the reason why only one peak is observed.



Figure II. 10. <sup>15</sup>N solid state MAS NMR spectrum of as synthesized  $Mg(NH_2)_2$ .

The DSC shows that Mg(NH<sub>2</sub>)<sub>2</sub> starts to decompose into MgNH around 350°C (*cf.* Figure II. 11). Here, the decomposition involves two endothermic-steps which might be due to a difference in the crystallites size. Indeed, after annealing, the product always consists in two different parts: a fine powder and a heap of agglomerate powder, in which the crystallites could have different sizes. Similar multi-step decompositions have been observed in the literature and they are also attributed to inhomogeneities in the sample.<sup>19</sup> At higher temperatures, MgNH decomposes into Mg<sub>3</sub>N<sub>2</sub> (around 500°C). The complete decomposition of Mg(NH<sub>2</sub>)<sub>2</sub> is described according to the following reaction<sup>20</sup>:



 $Mg(NH_2)_2 \rightarrow MgNH + NH_3 \rightarrow 1/3 Mg_3N_2 + 4/3 NH_3$  Equation II. 4

Figure II. 11. DSC of as-synthesized  $Mg(NH_2)_2$  recorded at 5°C/min under Ar flow.

#### II-4. Study of Mg(BH<sub>4</sub>)(NH<sub>2</sub>)

#### II-4a. Synthesis

Noritake *et al.* ball-milled Mg(BH<sub>4</sub>)<sub>2</sub> with Mg(NH<sub>2</sub>)<sub>2</sub> and then annealed the mixture to obtain Mg(BH<sub>4</sub>)(NH<sub>2</sub>).<sup>2,3</sup> In their study, in-situ X-ray diffraction was performed upon heating up the mixture. They determined that Mg(BH<sub>4</sub>)(NH<sub>2</sub>) starts to crystallize around 120°C and becomes amorphous at about 180°C. The dehydrogenation of the material happens at 200°C. The as-reported synthesis is hardly reproducible as only few parameters are known: a planetary ball milling was used and the milling duration was 2 h. No indication is given about the rotation speed or the balls to powder weight ratio. In their case, the ball-milling was strong enough to amorphize the precursors and only weak peaks of Mg(NH<sub>2</sub>)<sub>2</sub> remained. The annealing parameters are also difficult to reproduce as the study was performed with a small amount of powder in a capillary during their synchrotron XRD experiments. In the work of Higashi *et al.*, the same procedure as that of Noritake *et al.* was used, *i.e.* ball-milling with subsequent annealing but again, no parameters are given.<sup>1</sup> The third and last paper reporting the synthesis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) comes from Yang *et al.*.<sup>21</sup> The formation of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) was observed while heating up a mixture of Mg(BH<sub>4</sub>)<sub>2</sub>.2NH<sub>3</sub> and MgH<sub>2</sub>. At 100°C, pure Mg(BH<sub>4</sub>)(NH<sub>2</sub>) was detected by XRD.

Owing to this literature, we decided to synthesize Mg(BH<sub>4</sub>)(NH<sub>2</sub>) by ball-milling and subsequent annealing as described by Noritake *et al.*. The main problematic of this synthesis was to find the correct ball-milling and annealing parameters as none of them are reported in detail. X-ray diffraction was measured for each set of parameters to determine which one were optimal to obtain purely crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>). The procedure of the synthesis optimization is summarized in Figure II. 12, the different synthesis parameters tested are described in Table II. 1 and the XRD pattern of the products are presented on Figure II. 13.

[62]



Figure II. 12. Diagram summarizing the synthesis route for Mg(BH<sub>4</sub>)(NH<sub>2</sub>).

The first batch was made from the ball-milling of 1 g of an equimolar mixture of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub> performed at 600 rpm for 2 h with 2 min break every 30 min and a balls to powder weight ratio of 105:1. The ball milled powder does not show any diffraction peaks as all the precursors are amorphized (*cf.* Figure II. 14). After ball-milling, the powder has been annealed at 160°C for 48 h under 1 bar of Ar<sub>(g)</sub>. The as-obtained product was totally amorphous (sample 1 on Figure II. 13) and the powder turned into a porous solid (i.e. a foam) indicating the formation of gas during the annealing and thus a degradation. This was unexpected as Noritake *et al.* reported that Mg(BH<sub>4</sub>)(NH<sub>2</sub>) is stable up to 180°C. Moreover, none of the reactants shows degradation at 160°C (*cf.* Figure II. 5 and Figure II. 11). Nevertheless, this unexpected degradation was correlated to the formation of MgNH. Indeed, stretching bands attributed to the magnesium imide MgNH were observed by infrared spectroscopy around 3180 cm<sup>-1</sup> (*cf.* Figure II. 15).<sup>17</sup>

Chapter II – The known parts of the  $Mg(BH_4)_2$ - $Mg(NH_2)_2$  binary phases diagram:  $Mg(BH_4)_2$ ,  $Mg(NH_2)_2$  and  $Mg(BH_4)(NH_2)$ 

		Ball		Annealing conditions		
Sample name	Mg(BH <sub>4</sub> ) <sub>2</sub> precursor	milling speed (rpm)	Ball:powder mass ratio	Temp. (°C)	Time (h)	Atmosphere
D	$\gamma$ and $\alpha$	500	38:1	120	72	10 bar $H_{2(g)}$
12	$\gamma$ and $\alpha$	400	38:1	120	72	10 bar $H_{2(g)}$
11	γ	400	38:1	120	24	10 bar $H_{2(g)}$
10	γ	400	38:1	120	48	10 bar $H_{2(g)}$
С	γ	400	38:1	120	72	10 bar H <sub>2(g)</sub>
9	γ	400	38:1	120	96	10 bar $H_{2(g)}$
8	γ	300	38:1	120	96	10 bar $H_{2(g)}$
7	γ	200	38:1	130	48	10 bar $H_{2(g)}$
А	γ	200	38:1	130	48	1 bar Ar <sub>(g)</sub>
В	γ	200	38:1	120	96	1 bar Ar <sub>(g)</sub>
6	γ	100	38:1	120	96	1 bar Ar <sub>(g)</sub>
5	γ	100	38:1	120	48	1 bar Ar <sub>(g)</sub>
4	γ	0	/	120	96	1 bar Ar <sub>(g)</sub>
3	γ	0	/	120	48	1 bar Ar <sub>(g)</sub>
2	γ	0	/	160	48	1 bar Ar <sub>(g)</sub>
1	γ	600	105:1	160	48	1 bar Ar <sub>(g)</sub>

Table II. 1. Synthesis parameters investigated for the Mg(BH<sub>4</sub>)(NH<sub>2</sub>) synthesis.



Figure II. 13. XRD patterns smoothed and normalized of the products obtained with different ball-milling and annealing parameters as described in Table II. 1.
Chapter II – The known parts of the  $Mg(BH_4)_2$ - $Mg(NH_2)_2$  binary phases diagram:  $Mg(BH_4)_2$ ,  $Mg(NH_2)_2$  and  $Mg(BH_4)(NH_2)$ 



Figure II. 14. XRD patterns smoothed and normalized of the products after ball-milling of  $Mg(BH_4)_2$  and  $Mg(NH_2)_2$  at different milling speeds.

To avoid the formation of MgNH, the same annealing at 160°C for 48h under Ar was performed on a mixture of Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub> simply mixed in an agate mortar. The resulting product was again amorphous (sample 2 on Figure II. 13). At this point, the annealing temperature was questioned as a too high temperature could be the cause of the degradation of the samples. So, the temperature was reduced to 120°C. This allowed us to obtain a product that was not amorphous but a mixture of remaining reactants, an unknown additional phase and weak peaks of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (sample 3 on Figure II. 13). Then, the annealing time was increased to 96h (sample 4 on Figure II. 13). The product was still not pure but similar to sample 3. So a temperature of 120°C seems to be high enough to obtain Mg(BH<sub>4</sub>)(NH<sub>2</sub>) but a simple mixing in an agate mortar does not allow an intimate mixture of the two reactants and a complete reaction.

We tried to optimize the ball-milling parameters starting with softer conditions than those used previously. The balls to powder weight ratio was decreased from 105:1 to 38:1 and the ball-milling speed reduced to 100 rpm for 1h. In this case, the ball-milling does not degrade  $Mg(NH_2)_2$ 

into MgNH as no bands corresponding to the imide appear on the infrared spectrum (cf. Figure II. 15). An annealing at 120°C has been performed for 48 h under 1 bar of Ar. It allowed the crystallization of a product that was still impure and mainly made of the unknown additional phase encountered before (sample 5 on Figure II. 13). A longer annealing of 96 h was performed. It leads up to a product with more  $Mg(BH_4)(NH_2)$  than the additional phase and no more reactant (sample 6 on Figure II. 13). Later, the ball milling was increased to 200 rpm and the sample was annealed in the same conditions as previously (i.e. at 120°C for 96h under 1 bar of Ar). The purity of this sample was similar to sample 5 with  $Mg(BH_4)(NH_2)$  more present than the additional phase (sample B on Figure II. 13). Another annealing was tried at 130°C for 48h after the same ball-milling of 200 rpm. This time, the sample contained mainly the additional phase (sample A on Figure II. 13). We noticed also that this sample appears foamy after the annealing treatment. We considered that the additional phase could be a decomposition product of the samples during annealing under Ar. Subsequently, the annealing atmosphere was changed from 1 bar of Ar to 10 bar of  $H_2$  to avoid any gas evolution during the synthesis. With this new annealing atmosphere, the product was not foamy anymore but it was impure and the additional phase was still present (sample 7 on Figure II. 13). For the next syntheses, the ball-milling speed was increased to 300 and 400 rpm and an annealing at 120°C for 96 h under 10 bar of H<sub>2</sub> was performed. With the ballmilling at 300 rpm, the amount of crystalline additional phase was greatly reduced (sample 8 on Figure II. 13). Finally, after the ball-milling at 400 rpm and subsequent annealing, the product consists only in crystalline  $Mg(BH_4)(NH_2)$  as revealed by X-ray diffraction (sample 9 on Figure II. 13). So the ball-milling has to be strong enough for the synthesis of pure crystalline  $Mg(BH_4)(NH_2)$ . To know if the ball milling is strong enough, one can look at the diffraction patterns of the powders right after ball-milling. On Figure II. 14, by increasing the ball-milling speed, the amorphisation of the reactants is increased and it is once the borohydride Mg(BH<sub>4</sub>)<sub>2</sub> is completely amorphous that the purest samples are obtained after annealing.



Figure II. 15. Infrared spectra of the equimolar mixture of Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub> before and after a high energy ball-milling and a low energy ball-milling.

An optimization was implemented to try to decrease the annealing time. The product ballmilled at 400 rpm was annealed at 120°C under 10 bar of  $H_2$  for 24 h, 48h and 72h. For the annealing of 24 h, the additional phase is present (sample 11 on Figure II. 13). Then, after 48h and 72h of annealing, the samples are pure Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (sample 10 and C respectively on Figure II. 13). The annealing time of 72h was chosen as optimal parameter to make sure that the reaction is completed.

Later during the PhD,  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> stopped to be commercialized. We started to do the synthesis from the magnesium borohydride consisting in a mixture of the  $\gamma$  and  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub>. We first used the same synthesis parameters than for sample C, *i.e.* a ball milling at 400 rpm for 1h with a balls to powder weight ratio of 38:1 and a subsequent annealing at 120°C for 72h under 10 bar of H<sub>2</sub>. The as-obtained product was mainly Mg(BH<sub>4</sub>)(NH<sub>2</sub>) but it was not pure (sample 12 on Figure II. 13). A new crystalline additional phase was present. It was different from the additional phase observed in samples A, B and C. From the previous syntheses, we know that one of the important parameters for improving the purity of the sample was the ball-milling speed. So a synthesis with an increased ball-milling speed (500 rpm) and the same annealing conditions was performed. As expected, the product appears as purely crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (sample D on Figure II. 13). The diffraction pattern of this sample and its profile matching are shown on Figure II. 16. The compound crystallizes with the space group I4<sub>1</sub> with Z = 8 and the cell parameters a =

5.768(5) Å, c = 20.486(2) Å, and V = 681.6(1) Å<sup>3</sup> which is in agreement with the literature (a = 5.814(1) Å, c = 20.450(4) Å and V = 691.3(2) Å<sup>3</sup>).<sup>2</sup>

In the following sections, the samples labeled A, B, C and D will be compared due to their different compositions, especially regarding the content of additional phase as observed by XRD (*cf.* Figure II. 13). Their purity will be further analyzed by <sup>11</sup>B solid-state MAS NMR spectroscopy. The thermal stability of the samples will be evaluated and the influence of the additional phase on the ionic conductivity will be investigated by electrochemical impedance spectroscopy (EIS).



Figure II. 16. a) XRD pattern of sample D and its profile matching. b) Crystal structure of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) drawn with VESTA.

#### II-4b. MAS-NMR spectroscopy

To verify the purity of our materials and the local environment of boron in Mg(BH<sub>4</sub>)(NH<sub>2</sub>), <sup>11</sup>B MAS-NMR analyses were performed on samples A, B, C and D (*cf.* Figure II. 17a). No peaks are detected around -20 ppm which indicate that no  $B_xH_y$  borane groups such as  $(B_3H_8)^-$ ,  $(B_{12}H_{12})^{2^-}$ ,  $(B_{10}H_{10})^{2^-}$  and BH<sub>3</sub> are present.<sup>22–24</sup> In Figure II. 17, the four <sup>11</sup>B NMR spectra display strong peaks

between -37 ppm and -40 ppm, which can be unambiguously attributed to  $(BH_4)^-$  anions.<sup>12,25</sup> Samples A and B show actually two peaks in this chemical shift area: a first one at about -37.6 ppm and a second one at about -39.6 ppm (*cf.* Figure II. 17b). We can consider that one of the NMR peak is due to  $(BH_4)^-$  in Mg $(BH_4)(NH_2)$  and the other one to  $(BH_4)^-$  in a slightly different environment as in the additional phase detected by XRD. To assign the two peaks, the spectra were fitted with two components and the percentage of boron atoms contributing to each environment (*cf.* Figure II. 17d) was extracted and compared to the relative proportion of the two crystalline phases observed by XRD analyses (*cf.* Figure II. 13). The percentage of boron atoms corresponding to the peak at -37.6 ppm increases from sample A to sample B, so with increasing proportion of Mg $(BH_4)(NH_2)$ . In the same time, the percentage of boron atoms contributing to the peak at -39.6 ppm decreases from sample A to sample B, with the decrease of the additional phase content. We conclude therefore that the peak at -37.6 ppm is due to the  $(BH_4)^-$  anions in Mg $(BH_4)(NH_2)$  and that the second peak at -39.6 ppm is due to  $(BH_4)^-$  present in the additional phase.

In the case of sample C and D, for which only Mg(BH<sub>4</sub>)(NH<sub>2</sub>) was observed by XRD (*cf.* Figure II. 13), only one peak was expected on the NMR spectrum as, in the crystal structure reported for Mg(BH<sub>4</sub>)(NH<sub>2</sub>), the boron atoms occupy a single Wyckoff site. Two NMR peaks are however detected in both samples. For sample C, the first peak (52 molar % of the boron in the sample) at -37.6 ppm is similar to samples A and B and confirms the assignment to Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (*cf.* Figure II. 17b). The second peak (48 molar %) differs from that in the other samples: it is slightly less shielded at -38.6 ppm. For sample D, the contribution at -37.7 ppm due to Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (79 molar %) is also present as well as the other one at -38.8 ppm (21 mol %). For sample D, Mg(BH<sub>4</sub>)(NH<sub>2</sub>) is in larger quantity than in sample C (*cf.* Figure II. 17d).

Additional information as crystallinity degree can be extracted from the Full Width at Half Maximum (FWHM) of the NMR peaks. The FWHM is in between 1.1-1.7 ppm for all peaks except for the additional phase in sample C and D which has a value of 3.8 and 3.0 ppm respectively (*cf.* Figure II. 17c). This peak broadening and the pure Gaussian shape reveal the amorphous character of the new additional phase. The very amorphous character of this additional phase explains its non-observation by XRD; even if it represents 48 molar % of the total boron atoms in sample C.



Figure II. 17. a) <sup>11</sup>B MAS-NMR spectra for the samples A, B, C and D. b) Chemical shifts and c) FWHM of the peaks attributed to  $Mg(BH_4)(NH_2)$  and the additional phase. d) Molar percentages of boron contributing to each peak.

A <sup>15</sup>N MAS-NMR spectrum was also recorded for sample D (*cf.* Figure II. 18). The peak observed at 5.0 ppm corresponds to the  $(NH_2)^{-1}$  anions and can be fitted with only one component.

This is in agreement with the crystalline structure of  $Mg(BH_4)(NH_2)$  described in the literature where the nitrogen atoms occupy only one Wyckoff site. It also means that if the additional phase contains  $NH_2$  groups, they are very similar to the ones of  $Mg(BH_4)(NH_2)$  and are not affected by the change of structure. Note also that the chemical shift is similar to the one measured for  $Mg(NH_2)_2$  but its FWHM is smaller (3.0 ppm instead of 5.1 ppm). Despite the similarity between the  $(NH_2)^-$  anions in the two compounds, the FWHM difference can be explained by the fact that the structure of  $Mg(BH_4)(NH_2)$  is described with only one  $NH_2$  and not three as that of  $Mg(NH_2)_2$ .



Figure II. 18. <sup>15</sup>N solid state MAS-NMR spectrum for sample D.

### II-4c. Infrared spectroscopy

The infrared spectrum shown on Figure II. 19 confirms that sample D features only BH<sub>4</sub> and NH<sub>2</sub> groups signatures as described in the previous sections about Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub>. Interestingly, the bending vibration bands of BH<sub>4</sub> groups have changed compared to Mg(BH<sub>4</sub>)<sub>2</sub>. In the borohydride Mg(BH<sub>4</sub>)<sub>2</sub>, there are several bending bands around 1200 cm<sup>-1</sup> (*cf.* Figure II. 4). In the as-synthesized Mg(BH<sub>4</sub>)(NH<sub>2</sub>), these bands are split into four distinct bands at 1109, 1230, 1439 and 1638 cm<sup>-1</sup>. This is explained by the deformation of the BH<sub>4</sub> tetrahedra with two B-H lengths shorter than the two others (*cf.* Table II. 2). The vibration due to NH<sub>2</sub> has also changed compared to the one of Mg(NH<sub>2</sub>)<sub>2</sub>. The asymmetric stretching at 3326 cm<sup>-1</sup> has a higher amplitude than the symmetric one at 3270 cm<sup>-1</sup> which is the opposite of the Mg(NH<sub>2</sub>)<sub>2</sub> amide (*cf.* Figure II. 9). The bending band at 1541 cm<sup>-1</sup> has lower amplitude than in the amide. These amplitude changes might be caused by the change in the N-H bond length (*cf.* Table II. 2) and the change in

the NH<sub>2</sub> environment. Note that few imide has been formed during the synthesis (small absorption bands around 3200 cm<sup>-1</sup>) and that no OH groups are present (no absorption bands around 3500 cm<sup>-1</sup>).



Figure II. 19. Infrared spectrum of sample D.

Table II. 2. B-H and N-H bond lengths in γ-Ν	Лg(BH4)2, Mg(NH2)2 and Mg(BH4)(NH2).
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Bond	Bond length (Å)	Ref.
γ-Mg(BH <sub>4</sub> ) <sub>2</sub>		
B1-H1	1.14	12
B1-H2	1.14	
Mg(NH <sub>2</sub> ) <sub>2</sub>		
N1-H1	0.92	
N2-H2	0.87	26
N3-H3	0.89	
N3-H4	0.94	
Mg(BH <sub>4</sub> )(NH <sub>2</sub>	2)	
B1-H1	1.17	
B1-H2	1.17	
B1-H3	1.29	2
B1-H4	1.22	
N1-H5	1.01	
N1-H6	1.06	

#### II-4d. Thermal stability

Figure II. 20 presents the differential scanning calorimetry (DSC) curves recorded for the samples A, B, C and D. As reported in the literature<sup>1</sup>, an endothermic phenomenon related to an amorphization occurs between 120°C and 170°C and then the product is exothermically decomposed above 200°C. A decrease in the onset temperature of the amorphization is observed, decreasing from 152°C, 142°C and finally 120°C for samples A, B and C, respectively. Then, for sample D, the onset temperature of amorphization is at 172°C with a maximum at 183°C which is close to the one reported in the literature at 181°C.<sup>1</sup>



Figure II. 20. DSC of the samples A, B, C and D recorded at 5°C/min.

By thermal gravimetric analysis (TGA) coupled with DTA (Differential Thermal Analysis), no important mass loss was observed below 190°C. Only a small release of NH<sub>3</sub> starts at the same temperature than the endothermic phenomenon (*cf.* Figure II. 21). The measurement was not recorded at higher temperatures because the sample starts to decompose around 200°C and to produce a lot of foam that goes outside the crucible used for the measurement and can damage the device.



Figure II. 21. (a) TGA coupled with DTA measurement of sample D recorded at 5°C/min. (b) Gas mass spectrometry of sample D recorded at 5°C/min showing both  $NH_3$  and  $H_2$  releases.

#### II-4e. Ionic conductivity

The ionic conductivities were measured by Electrochemical Impedance Spectroscopy (EIS) on pellets made from powders of the samples A, B, C and D. Figure II. 22b exhibits the Nyquist and the Bode plots at 100°C for sample A, B and C which were measured using 13 mm diameter pellets with a thickness of about 0.8 mm (experimental details in Annex I). For each sample, a semi-circle can be observed on the Nyquist plot at high frequencies (HF) with the presence of a semi-circle weakly marked at middle frequencies (MF). At lower frequency, a more vertical straight line (capacitive effect) characteristic of ion-blocking electrodes (Papyex foils) can be observed. This line is not perfectly vertical due to the surface roughness. The impedance spectroscopy measurement protocol has been improved for sample D, using a 6 mm diameter pellet with a thickness of about 1.1 mm (experimental details in Annex I). The semicircle appears clearly at high frequency and it is followed by a straight line due to the capacitive effect of the blocking electrodes (*cf.* Figure II. 22a).

As discussed previously, XRD and <sup>11</sup>B MAS-NMR analyses showed that each sample contains Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and an additional phase. By a simple observation of the Nyquist diagrams, it can be noticed that the proportion of the second phenomenon at middle frequencies increases with the quantity of the additional phase. The observation of the Bode plots at high and middle frequencies clearly shows the presence of two phenomena (cf. Figure II. 22a). With an appropriate equivalent circuit, the conductivity, the activation energy and the real capacitance can be extracted as a function of temperature to attribute the physical meaning of each phenomenon. We chose the brick layer model. Indeed, the sample preparation by ball-milling involves a good mixing of the different precursors. As the thermal treatment is performed on pellets, and the different phases are generated during this thermal treatment, we could consider that Mg(BH<sub>4</sub>)(NH<sub>2</sub>) is the grain and the additional phase the grain boundaries as in a brick layer model. By taking this model into account, the fitting of impedance signals were performed with the equivalent circuit shown on Figure II. 22c. The equivalent circuit is composed of an initial resistor R<sub>0</sub> for the device and current collectors resistance, in series with a first  $R_1//CPE_1$  ( $R_1$  for the bulk solid electrolyte resistance in parallel with a constant phase element  $CPE_1$  for the non-ideal capacitance) and a second  $R_2//CPE_2$ for the grain boundaries conduction (resistance and capacitance) and, finally, another constant phase element (CPE<sub>3</sub>) for the impedance of both the top and bottom electrode-electrolyte junctions to consider the roughness of the electrical contact. As described previously, R1 could be associated to the conduction of  $Mg(BH_4)(NH_2)$  and  $R_2$  to the grain boundaries constituted by the additional phase.

