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BRIEF COMMUNICATION

# $Mg(BH_4)_2$-$CH_3NH_2BH_3$@MgO solid state electrolyte for magnesium batteries

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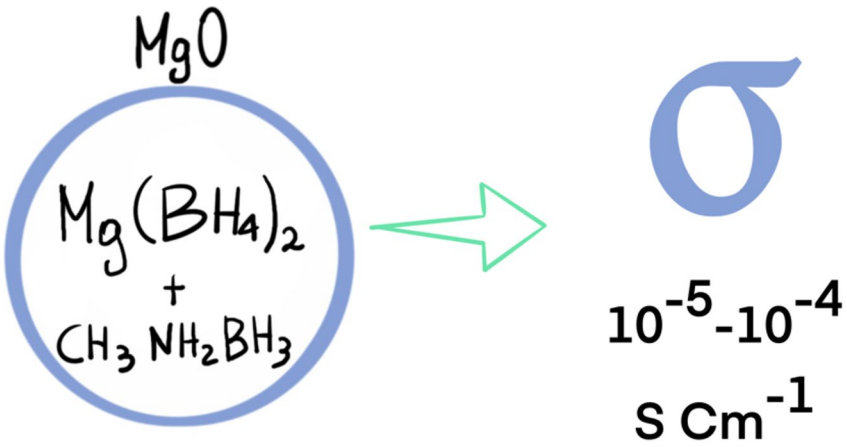
**Abstract**

New electrolytes are necessary for the development of eco-friendly and cost-effective solid-state magnesium batteries. Methylamine borane-magnesium borohydride $Mg(BH_4)_2$-$CH_3NH_2BH_3$ combined with MgO is suggested as a novel solid state electrolyte. In fact, $Mg(BH_4)_2$-$CH_3NH_2BH_3$ 0.33–0.67 (molar fraction) is a viscous liquid at room temperature, but it can be stabilized in the solid state after the incorporation of 75 wt% of MgO. The obtained composite exhibits remarkable $Mg^{2+}$ conductivity, achieving approximately $10^{-5}$ S $cm^{-1}$ at 25 °C and $10^{-4}$ S $cm^{-1}$ at 65 °C.

**Graphical abstract**




**Keywords** Complex hydrides · EIS · DSC · PXRD · Solid state electrolytes · Magnesium batteries

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**Abbreviations**

| | |
|---|---|
| SSE | Solid State Electrolyte |
| SSB | Solid State Battery |
| MeAB | CH3NH2BH3 |
| XRD | X-ray diffraction |
| DSC | Differential scanning calorimeter |
| EIS | Electrochemical Impedance Spectroscopy |

## Introduction

Solid state electrolytes (SSEs) have enabled the development of all solid-state batteries (SSB) [1]. They have several advantages with respect to the currently available Li-ion batteries, including a reduction in weight and volume, an increased energy density, a higher energy efficiency and limited energy loss and flammability [2]. Mg-ion batteries seem promising due to the greater abundance of magnesium compared to lithium, positioning them as strong contenders in the field of battery technology.

