Mg\(_3\)(BH\(_4\))_4(NH\(_2\))_2\) as Inorganic Solid Electrolyte with High Mg\(^{2+}\) Ionic Conductivity

Ronan Le Ruyet, Benoit Fleutot, Romain Berthelot, Yasmine Benabed, Geoffroy Hautier, Yaroslav Filinchuk, Raphael Janot

To cite this version:

Ronan Le Ruyet, Benoit Fleutot, Romain Berthelot, Yasmine Benabed, Geoffroy Hautier, et al.. Mg\(_3\)(BH\(_4\))_4(NH\(_2\))_2\) as Inorganic Solid Electrolyte with High Mg\(^{2+}\) Ionic Conductivity. ACS Applied Energy Materials, ACS, 2020, 3(7), pp.6093-6097. 10.1021/acsaem.0c00980 . hal-02924388
Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ as Inorganic Solid Electrolyte with High Mg$^{2+}$ Ionic Conductivity

Ronan Le Ruyet,$^{a,d}$ Benoît Fleutot,$^{a,d}$ Romain Berthelot,$^{b,d}$ Yasmine Benabed,$^{c,e}$ Geoffroy Hautier,$^{c}$ Yaroslav Filinchuk,$^{c}$ and Raphaël Janot$^{a,d,*}$

$^a$ Laboratoire de Réactivité et Chimie des Solides (LRCS), Université de Picardie Jules Verne, UMR 7314 CNRS, 33 Rue Saint Leu, Amiens 80039, France.

$^b$ ICGM, Univ. Montpellier, UMR 5253 CNRS, ENSCM, Montpellier, France.

$^c$ Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Place L. Pasteur 1, Louvain-la-Neuve 1348, Belgium.

$^d$ Réseau sur le Stockage Electrochimique de l’Energie (RS2E), FR 3459 CNRS, 33 Rue Saint Leu, Amiens 80039, France.

$^e$ Department of Chemistry, Université de Montréal, Montreal, H3T1J4, Canada.

* Corresponding author: Raphaël Janot: raphael.janot@u-picardie.fr

Co-authors: Ronan Le Ruyet: ronan.leruyet@u-picardie.fr
Benoît Fleutot: benoit.fleutot@u-picardie.fr
Romain Berthelot: romain.berthelot@umontpellier.fr
Yasmine Benabed: y.benabed@hotmail.fr
Geoffroy Hautier: geoffroy.hautier@uclouvain.be
Yaroslav Filinchuk: yaroslav.filinchuk@uclouvain.be
Abstract

Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ compound was synthesized through the investigation of the Mg(BH$_4$)$_2$-Mg(NH$_2$)$_2$ phase diagram; its crystal structure was solved in a tetragonal unit cell with the space group I-4. Interestingly, Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ has a high thermal stability with a decomposition temperature above 190°C and exhibits a high Mg$^{2+}$ ionic conductivity of 4.1x10$^{-5}$ S.cm$^{-1}$ at 100°C with a low activation energy (0.84 eV). The reversible Mg deposition/stripping was demonstrated at 100°C when using Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ as solid electrolyte. Thus, Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ is a compound that could help to develop rechargeable Mg-ion solid-state batteries.

Keywords: ionic conductor, Mg-ion battery, borohydride, crystal structure, impedance spectroscopy

In order to develop rechargeable batteries with better energy density and more sustainable materials than the lithium-based batteries, post-Li-ion technologies are being developed.$^1$ Among them, magnesium-based batteries are studied as Mg has the advantages of being abundant in the earth crust (21100 ppm vs. 10 ppm for Li),$^2$ to have a low redox potential (-2.356 V vs. NHE) and a high volumetric capacity (3833 mAh.cm$^{-3}$ vs. 2046 mAh.cm$^{-3}$ for Li). Nevertheless, the development of Mg batteries is slowed down by the difficulty of finding proper electrolytes. Until now, most of the liquid electrolytes used in Mg-ion batteries were made on Cl-containing salts (e.g. Grignard reagents), which cause severe corrosions to the electrochemical cell if the working potential is too high.$^{3,4}$ Recent progress has been made with fluoro-alkoxy-borates salts, such as Mg(B(hfip)$_4$)$_2$ with hfip = OCH(CF$_3$)$_2$, which are chlorine-free and show high electrochemical stability up to 4.5 V (vs. Mg$^{2+}$/Mg).$^5$ Interestingly,
hydroborate and carbo-borate based compounds (e.g. Mg(BH₄)₂ and Mg(CB₁₁H₁₂)₂) were also recently investigated as Mg²⁺ salts.⁶ These liquid electrolytes remain however limited for high energy density devices due to reactions occurring at the electrolyte/positive electrode interface. In addition, all these liquid electrolytes suffer from the use of ether-based solvents (often THF or DME) which are very volatile and flammable. Finally, quite recently, it has been demonstrated that the long thought non-dendritic formation in the case of Mg-ion batteries is false: several groups have reported that Mg dendritic growth can also occur and lead to fatal failures.⁷-⁸