Chapter II



Figure II. 22. Nyquist plots and Bode plots at 100°C from EIS measurements of a) sample D (with a 6 mm diameter pellet) and of b) samples A, B and C (with 13 mm diameter pellets). c) Equivalent circuit model used to fit the experimental data.

The conduction phenomena at high and middle frequencies can be separated by the equivalent circuit described previously and described by their intrinsic characteristics: their activation energy (Ea) and their real capacitances. These characteristics helped us to validate or not our model. To extract the activation energy of each phenomenon,  $ln(\sigma.T)$  is plotted as a function of 1/T for each sample as shown on Figure II. 23a. For the samples A, B and C, a clear difference of behavior can be observed for the two phenomena. The Ea for the middle frequency phenomenon remains constant around 1.3 eV whereas the one at high frequency decreases as the sample is getting higher purity in Mg(BH<sub>4</sub>)(NH<sub>2</sub>), evolving from 1.3 eV to 1.0 eV, which confirms our attribution of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) as the grain in our model. These Ea values are similar to those reported in the literature for the same material (1.31 eV) and other Mg<sup>2+</sup> ionic conductors.<sup>6,27</sup> For sample D, the activation energy is about 1.0 eV for the high frequency phenomenon and 0.9 eV for the middle frequency one.

To evaluate our fit, model and physical meaning, the real capacitance values of each conduction phenomenon is extracted for the R//CPE couple. The calculated capacitances for each phenomenon are plotted versus the temperature on Figure II. 23b. They remain constant as a function of temperature, which is scientifically sound as the capacitance is only dependent on the electrical permittivity of the phases and their geometrical dimensions, these parameters being independent of the temperature. For the phenomenon at high frequency, a real capacitance of the order of 10<sup>-10</sup> F.cm<sup>-2</sup> is obtained for all the samples whereas for the one at middle frequency, the real capacitance is around 10<sup>-9</sup> F.cm<sup>-2</sup> for sample A, B and C but around 10<sup>-8</sup> F.cm<sup>-2</sup> for sample D. Capacitance values around 10<sup>-9</sup>-10<sup>-10</sup> F.cm<sup>-2</sup> are typical of ionic conduction phenomena<sup>28</sup> and, hence, confirm our assumption that the high and middle frequencies phenomena are due to the ionic conduction in both phases. The value of 10<sup>-8</sup> F.cm<sup>-2</sup> corresponds to an interface between the electrode and the electrolyte. So, for sample D, the fitted middle frequency phenomenon is not due to the additional phase. The additional phase is in too low quantity in this sample to form grain boundaries detectable by EIS. For the other samples (A,B and C), the interface did not need to be modeled even though they were measured with the same electrodes. Thus, the equivalent circuit with two components was not appropriate for sample D. The data were fitted with a second equivalent circuit made of only one R//CPE component (cf. Figure II. 24). This model fits very well the data. The calculated activation energy (1.0 eV) and real capacitance (10<sup>-10</sup> F.cm<sup>-2</sup>) are the same than the one found for the phenomenon at high frequency while using a model with two R//CPE. So, an equivalent circuit with one R//CPE is more appropriate to model the ionic conduction in sample D.



Figure II. 23. a)  $ln(\sigma.T) = f(1/T)$  used to calculate the activation energies of the two ionic conduction phenomena (at high and middle frequency, HF and MF. b)Real capacitance values for the two conduction phenomena as a function of the temperature.



Figure II. 24. EIS measurements of sample D fitted with one R//CPE. a) Nyquist plot at 100°C. b) Equivalent circuit model used to fit the experimental data. c) Real capacitance as a function of the temperature. d)  $ln(\sigma.T) = f(1/T)$  used to calculate the activation energy.

Once the models were validated, the ionic conductivity for each sample was calculated. For samples A, B and C the ionic conductivity is calculated from R1 and R2 as both were determined to be linked to ionic conduction phenomena. The equation used is as follow:

$$\sigma = \frac{1}{(R_1 + R_2)} \cdot \frac{l}{S}$$
 Equation II. 5

For sample D, only R1 was used in Equation II. 5. The results are plotted on Figure II. 25 as a function of 1/T. The ionic conductivity increases gradually from sample A to D. This increase can be correlated to the increase of the amount of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) present in the samples. The more Mg(BH<sub>4</sub>)(NH<sub>2</sub>) is present, the highest is the conductivity. Very interestingly, the ionic conductivity reaches  $1\times10^{-5}$  S.cm<sup>-1</sup> at 100°C for sample D. This conductivity is four orders of magnitude higher than the one reported by Higashi *et al.*<sup>1</sup> for the same compound (*cf.* black dots on Figure II. 25). This value of ionic conductivity is one of the highest reported at this temperature, getting close to the one obtained by Roedern et al. for Mg(en)<sub>1</sub>(BH<sub>4</sub>)<sub>2</sub> (en = ethylene-diamine).<sup>6</sup> These results could be explained by the presence of the additional phase. Especially, once this phase gets amorphous

as shown by <sup>11</sup>B MAS-NMR spectroscopy, it would create a glass-ceramic-like composite material with improved ionic conduction, as previously described by Tsukasaki et al. on Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glassceramics.<sup>29</sup> In their study, nano-crystals of Li<sub>3</sub>PS<sub>4</sub> were observed by TEM within an amorphous matrix in  $Li_2S-P_2S_5$  glass-ceramics explaining the improvement in ionic conductivity compared to the glasses. This assumption is also supported in our study by the fact that the ionic conductivity of the pellet decreases with the increase of the proportion of crystalline additional phase. Nevertheless, it is hard to observe this kind of glass-ceramic structure by TEM on our samples without exposing them to air during the transfer into the microscope and without damaging them with the electronic beam. The enhancement of the ionic conductivity can also be related to the study of Yan et al. in which they demonstrate that adding an excess of BH<sub>4</sub> in Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> would create a solid solution with disorder in the structure which enables fast Li<sup>+</sup> diffusion<sup>30</sup>. In our case, the Mg(BH<sub>4</sub>)(NH<sub>2</sub>)-based composite material could have a similar behavior but the nature of the additional phase needs to be clearly characterized to support this hypothesis. Another explanation would be that the compound studied by Higashi et al. was not pure Mg(BH<sub>4</sub>)(NH<sub>2</sub>) but contained an important amount of amorphous additional phase (> 50 molar %). Again, further information as the synthesis parameters or <sup>11</sup>B MAS solid sate NMR measurements on their sample would have been very useful.



Figure II. 25. Ionic conductivity of samples A, B, C and D as a function of 1/T. The results are compared to the measurement of Higashi et al..<sup>1</sup>

#### **II-5.** Conclusion

 $Mg(BH_4)(NH_2)$  has been synthesized by ball-milling of  $Mg(BH_4)_2$  and  $Mg(NH_2)_2$  and a subsequent annealing. The crystalline phase of  $Mg(BH_4)_2$  used for the reaction is important as the synthesis parameters needed to obtain pure crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>) are different depending on the precursor used. The other critical parameters are the ball milling speed and the annealing conditions. The ball-milling speed must be not too strongly energetic in order to avoid the decomposition of the reactants but strong enough to make an intimate mixture of the two reactants. Besides the ball milling, the annealing has to be properly performed as well. The annealing temperature should not be too high, otherwise the product will decompose, but the temperature should be high enough to crystallize  $Mg(BH_4)(NH_2)$ . We also found out that a back pressure of  $H_2$  helps to keep the product stable during the synthesis and that the time of annealing has to be long enough to get a complete reaction. To obtain a compound with no other crystalline phase than Mg(BH<sub>4</sub>)(NH<sub>2</sub>) using pure  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2</sub> as precursor, a ball-milling at 400 rpm and a subsequent annealing at 120°C for 72h under 10 bar of H<sub>2</sub> were performed. Whereas with a borohydride made of the  $\gamma$  and  $\alpha$ -phases, a more energetic ball-milling at 500 rpm and the same subsequent annealing were needed. <sup>11</sup>B MAS-NMR spectroscopy revealed that even if by X-ray diffraction only crystalline  $Mg(BH_4)(NH_2)$  appears in samples C and D, an additional amorphous phase was still present. It was observed that this additional phase could be crystallized in samples for which the synthesis parameters were not optimized.

The content in additional phase present in the samples strongly influences the ionic conductivity. If the sample contains a large amount of the additional phase, its ionic conductivity will be lower than if it contains less of it. An ionic conductivity of  $1.10^{-5}$  S.cm<sup>-1</sup> was obtained for sample D that is made of 80 molar % of crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and 20 molar % of the amorphous additional phase. This conductivity is four orders of magnitude higher than the one previously reported by Higashi *et al.*. The activation energy is also lower than the one reported, 1.0 eV *vs.* 1.31 eV, indicating an improved Mg<sup>2+</sup> mobility. The ionic conductivity values become especially high once this additional phase is amorphous forming a glass-ceramic-like composite material. This could explain why the ionic conductivity values measured are several orders of magnitude higher than the one reported in the literature. We can also consider that the additional phase is actually detrimental for the ionic conductivity. However, it is necessary to know if the compound of Higashi *et al.* contained the additional phase or not to be able to conclude if it has a benefic or detrimental effect on the ionic conductivity.

The nature of the additional phase remained unclear but its strong influence on the properties of the as-synthesized Mg(BH<sub>4</sub>)(NH<sub>2</sub>) is interesting. The first assumption was that this additional phase was an Mg(BH<sub>4</sub>)<sub>2-x</sub>(NH<sub>2</sub>)<sub>x</sub> substoichiometric compound. Indeed, it is not a decomposition product and it was encountered in large proportion in samples for which the reaction was not fully completed. From <sup>11</sup>B MAS-NMR spectroscopy, we observed that it had slightly different environments for the BH<sub>4</sub> groups as compared to Mg(BH<sub>4</sub>)(NH<sub>2</sub>). Unfortunately, no compound of such composition has ever been reported so far. Therefore, we decided to explore the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram to try to identify this additional phase.

### References

- 1. Higashi, S., Miwa, K., Aoki, M. & Takechi, K. A novel inorganic solid state ion conductor for rechargeable Mg batteries. *Chem. Commun.* **50**, 1320–1322 (2014).
- 2. Noritake, T. *et al.* Synthesis and crystal structure analysis of complex hydride Mg(BH<sub>4</sub>)(NH<sub>2</sub>). *Int. J. Hydrogen Energy* **38**, 6730–6735 (2013).
- 3. Noritake, T. *et al.* Dehydrogenation properties and crystal structure analysis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>). *J. Alloys Compd.* **580**, S85–S89 (2013).
- Zavorotynska, O., El-Kharbachi, A., Deledda, S. & Hauback, B. C. Recent progress in magnesium borohydride Mg(BH<sub>4</sub>)<sub>2</sub>: Fundamentals and applications for energy storage. *Int. J. Hydrogen Energy* **41**, 14387–14403 (2016).
- 5. Mohtadi, R., Matsui, M., Arthur, T. S. & Hwang, S.-J. Magnesium borohydride: From hydrogen storage to magnesium battery. *Angew. Chemie Int. Ed.* **51**, 9780–9783 (2012).
- 6. Roedern, E., Kühnel, R.-S., Remhof, A. & Battaglia, C. Magnesium ethylenediamine borohydride as solid-State electrolyte for magnesium batteries. *Sci. Rep.* **7**, 46189 (2017).
- 7. Nakamori, Y., Kitahara, G. & Orimo, S. Synthesis and dehydriding studies of Mg–N–H systems. *J. Power Sources* **138**, 309–312 (2004).
- 8. Leng, H. Y., Ichikawa, T., Hino, S. & Hanada, N. New Metal-N-H System Composed of Mg(NH<sub>2</sub>)<sub>2</sub> and LiH for Hydrogen Storage. 8763–8765 (2004).
- 9. Leng, H. Y. *et al.* Synthesis and decomposition reactions of metal amides in metal–N–H hydrogen storage system. *J. Power Sources* **156**, 166–170 (2006).
- Filinchuk, Y., Černý, R. & Hagemann, H. Insight into Mg(BH<sub>4</sub>)<sub>2</sub> with synchrotron X-ray diffraction: structure revision, crystal chemistry, and anomalous thermal expansion. *Chem. Mater.* **21**, 925–933 (2009).
- 11. Filinchuk, Y. *et al.* Porous and dense magnesium borohydride frameworks: Synthesis, stability, and reversible absorption of guest species. *Angew. Chemie Int. Ed.* **50**, 11162–11166 (2011).
- 12. David, W. I. F. *et al.* The structure, thermal properties and phase transformations of the cubic polymorph of magnesium tetrahydroborate. *Phys. Chem. Chem. Phys.* **14**, 11800–11807 (2012).
- 13. Dimitrievska, M. *et al.* Structure-dependent vibrational dynamics of Mg(BH<sub>4</sub>)<sub>2</sub> polymorphs probed with neutron vibrational spectroscopy and first-principles calculations. *Phys. Chem. Chem. Phys.* **18**, 25546–25552 (2016).
- 14. D'Anna, V., Spyratou, A., Sharma, M. & Hagemann, H. FT-IR spectra of inorganic borohydrides. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **128**, 902–906 (2014).
- 15. Ma, L. *et al.* Enhanced Hydrogen storage properties of Li–Mg–N–H system prepared by reacting Mg(NH<sub>2</sub>)<sub>2</sub> with Li<sub>3</sub>N. *J. Phys. Chem. C* **113**, 9944–9949 (2009).
- 16. Moriwaki, T., Akahama, Y., Kawamura, H., Nakano, S. & Takemura, K. Structural phase transition of rutile-type MgH<sub>2</sub> at high pressures. *J. Phys. Soc. Japan* **75**, 2–7 (2006).

- 17. Linde, G. & Juza, R. IR-Spektren von Amiden und Imiden zwei- und dreiwertiger Metalle gestellt ; wenn das Praparat bisher noch nicht untersucht worden ist , werden. *Z. Anorg. Allg. Chem.* **409**, 199–214 (1974).
- 18. Luo, W. & Sickafoose, S. Thermodynamic and structural characterization of the Mg-Li-N-H hydrogen storage system. *J. Alloys Compd.* **407**, 274–281 (2006).
- 19. Dolci, F. *et al.* Magnesium imide: Synthesis and structure determination of an unconventional alkaline earth imide from decomposition of magnesium amide. *Inorg. Chem.* **50**, 1116–1122 (2011).
- 20. Hino, S., Ichikawa, T. & Kojima, Y. Thermodynamic properties of metal amides determined by ammonia pressure-composition isotherms. *J. Chem. Thermodyn.* **42**, 140–143 (2010).
- 21. Yang, Y. *et al.* Hydrogen storage properties and mechanisms of Mg(BH<sub>4</sub>)<sub>2</sub>.2NH<sub>3</sub>-xMgH<sub>2</sub> combination systems. *J. Alloys Compd.* **585**, 674–680 (2014).
- 22. Remhof, A. *et al.* Solvent-free synthesis and stability of MgB<sub>12</sub>H<sub>12</sub>. *J. Mater. Chem. A* **2**, 7244–7249 (2014).
- 23. Huang, J. *et al.* A novel method for the synthesis of solvent-free Mg(B<sub>3</sub>H<sub>8</sub>)<sub>2</sub>. *Dalt. Trans.* **45**, 3687–3690 (2016).
- 24. Au, Y. S., Yan, Y., de Jong, K. P., Remhof, A. & de Jongh, P. E. Pore confined synthesis of magnesium boron hydride nanoparticles. *J. Phys. Chem. C* **118**, 20832–20839 (2014).
- 25. Yang, Y., Liu, Y., Li, Y., Gao, M. & Pan, H. Synthesis and thermal decomposition behaviors of magnesium borohydride ammoniates with controllable composition as hydrogen storage materials. *Chem. Asian J.* **8**, 476–481 (2013).
- 26. Jacobs, H. Die kristallstruktur des magnesiumamids. *Zeitschrift fur Anorg. und Allg. Chemie* **382**, 97–109 (1971).
- Ikeda, S., Takahashi, M., Ishikawa, J. & Ito, K. Solid electrolytes with multivalent cation conduction. 1. Conducting species in Mg-Zr-PO<sub>4</sub> system. *Solid State Ionics* 23, 125–129 (1987).
- Irvine, B. J. T. S., Sinclair, D. C. & West, A. R. Electroceramics : Characterization by Impedance Spectroscopy. 2, 132–138 (1990).
- 29. Tsukasaki, H., Mori, S., Morimoto, H., Hayashi, A. & Tatsumisago, M. Direct observation of a non-crystalline state of Li<sub>2</sub>S–P<sub>2</sub>S<sub>5</sub> solid electrolytes. *Sci. Rep.* **7**, 4142 (2017).
- 30. Yan, Y. *et al.* A lithium amide-borohydride solid-state electrolyte with lithium-ion conductivities comparable to liquid electrolytes. *Adv. Energy Mater.* **1700294**, 1–7 (2017).

# <u>Chapter III –</u> The exploration of the unknown parts of the $Mg(BH_4)_2$ - $Mg(NH_2)_2$ binary phases diagram

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Chapter III – The exploration of the unknown parts of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram

#### III-1. Introduction

In the previous chapter, the formation of unknown phases has been observed during the synthesis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>). It was determined that these phases were not decomposition products but were rather obtained from non-optimized synthesis. Thus, the hypothesis of the existence of other compounds with different Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> stoichiometries was made. All the known parts of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram have been described in the previous chapter, namely: Mg(BH<sub>4</sub>)<sub>2</sub>, Mg(NH<sub>2</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)(NH<sub>2</sub>). Nevertheless, other borohydride-amide binary systems have been studied in other works. The most studied one is the LiBH<sub>4</sub>-LiNH<sub>2</sub> binary phases diagram. Besides LiBH<sub>4</sub>, LiNH<sub>2</sub> and Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>), other crystalline compounds were obtained such as Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub> and Li<sub>3</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>2</sub>.<sup>1-8</sup> The Li<sup>+</sup> ionic conduction properties of these compounds are higher compared to Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>) so it was important to know if similar phases do exist or not in the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram and if so, to characterize their Mg<sup>2+</sup> ionic conduction properties.

In this chapter, the exploration of the  $Mg(BH_4)_2-Mg(NH_2)_2$  binary phases diagram is presented. Looking for new  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$  compounds, a series of synthesis with different stoichiometries has been performed. It actually confirmed the existence of new phases. Then, the synthesis parameters were optimized to try to improve the purity of these new phases and to characterize them more precisely.

### III-2. First exploratory syntheses with different Mg(BH<sub>4</sub>)<sub>2</sub>:Mg(NH<sub>2</sub>)<sub>2</sub> ratios

The unknown phases observed during the synthesis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) were actually assumed as never reported Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> compounds. The last sample for which one of these phases appeared was sample 12 (*cf.* Chapter II). So the same annealing and ball-milling parameters were used but the Mg(BH<sub>4</sub>)<sub>2</sub>:Mg(NH<sub>2</sub>)<sub>2</sub> molar ratio was changed. As a reminder, the synthesis parameters were a ball-milling at 400 rpm for 1h and a subsequent annealing at 120°C for 72h under 10 bar of H<sub>2</sub>. The XRD patterns and the <sup>11</sup>B solid state MAS-NMR spectra of the as-obtained products are presented on Figure III. 1 and Figure III. 2, respectively. Interestingly, three new unreported crystalline phases were obtained. Two Mg(NH<sub>2</sub>)<sub>2</sub>-rich phases that were labeled the  $\alpha$ and the  $\beta$ -phase, and one Mg(BH<sub>4</sub>)<sub>2</sub>-rich phase labeled the  $\gamma$ -phase.

The  $\alpha$ -phase is the richest in Mg(NH<sub>2</sub>)<sub>2</sub>. By simple observation of the XRD pattern of the sample obtained for the ratio 1:4 (x = 0.20), it appears that the reflections of this new phase are similar to the ones of Mg(NH<sub>2</sub>)<sub>2</sub> but with an important shift towards lower angles, *i.e.* larger reticular distances. It is the typical behavior of a solid solution. The (BH<sub>4</sub>)<sup>-</sup> are substituting the (NH<sub>2</sub>)<sup>-</sup> in the structure of Mg(NH<sub>2</sub>)<sub>2</sub> and the shift towards lower angles is due to an expansion of the cell as (BH<sub>4</sub>)<sup>-</sup> anions are larger than (NH<sub>2</sub>)<sup>-</sup> (bond distances: B-H ~1.2 Å and N-H ~0.9 Å, see chapter II). The <sup>11</sup>B NMR spectrum indicates that there is only one type of BH<sub>4</sub> in this compound with a chemical shift at -40.2 ppm. This chemical shift is specific to this new phase.

The  $\beta$ -phase crystallizes for ratios 1:3 (x = 0.25) and 1:2 (x = 0.33). For the ratio 1:2 (x = 0.33), important X-ray diffraction peaks of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) are also observed but by <sup>11</sup>B NMR spectroscopy, it was probed that only 5 % of the product is made of crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (chemical shift at - 37.5 ppm, see chapter II). Another broad component can be fitted at -38.7 ppm, representing 51 % of the signal. This broad component is similar to the amorphous additional phase observed in sample C and D (see chapter II). The remaining 44 % is attributed to the crystalline  $\beta$ -phase with a shift at -39.5 ppm. For the ratio 1:3 (x = 0.25), only few crystalline Mg(NH<sub>2</sub>)<sub>2</sub> reflections are observed by XRD and the other diffraction peaks can be attributed to the  $\beta$ -phase. It is probed by <sup>11</sup>B NMR spectroscopy that a tiny amount of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) remains with a contribution at -37.3 ppm (2% of the signal). There is still a broad contribution that represents 60 % of the signal but it is shifted to -39.2 ppm. The peak corresponding to the  $\beta$ -phase (-39.3 ppm) is representing 38 % of the signal so its amount decreased even if by XRD, it seems well crystallized. This last observation may suggest that the broad contribution could be not only due to an amorphous phase but also to a disorder in the crystalline structure.



Figure III. 1. XRD patterns of the products obtained for different  $Mg(BH_4)_2-Mg(NH_2)_2$  ratios (different x of  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$ ).