Complex hydrides are a promising class of materials as solid-state electrolytes, for both Lithium-based and non-Lithium-based SSB, owing to their versatile crystal structure. For the beyond-lithium SSBs field, $Mg(BH_4)_2$-based compounds have been gaining attention as a potential SSE. $Mg(BH_4)_2$ typically exhibits a minimal cationic conductivity $\sim 10^{-12}$ S cm$^{-1}$ coupled with an electronic conductivity around $\sim 10^{-9}$ S cm$^{-1}$ [3]. Consequently, this material is classified as an insulator. Over recent years, a series of innovative compounds, denoted as $Mg(BH_4)_2 \cdot R$, where magnesium is coordinated with a neutral molecule, have been synthesized. In fact, when $Mg(BH_4)_2$ forms complexes with neutral molecules, such as ammonia ($NH_3$) [4] and ethylenediamine ($H_2NCH_2CH_2NH_2$)[5], the $Mg^{2+}$ conductivity increases by several orders of magnitude[6]. These compounds demonstrate elevated $Mg^{2+}$ conductivity even at moderate temperatures, laying the groundwork for the development of novel magnesium based SSBs [4, 5, 7]. Roedern et al.[5] reported an improvement in $Mg^{2+}$ conductivity to $6 \times 10^{-5}$ S cm$^{-1}$ at 70 °C by adding one molar ethylenediamine to $Mg(BH_4)_2$, creating an asymmetric coordination of $Mg^{2+}$ with one ethylenediamine and two $BH_4^-$ groups. Yan et al.[8] further studied the effect of the addition of $NH_3$, showing that both the crystal structure and ionic conduction properties of $Mg(BH_4)_2 \cdot nNH_3$ depend on the number of $NH_3$ molecules. For instance, $Mg(BH_4)_2 \cdot NH_3$, which forms flexible zigzag chains, exhibited an ionic conductivity of $3.3 \times 10^{-4}$ S cm$^{-1}$ at 80 °C. Adjusting the $NH_3$ content to non-integer values (e.g., $n = 1.6$) further improved conductivity, which can reach a value of $3.5 \times 10^{-4}$ S cm$^{-1}$ at 50 °C for $Mg(BH_4)_2 \cdot 1.6NH_3$. Among neutral molecules, ammonia borane proved to be a good candidate. At 30 °C, $Mg(BH_4)_2(NH_3BH_3)_2$ showcased an ionic conductivity of $1.3 \times 10^{-5}$ S cm$^{-1}$ [7]. Electrochemical cells utilizing $Mg(BH_4)_2(NH_3BH_3)_2$ as the SSE displayed reversible migration of Mg ions within the material, suggesting its suitability as a ionic conductor for SSB Mg-ion batteries.

Composite materials, obtained by mixing complex hydrides with oxides, have demonstrated the ability to create functional battery materials characterized by high thermal and mechanical stability, along with high $Mg^{2+}$ conductivity. An example of such a composites is $Mg(BH_4)_2 \cdot 1.6NH_3$ – MgO (75 wt %), which showed a $Mg^{2+}$ conductivity of the order of $10^{-5}$ S cm$^{-1}$ at room temperature [4].

In this study, the effect of a methylamine borane neutral substituent, $CH_3NH_2BH_3$ (MeAB), in $Mg(BH_4)_2$ has been investigated. The enhancements in $Mg^{2+}$ ionic conductivity in $Mg(BH_4)_2$ with the addition of MeAB is expected because of an increase in both the Mg – B bond distance and the volume of the tetrahedron surrounding the Mg ion, as well as in possible distortions of this tetrahedron. These structural changes are expected to promote the mobility of $Mg^{2+}$ ions. Because the mixture of $Mg(BH_4)_2$ with MeAB led to a jelly product, in order to assess the properties of $Mg(BH_4)_2$-MeAB 0.33–0.67 as SSE, MgO was used as a scaffolder.

## Experimental

A sample of $Mg(BH_4)_2$-$CH_3NH_2BH_3$ ($Mg(BH_4)_2$-MeAB) with 0.33–0.67 molar fraction was prepared by hand mixing the parent compounds in agate mortar for one minute. The resulting product was a white pearlescent viscous liquid (Figure S1 in the Supplementary Information (SI)). $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO sample was prepared via ball milling. The ball-to-sample mass ratio was 30:1 and approximately 1 g of mixture was prepared. The mechanochemical treatment was performed for a total time of 2 h under argon atmosphere at 200 rpm for periods of 2 min of milling, separated by 2 min breaks to avoid overheating. Nanopowder MgO from Thermo Fischer (purity > 99%) with a surface area ≥ 30 m²/g was employed for the synthesis after drying at 300 °C under dynamic vacuum for 8 h.

X-ray diffraction (XRD) measurements were performed at different temperatures. The sample was cooled and heated in a Differential Scanning Calorimeter (DSC) in the – 140/20°C temperature range at 5 °C/min, under 2 bar of He.