As for Li-ion and Na-ion batteries, there is an increasing interest for all-solid-state batteries in the case of Mg-ion as it could definitively solve the issues of solvent leakage and flammability. In addition, it could possibly allow the use of Mg metal at the negative electrode without any magnesium dendritic formation if the solid electrolyte pellet is dense enough. Thus, inorganic solid electrolytes could largely improve rechargeable Mg batteries if their ionic conductivity and electrochemical stability window are high. Unfortunately, inorganic solid compounds with Mg²⁺ cations have very low ionic conductivities, due to the very sluggish diffusion of divalent Mg²⁺ in the solid. Two recent reviews give a nice picture of the family of materials exhibiting decent Mg²⁺ ionic conductivities.⁹,¹⁰ Among them, the NASICON-like phosphates (e.g. MgZr₄(PO₄)₆) show a high ionic conductivity of about 10⁻³ S.cm⁻¹, however at high temperature (800°C),¹¹ and thus are unsuitable for Mg²⁺ rechargeable batteries. Searching for compounds with higher conductivities, and similarly to what is known for lithium, oxygen can be replaced by sulfur in Mg²⁺ ionic solid conductors. Indeed, sulfide glasses and glass-ceramics (e.g. MgS-P₂S₅) show an improved Mg²⁺ cation mobility at lower temperatures, but the ionic conductivity is still too low for applications (around 10⁻⁸ S.cm⁻¹ at 200°C).¹² A recent class of materials with high ionic conductivities are the ternary spinels,¹³ such as MgSc₂Se₄ (10⁻⁴ S.cm⁻¹ at 25°C), but unfortunately, these conductivities are accompanied by high electronic
ones (about 4x10⁻⁸ S.cm⁻¹), which impede their possible use as solid electrolytes.¹⁴ As a matter of fact, similarly to the recently developed Mg²⁺ salts based on Mg(BH₄)₂ for liquid electrolytes, the most interesting materials for solid electrolytes are today based on the same compound and derivatives.¹⁵ Very recent studies have shown the possibility to reach high ionic conductivities of about 10⁻⁵ S.cm⁻¹ close to room temperature by adding neutral molecules to Mg(BH₄)₂. In this manner, Mg(en)₂(BH₄)₂ with en being ethylene-diamine, Mg(BH₄)₂-NH₃ and Mg(BH₄)₂(NH₂BH₃)$_₂$ reach ionic conductivities of 6x10⁻⁵ S.cm⁻¹ at 70°C,¹⁶ 8.5x10⁻⁵ S.cm⁻¹ at 70°C,¹⁷ and 8.4x10⁻⁵ S.cm⁻¹ at 40°C,¹⁸ respectively. The latter is indeed the solid compound with the highest Mg²⁺ ionic conductivity reported so far. The ionic conductivity enhancement when adding these neutral N-H containing molecules is attributed to a network of dihydrogen N-H$.\cdot$.H-B bonds allowing a high degree of structural flexibility, as already observed in the field of hydrogen storage materials,¹⁹ and to the large volume of the tetrahedra surrounding the Mg²⁺ cations allowing a facilitated Mg²⁺ ionic motion.

In the literature, Mg(BH₄)(NH₂) compound was reported to have an ionic conductivity of 1x10⁻⁶ S.cm⁻¹ at 150°C,²⁰ but we have recently demonstrated that this conductivity could be improved up to 3x10⁻⁶ S.cm⁻¹ at only 100°C by synthesizing a glass-ceramic-like material.²¹ This was due to the presence of an unknown additional amorphous compound that was assumed as another phase existing in the Mg(BH₄)₂-Mg(NH₂)₂ binary system. Indeed, in similar systems such as LiBH₄-LiNH₂, several compounds can be obtained for different compositions.²² Searching for other magnesium ionic conductors, we explored different compositions in the hitherto unknown Mg(BH₄)₂-Mg(NH₂)₂ binary phase diagram (cf. Figure S1) by ball-milling and annealing of various mixtures of Mg(BH₄)₂ and Mg(NH₂)₂.