The γ-phase is rich in borohydride. From XRD measurements, it is identical to the unknown phase appearing in addition to  $Mg(BH_4)(NH_2)$  in sample 12 (see chapter II). It is confirmed by <sup>11</sup>B NMR spectroscopy as the spectrum of this sample can be fitted with a component at -37.8 ppm which is due to Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and one at -39.3 ppm which is the chemical shift observed for the y-phase. Note that in this sample, these two components represent respectively 27 and 21 % of the signal and that the remaining 52 % are due to an amorphous phase with a chemical shift at -38.4 ppm. For the ratio 2:1 (x = 0.66), some weak diffraction peaks due to  $Mg(BH_4)(NH_2)$  can be observed. Then, crystalline  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2</sub> starts also to be observed for the ratio 3:1 (x = 0.75) and even more clearly for the ratio 4:1 (x = 0.8). It was assumed that the  $\gamma$ -phase was a defined compound with a composition between the 2:1 ratio (x = 0.66) and the 3:1 ratio (x = 0.75). So a synthesis with a 2.5:1  $Mg(BH_4)_2$ - $Mg(NH_2)_2$  ratio (x = 0.71) was done and a sample with solely the y-phase crystallizing was obtained. Nevertheless, the diffraction pattern is evolving with the composition as the  $\alpha$ -phase, so the  $\gamma$ -phase behaves like a solid solution. By looking at the <sup>11</sup>B NMR spectra of the composition 2:1 (x = 0.66), 2.5:1 (x = 0.71), 3:1 (x = 0.75) and 4:1 (x = 0.80), it can be observed that all of them exhibit mainly one BH<sub>4</sub> environment with a chemical shift at about -39.3 ppm which is close to the chemical shift of pure  $Mg(BH_4)_2$  (-39.6 ppm, see chapter II). Another shift around -41.4 ppm is also slightly detectable (< 7 % of the signal). It might be due to the presence of a Mg(NH<sub>2</sub>)<sub>2</sub>-rich phase as the  $\alpha$ -phase, as a consequence of an incomplete reaction.

So, three new crystalline phases have been identified by XRD, each of them has a characteristic chemical shift for the (BH<sub>4</sub>)<sup>-</sup> anion as determined by <sup>11</sup>B MAS-NMR spectroscopy. From the NMR spectra, it has been possible to determine the range of compositions where each new phase can be formed. In the next sections, the syntheses will be optimized in order to try to obtain pure phases and to perform further characterizations especially for solving their crystal structures and for measuring their ionic conduction properties.

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Figure III. 2. a) <sup>11</sup>B solid state MAS-NMR spectra of the products obtained for different  $Mg(BH_4)_2$ - $Mg(NH_2)_2$  ratios. b) Chemical shifts as a function of the  $Mg(BH_4)_2$  amount present in the compound. The area of the circles is proportional to the amount of each component.

	Primary component			Seco	ndary compo	nent	Third component			
x Mg(BH <sub>4</sub> ) <sub>2</sub>	Chemical shift (ppm)	B molar percentage (%)	FWHM (ppm)	Chemical shift (ppm)	B molar percentage (%)	FWHM (ppm)	Chemical shift (ppm)	B molar percentage (%)	FWHM (ppm)	
0.80	-39.43	99.5	2.74	-41.5	0.5	0.19	/	/	/	
0.75	-39.45	100	2.54	/	/	/	/	/	/	
0.71	-39.3	93.8	1.81	-41.3	6.2	1.18	/	/	/	
0.67	-39.3	95.9	2.01	-41.4	4.1	1.05	/	/	/	
0.50	-38.4	52.3	2.97	-37.8	26.7	0.95	-39.3	21.0	1.46	
0.33	-38.7	50.4	2.77	-39.5	44.3	0.95	-37.5	5.3	0.69	
0.25	-39.2	60.3	1.55	-39.3	37.4	0.7	-37.3	2.3	1.27	
0.20	-40.18	100	0.95	1	1	1	1	1	1	

Table III. 1. Fitted parameters of the different components of the <sup>11</sup>B solid state MAS NMRspectra presented on Figure III. 2 for different Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub>.

### III-3. The $\alpha$ phase: Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> (x = 0.17, 0.20 and 0.25)

#### III-3a. Structural analysis of the $\alpha$ -phase

Here above, a solid solution where the (BH<sub>4</sub>)<sup>-</sup> replace the (NH<sub>2</sub>)<sup>-</sup> anions in the crystal structure of Mg(NH<sub>2</sub>)<sub>2</sub> was obtained for x = 0.20 (*i.e.*  $\alpha$ -Mg(BH<sub>4</sub>)<sub>0.40</sub>(NH<sub>2</sub>)<sub>1.60</sub>). A new synthesis for this stoichiometry was performed but this time the ball-milling speed was increased to 600 rpm to make sure that a maximum amount of Mg(NH<sub>2</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)<sub>2</sub> have reacted. The XRD pattern of the as-synthesized sample is presented in Figure III. 3. Only weak reflections of Mg(NH<sub>2</sub>)<sub>2</sub> are still observed so the increase of the ball-milling speed was successful in enhancing the reaction yield. Assuming that this compound is a solid solution with the same structure as Mg(NH<sub>2</sub>)<sub>2</sub>, the new cell parameters have to be determined. In the case of Mg(NH<sub>2</sub>)<sub>2</sub>, the (200) and (004) reflections produce a double weak peak at 17.1° and 17.3°. This double peak is also present on the XRD pattern of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>0.40</sub>(NH<sub>2</sub>)<sub>1.60</sub>. It is shifted to lower angles at 16.2° and 16.5°. The new cell parameters are roughly equal to a = 10.9 Å and c = 21.5 Å. These values were used as starting parameters to refine the XRD pattern of the  $\alpha$ -phase. A good fitting of the Bragg positions was obtained and after refinement, the unit cell parameters are a = 10.9945(6) Å and c = 21.624(3) Å (*cf.* Figure III. 4). This confirms that the  $\alpha$ -phase crystallizes in a tetragonal unit cell with the same space group as Mg(NH<sub>2</sub>)<sub>2</sub>, *i.e.* 141/acd.<sup>9</sup>



Figure III. 3. XRD pattern of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>0.40</sub>(NH<sub>2</sub>)<sub>1.60</sub>. The inset is a zoom on the (200) and (004) reflections for the space group I4<sub>1</sub>/acd.

To make sure that the  $\alpha$ -phase is a solid solution, another synthesis was performed for x = 0.17 with a ball-milling speed of 600 rpm Compared to the  $\alpha$ -phase at x = 0.20, the one at x = 0.17 has smaller cell parameters. Surprisingly, the ball-milling at 600 rpm seems to help the stabilization of the  $\alpha$ -phase for x = 0.25 instead of the  $\beta$ -phase that was obtained with a ball-milling at 400 rpm (*cf.* Figure III. 1). The  $\alpha$ -phase obtained for x = 0.25 has larger cell parameters; so the cell parameters increase with x (*cf.* Figure III. 5). These observation confirms that the  $\alpha$ -phase is a solid solution crystallizing in the same structure as Mg(NH<sub>2</sub>)<sub>2</sub>, for which the (BH<sub>4</sub>)<sup>-</sup> anions are substituting the (NH<sub>2</sub>)<sup>-</sup> leading to the expansion of the unit cell. The cell parameters are not following a Vegard's law as they are not changing linearly with x.

In order to determine where the  $(BH_4)^-$  anions were exactly located in the crystal structure, a Rietveld refinement was performed on each compound using the structure of Mg(NH<sub>2</sub>)<sub>2</sub>. A change in one of the N sites occupancy could mean that it is the actual location of the B. The H atoms are not taken into account due to their very low scattering effect. Before that the occupancies of the N sites were fitted, the structure of the different compounds could already be well fitted with exactly the same structure as  $Mg(NH_2)_2$  (cf. Figure III. 4). This result can be explained by the fact that  $(NH_2)^-$  and  $(BH_4)^-$  anions have exactly the same number of electrons, 9 electrons each. Indeed, X-rays interact with the electronic cloud of the atoms so in our case it is difficult to have enough contrast between these two anions using standard powder X-ray diffraction (PXRD). After fitting, the N sites occupancies vary around their initial values but without important variation (cf. Table III. 3a). The variations are too low to be significant considering that only light elements are present in the structure and that an error is added because of the intensity correction from the Be window. Nevertheless, for x = 0.25, the occupancy of the site of the atom N1 decreased more than the others. Another fit was realized exchanging the N1 atom on this site by a B atom (cf. Table III. 3b). It resulted in occupancies values higher than the initial one (0.5) meaning that this site is not occupied only by B atoms. This result confirmed that our PXRD data do not allow a complete resolution of the structure. It is assumed that the BH<sub>4</sub> randomly substitute the NH<sub>2</sub> in the structure.

To go further in the determination of the structure of the solid solution, neutron diffraction was considered as B and N atoms have a large difference of neutron absorption. However, for this kind of compound, it is really challenging to perform neutron diffraction because of the presence of incoherently scattering H and strongly absorbing B. A test was done on the sample x = 0.25 but no neutron diffraction peaks were observed (*cf.* Annex II). To avoid these negative effects, the solution would be to enrich the sample in <sup>2</sup>D and <sup>11</sup>B.

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Figure III. 4. XRD patterns and Rietveld refinements of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> for compositions x = 0, 0.17, 0.20 and 0.25.



Figure III. 5. Cell parameters of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> as a function of x.

Table III. 2. Cell parameters of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> for compositions x = 0, 0.17, 0.20 and 0.25 from the Rietveld refinements presented on Figure III. 4.

	<b>-</b> <sup>1</sup>					
x Mg(BH <sub>4</sub> ) <sub>2</sub>	a (Å)	a (Å) c (Å) V (ų)		Weight % Mg(NH <sub>2</sub> ) <sub>2</sub>	R <sub>Bragg</sub> (%)	χ²
0.25	11.0330(6)	21.968(3)	2674.2(4)	0	7.64	427
0.2	10.9945(6)	21.624(2)	2613.9(3)	1.28	1.86	220
0.17	10.9403(9)	21.336(4)	2553.8(5)	4.08	7.66	226
0	10.393(1)	20.088(3)	2170.0(5)	/	1.91	22.2

Space group: 14	/acd, 7	2 = 32
-----------------	---------	--------

a)	Atom	Wyckoff	Occupancy	RBragg	X²	b)	Atom	Wyckoff	Occupancy	<b>R</b> Bragg	X²																							
		х	= 0.25					х	= 0.25																									
	Mg1	32g	1.000		335	0 225								Mg1	32g	1.000																		
	N1	16e	0.395(2)	-				B1	16e	0.610(4)	-																							
	N2	16d	0.522(5)	_				N2	16d	0.561(6)																								
	N3	32g	1.106(7)	- 2 5 0			2 5 0 2 2 5		N3	32g	1.081(8)	2.04	200																					
	H1	32g	1.000	3.50			H1	32g	1.000	2.94	296																							
	H2	32g	1.000			-	H2	32g	1.000	_																								
	H3	32g	1.000				H3	32g	1.000	_																								
	H4	32g	1.000	_			H4	32g	1.000																									
		х	a = 0.20					х	= 0.20																									
	Mg1	32g	1.000	_			Mg1	32g	1.000	-																								
	N1	16e	0.468(5)	_	106		B1	16e	0.728(9)	_																								
	N2	16d	0.542(7)	_			N2	16d	0.552(7)	_																								
	N3	32g	1.074(13)	- 6.00			N3	32g	1.085(14)	- 1 60	256																							
	H1	32g	1.000	-	-	-	-	-	-	- - -	0.00 190	0.00 190	- 0.00 190			-	-				-	190	- 0.00 190	190	190	190	0.00 190	0.00 190		H1	32g	1.000(0)	1.00	250
	H2	32g	1.000															H2	32g	1.000(0)	_													
	H3	32g	1.000											_				_	-	_													H3	32g
	H4	32g	1.000					H4	32g	1.000(0)																								
		х	a = 0.17					х	= 0.17																									
	Mg1	32g	1.000	_			Mg1	32g	1.000																									
	N1	16e	0.512(4)	_			B1	16e	0.801(7)	_																								
	N2	16d	0.584(5)	_			N2	16d	0.598(5)	_																								
	N3	32g	1.118(9)	- 1 50	254		N3	32g	1.133(9)	- 5 70	100																							
	H1	32g	1.000	1.59	254		H1	32g	1.000	5.79	100																							
	H2	32g	1.000	-	-	-	_	_	-	_					-			H2	32g	1.000	-													
	H3	32g	1.000											H3	32g	1.000	-																	
	H4	32g	1.000				H4	32g	1.000																									

Table III. 3. Refinement of the occupancy of the N site with a) the original atoms from the  $Mg(NH_2)_2$  structure and b) replacing the atom N1 by a B atom.

Looking at the FTIR spectra of the different compounds (*cf.* Figure III. 6), it can be noticed that the B-H bending bands around 1200 cm<sup>-1</sup> are different from the BH<sub>4</sub> of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and those of Mg(BH<sub>4</sub>)<sub>2</sub> (*cf.* Chapter II). The shape of the BH<sub>4</sub> tetrahedra must have changed. Then, the NH<sub>2</sub> anions are modified by the presence of BH<sub>4</sub> in their surroundings. The N-H bending band at 1564 cm<sup>-1</sup> is similar to the one of Mg(NH<sub>2</sub>)<sub>2</sub> but the intensity ratio between the asymmetric and symmetric stretching around 3300 cm<sup>-1</sup> has been modified. In the same way as in the case of Mg(BH<sub>4</sub>)(NH<sub>2</sub>), their intensities have been reversed, and this can be due to a change of dipolar moment. The dipolar moment of the NH<sub>2</sub> are attracted by the H<sup>δ-</sup> of the BH<sub>4</sub>. The positions of the bands have also changed: they are shifted to higher wavenumbers indicating a change of the N-H bond. This change can be explained by a modification of the Mg-N bonding strength caused by the replacement of some of these bindings by Mg-BH<sub>4</sub> ones.



Figure III. 6. a) FTIR spectra of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> for compositions x = 0, 0.17, 0.20 and 0.25. b) Zoom on the stretching vibration bands of N-H bonds.

<sup>11</sup>B solid state MAS-NMR spectroscopy was also performed on these phases (*cf.* Figure III. 7a). As observed with the synthesis at 400 rpm (*cf.* Figure III. 2), the chemical shifts of the (BH<sub>4</sub>)<sup>-</sup> anion for the  $\alpha$ -phase are at about -40 ppm which is slightly different than the chemical shifts of Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (see chapter II). This observation can be correlated with the difference of B-H vibrations probed by FTIR and confirms that the BH<sub>4</sub> environment is specific to this phase. The chemical shift slightly moves towards more negative values as x increases, indicating that the shape of the BH<sub>4</sub> is also slightly changing with x (*cf.* Figure III. 7b). The FWHM (Full Width at Half Maximum) decreases with x (*cf.* Figure III. 7c). This change might be due to an ordering of the BH<sub>4</sub> in the structure or an increase of the rotational mobility of the (BH<sub>4</sub>)<sup>-</sup> anions as their quantity increases in the solid solution.



Figure III. 7. a) <sup>11</sup>B MAS-NMR spectra of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> x = 0.17, 0.20 and 0.25. b) <sup>11</sup>B chemical shift and c) Full Width at Half Maximum (FWHM) as a function of x.

#### III-3b. Ionic conductivity of the $\alpha$ -phase

The ionic conductivity was measured by EIS (Electrochemical Impedance Spectroscopy) using 6 mm diameter pellets of about 0.9 mm thickness (*cf.* Figure III. 8). In the case of Mg(NH<sub>2</sub>)<sub>2</sub>, the Nyquist plot at 100°C displays only a straight line generated by the purely capacitive behavior of the sample. Mg(NH<sub>2</sub>)<sub>2</sub> does not conduct ions nor electrons. For x = 0.17, 0.20 and 0.25, a semicircle starts to appear around 90°C and it is followed by a straight line at lower frequencies. The semicircle is attributed to the bulk ionic conduction of the materials. The straight line is the capacitance formed by the carbon blocking electrodes on the two sides of the solid electrolyte. The data are fitted with one R//CPE to model the bulk ionic conduction in series with a resistance for the electrical resistance of the cell and a CPE for the capacitance at low frequency. The resistances below 80°C for x = 0.25 and below 90°C for x = 0.17 and 0.20 are too high to be measured precisely so the ionic conductivity cannot be determined below these temperatures. The values obtained at 100°C for x = 0.17, 0.20 and 0.25 are  $4x10^{-9}$ ,  $5x10^{-9}$  and  $2x10^{-8}$  S.cm<sup>-1</sup>, respectively. High activation energies of about 1.6-1.7 eV were calculated for these compounds, revealing the relatively low Mg<sup>2+</sup> mobility in these  $\alpha$ -phases. The ionic conductivity values are

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quite low but it is interesting to see that adding Mg(BH<sub>4</sub>)<sub>2</sub> into the structure of Mg(NH<sub>2</sub>)<sub>2</sub> improves its ionic conductivity. Even more, the ionic conductivity continuously increases with x as presented on Figure III. 8d.



Figure III. 8. a) Nyquist plots at 100°C of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> for x = 0.17, 0.20 and 0.25. b) lonic conductivity as a function of 1/T. c) ln( $\sigma$ .T) as a function of 1/T. d) lonic conductivity at 100°C as a function of x.
### Chapter III – The exploration of the unknown parts of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram

The improvement of the ionic conductivity can be explained by the evolution of the structure. By XRD, it was shown that the cell parameters were increasing with x. The expansion of the unit cell can help the mobility of the Mg<sup>2+</sup> ions forming a larger pathway through the structure for the Mg<sup>2+</sup> cations. The <sup>11</sup>B NMR spectroscopy showed also that there might be an increase of the BH<sub>4</sub> rotational mobility with x. It could promote the Mg<sup>2+</sup> mobility through the paddle wheel mechanism, well described in the literature, where the rotating anions shovels the cations.<sup>10</sup>

### III-3c. Thermal analysis and $\alpha$ to $\beta$ phase transition

DSC measurements at 5 °C/min were performed on the samples obtained after ball-milling and before the annealing of the compounds (*cf.* Figure III. 9). All the samples undergo an endothermic phenomenon at low temperatures (65-80°C). This endothermic peak has a low enthalpy; between 16 and 19 J.g<sup>-1</sup> (~0.8-1 kJ/mol, *cf.* Table III. 4) and its onset temperature gradually shifts towards lower temperature as x increases. This phenomenon might be due to the organization of the (BH<sub>4</sub>)<sup>-</sup> anions into the Mg(NH<sub>2</sub>)<sub>2</sub> structure to form the  $\alpha$ -phase. After 200°C, an exothermic phenomenon happens. This phenomenon is related to the degradation of the products and is similar to what was observed previously with Mg(BH<sub>4</sub>)(NH<sub>2</sub>) at 200°C with the release of gases (H<sub>2</sub> and NH<sub>3</sub>) and the formation of a very foamy solid residue (*cf.* Chapter II).



Figure III. 9. DSC recorded at 5°C/min under Ar flow of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.17, 0.20 and 0.25 before annealing.

X Mg(BH <sub>4</sub> ) <sub>2</sub>	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	∆H (J.g <sup>-1</sup> )	ΔH (kJ.mol <sup>-1</sup> )
0.25	58.5	65.7	16	0.891
0.2	64.3	71.1	17	0.949
0.17	73	79.1	19	1.062

Table III. 4. Enthalpy and temperatures of the endothermic phenomenon for different  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> compositions.



Figure III. 10. TGA coupled with DTA recorded at 1°C/min under Ar flow of  $\alpha$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> for x = 0.17, 0.20 and 0.25.

x Mg(BH <sub>4</sub> ) <sub>2</sub>	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	∆H (J.g⁻¹)	ΔH (kJ.mol <sup>-1</sup> )
0.25	149.9	159	111	6.183
0.20	140.1	154.1	105	5.862
0.17	152.2	160.1	102	5.701

Table III. 5. Enthalpy and temperatures values of the endothermic phenomenon recorded by DSC for different  $\alpha$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> compositions.

Then, the thermal stability of the samples obtained after annealing, *i.e.* the  $\alpha$ -phases, was measured by TGA coupled with DTA (*cf.* Figure III. 10). The endothermic phenomenon observed before annealing has disappeared so it can be attributed to the formation of the  $\alpha$ -phase. All the annealed samples undergo an endothermic phenomenon at about 150°C. The enthalpy of this phenomenon is approximately 105 J.g<sup>-1</sup> (~5.9 kJ.mol<sup>-1</sup>, *cf.* Table III. 5) and there is no mass loss as observed on the TGA curves.

To determine the nature of this endothermic phenomenon, a DSC measurement was performed on the sample for x = 0.25 upon heating, until to 170°C, and cooling. This phenomenon is irreversible. Then, the sample with x = 0.25 has been annealed at 170°C for 12h under 1 bar of Ar to see what happens to the  $\alpha$ -phase. The crystalline  $\beta$ -phase was formed. So, the  $\alpha$ -phase turns irreversibly into the  $\beta$ -phase at about 150°C through an endothermic structural transition caused by the reorganization of the structure. As the  $\beta$ -phase remains stable at room temperature, it can be considered that the  $\alpha$ -phase with x = 0.25 is actually metastable. This metastability is highlighted by the fact that only a powerful ball-milling can lead to its synthesis. As a matter of fact, for x = 0.25, a ball-milling at 400 rpm leads to the formation of the  $\beta$ -phase (*cf.* Figure III. 1) whereas the  $\alpha$ -phase is obtained at 600 rpm.



Figure III. 11. a) DSC recorded at 1°C.min<sup>-1</sup> under Ar flow upon heating up to 170°C and cooling of  $Mg(BH_4)_x(NH_2)_{2-x}$  for x = 0.25. b) XRD patterns of the sample before and after annealing at 170°C for 12h under Ar.

# III-4. The $\beta$ phase: Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> (x = 0.25 and 0.33)

## III-4a. Crystal structure of the 6-phase

In the previous paragraph, the  $\beta$ -phase was obtained for x = 0.25 by annealing of the  $\alpha$ -phase or by ball-milling at lower speed (400 rpm). Another synthesis was performed for x = 0.33 with a ball-milling at 600 rpm followed by an annealing at 120°C for 72h under 10 bar of H<sub>2</sub>. The as-obtained sample is very amorphous and only weak reflections of the  $\beta$ -phase appear (*cf*. Figure III. 12). The low crystallinity of the sample might be due to a low stability of the phase with this stoichiometry. It is interesting to compare XRD pattern of the  $\beta$ -phase to the one of sample A which was obtained for a non-optimized synthesis of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and contains mainly a crystalline additional phase. Indeed, the reflections of the  $\beta$ -phase but with slightly different unit cell parameters. Therefore, the  $\beta$ -phase seems to behave like a solid solution as the  $\alpha$ -phase does. No space group was found so far to explain the XRD pattern of the  $\beta$ -phase. It matched only with monoclinic cells but even the indexing in such low symmetry space group was not fully adequate (*cf*. Annex II)



Figure III. 12. XRD patterns of  $\beta$ - Mg(BH<sub>4</sub>)<sub>0.5</sub>(NH<sub>2</sub>)<sub>1.5</sub> compared with  $\beta$ -Mg(BH<sub>4</sub>)<sub>0.67</sub>(NH<sub>2</sub>)<sub>1.33</sub> and sample A.