Electrochemical Impedance Spectroscopy (EIS): Mg-ion conductivity was assessed using EIS employing a potentiostat. The frequency range was set between 500 Hz and 7 MHz, with an applied voltage of 5 mV. The pellet were prepared by placing approximately 50 mg of sample powder into a PEEK (polyether ether ketone) cylinder with a 10 mm

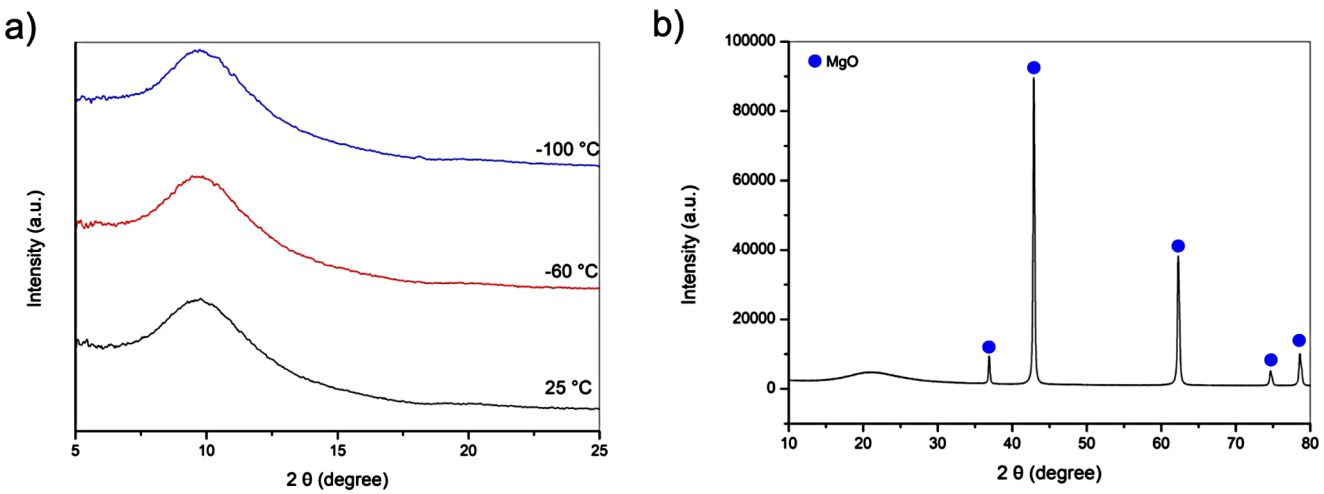


**Fig. 1** **a**) XRD patterns for sample $Mg(BH_4)_2$- MeAB 0.33–0.67 at 25 °C (bottom), -60 °C (middle) and − 100 °C (top); **b**) XRD pattern for sample $Mg(BH_4)_2$- MeAB 0.33–0.67@75%wt MgO

diameter, followed by cold pressing at 0.8 ton between two stainless steel pistons.

A custom made cell, based on a design suggested by Utrecht University [9], was used to measure Mg-ion conductivity in $Mg(BH_4)_2$- MeAB@MgO. A custom-made cell was specifically developed for measuring the Mg-ionic conductivity of $Mg(BH_4)_2$-MeAB. The cell design was created using a CAD (Computer-Aided Design) program (Shapr3D), and it was 3D printed in PLA with 15% infill and a 2.4 mm border thickness. Stainless steel electrodes were fixed to the cell using UV resin to ensure a fully sealed connection, and a Viton O-ring was used to maintain an air-tight condition within the cell chamber. The scheme of the cell is shown in Figure S3 of the SI. The cell was properly calibrated, in order to acquire the cell constant using standard solutions of $Na_2SO_4$ e $MgSO_4$ at concentrations of 0.1, 0.5, 1, and 1.5 M. EIS measurements were conducted every 5 °C within the temperature range of $25 \leq T \leq 65$ °C. Impedance data were analyzed using the EC-LaB software.

## Results and discussion

Obtained XRD patterns are reported in Fig. 1a. A broad band is present at low angle at 25 °C, suggesting that the energy of the hand mixing synthesis was enough to allow the reaction between $Mg(BH_4)_2$ and MeAB, leading to the formation of a non-crystalline product. The product of the solid-state reaction is possibly an ionic solution in which MeAB acts as a solvent. Therefore, a eutectic pseudo-binary system, with the eutectic temperature below room temperature, is likely formed between $Mg(BH_4)_2$ and MeAB.