### III-4b. Ionic conductivity of the 6-phase

The ionic conductivity of the  $\beta$ -phase was measured by EIS using 6 mm diameter pellets of about 0.9 mm thickness. The results were fitted with the same model as the one used previously for the  $\alpha$ -phase. For the sample obtained after annealing of the  $\alpha$ -phase, the resistances were too high to be measured at low temperatures (*cf.* Figure III. 13). The value of ionic conductivity at 100°C is approximately the same as the  $\alpha$ -phase, 2.10<sup>-8</sup> S.cm<sup>-1</sup>. However, the activation energy increased, reaching a high value of about 2 eV.



Figure III. 13. a) Nyquist plots at 100°C of  $\beta$ -Mg(BH<sub>4</sub>)<sub>0.5</sub>(NH<sub>2</sub>)<sub>1.5</sub>. b) Ionic conductivity as a function of 1/T. c) In( $\sigma$ .T) as a function of 1/T.

The results of the EIS measurements on the sample synthesized with a ball-milling of 600 rpm for x = 0.33 are presented on Figure III. 14. In term of ionic conductivity, the as-obtained sample has a higher conductivity than the compounds obtained for x = 0.25,  $\sigma_{100^{\circ}C}$  = 2.10<sup>-7</sup> S.cm<sup>-1</sup>. The activation energy is similar to the one of the  $\alpha$ -phase, 1.6 eV. The conductivity in the  $\beta$ -phase seems to increase with x as observed in the  $\alpha$ -phase. Nevertheless, the two samples were not synthesized with the same route so the comparison remains difficult and not fully conclusive.



Figure III. 14. a) Nyquist plots at 100°C of  $\beta$ -Mg(BH<sub>4</sub>)<sub>0.67</sub>(NH<sub>2</sub>)<sub>1.33</sub>. b) Ionic conductivity as a function of 1/T. c) In( $\sigma$ .T) as a function of 1/T.

### III-4c. Thermal analysis of the 6-phase

Thermal analyses were performed on the sample with x = 0.33 synthesized at 600 rpm. The DSC performed on the mixture after ball-milling and before annealing is similar to what was obtained for the compositions x = 0.17, x= 0.20 and x =0.25 (*cf.* Figure III. 9 and Figure III. 15). An endothermic phenomenon occurs at low temperature, 47°C. Its enthalpy of 14 J.g<sup>-1</sup> (0.8 kJ.mol-1, *cf.* Table III. 6) is closed to the ones described previously. The DSC curve shows an important noise after 200°C due to the decomposition of the sample.

Then, TGA coupled with DTA was performed on the sample obtained for x = 0.33 after annealing. It shows that no thermal phenomenon happens below 180°C but, after this temperature, a slight mass loss is noticed which is related to the beginning of the material decomposition.



Figure III. 15. a) DSC recorded at 5°C/min under Ar flow of  $\beta$ -Mg(BH<sub>4</sub>)<sub>0.67</sub>(NH<sub>2</sub>)<sub>1.33</sub> before annealing. b) TGA coupled with DSC recorded at 1°C/min under Ar flow of  $\beta$ -Mg(BH<sub>4</sub>)<sub>0.67</sub>(NH<sub>2</sub>)<sub>1.33</sub> after annealing.

Table III. 6. Enthalpy and temperatures of the endothermic phenomenon recorded by DSC for  $\beta$ -Mg(BH<sub>4</sub>)<sub>0.67</sub>(NH<sub>2</sub>)<sub>1.33</sub> before annealing.

x Mg(BH <sub>4</sub> ) <sub>2</sub>	T <sub>onset</sub> (°C)	T <sub>max</sub> (°C)	ΔH (J.g⁻¹)	ΔH (kJ.mol⁻¹)	
0.33	47.2	53.9	14	0.777	

# III-5. The γ-phase: Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> (x = 0.67, 0.71 and 0.75)

## III-5a. Structural analysis of the γ-phase

The last part of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram that was explored is the one rich in borohydride with x = 0.67, 0.71 and 0.75. To get samples as pure as possible, syntheses were done with a ball-milling speed of 600 rpm for 1h. The same subsequent annealing as that previously used was performed, *i.e.* 120°C for 72h under 10 bar of H<sub>2</sub>. The XRD patterns of the assynthesized samples are presented on Figure III. 16a. For x = 0.66, weak peaks of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) are observed. The  $\gamma$ -phase has a completely new unknown crystal structure. This structure changes depending on the stoichiometry so it behaves like a solid solution as observed for the  $\alpha$ -phase. To emphasize this structural evolution, Figure III. 16b displays the double peak observed at about 20° that obviously shifts as x is changing.



Figure III. 16. a) XRD patterns of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.66, 0.71 and 0.75. b) Zoom on the most intense reflections.

The structure of the  $\gamma$ -phase can be indexed in a tetragonal unit cell with space group I-4 (No.: 82) (*cf.* Figure III. 17). The fitted unit cell parameters reveal that the increase of the amount of (BH<sub>4</sub>)<sup>-</sup> anion leads to an expansion of the cell (*cf.* Figure III. 18). This expansion is similar to the one observed in the  $\alpha$ -phase so the  $\gamma$ -phase is also a solid solution in which (NH<sub>2</sub>)<sup>-</sup> anions can be partially substituted by (BH<sub>4</sub>)<sup>-</sup> ones. It is also interesting to note that this cell has a tetragonal symmetry as other compounds in the Mg(BH<sub>4</sub>)<sub>2</sub>:Mg(NH<sub>2</sub>)<sub>2</sub> binary system: Mg(NH<sub>2</sub>)<sub>2</sub> (s.g.: I4<sub>1</sub>/acd), Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (s.g.: I4<sub>1</sub>) and  $\delta$ -Mg(BH<sub>4</sub>)<sub>2</sub> (s.g.: I4<sub>1</sub>/acd).



Figure III. 17. a) XRD patterns and profile matching of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.67, 0.71 and 0.75. b) Cell parameters and unit cell volume as a function of x.



Figure III. 18. Cell parameters of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> as a function of x.

Table III. 7. Refined unit cell parameters of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.66, 0.71 and 0.75. Space group: I-4

x Mg(BH <sub>4</sub> ) <sub>2</sub>	a (Å)	c (Å)	V (ų)	χ²
0.75	14.1190(9)	6.2421(4)	1244.4(1)	98.9
0.71	14.171(1)	6.1330(5)	1231.7(2)	325
0.67	14.2365(7)	6.0056(2)	1208.48(9)	89.4

The crystalline structure is still under investigation in collaboration with Pr. Yaroslav Filinchuk (University of Louvain, Belgium). A first structure has been proposed for x = 0.67, *i.e.*  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (*cf.* Figure III. 19). It is a complex structure with 3 independent Mg atoms, two sites for B atoms and one for the N atoms (*cf.* Table III. 8). This structure still needs to be confirmed and optimized by DFT calculations, especially for the H atom positions. Better XRD data would be also useful.



Figure III. 19. a) Rietveld refinement of  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and b) its structure drawn with the software VESTA.

Table III. 8. Proposed structure for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>.

Space group: I-4 Z = 4 a = 14.1801(8) Å c = 6.002(4) Å V = 1207.0(1) Å<sup>3</sup>

Atom	Wyckoff site	Occ.	x	У	z
Mg1	2c	1	0	0.5	0.25
Mg2	2a	1	0	0	0
Mg3	8g	1	0.7455	0.6791	0.8994
B1	8g	1	0.9504	0.3932	0.5041
H1	8g	1	0.9270	0.3478	0.3740
H2	8g	1	0.9470	0.3542	0.6714
H3	8g	1	1.0349	0.4094	0.4824
H4	8g	1	0.9144	0.4641	0.5178
B2	8g	1	0.0801	0.8501	0.8560
H5	8g	1	0.0158	0.8703	0.7628
H6	8g	1	0.0746	0.8791	1.0323
H7	8g	1	0.0871	0.7680	0.8684
H8	8g	1	0.1484	0.8799	0.7813
N1	8g	1	0.7445	0.3396	0.8878
H9	8g	1	0.7882	0.3011	0.8642
H10	8g	1	0.7178	0.3640	0.7639

The infrared (IR) spectra for each sample are presented on Figure III. 20. The N-H stretching and bending bands have the same wavenumbers as those of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) but the stretching bands present a small shoulder at higher wavenumber. This shoulder can be due to the presence of different N-H bonds similar to the one encountered in the  $\alpha$ -phase. In the B-H bending region, vibrations are observed around the same position as in Mg(BH<sub>4</sub>)(NH<sub>2</sub>) but in these compounds the vibrations are split in two. This splitting could be explained by a distortion of the (BH<sub>4</sub>)<sup>-</sup> anions.



Figure III. 20. IR spectra of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.66, 0.71 and 0.75.

### *III-5b. Ionic conductivity of the γ-phase*

The ionic conductivities of the samples containing the  $\gamma$ -phases were measured by impedance spectroscopy using 6 mm diameter pellets of about 1.1 mm thickness (*cf.* Figure III. 21). The Nyquist plots show only one semicircle at high frequency that is attributed to the ionic conduction in the materials. The semicircle is followed by a straight line that is the capacitance formed by the carbon blocking electrodes placed on both sides of the samples. In the same way than for the  $\alpha$  and the  $\beta$ -phases, the data are fitted with one R//CPE for the bulk ionic conduction in series with a resistance for the cell and with a CPE for the capacitance formed by the electrical contacts on both sides of the electrolyte. The ionic conductivity values extracted from these fits are presented as a function of the temperature on Figure III. 21b. At 100°C, the ionic conductivity is 0.8x10<sup>-5</sup>, 2x10<sup>-5</sup> and 4x10<sup>-5</sup> S.cm<sup>-1</sup> for x = 0.75, 0.71 and 0.67, respectively (*cf.* Figure III. 21d). These values are the highest ever recorded for an inorganic Mg<sup>2+</sup> solid ionic conductor at such low

### Chapter III – The exploration of the unknown parts of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram

temperature. The ionic conductivity is increasing as x is decreasing in the  $\gamma$ -phase. This trend is opposite to what was observed for the  $\alpha$  and  $\beta$ -phases.

The activation energies determined from these measurements are low with values equal to about 0.8, 0.9 and 1.0 eV for x = 0.67, 0.71 and 0.75, respectively (*cf.* Figure III. 21c). These activation energies are low for an inorganic Mg<sup>2+</sup> solid ionic conductor, indicating a high mobility of the Mg<sup>2+</sup> cations in the  $\gamma$ -phase. This mobility is increasing as x decreases which is also confirmed by the ionic conductivity values.

Thanks to the good mobility of  $Mg^{2+}$  in the  $\gamma$ -phase, it was possible, for the sample x = 0.71, to record <sup>25</sup>Mg solid state MAS NMR spectra with a good signal in a short time without isotopic enrichment in <sup>25</sup>Mg. A good spectrum could be recorded in 5h whereas, for Mg(BH<sub>4</sub>)(NH<sub>2</sub>), an acquisition of about 15h was necessary. This improvement of the signal allowed us to do measurement in temperature and to try to obtain more information about the Mg<sup>2+</sup> mobility in this  $\gamma$ -phase (*cf.* Figure III. 22a). Tries were attempted to measure the spin-lattice relaxation time T<sub>1</sub> at different temperatures to calculate an activation energy using the Bloembergen-Purcell-Pound formula. Indeed, from this formula, a Mg<sup>2+</sup> motion correlation time  $\tau$  can be obtained. This correlation time should follow an Arrhenius behavior from which the activation energy can be calculated. Unfortunately, the variation of T<sub>1</sub> was too small and in the range of the signal-to-noise ratio of the measurement. So, it was not possible to determine the activation energy with this technique.

Still, with these measurements in temperature, a clear decrease of the FWHM of the peak was observed, indicating an increase of the Mg<sup>2+</sup> mobility with the temperature. Looking at the <sup>1</sup>H solid state MAS-NMR spectra recorded in the same conditions, no changes of the shape of the peak can be observed. These two measurements prove that the mobile species in this phase are Mg<sup>2+</sup> cations and definitively not H.



Figure III. 21. a) Nyquist plots at 100°C of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>x</sub>(NH<sub>2</sub>)<sub>2-x</sub> for x = 0.67, 0.71 and 0.75. b) Ionic conductivity as a function of 1/T. c) In( $\sigma$ .T) as a function of 1/T. d) Ionic conductivity at 100°C as a function of x.



Figure III. 22. a) <sup>25</sup>Mg and b) <sup>1</sup>H solid state MAS NMR spectra of γ-Mg(BH<sub>4</sub>)<sub>1.42</sub>(NH<sub>2</sub>)<sub>0.58</sub> at different temperatures.

## *III-5c. Thermal stability of the γ-phase*

DSC was measured on samples for x = 0.67, 0.71 and 0.75 just after the ball-milling step and before the annealing (*cf.* Figure III. 23). As the  $\alpha$ -phase, these compounds undergo an endothermic phenomenon at low temperature, around 60°C. Here, the enthalpy is higher with values ranging from 25 to 37 J.g<sup>-1</sup> (1.4 to 2.0 kj.mol-1, *cf.* Table III. 9). The enthalpy and the onset temperature of this phenomenon decrease with x. It could be due to a rearrangement of the crystalline structure. At about 110°C, an exothermic phenomenon occurs with a higher enthalpy, about -160 J.g<sup>-1</sup> (~9 kJ.mol<sup>-1</sup>). This exothermic phenomenon is related to the crystallization of the  $\gamma$ -phase. At 200°C, there is another endothermic phenomenon followed by the degradation of the product. This last phenomenon might be the melting of the products as observed for Li<sub>2</sub>(BH<sub>4</sub>)(NH<sub>2</sub>) and Li<sub>4</sub>(BH<sub>4</sub>)(NH<sub>2</sub>)<sub>3</sub>.<sup>6</sup>



Figure III. 23. DSC recorded at 5°C/min under Ar flow of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.67, 0.71 and 0.75 before annealing.

Table III. 9. Temperatures and enthalpy values of the endothermic and exothermic phenome	na
recorded by DSC for different $\gamma$ -Mg(BH <sub>4</sub> ) <sub>2x</sub> (NH <sub>2</sub> ) <sub>2(1-x)</sub> compositions.	

x Mg(BH <sub>4</sub> ) <sub>2</sub>	T <sub>onset 1</sub> (°C)	T <sub>max 1</sub> (°C)	ΔH <sub>1</sub> (J.g <sup>-1</sup> )	ΔH₁ (kJ.mol <sup>-1</sup> )	T <sub>onset 2</sub> (°C)	T <sub>max 2</sub> (°C)	ΔH <sub>2</sub> (J.g <sup>-1</sup> )	ΔH <sub>2</sub> (kJ.mol <sup>-1</sup> )
0.75	59.4	66.2	37.34	2.017	109.8	116.5	-153	-8.341
0.71	56.1	63.8	29.16	1.583	107.3	115.4	-170.6	-9.316
0.67	55.4	62.3	25.11	1.367	108.9	116.3	-156.1	-8.539

TGA coupled with DTA measurements were performed on the final products, after annealing. These measurements do not show any thermal phenomenon occurring before 190°C. Only the sample obtained for x = 0.67 seems to start to degrade around 180°C. At 200°C, the samples are decomposed as shown by the DSC previously recorded (*cf.* Figure III. 23). These results are interesting because they mean that the  $\gamma$ -phases are more thermally stable than Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and could be used at higher temperatures up to 180°C.



Figure III. 24. TGA coupled with DTA recorded at 1°C/min under Ar flow of  $\gamma$ -Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> for x = 0.67, 0.71 and 0.75.

# III.6. Comparative study of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram

From the data presented here above and the ones obtained in the chapter II, a pseudobinary Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> phases diagram is proposed between room temperature and 200°C (*cf*. Figure III. 25). The new Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> phases found and described above are included in this diagram. The content of the unexplored regions are assumed from our experimental observations. On both extreme parts are the magnesium amide and borohydride, and in the center Mg(BH<sub>4</sub>)(NH<sub>2</sub>) which decompose into an amorphous compound around 180°C. Between, Mg(NH<sub>2</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)(NH<sub>2</sub>), two new phases have been observed: the  $\alpha$  and the  $\beta$  phase. The  $\alpha$ -phase is a solid solution crystallizing in the Mg(NH<sub>2</sub>)<sub>2</sub> tetragonal structure (s.g.: 14<sub>1</sub>/acd) which expands as (NH<sub>2</sub>)<sup>-</sup> anions are substituted by larger (BH<sub>4</sub>)<sup>-</sup>. It undergoes a phase transition at about 150°C and turns into the  $\beta$ -phase. The  $\beta$ -phase was observed up to x = 0.33 but seems to be less stable as x is getting close to 0.5. On the other side, between Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(BH<sub>4</sub>)(NH<sub>2</sub>), only one new phase was observed: the  $\gamma$ -phase. This phase is also a solid solution crystallizing in a tetragonal structure with the space group I-4. Its structure also expands as x increases.



Figure III. 25. Pseudo binary Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> phases diagram. The full areas are the known ones and the shaded ones are assumed.

Another diagram showing the values of ionic conductivity at 100°C as a function of x, obtained for the different compounds, is shown in Figure III. 26. There are no data for  $Mg(BH_4)_2$ and  $Mg(NH_2)_2$  as they are very bad ionic conductor. The ionic conductivity of  $Mg(NH_2)_2$  was too low to be measured and the one of  $Mg(BH_4)_2$  is reported to be about  $10^{-9}$  S.cm<sup>-1</sup> at 150°C.<sup>11</sup> So it is interesting to see that the phases based on a mixture of this two compound show better ionic conductivities. For instance, the substitution of  $(NH_2)^-$  anions by  $(BH_4)^-$  in the  $\alpha$ -phase improves the ionic conductivity, reaching  $2x10^{-8}$  S.cm<sup>-1</sup> for x = 0.25. This increasing trend is followed by the  $\beta$ -phase as well with an ionic conductivity of 2x10<sup>-7</sup> S.cm-1 for x = 0.33. In the center, Mg(BH<sub>4</sub>)(NH<sub>2</sub>) has a good ionic conductivity of 1x10<sup>-5</sup> S.cm<sup>-1</sup> and a low activation energy of 1.0 eV. Finally, the phase rich in borohydride, the  $\gamma$ -phase, is the one having the highest ionic conductivity and the lowest activation energy with  $4x10^{-5}$  S.cm<sup>-1</sup> and 0.8 eV for x = 0.67. In this phase, the ionic conductivity decreases as x increases. Overall, even if the crystalline structure changes from one compound to another, a trend appears in terms of ionic conductivities. Indeed, the maximum was measured for the  $\gamma$ -phase at x = 0.67. From this point, the ionic conductivity gradually decreases and it is true from one compound to the other. This trend is not random and is concomitant to the evolution of the structures and of the different substitutions of  $(NH_2)^-$  anions by  $(BH_4)^-$ .



Figure III. 26. Ionic conductivity at 100°C and activation energy as a function of x in  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$ .

Chapter III

## **III-7.** Conclusions

In this chapter, the discovery of three new crystalline phases in the  $Mg(BH_4)_2-Mg(NH_2)_2$ binary phases diagram has been reported. These phases behave as solid solutions with different  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$  compositions.

Two phases, named the α-phase and the β-phase, have a composition rich in amide. The αphase crystallizes with the same structure as Mg(NH<sub>2</sub>)<sub>2</sub> in which (BH<sub>4</sub>)<sup>-</sup> anions are substituting the (NH<sub>2</sub>)<sup>-</sup>. This substitution leads to an expansion of the unit cell and an improvement of the ionic conductivity at 100°C, increasing from  $4\times10^{-9}$  S.cm<sup>-1</sup> for x = 0.17 to  $1\times10^{-8}$  S.cm<sup>-1</sup> for x = 0.25. Upon heating, the α-phase undergoes an irreversible endothermic structural transition, forming the βphase. The β-phase crystallizes in a new unknown crystal structure and might be the one crystallizing in sample A in addition of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (*cf.* Chapter II). This phase transition has a little impact on the ionic conductivity of the material,  $\sigma_{100^{\circ}C} = 2\times10^{-8}$  S.cm<sup>-1</sup>, and the activation energy of the ionic conductivity increases from 1.7 eV to 2 eV. For x = 0.33, with a ball-milling at 600 rpm, poorly crystallized β-phase was obtained with an amorphous background visible by XRD. So, it might be less stable around this stoichiometry. The ionic conductivity at 100°C of this last compound is improved, as it reaches  $2\times10^{-7}$  S.cm<sup>-1</sup> and its activation energy is 1.6 eV.

The phase crystallizing in the borohydride-rich region was named the  $\gamma$ -phase. It crystallizes in a tetragonal structure with the space group I-4. Similarly to the  $\alpha$ -phase, adding more BH<sub>4</sub> into this compound increases the unit cell volume but decreases the ionic conductivity. The  $\gamma$ -phase exhibits high ionic conductivity values that decrease with x, while the activation energy increases. The best ionic conductor is  $\gamma$ -Mg(BH<sub>4</sub>)<sub>1.33</sub>(NH<sub>2</sub>)<sub>0.67</sub> (which can be also written  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>) with an ionic conductivity at 100°C of 4x10<sup>-5</sup> S.cm<sup>-1</sup> and an activation energy of 0.8 eV. These values mean that it features one of the best Mg<sup>2+</sup> mobility in an inorganic solid ionic conductor reported so far. The good mobility of Mg<sup>2+</sup> was confirmed by <sup>25</sup>Mg solid state MAS-NMR spectroscopy with a significant narrowing of the NMR peak upon heating. The  $\gamma$ -phase has also a good thermal stability as no thermal event nor mass loss was detected below 190°C.

A pseudo binary phases diagram was proposed. It helps us to understand the complexity of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> system. A trend was observed for the ionic conductivity of the compounds as a maximum is reached for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> and then it decreases and this trend continues even if the crystal structure changes. Deeper structural (synchrotron) and theoretical (DFT) studies could allow to understand this trend that might depend on the crystalline structure (Mg<sup>2+</sup> mobility pathways) and the different substitution of (NH<sub>2</sub>)<sup>-</sup> anions by (BH<sub>4</sub>)- (interaction of Mg<sup>2+</sup> with its

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surrounding). Understanding this trend in this binary phases diagram could allow the design of better Mg<sup>2+</sup> ionic conductors based on other compounds.

The following chapter is dedicated to the characterization of two of the best  $Mg^{2+}$  ionic conductor studied,  $Mg(BH_4)(NH_2)$  and  $\gamma-Mg_3(BH_4)_4(NH_2)_2$ , as solid electrolytes for Mg batteries.

# References

- Pinkerton, F. E., Meisner, G. P., Meyer, M. S., Balogh, M. P. & Kundrat, M. D. Hydrogen desorption exceeding ten weight percent from the new quaternary hydride Li<sub>3</sub>BN<sub>2</sub>H<sub>8</sub>. J. Phys. Chem. B **109**, 6–8 (2005).
- 2. Noritake, T. *et al.* Crystal structure analysis of novel complex hydrides formed by the combination of LiBH<sub>4</sub> and LiNH<sub>2</sub>. *Appl. Phys. A* **83**, 277–279 (2006).
- 3. Chater, P., David, W. I. F. & Anderson, P. Synthesis and structure of the new complex hydride Li<sub>2</sub>BH<sub>4</sub>NH<sub>2</sub>. *Chem. Commun.* 4770 (2007).
- 4. Chater, P. A., David, W. I. F., Johnson, S. R., Edwards, P. P. & Anderson, P. A. Synthesis and crystal structure of Li<sub>4</sub>BH<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>. *Chem. Commun.* **0**, 2439 (2006).
- 5. Matsuo, M. *et al.* Complex hydrides with (BH<sub>4</sub>)<sup>-</sup> and (NH<sub>2</sub>)<sup>-</sup> anions as new lithium fast-ion conductors. *J. Am. Chem. Soc.* **131**, 16389–16391 (2009).
- 6. Zhou, Y. *et al.* Enhanced electrical conductivities of complex hydrides  $Li_2(BH_4)(NH_2)$  and  $Li_4(BH_4)(NH_2)_3$  by melting. *Mater. Trans.* **52**, 654–657 (2011).
- 7. Borgschulte, A. *et al.* Surface and bulk reactions in borohydrides and amides. *Energy Environ. Sci.* **5**, 6823 (2012).
- 8. Yan, Y. *et al.* A lithium amide-borohydride solid-state electrolyte with lithium-ion conductivities comparable to liquid electrolytes. *Adv. Energy Mater.* **1700294**, 1–7 (2017).
- 9. Jacobs, H. Die kristallstruktur des magnesiumamids. *Zeitschrift fur Anorg. und Allg. Chemie* **382**, 97–109 (1971).
- Skripov, A. V. *et al.* Nuclear magnetic resonance study of atomic motion in A<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (A = Na, K, Rb, Cs): Anion reorientations and Na<sup>+</sup> mobility. *J. Phys. Chem. C* **117**, 25961–25968 (2013).
- 11. Higashi, S., Miwa, K., Aoki, M. & Takechi, K. A novel inorganic solid state ion conductor for rechargeable Mg batteries. *Chem. Commun.* **50**, 1320–1322 (2014).

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# <u>Chapter IV –</u> Characterization of ionic conductors as solid electrolytes: towards all-solid-state Mg batteries

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batteries

**Chapter IV** 

## **IV-1.** Introduction

During this PhD thesis, new solid-state Mg<sup>2+</sup> conductors have been discovered but before to use them as solid electrolytes, it is crucial to know more about their chemical and electrochemical stabilities. Indeed, a solid electrolyte needs, of course, to be electronically insulative and to have a good ionic conductivity but other parameters are also very important. The chemical stability is important to make sure that the electrolyte will not react with one of the active or inactive material of the battery. Any unwanted reaction can hinder or make impossible the cycling of the electrochemical cell. The compatibility between the solid electrolyte and the electrodes is fundamental for a rechargeable device. A bad interface would lead to a quick fading of the device. Finally, the electrochemical stability window (ESW) of a solid electrolyte has to be as large as possible to avoid its reduction at low potential or its oxidation at high potential. A wide ESW would provide a larger choice in terms of usable electrodes for rechargeable Mg batteries.

In this chapter, Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> have been characterized as solid electrolytes. It was shown in the previous chapters that they have both good ionic conductivities (~10<sup>-5</sup> S.cm-1 at 100°C). First, different active and inactive materials that can be used in a rechargeable Mg battery have been selected. Then, the chemical stability of the ionic conductors was tested by annealing mixtures of electrode materials with the solid electrolytes. The electrochemical stability is evaluated by polarization and cyclic voltammetry measurements. The polarization is especially used to characterize the interface between the electrolyte and the anode. The cyclic voltammetry enables the determination of the ESW.

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# IV-2. Chemical stability

### IV-2a. Selection of electrode materials

First, it was needed to know if our solid electrolytes would react with components of a rechargeable all-solid-state Mg battery. Two different materials have been chosen for the anode: Mg and Bi. The Chevrel phase Mo<sub>6</sub>S<sub>8</sub> has been selected as the cathode material and carbon C45 has been used as electronic conduction additive. Each material is described here after.

### Magnesium metal anode

One of the main advantages of using a solid electrolyte should be the possibility of using a metallic anode. In the first chapter, the different properties of magnesium metal as negative electrode for batteries have already been described. As a reminder, its redox standard potential is -2.375 V *vs.* NHE and it has a gravimetric capacity of 2205 mAh.g<sup>-1</sup>. Commercial magnesium powder (Alfa Aesar, 99.8 % purity) was used. Magnesium metal is usually covered by a very stable layer of MgO. So, the powder was ball-milled under argon to break this oxide surface layer and make the Mg particles more reactive. The ball-milling was performed under Ar as followed: 2 g of commercial Mg powder was placed in a 50 cm<sup>3</sup> WC airtight jar and planetary ball-milled at 600 rpm for 2 h with a 2 min break every 30min and with a balls to powder weights ratio of 53:1. The XRD pattern of the Mg powder obtained after ball milling is presented on Figure IV. 1a. The diffractogram indicates that no crystalline impurities are present: only Mg metal is visible, crystallizing in a hexagonal structure with the space group P6<sub>3</sub>/mmc and the cell parameters a = 3.210(1) Å and c = 5.211(2) Å.

### **Bismuth anode**

Bismuth has been considered as a second solution for the anode in case of reactivity and/or instability of the interface between Mg and the solid electrolytes. The Mg-Bi binary phases diagram indicates that no solid solution exists between these two elements and that only the intermetallic compound Mg<sub>3</sub>Bi<sub>2</sub> can be formed. The magnesiation of Bi leads to the formation of a biphasic mixture of Bi and Mg<sub>3</sub>Bi<sub>2</sub> as follows: <sup>1,2</sup>

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$$3x \operatorname{Mg}^{2+} + 2 \operatorname{Bi} + 6x \operatorname{e} \rightarrow x \operatorname{Mg}_3 \operatorname{Bi}_2 + (2 - 2x) \operatorname{Bi}$$
 Equation IV. 1

This reaction happens at ~ 0.27 V vs Mg<sup>2+</sup>/Mg and has a specific capacity of 385 mAh.g<sup>-1</sup>. Bi powder obtained after ball-milling of Bi ingots (Prolabo, 99.999 % purity) was used. The ballmilling parameters were the same than the ones described previously for Mg. After ball-milling, the powder was sieved to separate large aggregates from the fine powder. Then it was stored in an Ar filled glovebox. The powder does not show any traces of impurities as analyzed by XRD. The only seen peaks are from Bi crystallizing in a hexagonal structure with the space group R-3m and the cell parameters a = 4.5438(4) Å and c= 11.854(1) Å (*cf.* Figure IV. 1b).

### Mo<sub>6</sub>S<sub>8</sub> Chevrel phase as cathode

For the cathode, the Chevrel phase  $Mo_6S_8$ ,<sup>3</sup> which is commonly used for Mg intercalation, <sup>4,5</sup> has been selected. It has been synthesized at the ICGM in Montpellier from  $Cu_{2.5}Mo_6S_8$  by acid leaching in a solution of HCl to remove Cu. The reaction with Mg is as follows:

$$x Mg^{2+} + Mo_6S_8 + 2x e \rightarrow Mg_xMo_6S_8$$
 Equation IV. 2

The intercalation occurs in two steps: a first one at 1.2 V vs. Mg<sup>2+</sup>/Mg and a second one at 1.0 V vs Mg<sup>2+</sup>/Mg. Each step corresponds to the intercalation of Mg into two different crystallographic sites. The maximum quantity of Mg that can be intercalated is x = 2 for a theoretical specific capacity of 122 mAh.g<sup>-1</sup>. This maximum capacity is hard to reach as, upon charge, the ionic conductivity decays as the concentration of Mg ions decreases, leading to the entrapment of Mg ions. From our XRD measurement, pure crystalline Mo<sub>6</sub>S<sub>8</sub> is obtained with the hexagonal space group R-3 and the cell parameters a = 9.1837(8) Å, c = 10.869(1) Å and V = 793.8(1) Å<sup>3</sup> (cf. Figure IV. 1c).

# C45 carbon black

To enhance the electronic conductivity of the electrodes, it is necessary to use a carbon additive. Carbon black C45 (Imerys) was used. It has a specific surface area of 45 m<sup>2</sup>.g<sup>-1</sup>. Before use, C45 is placed under dynamic vacuum at 750°C overnight to remove all molecules adsorbed onto the carbon surface. It is then stored in an Ar filled glovebox. Carbon black consists in a poorly graphitized carbon and this low crystallinity causes a broad diffraction peak around 26° as observed on the XRD pattern on Figure IV. 1d.



Figure IV. 1. XRD patterns of the different electrode materials: a) Ball-milled Mg powder, b) Bi powder, c)  $Mo_6S_8$  and d) carbon C45.

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### IV-2b. Chemical stabilities of $Mg(BH_4)(NH_2)$ and $\gamma$ - $Mg_3(BH_4)_4(NH_2)_2$

To characterize the chemical stability of our solid electrolytes, Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (sample D in Chapter II) and  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> were mixed with the electrode materials described above in a 1:1 mass ratio. The mixtures were done in an Ar filled glovebox by hand with an agate mortar. They were subsequently annealed under Ar for 12h at 100°C for Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and 150°C for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> as it was observed in Chapter III that this compound is thermally stable at least up to 180°C. The powders are then recovered after annealing and analyzed by XRD.

For the mixture of the solid electrolytes with the anode materials: Mg and Bi (*cf.* Figure IV. 2 and Figure IV. 3), and with the carbon additive C45 (*cf.* Figure IV. 4), only the reflections of the solid electrolytes and the electrode materials are visible. The refined cell parameters of the Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> change slightly compare to the ones obtained in the previous chapters. Nevertheless, the volume of cell is similar to the one of the raw materials. So, no bulk reaction has occurred. This is an interesting result, because it indicates that the solid electrolytes do not react with the anode materials. Indeed, some liquid electrolytes are not stable at low potential and form a passivation layer on the anode. This passivation layer is blocking the Mg<sup>2+</sup> ions diffusion and thus makes impossible the cycling of the cell.<sup>6</sup> With these solid electrolytes, the interface with the anode would be chemically stable.

On the contrary, the mixture with Mo<sub>6</sub>S<sub>8</sub> led to a clear reaction between the solid electrolyte and the electrode material. The magnesiation of the Chevrel phase occurs forming Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub>. A profile matching was performed on the XRD pattern of the mixture after annealing. The refined unit cell parameters of Mg<sub>x</sub>Mo<sub>6</sub>S<sub>8</sub> are a = 9.7693(4) Å and c= 10.3734(8) Å (V = 857.31 Å<sup>3</sup>) for the mixture with Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and a = 9.7549(8) Å and c= 10.362(2) Å (V = 853.8(2) Å<sup>3</sup>) for the one with  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. These parameters correspond to the Chevrel phase with x = 2 so it has been completely magnesiated (the cell parameters of Mo<sub>6</sub>S<sub>8</sub> are a = 9.1837(8) Å, c = 10.869(1) Å and V = 793.8(1) Å<sup>3</sup>). The solid electrolytes are therefore oxidized in contact with the cathode. This oxidation forms amorphous products that are not detected by XRD. It even leads to a complete amorphization of the solid electrolyte for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. This kind of reaction was also observed in the study of Unemoto *et al.* where the lithiation of TiS<sub>2</sub> in contact with LiBH<sub>4</sub> is observed.<sup>7</sup> Titanium disulfide has a working potential of about + 2.3 V vs. Li<sup>+</sup>/Li and recent studies showed that the actual stability of LiBH<sub>4</sub> is + 2.0 V vs. Li<sup>+</sup>/Li.<sup>8,9</sup> So, LiBH<sub>4</sub> can be spontaneously oxidized by TiS<sub>2</sub>. Similarly, our results indicate that the oxidation potential of our solid electrolytes is lower than the working potential of Mo<sub>6</sub>S<sub>8</sub>. Chapter IV – Characterization of ionic conductors as solid electrolytes: towards all-solid-state Mg

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Figure IV. 3. XRD patterns of the 1:1 mixture of Bi with  $Mg(BH_4)(NH_2)$ after annealing at 100°C for 12h under Ar.



Figure IV. 4. XRD patterns of the 1:1 mixture of C45 with a)  $Mg(BH_4)(NH_2)$  and b)  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> after respective annealing at 100°C and 150°C for 12h under Ar.



Figure IV. 5. XRD patterns of the 1:1 mixture of  $Mo_6S_8$  with a)  $Mg(BH_4)(NH_2)$  and b)  $\gamma$ - $Mg_3(BH_4)_4(NH_2)_2$  after respective annealing at 100°C and 150°C for 12h under Ar.

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# **IV-3. Electrochemical stability**

## III-3a. Anode/electrolyte compatibility

To determine the compatibility between the electrolyte and the anode, galvanostatic polarization measurements were performed on a symmetrical cell. The cell was simply made of a parallel stack of two anodes (Mg or Bi) separated by the solid electrolyte. Ideally, the anodes are pressed onto the electrolyte to form a self-standing stack and to get good electrical contacts. Unfortunately, Mg is a relatively hard metal and it cannot be stacked onto the electrolyte. Mg has a Brinell hardness (HB) of 260 at room temperature which is close to the HB of Al (245) for instance.<sup>10</sup> By comparison, alkaline elements like Na or K have HB < 1. This means that Mg is not a soft metal and it does not easily form good contact with other materials. So, instead, our stack was made with two magnesium discs made from cold pressed powder and a pellet of solid electrolyte. This assembly was not optimum for good contacts but it was the only way to use Mg powder as anode in a symmetrical cell.

The results for Mg(BH<sub>4</sub>)(NH<sub>2</sub>) are presented on Figure IV. 6. A current of  $\pm 5 \ \mu$ A.cm<sup>-2</sup> was applied for 2h and each polarization was separated by 5 min of rest. During the first cycles, the potential evolved slowly before reaching its steady-state equilibrium with a plateau at about 0.5 V. This evolution of the potential can be due to the slow diffusion of Mg<sup>2+</sup> in the solid electrolyte. If the ionic conductivity of our pellet is 1x10<sup>-5</sup> S.cm<sup>-1</sup> at 100°C, the expected polarization potential should be around 25 mV. The measured polarization was 20 times higher. The bad contacts between the electrolyte and the electrodes might be the cause of this over potential, creating a high interfacial resistance. The interfacial resistance was estimated to be about 120 k $\Omega$  (152 k $\Omega$ .cm<sup>-2</sup>). As the cycling continued, the interfacial resistance increased and, after 60 h of cycling, the polarization did not reach a steady-state anymore but reached a maximum before slowly decreasing. This new evolution of the potential can be due to side reactions happening, as inhomogeneous deposition of Mg (dendrites, foam, *etc.*)<sup>11</sup> or decomposition of the solid electrolyte. Therefore, this symmetrical cell measurement indicates that the interface between Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and Mg is electrochemically unstable for such stack.



Figure IV. 6. Galvanostatic measurement at 100°C of a symmetrical cell Mg/Mg(BH<sub>4</sub>)(NH<sub>2</sub>)/Mg cycled with a current of 5  $\mu$ A.cm<sup>-2</sup> for 2h with 5 min rest between each polarization.

A different anode was then used, the magnesiated form of Bi, *i.e.* Mg<sub>3</sub>Bi<sub>2</sub>. With this anode, no metal deposition/stripping process occurs anymore but a biphasic reaction instead as described in Equation IV. 1. For polarization measurements, the same redox reaction is needed at both electrodes to be able to reach equilibrium and to be sure that the polarization evolution is only due to the interface evolution and not to electrochemical reactions occurring at the electrodes. Thus, Mg<sub>3</sub>Bi<sub>2</sub> cannot be used directly otherwise on one side would occur the biphasic reaction described in Equation IV. 1 and, on the other side, Mg deposition:

$$x Mg^{2+} + 2x e^{-} \rightarrow x Mg$$
 Equation IV. 3
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An electrode was prepared by ball-milling Mg and Bi with the objective that only half of the Bi was magnesiated. In an Ar filled glovebox, 0.177g of Mg were mixed with 1.840g of Bi. The mixture was placed in a stainless steel jar with 12 stainless steel balls of 8 mm diameter for a balls to powder weights ratio of 12:1. The ball-milling is performed using a Spex mill for 5h. The XRD pattern of the as-obtained product is presented on Figure IV. 7. A Rietveld refinement confirmed that a mixture of Mg<sub>3</sub>Bi<sub>2</sub> + Bi was obtained with 46 mass % of Mg<sub>3</sub>Bi<sub>2</sub> and 54 mass % of Bi. With this mixture, only the biphasic redox reaction (*cf.* Equation IV.1) would occur at both electrodes. Finally, to use this material, 10 wt% of C45 was added to ensure a good electronic conductivity as Bi is a bad electronic conductor. The electrodes were cold pressed into discs and used in the same configuration as with the Mg electrodes.

Even if Bi has a lower hardness than Mg (HB<sub>Bi</sub> = 94.2), it is still too hard to stick to the solid electrolyte. A low current density had to be used for the galvanostatic measurements to avoid a too important polarization. Already, with a current density of 1  $\mu$ A.cm<sup>-2</sup>, the polarization potential was about 1 V (cf. Figure IV. 8) so the interfacial resistance was about 1.2 M $\Omega$  (1.5 M $\Omega$ .cm<sup>-2</sup>). This huge resistance was not due to chemical reactivity as shown in the previous section. The interface was inhomogeneous as the electrode surface was made of Bi, Mg<sub>3</sub>Bi<sub>2</sub> and C45 and this inhomogeneity could explain the initial bad interface. The first polarization cycles were stable and featured the formation of an arc before to reach a steady-state. Rapidly, the polarization turned into an unstable state and the potential increased. The complex shape of the polarization observed after several cycles might be due to a detrimental evolution of the contact between the electrode and the solid electrolyte because of the volumetric expansion of Bi upon cycling. The volume increases of 73 % when Bi transforms into Mg<sub>3</sub>Bi<sub>2</sub>. Actually, important volume changes are very problematic in all-solid-state batteries because it cannot be compensated by any change of shape or mechanical flexibility. It can also be assumed that upon cycling some of the Bi or Mg<sub>3</sub>Bi<sub>2</sub> particles could lose their electrical contact with the carbon. So, the change of Mg metal for Bi anode unfortunately did not improve the compatibility of the anode with the solid electrolyte.



Figure IV. 7. XRD pattern of the as-prepared Mg<sub>3</sub>Bi<sub>2</sub> + Bi electrode material and its Rietveld refinement.



Figure IV. 8. . Galvanostatic measurement at 100°C of a symmetrical cell  $Mg_3Bi_2 + Bi + C45/Mg(BH_4)(NH_2)/Mg_3Bi_2 + Bi + C45$  cycled with a current of 1  $\mu$ A.cm<sup>-2</sup> for 2h with 5 min rest between each polarization.

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#### III-3a. Electrochemical stability window

One of the most important parameter to know about our solid electrolytes is their electrochemical stability window (ESW). To determine the ESW of our materials, cyclic voltammetry was performed using a cell made of a Mg anode versus a composite positive electrode made of the solid electrolyte mixed with 10 wt% C45. Both electrodes were separated by the solid electrolyte. The cyclic voltammetry was performed with a slow scanning rate of 0.05 mV.s<sup>-1</sup> at 100°C starting by the reduction process. Figure IV. 9a and b show the results for Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>, respectively. For both phases, the Mg deposition/stripping happens around 0 V vs. Mg<sup>2+</sup>/Mg. No reduction other than the Mg deposition occurred so these solid electrolytes are stable at low potentials. This was confirmed by the chemical stability experiments described in the previous section.

On the other side, the oxidation of the solid electrolytes was observed. It started in both cases around 1 V vs  $Mg^{2+}/Mg$  and had an onset potential of about 1.49 V vs  $Mg^{2+}/Mg$  for Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and 1.48 V vs Mg<sup>2+</sup>/Mg for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (cf. Figure IV. 9c and d). The composition does not seem to have a strong influence on the ESW. In the case of  $Mg(BH_4)(NH_2)$ , the oxidation potential is lower than that reported by Higashi *et al.*<sup>12</sup> In their work, they assumed that  $Mg(BH_4)(NH_2)$  would not be oxidized before 3V vs  $Mg^{2+}/Mg$ . This value was clearly overestimated as they performed their cyclic voltammetry using a flat Pt electrode as counter electrode and a fast scanning rate of 1 mV.s<sup>-1</sup>. The use of a flat counter electrode does not allow a good contact with the solid electrolyte and can hinder the oxidation reaction as only a few amount of the electrolyte would react and the measured current is therefore very low. The measured current will be even lower if the scanning rate is fast (kinetic limitation). A recent study showed that using carbon with different specific surface area changed the kinetic of oxidation reaction and changed the observed oxidation potential.<sup>9</sup> The most accurate measurements were obtained for composite electrodes using high specific surface area carbon blacks. The high contact surface area allows a good electronic percolation through the solid electrolyte and hence ensures a precise measurement of the oxidation potential. This highlights once more the importance of the contact surface area between the counter electrode and the solid electrolyte. In our case, the fact that a composite counter electrode was used instead of a flat electrode explains the discrepancy between the ESW measured for  $Mg(BH_4)(NH_2)$  and the results of Higashi *et al.*. With an oxidation starting at about 1 V vs Mg<sup>2+</sup>/Mg, it is obvious that these solid electrolytes are unstable versus cathode electrodes as  $Mo_6S_8$  that has a working potential around 1.2 V vs

 $Mg^{2+}/Mg$ . This explains why the solid electrolytes are oxidized by  $Mo_6S_8$  to form  $Mg_2Mo_6S_8$  and amorphous decomposition products.



Figure IV. 9. Cyclic voltammetry measurements of cells made of Mg/solid electrolyte/solid electrolyte + C45 (90:10) recorded at 0.05 mV.s<sup>-1</sup> at 100°C with a) Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and b) γ-Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. The insets are the coulombic efficiencies of the Mg deposition/stripping. c) and d) are the zoom on the first oxidation observed on a) and b) respectively.

Another information that could be extracted from the cyclic voltammetry curve was the coulombic efficiency of the Mg deposition/stripping that is shown on the inset of Figure IV. 9a and b. For Mg(BH<sub>4</sub>)(NH<sub>2</sub>), during the first cycle, the coulombic efficiency is about 60%. This low value can be due to the low conductivity of the solid electrolyte. Upon cycling, this efficiency dropped to 20% and then stayed stable. This drop reveals that the oxidation of the electrolyte created a passivation layer with low conductivity. Note that the coulombic efficiency for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>

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was already at 20% during the first cycle. It was because the cell had already undergone a cycle before this measurement but the current range selected was too high. So, the following cycles had to be repeated with a lower current range to get the result shown on Figure IV. 9d. Hence, the passivation layer formed by the oxidation of the solid electrolytes is detrimental to the cyclability of the cell.