For the evaluation of a possible crystallization of the highly viscous liquid phase obtained at room temperature,

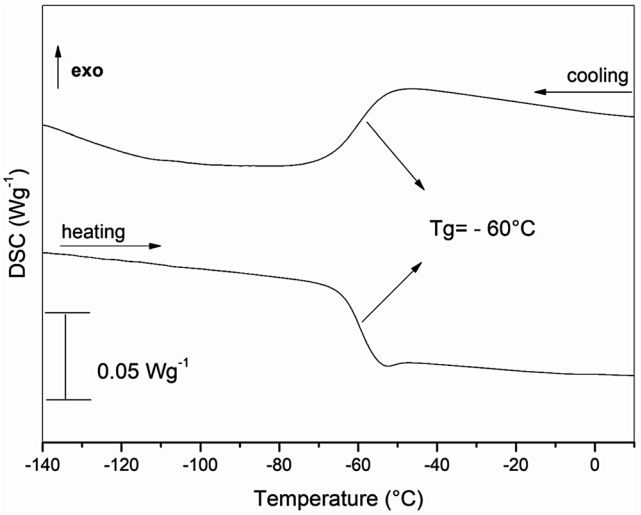


**Fig. 2** Low temperature DSC trace of sample $Mg(BH_4)_2$-MeAB 0.33–0.67

the XRD measurements were also performed at lower temperatures by using a cryostream with a cooling ramp of 5 °C/min. As shown in Fig. 1a, in all the acquired XRD patterns, both at -60 °C and − 100 °C, only a broad band has been observed at low angles, related to a non-crystalline structure. In light of these results, it is possible to state that the material does not undergo crystallization under cooling.

In order to support the XRD results regarding the non-crystalline structure of $Mg(BH_4)_2$-MeAB 0.33–0.67, a low temperature DSC measurement was performed. A step DSC signal has been detected at -60 °C in both the heating and cooling ramp of the measurement (Fig. 2), and it can be correlated to the glass transition of the sample. The DSC results are coherent to what was observed during low temperature XRD measurements, suggesting that, at low temperatures, $Mg(BH_4)_2$-MeAB 0.33–0.67 becomes a glass.

The addition of 75% by weight of MgO to the $Mg(BH_4)_2$-MeAB 0.33-0.67mixture yielded a solid product (Figure S2 in the SI). Figure 1b displays the XRD pattern of $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO, revealing distinct crystalline peaks corresponding to the MgO cubic phase, alongside a broad peak at lower angles. This result shows the possible integration of $Mg(BH_4)_2$-MeAB 0.33–0.67 within the MgO structure, without inducing any crystallization of the starting mixture. The nature of the interaction between $Mg(BH_4)_2$-MeAB 0.33–0.67 and MgO is still unclear. Our initial hypothesis is that MgO acts as a scaffold, with the liquid filling the pores of the metal oxide. However, additional experiments are planned to determine whether MgO functions solely as a scaffold or specific chemical interactions are acting between the oxide and $Mg(BH_4)_2$-MeAB.

The viscous liquid showed a remarkable ionic conductivity, reaching $6.27\times10^{-4}$ S cm$^{-1}$ at 25 °C and $1.64\times10^{-3}$ S cm$^{-1}$ at 65 °C. $Mg^{2+}$ ionic conductivity measurements on $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO were conducted between 25 °C and 65 °C, since a heating up to 75 °C resulted in the loose of the solid state. As an example, the Nyquist plots of $Mg(BH_4)_2$-MeAB 0.33–0.67 at 60 °C and $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO at 55 °C, together with the relative circuit used to fit data, are reported in Figure S4 in the SI.

Figure 3 reports the ionic conductivity for $Mg(BH_4)_2$-MeAB 0.33–0.67 and $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO, as a function of the inverse of temperature, alongside previously documented $Mg(BH_4)_2$-based $Mg^{2+}$ ionic conductors[4, 5, 7] and Mg based ionic liquid and gel electrolytes [10, 11].