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#### **IV-4.** Conclusions

Two of our best ionic conductors found in the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> phases diagram have been evaluated as possible solid electrolytes: Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. Interestingly, they do not react with the carbon additive and the anode materials: Mg and Bi. However, they reacted with the cathode material: Mo<sub>6</sub>S<sub>8</sub>. In contact with Mo<sub>6</sub>S<sub>8</sub>, they were oxidized to form Mg<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> and amorphous decomposition products. The compatibility of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) with the Mg anode was also tested by a polarization measurement in a symmetrical cell using Mg electrodes. A large interfacial resistance was observed. It could be explained by a poor contact between the electrolyte and Mg, especially because Mg is a hard metal and sticks very poorly on the solid electrolyte pellet. The interfacial resistance increased upon cycling indicating its instability upon Mg deposition/stripping. The same experiment was performed with "Mg<sub>3</sub>Bi<sub>2</sub> + Bi" electrodes, but unfortunately the interfacial resistance was even larger than that with Mg. This could be due to the inhomogeneity of the surface in contact with the solid electrolyte as the electrode is made of Mg<sub>3</sub>Bi<sub>2</sub>, Bi, and C45. The interfacial resistance increased upon cycling, which could be caused by the important volume change between Mg<sub>3</sub>Bi<sub>2</sub> and Bi.

The electrochemical stability windows of the two solid electrolytes were measured by cyclic voltammetry. Magnesium deposition/stripping is observed around 0 V vs. Mg<sup>2+</sup>/Mg, which represents a nice result as it has been very rarely reported for a solid Mg<sup>2+</sup> ionic conductor. The oxidation of the solid electrolytes starts at about 1.0 V vs. Mg<sup>2+</sup>/Mg and had an onset potential around 1.5 V vs. Mg<sup>2+</sup>/Mg. The oxidation potential was not affected by the composition of the phase studied. The coulombic efficiency values of the Mg deposition/stripping decreased upon cycling probably because the oxidation of the electrolytes leads to the formation of non-conductive passivation layers.

So, on one hand, these materials are unstable at potentials higher than 1.0 V vs.  $Mg^{2+}/Mg$ and would be oxidized by cathodes such as  $Mo_6S_8$ . This oxidation leads to the detrimental formation of non conducting compounds. On the other hand, they are stable chemically and electrochemically versus the anode materials. Unfortunately, it is hard to obtain a good interface between the anode and the solid electrolytes due to the important hardness of Mg metal. This point is critical to develop all-solid-state Mg batteries and might be improved by using foldable Mg thin foils or very fine powder of the anode material that could be dispersed in a composite electrode with the solid electrolyte.

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#### References

- 1. Murgia, F., Stievano, L., Monconduit, L. & Berthelot, R. Insight into the electrochemical behavior of micrometric Bi and Mg<sub>3</sub>Bi<sub>2</sub> as high performance negative electrodes for Mg batteries. *J. Mater. Chem. A* **3**, 16478–16485 (2015).
- 2. Arthur, T. S., Singh, N. & Matsui, M. Electrodeposited Bi, Sb and  $Bi_{1-x}Sb_x$  alloys as anodes for Mg-ion batteries. *Electrochem. commun.* **16**, 103–106 (2012).
- 3. Chevrel, R., Sergent, M. & Prigent, J. Un nouveau sulfure de molybdene : Mo<sub>3</sub>S<sub>4</sub> preparation, propriétés et structure cristalline. *Mater. Res. Bull.* **9**, 1487–1498 (1974).
- 4. Levi, M. D. *et al.* Kinetic and thermodynamic studies of Mg<sup>2+</sup> and Li<sup>+</sup> ion insertion into the Mo<sub>6</sub>S<sub>8</sub> Chevrel phase. *J. Electrochem. Soc.* **151**, A1044 (2004).
- 5. Aurbach, D. *et al.* Prototype systems for rechargeable magnesium batteries. *Nature* **407**, 724–727 (2000).
- 6. Mohtadi, R. & Mizuno, F. Magnesium batteries: Current state of the art, issues and future perspectives. *Beilstein J. Nanotechnol.* **5**, 1291–1311 (2014).
- 7. Unemoto, A. *et al.* Stable interface formation between TiS<sub>2</sub> and LiBH<sub>4</sub> in bulk-type all-solid-state lithium batteries. *Chem. Mater.* **27**, 5407–5416 (2015).
- 8. Gulino, V. *et al.* Phase stability and fast ion conductivity in the hexagonal LiBH<sub>4</sub>–LiBr–LiCl solid solution. *Chem. Mater.* **31**, 5133–5144 (2019).
- 9. Asakura, R. *et al.* Electrochemical oxidative stability of hydroborate-based solid-state electrolytes. *ACS Appl. Energy Mater.* **2**, 6924–6930 (2019).
- 10. Samsonov, G. V. Handbook of the Physicochemical Properties of the Elements. (Springer US, 1968).
- 11. Chen, K. *et al.* Dead lithium: Mass transport effects on voltage, capacity, and failure of lithium metal anodes. *J. Mater. Chem. A* **5**, 11671–11681 (2017).
- 12. Higashi, S., Miwa, K., Aoki, M. & Takechi, K. A novel inorganic solid state ion conductor for rechargeable Mg batteries. *Chem. Commun.* **50**, 1320–1322 (2014).

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### **General conclusion**

The main aims of this PhD thesis were to enhance the ionic conductivity of known Mg<sup>2+</sup> inorganic ionic conductors, to find new ones and to characterize them electrochemically in order to know if they could be used as solid electrolytes in Mg batteries. The first studied material was Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (cf. Chapter II). It has been synthesized by ball-milling of Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub> and a subsequent annealing. The synthesis parameters were not described in the literature so they had to be determined. Different ball-milling speeds and annealing times, temperatures and atmospheres were tested. The purest sample was obtained with a ball-milling at 500 rpm for 1h and a subsequent annealing at 120°C for 72h under 10 bar of H<sub>2</sub>. The X-ray diffraction pattern of this sample showed only Mg(BH<sub>4</sub>)(NH<sub>2</sub>), crystallizing in the space group  $I4_1$  with Z = 8 and the cell parameters a = 5.768(5) Å, c = 20.486(2) Å, and V = 681.6(1) Å<sup>3</sup> which are in agreement with the literature.<sup>1</sup> During the synthesis optimization, composite samples made of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) and an unknown crystalline additional phase were obtained. <sup>11</sup>B MAS-NMR spectroscopy experiments, that were performed for the first time on these compounds, revealed that even in samples presenting only crystalline Mg(BH<sub>4</sub>)(NH<sub>2</sub>) by X-ray diffraction, the additional phase was nevertheless present as an amorphous phase. The additional phase content determined by <sup>11</sup>B MAS-NMR spectroscopy strongly influences the ionic conductivity. The sample containing mainly the additional phase (73 %) has an ionic conductivity of 8.10<sup>-8</sup> S.cm<sup>-1</sup> at 100°C with an activation energy of 1.3 eV; while the sample containing less additional phase (20 %) has an ionic conductivity of 1x10<sup>-5</sup> S.cm<sup>-1</sup> at 100°C with an activation energy of 1.0 eV. This last ionic conductivity value is four order of magnitude higher than the one previously reported by Higashi et al. (~10<sup>-9</sup> S.cm<sup>-1</sup> at 100°C and Ea = 1.31 eV).<sup>2</sup> Two hypotheses can be made to explain this discrepancy. In the first hypothesis, the material of Higashi et al. is considered as 100 % pure Mg(BH<sub>4</sub>)(NH<sub>2</sub>), then the presence of the additional phase in our composite samples would enhance the ionic conductivity, especially, once it becomes amorphous forming a glass/ceramiclike material with enhanced Mg<sup>2+</sup> mobility.<sup>3</sup> For the second hypothesis, the additional phase has actually a negative effect on Mg<sup>2+</sup> mobility. Indeed, it was observed in our study that the lowest is its content; the highest is the ionic conductivity. In that case, the material of Higashi et al. would contain an important amount of amorphous additional phase, lowering its ionic conductivity. To validate one of these two hypotheses, a precise description of the synthesis parameters used by Higashi et al. and <sup>11</sup>B MAS-NMR spectroscopy measurements on their sample would have been very useful. However, in both cases, the additional phase has clearly an impact on the ionic

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conductivity and it was important to try to obtain it pure. As it contains  $(BH_4)^-$  anions, as-probed by <sup>11</sup>B MAS-NMR spectroscopy, that it was not a decomposition product and that it was obtained for non-optimized synthesis, the assumption was made that it was actually a never reported Mg $(BH_4)_{2x}(NH_2)_{2(1-x)}$  compound.

Then, to try to identify this additional phase and to find new Mg<sup>2+</sup> ionic conductors, the  $Mg(BH_4)_2-Mg(NH_2)_2$  binary phases diagram has been explored (cf. Chapter III). Three new  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$  crystalline phases were discovered. Two phases with a composition rich in amide were named the  $\alpha$ -phase and the  $\beta$ -phase. The  $\alpha$ -phase crystallizes with the same crystal structure as  $Mg(NH_2)_2$  in which large  $(BH_4)^{-}$  anions are substituting the  $(NH_2)^{-}$ . This substitution leads to an expansion of the unit cell and an improvement of the ionic conductivity, increasing from  $4x10^{-9}$  S.cm<sup>-1</sup> for x = 0.17 to  $1x10^{-8}$  S.cm<sup>-1</sup> for x = 0.25. Upon heating, the  $\alpha$ -phase undergoes an irreversible endothermic structural transition, forming the  $\beta$ -phase. The  $\beta$ -phase crystallizes in a new unknown crystal structure. This phase transition has a little impact on the ionic conductivity of the material,  $\sigma_{100^{\circ}C} = 2 \times 10^{-8}$  S.cm<sup>-1</sup>, and the activation energy of the ionic conductivity increases from 1.7 eV to 2 eV. For x = 0.33, with a ball-milling at 600 rpm, poorly crystallized  $\beta$ -phase was obtained with an amorphous background visible by XRD. The ionic conductivity at 100°C of this last compound is improved, as it reaches 2x10<sup>-7</sup> S.cm<sup>-1</sup> and its activation energy is 1.6 eV. The βphase might be the additional phase present in the composite materials described in Chapter II during the  $Mg(BH_4)(NH_2)$  synthesis. Indeed, for the samples with the crystalline additional phase, the X-ray diffraction patterns and ionic conductivity values are similar. This observation would confirm the second hypothesis we have made, considering that the presence of additional phase decreases the ionic conductivity of the composite materials.

Another phase crystallizes in the borohydride-rich region of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> phases diagram: it was named the  $\gamma$ -phase. It has a tetragonal structure with the I-4 space group. Similarly to the  $\alpha$ -phase, adding more (BH<sub>4</sub>)<sup>-</sup> anions into this compound increases the unit cell volume but, here, it decreases the ionic conductivity. The best ionic conductor is  $\gamma$ -Mg(BH<sub>4</sub>)<sub>1.33</sub>(NH<sub>2</sub>)<sub>0.67</sub> (which can be also written  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>) with an ionic conductivity at 100°C of 4x10<sup>-5</sup> S.cm<sup>-1</sup> and an activation energy of 0.8 eV. These values mean that it features one of the best Mg<sup>2+</sup> mobility in an inorganic solid ionic conductor reported so far. The good mobility of Mg<sup>2+</sup> was confirmed by <sup>25</sup>Mg solid state MAS-NMR spectroscopy with a significant narrowing of the NMR peak upon heating. The  $\gamma$ -phase has also a good thermal stability as no thermal event nor mass loss was detected below 190°C. A pseudo-binary Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> phases diagram was proposed. It helps us to understand the complexity of this Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> system. A trend was observed for the ionic

conductivity of the compounds as a maximum is reached for  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. This trend continues even if the crystal structure changes. So, good Mg<sup>2+</sup> ionic conductors were found in this binary phases diagram but they still needed to be characterized as solid electrolyte in order to know if they could be used in Mg batteries.

Two of our best ionic conductors found in the  $Mg(BH_4)_2$ - $Mg(NH_2)_2$  phases diagram have been evaluated as possible solid electrolytes:  $Mg(BH_4)(NH_2)$  and  $\gamma-Mg_3(BH_4)_4(NH_2)_2$ (cf. Chapter IV). Interestingly, they do not react with the carbon additive and the anode materials: Mg and Bi. However, they reacted with the  $Mo_6S_8$  cathode material. In contact with  $Mo_6S_8$ , they were oxidized to form Mg<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> and amorphous decomposition products. The compatibility of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) with the Mg anode was also tested by a polarization measurement in a symmetrical cell using Mg electrodes. A large interfacial resistance was observed. It could be explained by a poor contact between the electrolyte and Mg, especially because Mg is a hard metal and sticks very poorly on the solid electrolyte pellet. The interfacial resistance increased upon cycling indicating its instability upon Mg deposition/stripping. The same experiment was performed with "Mg<sub>3</sub>Bi<sub>2</sub> + Bi" electrodes, but unfortunately the interfacial resistance was even larger than that with Mg. The interfacial resistance increased upon cycling, which could be caused by the important volume change between Mg<sub>3</sub>Bi<sub>2</sub> and Bi. The electrochemical stability windows of the two solid electrolytes were measured by cyclic voltammetry. Magnesium deposition/stripping is observed around 0 V vs. Mg<sup>2+</sup>/Mg, which represents a very positive result as it has been very rarely reported for a solid Mg<sup>2+</sup> ionic conductor. The oxidation of the solid electrolytes starts at about + 1.0 V vs.  $Mg^{2+}/Mg$  and had an onset potential around + 1.5 V vs.  $Mg^{2+}/Mg$ . The oxidation potential was not affected by the composition of the phase studied. Unfortunately, it is hard to obtain a good interface between the anode and the solid electrolytes due to the important hardness of Mg metal. This point is critical to develop all-solid-state Mg batteries and might be improved by using foldable Mg thin foils or very fine powder of the anode material that could be dispersed in a composite electrode with the solid electrolyte.

To summarize, through the exploration of the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> phases diagram, we have discovered new solid inorganic Mg<sup>2+</sup> ionic conductors. A trend appears between the ionic conductivity and the composition of these materials. One of them reaches one of the highest ionic conductivity ever reported for an inorganic Mg<sup>2+</sup> ionic conductor (4x10<sup>-5</sup> S.cm<sup>-1</sup> at 100°C) and has also one of the lowest activation energy (0.8 eV). Deeper structural (synchrotron X-ray diffraction) and theoretical studies (DFT) could help to understand this trend. It might depend on the crystalline structure (Mg<sup>2+</sup> mobility pathway) and the different substitution of (NH<sub>2</sub>)<sup>-</sup> anions by

(BH<sub>4</sub>)<sup>-</sup> (*i.e.* interaction of Mg<sup>2+</sup> with its surrounding). Understanding this trend in this binary phases diagram could allow the design of better Mg<sup>2+</sup> ionic conductor based on other compounds. For instance, the substitution of  $(NH_2)^{-1}$  and  $(BH_4)^{-1}$  by other anions such as  $(B_{12}H_{12})^{2-1}$  (as demonstrated with  $Na_3(B_{12}H_{12})(NH_2))^4$  or  $(CB_{11}H_{12})^-$  could lead to the discovery of better ionic conductors. To obtain this kind of compounds, important effort on the synthesis process would be needed as there is no report of pure magnesium closo-borane or carborane synthesis. They are stabilized only with solvent molecules or in carbon scaffolds.<sup>5,6</sup> Synthesis process could be imagined to react  $Mg(BH_4)(NH_2)$  with solid or liquid  $B_{10}H_{14}$  for instance, similarly to what is done to get  $Li_2B_{12}H_{12}$  and Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>.<sup>7</sup> In terms of electrochemistry, it is hard to imagine using these materials directly as bulk solid electrolytes. However, their chemical and electrochemical stability vs. the Mg anode makes them interesting as coating materials. Indeed, it is possible to think about a system where the electrodes are coated by a thin layer of stable electrolytes and separated by a good solid or liquid ionic conductor. Then, of course, the contact with Mg metal will have to be optimized and our materials will have to be chemically stable with the bulk electrolyte. If a coating is necessary at the cathode, materials such as phosphates should be stable.<sup>8</sup> Other compounds such as magnesium halides are studied by Canepa's group to form stable interfaces that are crucial for rechargeable batteries.<sup>9</sup>

For bulk solid state electrolyte, more studies could also be done on Mg<sub>2</sub>P<sub>2</sub>S<sub>6</sub>. Indeed, this compound has been reported only once in the work of Yamanaka *et al.*, where it was obtained as a side product studying MgS-P<sub>2</sub>S<sub>5</sub>-MgI<sub>2</sub> glass-ceramics.<sup>10</sup> A recent study showed that Zn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> features a good Zn<sup>2+</sup> mobility with an ionic conductivity of about 10<sup>-7</sup> S cm<sup>-1</sup> at 60°C and more interestingly, a very low activation energy of  $351 \pm 99 \text{ meV}$ .<sup>11</sup> So it is possible that Mg<sub>2</sub>P<sub>2</sub>S<sub>6</sub> also has good Mg<sup>2+</sup> mobility because it has a very similar crystal structure as that of Zn<sub>2</sub>P<sub>2</sub>S<sub>6</sub> (Mg<sub>2</sub>P<sub>2</sub>S<sub>6</sub>: C2/m, Z = 2, a = 6.085(1) Å, b = 10.560(2) Å, c = 6.835 (1) Å,  $\beta = 106.97(3)^{\circ}$  and Zn<sub>2</sub>P<sub>2</sub>S<sub>6</sub>: C2/m, Z = 2, a = 5.9717(4) Å, b = 10.3424(8) Å, c = 6.7565(5),  $\beta = 107.139(4)^{\circ}$ ). So, inorganic solid electrolytes for Mg batteries are still worth of investigation and there are plenty of rooms to improve their ionic conductivity/mobility and stability. The implementation of solid electrolytes in Mg batteries would help to develop systems with high energy densities such as the Mg-S batteries and, thus, to bring more options to the world of energy storage.

#### References

- 1. Noritake, T. *et al.* Synthesis and crystal structure analysis of complex hydride Mg(BH<sub>4</sub>)(NH<sub>2</sub>). *Int. J. Hydrogen Energy* **38**, 6730–6735 (2013).
- 2. Higashi, S., Miwa, K., Aoki, M. & Takechi, K. A novel inorganic solid state ion conductor for rechargeable Mg batteries. *Chem. Commun.* **50**, 1320–1322 (2014).
- 3. Le Ruyet, R. *et al.* Investigation of Mg(BH<sub>4</sub>)(NH<sub>2</sub>)-based composite materials with enhanced Mg<sup>2+</sup> ionic conductivity. *J. Phys. Chem. C* **123**, 10756–10763 (2019).
- 4. He, L. *et al.* Na<sub>3</sub>NH<sub>2</sub>B<sub>12</sub>H<sub>12</sub> as high performance solid electrolyte for all-solid-state Na-ion batteries. *J. Power Sources* **396**, 574–579 (2018).
- 5. Remhof, A. *et al.* Solvent-free synthesis and stability of MgB<sub>12</sub>H<sub>12</sub>. *J. Mater. Chem. A* **2**, 7244 (2014).
- 6. Tutusaus, O. *et al.* An efficient halogen-free electrolyte for use in rechargeable magnesium batteries. *Angew. Chemie Int. Ed.* **54**, 7900–7904 (2015).
- He, L., Li, H., Hwang, S. & Akiba, E. Facile solvent-free synthesis of anhydrous alkali metal dodecaborate M<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (M = Li, Na, K). *J. Phys. Chem. C* **118**, 6084–6089 (2014).
- 8. Su, J. *et al.* Atomic layer deposition of a magnesium phosphate solid electrolyte. *Chem. Mater.* **31**, 5566–5575 (2019).
- 9. Chen, T., Sai Gautam, G. & Canepa, P. Ionic transport in potential coating materials for Mg batteries. *Chem. Mater.* **31**, 8087–8099 (2019).
- Yamanaka, T., Hayashi, A., Yamauchi, A. & Tatsumisago, M. Preparation of magnesium ion conducting MgS–P<sub>2</sub>S<sub>5</sub>–Mgl<sub>2</sub> glasses by a mechanochemical technique. *Solid State Ionics* 262, 601–603 (2014).
- 11. Martinolich, A. J. *et al.* Solid-state divalent ion conduction in ZnPS<sub>3</sub>. *Chem. Mater.* **31**, 3652–3661 (2019).

## <u>Annex I –</u> Experimental methods

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#### Annex I – Experimental methods

#### AI.1 – Note on the air sensitivity of the materials

The studied materials are extremely moisture and O<sub>2</sub> sensitive so all the experimental techniques have been adapted to be able to keep the materials protected. The storage and all the handling of the different products were done in an Ar filled glovebox. All the different syntheses and measurements were performed using airtight set-ups. In contact with H<sub>2</sub>O or O<sub>2</sub>, the hydrides, borohydrides and the amides would form very exothermically oxides and hydroxides and release an important quantity of gases such as H<sub>2</sub> and NH<sub>3</sub>. This can be dangerous for instance if an important quantity of material is exposed to H<sub>2</sub>O, especially if the material is powdery. In cases where the materials have to be exposed to air, like for the cleaning of the ball milling jar, it is important to neutralize them quickly after exposition to air and if possible under a fume hood. For the neutralization, it is better to use ethanol as the production of gases will be slower than with water and thus avoid explosions (*cf.* Figure AI. 1).



Figure AI. 1. Picture taken while pouring deionized water on the remaining powder in a jar used to ball-mill a mixture of Mg(BH<sub>4</sub>)<sub>2</sub> and Mg(NH<sub>2</sub>)<sub>2</sub>. It illustrates the reactivity of these compounds and that they can lead to explosions if not manipulate with care.

#### AI.2 – Synthesis methods

#### AI.2a – Ball-milling

Ball-milling was used to perform mechanochemical syntheses and also to reduce the grains size of powders. Two kinds of ball-milling were used during this work: the planetary ball-milling and the Spex ball-milling. Planetary ball milling will produce frictions while the balls rolls on the walls of the jar and compression when the balls are projected from one side of the jar to the other. The Spex ball milling will mainly shake the balls and the powder describing a 3D 8-shape rotation. The planetary ball-milling was performed with a Retsch PM100 mill and a 50cm<sup>3</sup> tungsten carbide (WC) jar with 10 mm diameter WC balls. The ball-milling jar was sealed by a rubber o-ring encased in its cap which is tight together with the jar with a clamping bracket. The spex ball-milling was performed with a Spex 8000M mill. To perform the Spex ball-milling under NH<sub>3</sub> atmosphere, a 25 cm<sup>3</sup> stainless steel Spex jar equipped with a gas inlet was used (*cf.* Figure AI. 2). The atmosphere inside the jar was changed using the same montage than described here after for the annealing reactor. For Spex ball-milling under Ar, a jar without gas inlet was used. 8 mm diameter stainless steel balls were used. The Spex jars were airtight thanks to a rubber o-ring encased in the jar and tight with the cap using screws.



Figure AI. 2. Picture of the Spex jar equipped with a gas inlet.

#### AI.2b – Annealing under controlled atmosphere

Annealing was needed to crystallize samples or to promote chemical reactions. A stainless steel airtight reactor was used (*cf.* Figure AI. 3). The sealing of the reactor is ensured by a copper ring that is strongly tightened between the body of the reactor and the cap. The cap was equipped with a gas valve using graphite seals. With such reactor, the annealing can be performed at high temperature and under several bar of gas pressure. During this thesis, three different atmosphere of annealing had to be used: Ar, H<sub>2</sub> and NH<sub>3</sub>. To do annealing under Ar atmosphere, the atmosphere of the Ar filled glovebox in which the samples were loaded in the reactor was used. Then to place the reactor under different atmospheres, a montage was assembled. It was made of a vacuum pump and a gas inlet (H<sub>2</sub> or NH<sub>3</sub>), both connected to a series of pipes and valves. The montage allowed to vacuum the reactor up to  $1x10^{-5}$  bar. Then, by closing the valve of the vacuum and opening the one of the gas inlet, the reactor could be refilled without any air contamination.



Figure AI. 3. Picture of the stainless steel reactor used for our syntheses.

#### AI.3 – Structural analysis

#### AI.3a – Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was performed on Bruker D8 diffractometers using Co  $K_{\alpha 1}$ - $K_{\alpha 2}$  or Cu  $K_{\alpha 1}$ - $K_{\alpha 2}$  radiation in a  $\theta$ - $\theta$  configuration. For the measurements, the LeRiCh'S cell that has been developed in the lab was used.<sup>1</sup> It is airtight and uses a X-ray-transparent Be window.

The Fullprof suite was used to analyze our data. Le Bail method<sup>2</sup> (profile matching) was used to determine the unit cell parameters. Rietveld refinement<sup>3</sup> was used to get information on the complete crystalline structure of the unit cell and also to quantify the amount of phases present in some samples. For unknown structures, the software DICVOL<sup>4</sup> was used to find the symmetry of the unit cell and the software checkcell helped us to find the best space group based on the extinction rule.

To perform correctly the Rietveld refinements, the measured intensity had to be corrected from the absorption of the X-ray by the Be window. The correction was done with the Beer Lambert law:

$$I = I_0 \exp(-\mu x)$$
 Equation AI. 1

with I: the X-ray intensity after absorption

I<sub>0</sub>: the X-ray intensity before absorption

 $\mu$ : the mass absorption coefficient of Be (m<sup>-1</sup>)

x: the distance travelled by the X-ray in the Be window (m)

The mass absorption coefficient does not follow a linear behavior as a function of the photons wavelength so it has to be calculated for each radiation (*cf.* Figure AI. 4). The National Institute of Standards and Technology (NIST) provides a table corresponding to the mass absorption coefficient of Be for different photon energies.<sup>5</sup> It is from this table that can be calculated the mass absorption coefficient corresponding to the photons from Co ( $\lambda$  = 1.78897 Å, *i.e.* E = 6935 eV) and Cu ( $\lambda$  = 1.54060 Å, *i.e.* E = 8053 eV) sources:

$$\mu_{\lambda Co}$$
 = 29.9 m<sup>-1</sup> and  $\mu_{\lambda Cu}$  = 20.5 m<sup>-1</sup>

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Figure AI. 4. Mass absorption coefficient of Be for different values of photon energy.<sup>5</sup>

The distance x is determined by trigonometry knowing the angle of measure ( $\theta$ ) and the thickness of the Be window (h):

$$x = 2.\frac{h}{\sin(\theta)}$$
 Equation Al. 2

with h: thickness of the Be window (300  $\mu$ m)

θ: detector angle (°)



*Figure 3. Illustration of the path of the incident X-ray beam through the Be window during diffraction measurement.* 

#### AI.3b – Solid state MAS NMR spectroscopy

The solid state MAS NMR spectroscopy measurements were performed and analyzed at the CEMHTI in Orléans by Elodie Salager and Pierre Florian.

<sup>11</sup>B, <sup>15</sup>N, <sup>25</sup>Mg and <sup>1</sup>H solid-state MAS-NMR spectroscopy measurements were performed using a 20 T Avance III Bruker spectrometer operating at 272.7 MHz, 86.16 MHz, 52.05 MHz and 850 MHz, respectively. All samples were handled and packed in rotors in an Ar filled glovebox.

<sup>11</sup>B solid-state MAS-NMR spectroscopy measurements were performed using a 2.5 mm CP-MAS probe. The spectra were obtained at a magic angle spinning rate of 30 kHz under pure nitrogen at 278 K. The one pulse <sup>11</sup>B experiments were recorded with a RF power of 50 kHz and a short excitation pulse ( $<\pi/18$ ). Spinal-64 <sup>1</sup>H heteronuclear decoupling was applied at 100 kHz during acquisition (8 ms). All spectra are referenced to a 1 mol.L<sup>-1</sup> solution of B<sub>2</sub>O<sub>3</sub> set at 20.5 ppm and processed with a 3 Hz exponential broadening.

<sup>15</sup>N, <sup>25</sup>Mg and <sup>1</sup>H solid-state MAS-NMR spectroscopy measurements were performed using a 4 mm CP-MAS probe.

The <sup>15</sup>N experiments were recorded at a magic angle spinning rate of 14 kHz under pure nitrogen at 278 K using a <sup>1</sup>H-<sup>15</sup>N cross-polarization (CP) experiment with a contact time of 1.4 ms. Spinal-64 <sup>1</sup>H heteronuclear decoupling was applied at 50 kHz during the acquisition period (15 ms). The recycle delay was 1 s, for a total experiment time of approximately 15 h. All spectra are referenced to a (NH<sub>4</sub>)(NO<sub>3</sub>) sample set at 22 ppm and processed with a 50 Hz exponential broadening.

The <sup>25</sup>Mg and <sup>1</sup>H variable temperature experiments were recorded at a magic angle spinning rate of 10 kHz under pure nitrogen for temperatures ranging from -25°C to +100°C.

The <sup>1</sup>H spectra were recorded with a rotor-synchronized Hahn echo ( $\pi/2$ -tau- $\pi$ -tau) using a RF power of 110 kHz and a tau delay of 3 rotor periods. The recycle delay was 2 s, for a total experiment time of approximately 30 s. All spectra were referenced to pure TMS set at 0 ppm.

The <sup>25</sup>Mg signal was enhanced through a double-frequency sweep (DFS) followed by a rotor-synchronized Hahn echo. The Hahn echo pulses were performed using a RF power of 360 W (25 kHz for MgCl<sub>2</sub> solution). Spinal-64 <sup>1</sup>H heteronuclear decoupling was applied at 100 kHz during evolution (200µs) and acquisition (8 ms). The recycle delay was 1.5 s, for a total experiment time of approximately 5 hours. All spectra are referenced to a 1 mol.L<sup>-1</sup> solution of MgCl<sub>2</sub> set at 0 ppm.

Baseline correction and removal of the probe background were performed using a homemade Matlab program. The spectra were fitted with the DMfit software.<sup>6</sup>

NMR spectroscopy was used to identify the phases present in our compounds. From <sup>11</sup>B NMR spectroscopy, the measured chemical shift can be compared with the literature to know what is the environment around the B atoms. The full width at half maximum (FWHM) of the peaks gave us an information on the crystallinity of the present phases as a broad peak suggest that the phase is disordered and might be amorphous. Then <sup>15</sup>N NMR was performed to have more information on the structure of our phases. Finally, <sup>25</sup>Mg and <sup>1</sup>H NMR were performed in temperature to confirm that Mg<sup>2+</sup> was the mobile specie and not H<sup>+</sup>.

#### AI.3c – Infrared spectroscopy

Fourrier transform infrared (FTIR) spectroscopy was performed in transmission mode. In an argon filled glovebox, the samples were mixed with dried KBr powder and pelletized into thin transparent 13 mm diameter pellets. KBr is used as IR-transparent matrix to support our sample. The pellet is placed in an airtight sample holder that has two thick IR-transparent KCl windows. The measurements were performed on Nicolet iS10 spectrometer (Thermo Scientific company) from 4000 to 600 cm<sup>-1</sup> with 100 spectra recorded by measurement.

The infrared spectroscopy gave us information on the B-H and N-H bonds in the different samples. It also indicates if some impurities such as –OH groups are present in our samples. These information are given by the vibration that are observed and by their wavenumbers.

#### AI.4 – Thermal analysis

The thermal analysis measurements were performed by Matthieu Courty (LRCS, Amiens).

#### AI.4a – Differential scanning calorimetry

The differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC 204 F1 heat flux differential calorimeter at a heating rate of 5°C.min<sup>-1</sup> under a constant argon flow of 50 mL.min<sup>-1</sup>. The samples were placed in aluminum crucibles which were sealed in a Ar filled glovebox and their lids were pierced under argon flow prior to the measurement to allow gas release upon heating. The onset and starting temperatures of the heat flow peaks were determined with the software Proteus Analysis. The same software was used to measure the enthalpy of each thermal phenomenon.

The DSC tells us if the samples will undergo exothermic or endothermic thermal phenomena. To determine at which temperature a thermal phenomenon occurs, three values can be defined: the starting temperature ( $T_{onset}$ ), the temperature at the maximum of the peak ( $T_{max}$ ) and the finishing temperature ( $T_{offset}$ ). The DSC also gives the enthalpy of each phenomenon by integration of the area under each peak.



*Figure 4. Illustration of a DSC peak with its characteristic temperatures.* 

#### AI.4b – Thermal gravimetric analysis

Thermogravimetric analyses (TGA) coupled with differential thermal analysis (DTA) and gas mass spectrometry (MS) were performed between 25°C and 190°C under a constant flow of dry argon (50 mL/min) using a Simultaneous Thermal Analyzer STA 449C Jupiter/ STA 449F3 from Netzsch, and a heating/cooling rate of 1 K/min. The isothermal drift and sensitivity values are 0.6  $\mu$ g/h and 0.1  $\mu$ g, respectively. Alumina (or Platinum with an Al<sub>2</sub>O<sub>3</sub> insert) crucibles were loaded with 3-6 mg of sample powder in an Ar filled glovebox.

The MS was done on a quadrupole QMS403D Aëolos<sup>®</sup> mass spectrometer with a stainless steel capillary heated at 230°C and a SEV detector (Channeltron). The counting time for mass spectrometer is of 20 ms per m/z values (scanning width: m/z = 1-100) with a resting time of 1 s. This measurement was performed under Ar atmosphere in a glovebox. The mass spectrometry (MS) was coupled to the TGA measurements to identify any gas molecule that would be released. At the entrance of the device, the gases are ionized and then separated by their mass-to-charge ratio (m/z).

#### AI.5. Electrochemical analysis

#### AI.5a – Electrochemical Impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were realized with a MTZ-35 frequency response analyzer (BioLogic Company) coupled with an Intermediate Temperature System (ITS) controlling the sample temperature by Peltier effect. Pellets of our samples were loaded in a Controlled Environment Sample Holder (CESH) in which two gold discs are the electrodes. Papyex discs (flexible graphite previously dried under vacuum at 150°C) were placed on both side of the pellets to improve the electrical contact between the gold electrodes and the pellets. The combined Papyex foil and gold disk ensure an ion blocking electrode. Once the sample is loaded, the CESH was placed in the ITS. AC impedance spectra were recorded in the frequency range from 30 MHz to 500 mHz with an excitation signal of 50 mV amplitude and from 50°C to 100°C upon heating and cooling (1°C.min<sup>-1</sup>) with a temperature stabilization of 15 min before impedance measurement every 10°C. The results shown are the one recorded upon cooling. At the beginning of this thesis, the samples were cold pressed into pellets of 13 mm diameter under a pressure of 6 tons with 100 mg of powder per pellet. A thickness of about 0.8 mm was obtained, corresponding to a density close to 95% of the crystalline density in the case of Mg(BH<sub>4</sub>)(NH<sub>2</sub>) (calculated from the crystallographic density: 0.9966 g.cm<sup>-3</sup>). The pellets were simply sandwiched between two Papyex foils. Later, the pellets were prepared with a 6 mm diameter die in which they were cold pressed directly between two Papyex foils. With this method, the Papyex foils are stuck to the solid electrolyte. It improves a lot the contacts and thus the quality of the measurements. It also needs less powder as only 30 mg of powder was pressed under 2 tons for a final thickness of about 1.1 mm, so also a density close to 95% in the case of Mg(BH<sub>4</sub>)(NH<sub>2</sub>).

The following equation was used to determine the ionic conductivity of our materials from EIS measurements:

$$\sigma = \frac{1}{R} \cdot \frac{l}{S}$$
 Equation AI. 3

with  $\sigma$ : is the conductivity (S.cm<sup>-1</sup>)

R: is the resistance ( $\Omega$ )

I: the thickness of the pellet (cm)

S: the cross-sectional area of the pellet (cm<sup>2</sup>)

The value of the resistance is obtained from the Nyquist diagram that is fitted with the proper model. For the measurement of a solid electrolyte between two blocking electrodes, a Nyquist plot as shown on Figure AI. 5a is obtained. The semicircle at high frequency is due to the bulk ionic conduction of the solid electrolyte. The following straight line is due to the capacitance formed by the contact with the blocking electrodes. The diameter of the semi-circle is the resistance R. The experimental data are fitted with an equivalent circuit model. The resistance of the external electrical circuit is modelled by a resistance R0 in series with a R1//CPE1 which model the ionic conductivity in the solid electrolyte and a CPE2 that models the capacitance formed by the blocking electrodes on both sides of the solid electrolyte (*cf.* Figure AI. 5). Constant phase elements (CPE) had to be used instead of ideal capacitances to model the roughness of the contacts between the solid electrolyte and the blocking electrodes. The impedance of a real capacitance would be expressed as:

$$Z_{Creal} = \frac{1}{j.C.\omega}$$
 Equation AI. 4

with C: the capacitance (F)

 $\omega = 2. \pi. f$ : the angular frequency (rad.s<sup>-1</sup>)

While the impedance of a CPE is expressed as:

$$Z_{CPE} = \frac{1}{Y_0.(j.\omega)^n}$$
 Equation AI. 5

#### with Y<sub>0</sub>: a prefactor

n: a factor comprised between 0 and 1, depending on the surface roughness or a nonuniform current distribution

Before to start fitting, the model needs to be fed with approximate values for R1 and CPE1. If R1 is difficult to approximate from the Nyquist plot, it can be extracted from the Bode plot. Indeed, the maximum on the Bode plot corresponds to the end of the semicircle (*cf.* Figure AI. 5b). Knowing the frequency at which is the maximum on Bode plot allows to find the point corresponding to this frequency on the Nyquist plot and thus to find R1. For the capacitance value, the point at the top of the semi-circle has to be used. At this specific point, the cut-off frequency is reached. This frequency is linked to the resistance R1 and the capacitance C1 by the relation:

$$f_{cut-off} = \frac{1}{2.\pi.R1.C1}$$
 Equation AI. 6

From Equation AI. 6, C1 can be calculated knowing R1 and  $f_{cut-off}$ . This value of C1 can be used as starting parameter for the CPE1, putting  $Y_0 = C1$  and n = 1.



Figure AI. 5. Typical a) Nyquist and b) Bode plots obtained for the measurement by EIS of a solid electrolyte with two blocking electrodes. c) The equivalent circuit used to simulate the data of the Nyquist and Bode plots.

From the fitting of the data, other information than the resistance R can be extracted. The real capacitance C linked to the ionic conduction phenomenon can be obtained. It is calculated from the real parts of Equation AI. 4 and Equation AI. 5:

$$R = \frac{1}{C.\omega}$$
 and  $R = \frac{1}{Y_{0}.\omega^{n}}$  Equation AI. 7  
Equation AI. 8

From Equation AI. 7 and Equation AI. 8 the relationship between the parameters of the CPE ( $Y_0$  and n) and the real Capacitance (C) is obtained:

$$C = R^{\frac{1-n}{n}} Y_0^{\frac{1}{n}}$$
 Equation AI. 9

The value of the real capacitance will change depending on the conduction phenomenon happening. The ionic conduction in the bulk and in the grain boundaries can be differentiated for instance as it is described in Chapter II.

The ionic conductivity should follow an Arrhenius law. Plotting the logarithm of the ionic conductivity values as a function of the reverse of the temperature gives us access to the activation energy of the ionic motion in our solid electrolyte. Indeed, the ionic conductivity in a solid electrolyte is given by the equation:

$$\sigma = \frac{\sigma_0}{T} \cdot \exp\left(\frac{-Ea}{k_B \cdot T}\right)$$
 Equation Al. 10

with  $\sigma_0$ : a constant (K.S.cm<sup>-1</sup>)

Ea: the activation energy of the ionic conductivity (eV)

A linear fit of  $\ln(\sigma.T)$  as a function of 1/T give us access to the activation energy Ea from the slope which is equal to Ea/k<sub>B</sub>.

#### AI.5b – Polarization

Galvanostatic cycling with potential limit (GCPL) was performed using a VSP potentiostat (Biologic company) equipped with a low current channel allowing us to work with current as low as the nA. The current was applied with a positive and negative alternatively for 2h and each polarization was separated by a 5 min rest. This resting time is used to remove the accumulate charges at the interfaces. The assembly of the stacks was hardly reproducible so the current density was set at a value for which the polarization would be at reasonable potential that is the reason why it was changed from a cell to another. As our electrolytes have interesting ionic conductivities only at elevated temperature, it was necessary to perform electrochemical measurements at 100°C with a specific cell. A high temperature electrochemical cell has been developped in our lab.<sup>7</sup> This cell is based on the design of swagelock cells. It is made of a glass tube that is closed on both side with swagelocks cells using teflon rings for sealing (*cf.* Figure AI. 6a). The sample is placed in the middle of the glass tube where it is squeezed between two long

plungers. The pressure in the cell is maintained by a spring placed at the back of one of the plunger. The glass part of the cell is placed in a homemade tubular oven that heats only the middle of the cell and hence avoids the warming up of the teflon rings that could be detrimental to the sealing. For the polarization measurements, a 10 mm diameter cold pressed pellet of a thickness of about 0.5 mm is placed between two 10 mm diameter discs of cold pressed Mg powder. In this configuration, the open circuit voltage (OCV) should be close to 0 V vs Mg<sup>2+</sup>/Mg. Nevertheless, for the first tries, the OCV was very unstable as shown on Figure AI. 6b and the measure was very noisy (*cf.* Figure AI. 6c). It was observed that the spring used previously was actually too stiff so when the cell was tight, the strength of the spring was large enough to push one of the swagelock parts that slid along the glass tube. It leads to the decompression of the cell making the contacts between the different parts of the stack very bad and that is the reason why the signal was so noisy. To avoid this, the initial spring was replaced by a less stiff one and it results in a perfect conservation of the mechanical pressure applied to the stack. After this change, the OCV of the cells was much more stable and the measurement had almost no noise (*cf.* Figure AI. 6b and d).



Figure AI. 6. a) Design of the high temperature electrochemical cell. b) Typical open circuit voltage (OCV) before and after optimization by changing the spring of the electrochemical cell. Polarization measurement c) before and d) after optimization.

The polarization measurements with symmetrical cells were used to determine the compatibility between the anode and the solid electrolyte. A stable interface should result in a stable polarization. If it is not the case, the polarization potential will increase and evolve in

different ways depending on the phenomena occurring at the interface (dendrite or foam formation, degradation of the solid electrolyte, lost of contacts, *etc.*).

#### AI.5c – Cyclic voltammetry

The cyclic voltammetry (CV) measurements were performed with a VSP potentiostat (Biologic company) with a scanning rate of 0.05 mV.s<sup>-1</sup> at 100°C using the high temperature electrochemical cell presented in the previous subsection. The samples were prepared in an argon filled glovebox where 20 mg of solid electrolyte were poured in a 6 mm diameter die, a first low pressure of 0.5 ton was applied only with the plunger of the die to tamp the powder. Then, the plunger was taken out and 10 mg of a composite electrode made of the solid electrolyte and carbon black (90:10 wt%) mixed by hand in an agate mortar was poured on the top of the tamped solid electrolyte in the die. A pressure of 2 tons was applied to obtain a dense pellet made on one side of the solid electrolyte and on the other side of the composite electrode (cf. Figure AI. 7). The fact to tamp the solid electrolyte in the die before to introduce the composite electrode ensure that there will be no carbon of the composite electrode passing on the other side of the pellet which would cause a short circuit. The side of the pellet made only of solid electrolyte is placed on a disc made from cold pressed Mg powder. They are stacked in the electrochemical cell where the pressure applied by a spring ensures the contact between them. As for polarization measurements, the CV measurements were hard to realize so the parameters as the voltage window or current range had to be modified depending on the cell (see chapter IV).

Cyclic voltammetry measurements were performed to measure the electrochemical stability window of our solid electrolytes. By measuring anodic and cathodic currents, it is possible to know at which potential our solid electrolytes are oxidized and/or reduced. If a measured electrochemical reaction is reversible, its coulombic efficiency can be calculated from a plot where the current is plotted as a function of time. On this plot, the area under the peak of oxidation or reduction gives the capacity of the electrochemical reaction in Ah. The coulombic efficiency of a reaction is the ratio between the measured areas of the reduction and oxidation during the same cycle.

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**Carbon foil Composite electrode** Solid electrolyte + carbon (90:10) Solid electrolyte

Mg

Figure AI. 7. Scheme of the assembling used to measure the electrochemical stability window by cyclic voltammetry.

#### References

- 1. Leriche, J. B. *et al.* An electrochemical cell for operando study of lithium batteries using synchrotron radiation. *J. Electrochem. Soc.* **157**, A606 (2010).
- 2. Le Bail, A. Whole powder pattern decomposition methods and applications: A retrospection. *Powder Diffr.* **20**, 316–326 (2005).
- 3. Rietveld, H. M. A profile refinement method for nuclear and magnetic structures. *J. Appl. Crystallogr.* **2**, 65–71 (1969).
- 4. Boultif, A. & Louër, D. Indexing of powder diffraction patterns for low-symmetry lattices by the successive dichotomy method. *J. Appl. Crystallogr.* **24**, 987–993 (1991).
- NIST: X-Ray Mass attenuation coefficients Beryllium. Available at: https://physics.nist.gov/PhysRefData/XrayMassCoef/ElemTab/z04.html. (Accessed: 12<sup>th</sup> November 2019)
- 6. Massiot, D. *et al.* Modelling one- and two-dimensional solid-state NMR spectra. *Magn. Reson. Chem.* **40**, 70–76 (2002).
- 7. Lalère, F. *et al.* An all-solid state NASICON sodium battery operating at 200°C. *J. Power Sources* **247**, 975–980 (2014).

#### Annex I – Experimental methods

## <u>Annex II</u> – Extra data

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## All.1 – Neutron diffraction of the $\alpha$ -phase for x = 0.25

Neutron diffraction was used to try to differentiate the position of  $(BH_4)^-$  to the one of  $(NH_2)^$ anions in the structure of the  $\alpha$ -phase obtained for x = 0.25 (*cf.* Chapter III). Indeed, from powder X-ray diffraction, it is difficult to differentiate the positions of these two anions, especially because they contain the same number of electrons (9 electrons). By neutron diffraction, B and N should be clearly identified as they have a large difference of neutron absorption, 679.977 and 1.684 barn respectively.