$Mg(BH_4)_2$-MeAB 0.33-0.67@MgO exhibits superior $Mg^{2+}$ ionic conductivity compared to $Mg(BH_4)_2(NH_3BH_3)_2$ and $Mg(en)(BH_4)_2$ SSEs. At temperatures ranging from 25 °C to 55 °C, $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO demonstrates superior $Mg^{2+}$ ionic conductivity compared to $Mg(BH_4)_2\cdot xNH_3$@MgO (where x = 1.5/1.6), and exhibits comparable $Mg^{2+}$ ionic conductivity between 60 °C and 65 °C. Moreover, $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO displays higher $Mg^{2+}$ ionic conductivity than $Mg(BH_4)_2\cdot xNH_3$ (x = 1.5/1.6) up to 45 °C, with slightly reduced, but still comparable, performance at higher temperatures. Overall, $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO shows superior ionic conductivity in the operating temperature range for batteries [12] compared to suggested $Mg(BH_4)_2$-based $Mg^{2+}$ ionic conductors, proving to be a suitable SSE candidate.

On the other hand, $Mg(BH_4)_2$-MeAB 0.33–0.67 alone shows ionic conductivity comparable to $Pyr_{1201}$TFSI[Mg(TFSI)][11], an ionic liquid electrolytes, and to PVdF/$Mg(AlEtBuCl_2)_2$/tetraglyme [10], a gel electrolyte. Ionic liquids generally exhibit high ionic conductivity due to their composition of only cations and anions [13], while gel-based electrolytes benefit from the synergistic interactions between the ionic conductor and the polymer,