The samples were sent to the ILL (Institut Laue-Langevin) in Grenoble and the diffraction measurements were performed by Emmanuel Suard with the beam line D2B (high resolution neutron powder diffractometer). The wavelength was 1.594 Å with a high flux resolution. The sample was placed in a 5.5 mm diameter vanadium tube sealed in an Ar filled glovebox.

Unfortunately, the measurement resulted in a quasi-total absorption of the neutrons and no diffraction was obtained (*cf.* Figure AII. 1). This strong absorption is due to the presence of incoherently scattering H and strongly absorbing B.



Figure All. 1. Neutron diffraction pattern of the  $\alpha$ -phase for x =0.25.

Annex II – Extra data

## All.2 – Structural analysis of the $\beta$ -phase for x = 0.25

The  $\beta$ -phase obtained after annealing at 170°C of the  $\alpha$ -phase for x = 0.25, crystallizes in an unreported crystalline structure. The only symmetry found for the  $\beta$ -phase was monoclinic. On Figure AII. 2, the XRD pattern of the  $\beta$ -phase for x =0.25 is fitted by profile matching using the monoclinic space group P2/m. The obtained cell parameters are a = 21.522(2) Å, b = 11.7689(5) Å, c = 10.428(5) Å, V = 2437.9(3) Å<sup>3</sup> and  $\beta$  = 112.625(3) °. They are similar to the tetragonal unit cell of the  $\alpha$ -phase for x = 0.25 (s.g.: I4<sub>1</sub>/acd, a = 11.0330(6) Å, c = 21.968(3) Å and V = 2674.2(4) Å<sup>3</sup>) but for the  $\beta$ -phase, the volume is slightly smaller and the  $\beta$  angle is deformed to 112.625(3) °. So the transition from  $\alpha$  to  $\beta$  could be related to a shrinkage of the unit cell along with a monoclinic deformation. Nevertheless, too many Bragg's positions of this space group do not correspond to experimental reflections. Further work is needed to find a more adequate space group and to fully solve the crystal structure.



Figure AII. 2. XRD pattern and profile matching of the  $\beta$ -phase for x = 0.25.

Annex II

Dans un monde qui consomme de plus en plus d'électricité, les batteries rechargeables jouent un rôle clé. Jusqu'à présent, elles étaient principalement utilisées pour l'électronique mobile mais de nouvelles demandes commencent à émerger de la part d'autres applications, notamment de la part des véhicules électriques. Ces derniers pourraient remplacer la majorité du parc automobile utilisant des moteurs à combustion dans les prochaines décennies. La production de batteries rechargeables pourrait aussi être accélérée par leur utilisation dans le domaine des énergies renouvelables. En effet, les énergies renouvelables sont pour la plupart intermittentes (solaire, éolien, *etc.*) et doivent donc être stockées pour permettre une utilisation continue de l'électricité.

Aujourd'hui, les batteries rechargeables les plus couramment utilisées sont les batteries Liion. Cette hégémonie est due à leur densité d'énergie qui est la plus élevée de toutes les technologies existantes (jusqu'à 200 Wh.kg<sup>-1</sup>). Leur fort impact sur la société à conduit à l'attribution du Prix Nobel de Chimie 2019 à John B. Goodenough, Stanley Whittingham et Akira Yoshino pour le développement des batteries Li-ion. Cette technologie est tellement versatile que sa production massive commence à créer des problèmes de développement durable. Des éléments tels que le cobalt, qui est utilisé dans les matériaux de cathode de la plupart des batteries Li-ion commerciales, sont rares et seulement présents dans certaines régions du monde. Pour ces raisons, leur prix et leur disponibilité peuvent fluctuer de façon importante. Des solutions sont à l'étude pour substituer ces éléments par des éléments plus abondants ou pour les remplacer totalement et dans ce cas utiliser des technologies dites post-Li-ion tel que les batteries Li-S. Audelà des batteries basées sur le lithium, d'autres technologies sont étudiées. Comme celles basées sur d'autres ions monovalents comme Na<sup>+</sup> ou K<sup>+</sup>. D'autres systèmes basés sur des ions multivalents comme Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup> ou Al<sup>3+</sup> sont aussi étudiés. Parmi ces éléments, le magnésium a été celui qui a attiré le plus l'attention durant les vingt dernières années.

Les batteries Mg rechargeables sont étudiées depuis le début des années 90 mais c'est seulement en 2000 qu'une cellule fonctionnelle fut assemblée par Aurbach *et al.*. Néanmoins, cette première cellule ne pouvait pas délivrer une importante quantité d'énergie. D'importants efforts ont été faits par la communauté scientifique pour concevoir de meilleures cellules qui puissent atteindre de grandes capacités ainsi que des hautes tensions pendant de nombreux cycles. Les principaux problèmes rencontrés proviennent des difficultés à trouver des matériaux de cathode qui permettent une insertion rapide des ions Mg<sup>2+</sup> et des électrolytes présentant une bonne conductivité ionique tout en possédant une large fenêtre de stabilité électrochimique. En

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vue d'améliorer les batteries Mg rechargeables, notre approche fut d'étudier la possibilité d'utiliser des électrolytes solides. En effet, les électrolytes solides pourraient être bénéfiques en termes de stabilité chimique et électrochimique et en termes de sécurité. Les candidats comme électrolytes solides ont été choisis parmi les conducteurs ioniques solides inorganiques de Mg<sup>2+</sup> existants (sans les conducteurs mixtes tels que les matériaux d'électrode). Très peu de matériaux sont rapportés du fait de la difficulté qu'ont les ions Mg<sup>2+</sup> à se mouvoir dans les solides. Ces matériaux sont listés dans le Chapitre I et ils peuvent être séparés en trois familles : les phosphates, les sulfures et les hydrures complexes. Les phosphates, basés sur Mg-Zr-PO<sub>4</sub>, ont des conductivités ioniques élevées mais seulement à hautes températures, typiquement ~10<sup>-3</sup> S.cm<sup>-1</sup> à 800°C. Ensuite, les sulfures, basés sur des verres du type MgS-P<sub>2</sub>S<sub>5</sub>, ont de trop faibles conductivités ioniques (~10<sup>-7</sup> S.cm<sup>-1</sup> à 200°C) pour être intéressants en tant qu'électrolytes solides. Finalement, les hydrures complexes, basés sur Mg(BH<sub>4</sub>)<sub>2</sub>, ont les meilleures conductivités ioniques à basses températures (~10<sup>-5</sup>-10<sup>-6</sup> S.cm<sup>-1</sup> en dessous de 150°C). De plus, ce sont les seuls matériaux qui ont été réellement caractérisés dans le but de les utiliser dans des batteries Mg (e.g. mesures de dépôt/dissolution du Mg, fenêtre de stabilité électrochimique, etc.). Il a donc été décidé de commencer notre étude avec Mg(BH<sub>4</sub>)(NH<sub>2</sub>) qui était rapporté comme un conducteur ionique solide prometteur pour les ions Mg<sup>2+</sup>.

Mg(BH<sub>4</sub>)(NH<sub>2</sub>) fut décrit pour la première fois par Noritake *et al.* en 2013. Ils le synthétisèrent à partir de Mg(BH<sub>4</sub>)<sub>2</sub> et Mg(NH<sub>2</sub>)<sub>2</sub> mais ils ne donnèrent aucun des paramètres de synthèse (vitesse de broyage, temps et température de recuit, *etc.*). Il a donc fallu dans un premier temps trouver les paramètres adéquats pour cette synthèse en testant différentes vitesse de broyage et différents temps, atmosphères et températures de recuit (*cf.* **Chapitre II**). L'échantillon le plus pur fut obtenu avec un broyage à 500 tr/min pendant 1 h et un recuit ultérieur à 120°C pendant 72 h sous 10 bar de H<sub>2</sub>. Le diffractogramme de cet échantillon montre seulement Mg(BH<sub>4</sub>)(NH<sub>2</sub>) qui cristallise dans le groupe d'espace I4<sub>1</sub>/acd avec Z = 8 et les paramètres de mailles a = 5.768(5) Å, c = 20.486(2) Å, et V = 681.6(1) Å<sup>3</sup> qui sont en adéquation avec ceux de la littérature. Lors de l'optimisation de la synthèse, des échantillons composites de Mg(BH<sub>4</sub>)(NH<sub>2</sub>) et d'une phase additionnelle cristalline inconnue furent obtenues. Des mesures par spectroscopie <sup>11</sup>B MAS-RMN révélèrent que même dans les échantillons ne présentant que Mg(BH<sub>4</sub>)(NH<sub>2</sub>) cristallin par diffraction des rayons X (DRX), la phase additionnelle subsistait mais elle était amorphe.

La teneur en phase additionnelle déterminée par spectroscopie RMN influence fortement la conductivité ionique. L'échantillon contenant principalement la phase additionnelle (73%) a une conductivité ionique de 8.10<sup>-8</sup> S.cm<sup>-1</sup> à 100°C avec une énergie d'activation de 1.3 eV; tandis que l'échantillon contenant le moins de phase additionnelle (20%) a une conductivité ionique de 1x10<sup>-</sup> <sup>5</sup> S.cm<sup>-1</sup> à 100°C avec une énergie d'activation de 1.0 eV. Cette dernière valeur de conductivité ionique est quatre ordres de grandeur supérieure à celle rapportée par Higash et al. (~10-9 S.cm-1 à 100°C et Ea = 1,31 eV). Deux hypothèses peuvent être émises pour expliquer cette différence. Pour la première hypothèse, le matériau de Higashi et al. est considéré comme étant Mg(BH<sub>4</sub>)(NH<sub>2</sub>) pur à 100%. Dans ce cas, la présence de la phase additionnelle dans nos échantillons composites améliorerait la conductivité ionique. En particulier, une fois qu'elle devient amorphe, elle forme un matériau de type vitrocéramique augmentant la mobilité de Mg<sup>2+</sup>. Pour la deuxième hypothèse, la phase supplémentaire a en fait un effet négatif sur la mobilité de Mg<sup>2+</sup>. En effet, il a été observé dans notre étude que moins elle est présente et plus la conductivité ionique est élevée. Dans ce deuxième cas de figure, le matériau de Higashi et al. contiendrait une quantité importante de phase additionnelle amorphe, diminuant sa conductivité ionique. Pour valider l'une de ces deux hypothèses, une description précise des paramètres de synthèse utilisés par Higashi et al. et des mesures de spectroscopie <sup>11</sup>B RMN sur leur échantillon auraient été très utiles. Cependant, dans les deux cas, la phase additionnelle a clairement un impact sur la conductivité ionique et il était important d'essayer de l'obtenir pure. Comme elle contient des anions (BH<sub>4</sub>)<sup>-</sup> observés par spectroscopie RMN, qu'il ne s'agit pas d'un produit de décomposition et qu'elle a été obtenu pour des synthèse non optimisées, il a été supposé qu'il s'agissait en réalité d'un composé du type  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$ .

Par la suite, pour tenter d'identifier cette phase additionnelle et pour identifier de nouveaux conducteurs ioniques de Mg<sup>2+</sup>, le diagramme de phases binaire Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> fut exploré (*cf.* **Chapitre III**). Trois nouvelles phases cristallines de type Mg(BH<sub>4</sub>)<sub>2</sub>x(NH<sub>2</sub>)<sub>2(1-x)</sub> furent découvertes. Deux phases avec une composition riche en amidure, appelées phase  $\alpha$  et phase  $\beta$ . La phase  $\alpha$  cristallise avec la même structure cristalline que Mg(NH<sub>2</sub>)<sub>2</sub>, dans laquelle les anions (BH<sub>4</sub>)<sup>-</sup> se substituent aux (NH<sub>2</sub>)<sup>-</sup>. Cette substitution conduit à une expansion de la maille cristalline et à une amélioration de la conductivité ionique, passant de 4x10<sup>-9</sup> S.cm<sup>-1</sup> pour x = 0.17 à 1x10<sup>-8</sup> S.cm<sup>-1</sup> pour x = 0,25. En montant en température, la phase  $\alpha$  subit une transition structurale endothermique irréversible formant la phase  $\beta$ . La phase  $\beta$  cristallise dans une nouvelle structure cristalline  $\sigma_{100^{\circ}C} = 2x10^{\cdot8}$  S.cm<sup>-1</sup>, et l'énergie d'activation de la conductivité ionique augmente de 1.7 eV à 2.0 eV. Pour x = 0,33, avec un broyage à 600 tr/min, la phase  $\beta$  fut obtenue mal cristallisée. La conductivité ionique à 100°C de ce dernier composé est améliorée car elle atteint 2x10<sup>-7</sup> S.cm<sup>-1</sup> et son énergie d'activation est de 1.6 eV. La phase  $\beta$  pourrait être la phase additionnelle présente dans les matériaux composites décrits dans le chapitre II lors de la synthèse de Mg(BH<sub>4</sub>)(NH<sub>2</sub>). En

effet, pour les échantillons avec la phase additionnelle cristalline, les diagrammes DRX et les valeurs de conductivité ionique sont similaires, même si la valeur de Ea de la phase  $\beta$  est plus élevée. Cette observation confirmerait la deuxième hypothèse que nous avons faite précédemment, pour laquelle il est considéré que la présence de la phase additionnelle diminue la conductivité ionique des matériaux composites.

Une autre phase cristallise dans la région riche en borohydrures, elle a été appelée la phase y. Elle a une structure tétragonale avec le groupe d'espace I-4. Comme pour la phase  $\alpha$ , l'ajout d'anions (BH<sub>4</sub>)<sup>-</sup> dans ce composé augmente le volume de la maille, mais diminue ici la conductivité ionique. La phase y présente des valeurs de conductivité ionique élevées qui diminuent avec x tandis que l'énergie d'activation augmente. Le meilleur conducteur ionique est y-Mg(BH<sub>4</sub>)<sub>1.33</sub>(NH<sub>2</sub>)<sub>0.67</sub> (qui peut également s'écrire  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>) avec une conductivité ionique à 100°C de 4x10<sup>-5</sup> S.cm<sup>-1</sup> et une énergie d'activation de 0.8 eV. Ces valeurs signifient que ce matériau présente l'une des meilleures mobilités des ions Mg<sup>2+</sup> dans un conducteur ionique solide inorganique jamais rapportées. La bonne mobilité des ions Mg<sup>2+</sup> a été confirmée par spectroscopie  $^{25}$ Mg RMN-MAS avec un affinement significatif du pic de RMN lors du chauffage. La phase y présente également une bonne stabilité thermique, aucun événement thermique ni aucune perte de masse n'ayant été détecté en dessous de 190°C. Un pseudo-diagramme de phases binaire Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> a été proposé. Il nous aide à comprendre la complexité de ce système. Une tendance a également été observée pour la conductivité ionique puisqu'un maximum est atteint pour  $\gamma$ -Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>. Cette tendance se poursuit même si la structure cristalline change. De bons conducteurs ioniques pour ions Mg<sup>2+</sup> ont été trouvés dans ce diagramme de phases binaire, mais ils devaient encore être caractérisés en tant qu'électrolytes solides pour savoir s'ils pourraient être utilisés dans des batteries Mg.

Deux des meilleurs conducteurs ioniques trouvés dans le diagramme de phases Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> furent caractérisés comme possibles électrolytes solides: Mg(BH<sub>4</sub>)(NH<sub>2</sub>) et γ-Mg<sub>3</sub>(BH<sub>4</sub>)<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub> (*cf.* **chapitre IV**). Premièrement, ils ne réagissent pas avec le carbone utilisé comme additif conducteur et ils ne réagissent pas non plus avec les matériaux d'anode: Mg et Bi. Cependant, ils réagissent avec le matériau de cathode Mo<sub>6</sub>S<sub>8</sub>. Au contact de Mo<sub>6</sub>S<sub>8</sub>, ils ont été oxydés pour former Mg<sub>2</sub>Mo<sub>6</sub>S<sub>8</sub> et des produits de décomposition amorphes. La compatibilité de Mg(BH<sub>4</sub>)(NH<sub>2</sub>) avec l'anode de Mg a également été testée par une mesure de polarisation dans une cellule symétrique utilisant des électrodes de Mg. Une grande résistance interfaciale a été observée. Cela pourrait s'expliquer par un mauvais contact entre l'électrolyte solide et Mg, notamment parce que Mg est un métal dur qui adhère très mal à l'électrolyte solide. La résistance

interfaciale augmente au fur et à mesure des cycles, indiquant son instabilité lors du dépôt/dissolution du Mg. La même expérience a été réalisée avec des électrodes «Mg<sub>3</sub>Bi<sub>2</sub> + Bi», mais malheureusement, la résistance interfaciale était encore plus grande que celle avec Mg. La résistance interfaciale a augmenté lors du cyclage, ce qui pourrait être causé par le changement important de volume entre Mg<sub>3</sub>Bi<sub>2</sub> et Bi. Les fenêtres de stabilité électrochimiques des deux électrolytes solides ont été mesurées par voltammétrie cyclique. Le dépôt/dissolution du Mg est observé autour de 0 V vs. Mg<sup>2+</sup>/Mg, ce qui représente un résultat positif car il a été très rarement rapporté pour un conducteur ionique solide d'ions Mg<sup>2+</sup>. L'oxydation des électrolytes solides commence à environ 1.0 V vs. Mg<sup>2+</sup>/Mg. Le potentiel d'oxydation n'est pas affecté par la composition de la phase étudiée.

En résumé, l'exploration du diagramme de phases  $Mg(BH_4)_2-Mg(NH_2)_2$  nous a permis de découvrir de nouveaux conducteurs ioniques inorganiques solides de  $Mg^{2+}$ . Une tendance apparaît entre la conductivité ionique et la composition de ces matériaux. L'un d'eux atteint l'une des conductivités ioniques les plus élevées jamais rapportées pour un conducteur ionique inorganique pour ions  $Mg^{2+}$  (4x10<sup>-5</sup> S.cm<sup>-1</sup> à 100°C) et possède également l'une des énergies d'activation les plus basses (0.8 eV). Des études cristallographiques plus approfondies (diffraction des rayons X par rayonnement synchrotron) et théoriques (DFT) pourraient aider à comprendre cette tendance. Elle peut dépendre de la structure cristalline (chemin de diffusion des ions  $Mg^{2+}$ ) et de la substitution des anions  $(NH_2)^-$  par  $(BH_4)^-$  (interaction des ions  $Mg^{2+}$  avec leur environnement). La compréhension de cette tendance dans ce diagramme de phases binaires pourrait permettre de trouver de meilleurs conducteurs ioniques de  $Mg^{2+}$ .

## Résumé

Cette thèse porte sur l'identification de nouveaux conducteurs d'ions Mg<sup>2+</sup> inorganiques pour les utiliser en tant qu'électrolyte solide dans des batteries Mg. Le choix a été fait d'étudier les composés du diagramme de phases binaire Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub>. Dans ce diagramme, seuls les composés Mg(BH<sub>4</sub>)<sub>2</sub>, Mg(NH<sub>2</sub>)<sub>2</sub> et Mg(BH<sub>4</sub>)(NH<sub>2</sub>) étaient connus. Mg(BH<sub>4</sub>)(NH<sub>2</sub>) avait été rapporté comme un bon conducteur ionique mais ses paramètres de synthèse n'étaient pas rapportés. Dans un premier temps, il a donc fallu déterminer les paramètres de synthèse nécessaires pour l'obtention de Mg(BH<sub>4</sub>)(NH<sub>2</sub>). Après avoir tester différentes vitesses de broyage, différents temps, atmosphères et températures de recuit, Mg(BH<sub>4</sub>)(NH<sub>2</sub>) a pu être obtenu. Au cours des différentes optimisations des paramètres de synthèse, une phase additionnelle inconnue fut identifiée. Cette phase a une influence importante sur la conductivité ionique des échantillons. L'hypothèse fut faite que cette phase était en fait un composé du type  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$ . A partir des paramètres de synthèse déterminés précédemment, de nouvelles synthèses furent réalisées avec différentes stœchiométries. Trois nouvelles phases cristallines du type Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> purent être identifiées et une tendance fut observée entre la stœchiométrie et la conductivité ionique des phases. Un maximum est atteint pour x = 0.67 avec une conductivité de  $4x10^{-5}$  S.cm<sup>-1</sup> à 100°C, ce qui représente l'une des meilleures conductivités ioniques pour Mg<sup>2+</sup> jamais mesurée dans un solide inorganique. Les propriétés d'électrolyte solide des meilleurs conducteurs ioniques identifiés lors de ces travaux furent caractérisées. Il apparut que ces composés ne sont pas stables à hauts potentiels. Ils commencent à s'oxyder aux alentours de + 1.0 V vs.  $Mg^{2+}/Mg$ . Néanmoins, ils sont stables vis-à-vis de Mg et permettent son dépôt et sa dissolution électrochimique.

Mots clés : batteries magnésium, électrolyte solide, hydrures complexes, conducteurs ioniques solides, stockage de l'énergie

### Abstract

This PhD thesis concerns the identification of new Mg<sup>2+</sup> inorganic solid ionic conductors for possible use as solid electrolytes in Mg batteries. The choice was made to study the compounds from the Mg(BH<sub>4</sub>)<sub>2</sub>-Mg(NH<sub>2</sub>)<sub>2</sub> binary phases diagram. In this phases diagram, only Mg(BH<sub>4</sub>)<sub>2</sub>, Mg(NH<sub>2</sub>)<sub>2</sub> and  $Mg(BH_4)(NH_2)$  were known.  $Mg(BH_4)(NH_2)$  was reported previously as a good ionic conductor but its synthesis parameters were unknown. First, it was necessary to determine the synthesis parameters of Mg(BH<sub>4</sub>)(NH<sub>2</sub>). After testing different ball milling speeds, and different annealing times, atmospheres and temperatures,  $Mg(BH_4)(NH_2)$  could be obtained. During the optimization of the synthesis parameters, an unknown additional phase was identified. This phase has a strong influence on the ionic conductivity of the samples. The hypothesis was made that it was actually a  $Mg(BH_4)_{2x}(NH_2)_{2(1-x)}$ type compound. From the synthesis parameters determined previously, new synthesis were performed with different stoichiometries. Three new crystalline Mg(BH<sub>4</sub>)<sub>2x</sub>(NH<sub>2</sub>)<sub>2(1-x)</sub> phases were identified and a trend was observed between the composition of the products and their ionic conductivity. A maximum is reached for x = 0.67 with an ionic conductivity of  $4x10^{-5}$  S.cm<sup>-1</sup> at 100°C, which is one of the best Mg<sup>2+</sup> ionic conductivity ever reported in an inorganic solid. The solid electrolyte properties of the best ionic conductors identified during this work were characterized. It appeared that these compounds are not stable at high potentials. They start to get oxidized around + 1.0 V vs. Mg<sup>2+</sup>/Mg. Nevertheless, they are stable against Mg and allow its electrochemical deposition and stripping.

Keywords: magnesium batteries, solid electrolyte, complex hydrides, solid ionic conductors, energy storage