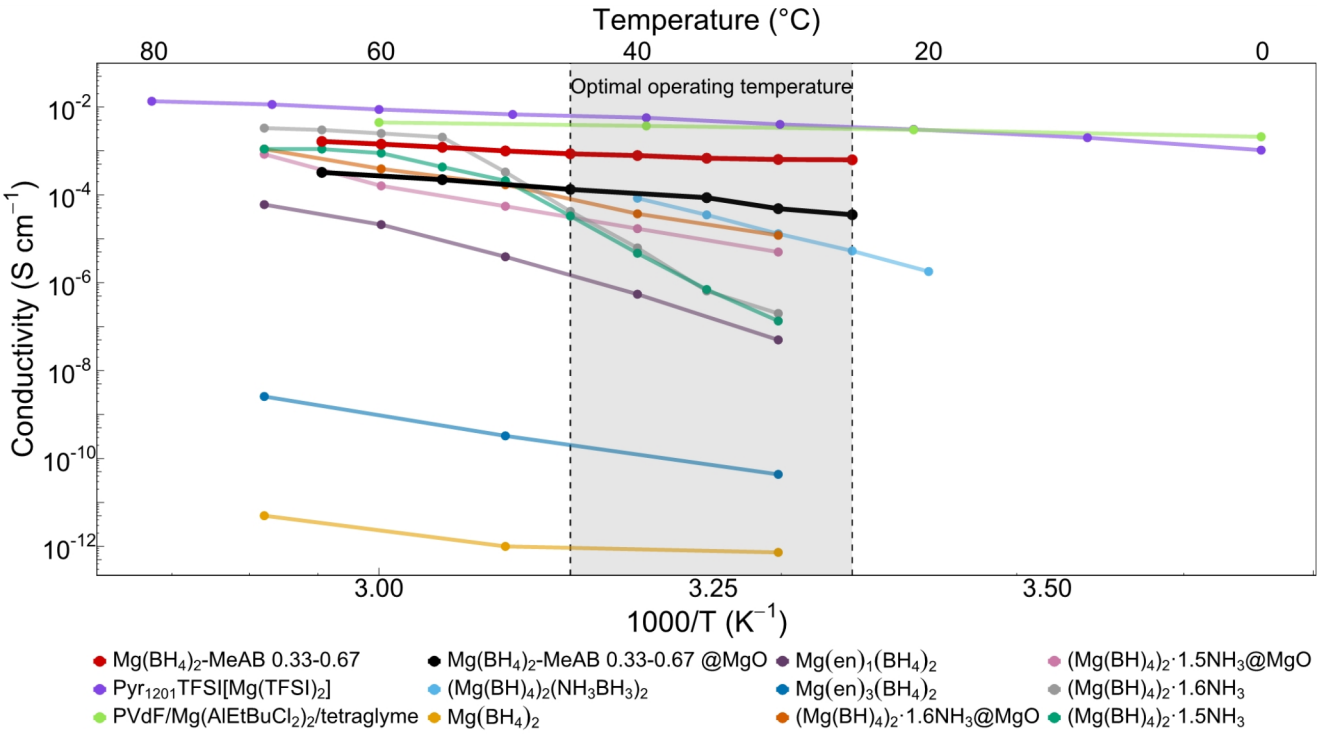


**Fig. 3** Ionic conductivity of $Mg(BH_4)_2$-MeAB 0.33–0.67 and $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO compared to $Mg(BH_4)_2$-based $Mg^{2+}$ ionic conductors[4, 5, 7], $Pyr_{1201}$TFSI [Mg(TFSI)][11] and PVdF/Mg( $AlEtBuCl_2)_2$/tetraglyme [10]

which enhances ionic mobility and thus increases ionic conductivity [14]. The exact nature of $Mg(BH_4)_2$-MeAB 0.33–0.67 is still under structural investigation, as it is unclear whether the highly viscous liquid is an ionic liquid or a solution. Incorporating $Mg(BH_4)_2$-MeAB 0.33–0.67 into a polymer matrix could be a potential method to further enhance its ionic conductivity, and this possibility will be explored in the future.

The activation energy for $Mg(BH_4)_2$-MeAB 0.33–0.67 and $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO was calculated following the equation $\sigma = \sigma_0 /T\ exp(-E_a/k_BT)$ where T is the temperature, $E_a$ is the activation energy, $k_b$ is Boltzmann's constant and $\sigma_0$ is the conductivity pre-factor. $Mg(BH_4)_2$-MeAB 0.33–0.67 and $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO shows an activation energy of 0.25 eV and 0.50 eV, respectively.

## Conclusions and future prospectives

In conclusion, we have identified a promising new candidate for Mg-based SSE applications. $Mg(BH_4)_2$MeAB 0.33–0.67@MgO has demonstrated favorable $Mg^{2+}$ ionic conductivity both at 25 °C ($3.53 \times 10^{-5}$ S cm$^{-1}$) and 65 °C ($3.25 \times 10^{-4}$ S cm$^{-1}$). The high Mg-ion conductivity achieved in the optimal operating temperature for commercial batteries place $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO as a candidate for application as SSE. $Mg(BH_4)_2$-MeAB 0.33-0.67shows an ionic conductivity higher of one order of magnitude compared to $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO both at 25 °C and 65 °C due to its non-crystalline nature which presents an intriguing area for further investigation. At this stage of our research, it is too early to assemble and test a battery, as further characterization of the newly discovered electrolytes is required. Liquid NMR and solid state NMR measurements are planned, in order to identify the nature of the bonds both in $Mg(BH_4)_2$-MeAB 0.33–0.67 and $Mg(BH_4)_2$-MeAB 0.33–0.67@MgO. A synchrotron PDF analysis will help in clarifying this aspect in developed material. To delve deeper, we plan to conduct more experiments, including the addition of different type of oxides, with different ratios. This will enable us to determine whether the observed high ionic conductivity is intrinsic to the $Mg(BH_4)_2$-MeAB 0.33–0.67 system or if it is an emergent property resulting from the ratio and type of added oxide. After having found the best candidate, the Mg plating and stripping behavior will be investigated, in order to assess the possibility to use $Mg(BH_4)_2$MeAB based systems as electrolytes. Finally, a battery will be assembled with Mg metal as the anode. All these insights are critical for advancing in the Mg SSB research field.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s40243-024-00278-3.

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**Authors contribution** Conceptualization: Baricco, Filinchuk; Methodology: Mazzucco, Sgroi, Tricerri, Lamacchia; Formal analysis and investigation: Mazzucco; Writing - original draft preparation: Mazzucco; Writing - review and editing: Mazzucco, Tricerri, Sgroi, Baricco; Funding acquisition: Baricco; Resources: Baricco, Filinchuk; Supervision: Baricco, Filinchuk.

**Data Availability** Raw data are available under request to authors. The raw EIS data both for $Mg(BH_4)_2$- MeAB and $Mg(BH_4)_2$- MeAB@MgO has been uploaded.

## Declarations

**Conflict of interest** All authors declare that they have no conflicts of interest.



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