After ball-milling and annealing at 120°C of a Mg(BH₄)₂:Mg(NH₂)₂ mixture in the 2:1 molar ratio (see the supporting information for the detailed synthesis conditions), a crystalline single-phase compound was obtained and, consequently, named Mg₃(BH₄)₄(NH₂)₂ (cf. Figure
S1 for the experimentally determined Mg(BH$_4$)$_2$-Mg(NH$_2$)$_2$ binary phase diagram). The corresponding XRD pattern has been well indexed in a tetragonal unit cell (cf. Figure 1a) like other compounds in the Mg(BH$_4$)$_2$-Mg(NH$_2$)$_2$ phase diagram, for instance: Mg(BH$_4$)(NH$_2$) (space group: I4$_1$)$_2^{23}$ Mg(NH$_2$)$_2$ (space group: I4$_1$/acd)$^{24}$ and δ-Mg(BH$_4$)$_2$ (space group: I4$_1$/acd)$^{25}$. From Rietveld refinement with the space group I-4, it was possible to propose a crystal structure for the so-called Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ with tetragonal cell parameters $a = 14.1801(8)$ Å and $c = 6.002(4)$ Å (cf. Figure 1b). Only few additional weak peaks of Mg(BH$_4$)(NH$_2$) can be observed (i.e. a content of only 1.1 wt.% as found from Rietveld refinement).

Crystal structure of Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$, solved in the space group I-4, is shown in Figure 1b. The presence of some weak peaks allowed to exclude the screw axis $4_1$ and the glide planes. Twelve Mg atoms per cell are distributed over three crystallographic sites, the anions were also attributed to three sites: $8 + 8$ for BH$_4$ groups and one 8-fold position for NH$_2$ (cf. Table S1). The site for the NH$_2$ group is clearly identified thanks to much shorter Mg-N bonds than Mg…B

![Figure 1](image-url)

Figure 1. a) Rietveld refinement of the XRD diagram of Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ and b) its crystal structure drawn with the software VESTA.
contacts, as well as by much narrower N-Mg-N angles compared to rather open B…Mg…B, as also seen in the crystal structures of Mg(NH₂)₂ and Mg(BH₄)₂. A possible anionic site disorder cannot be firmly excluded due to the small difference in the X-ray scattering power for the BH₄ and NH₂ anions, however it not supported the distinctly different structural chemistry of the anions. The B-H distance of 1.15 Å and N-H of 0.9 Å were taken as typical values for the apparent bond lengths for X-ray diffraction studies, the H-B-H and H-N-H angles were fixed as ideally tetrahedral (109.47°). The positions and the orientations of the anions, determined using the software FOX with the help of H…H anti-bump restraints, were fixed in the latter refinement. The experimental structure was DFT-optimized, improving accuracy of hydrogen positions (the major difference with the experimental structure is related to the anions’ orientations) and validating the experimental conclusions. The full crystallographic parameters can be found in Table S1. Two Mg sites (Mg1 and Mg2) are in the center of tetrahedra made of four (BH₄)⁻ anions as in Mg(BH₄)₂ and one site (Mg3) is in the center of a tetrahedron made of two (BH₄)⁻ anions and two (NH₂)⁻ anions as in Mg(BH₄)(NH₂). The calculated density for Mg₃(BH₄)₄(NH₂)₂ crystal structure is very low: 0.904 g.cm⁻³. This low crystallographic density is attractive for a solid-state electrolyte as it allows obtaining good ionic percolation in composite electrodes with a relatively low weight of electrolyte, thus ensuring reasonable electrochemical gravimetric capacities for the composite electrodes.

Infrared spectroscopy was performed on this Mg₃(BH₄)₄(NH₂)₂ compound (cf. Figure S2) and reveals N-H and B-H stretching/bending bands at very similar wave numbers to those found for the precursors, Mg(BH₄)₂ and Mg(NH₂)₂, and to the other compound in the binary diagram: Mg(BH₄)(NH₂). More specifically, two strong N-H stretching bands are observed at 3270 and 3326 cm⁻¹ which are characteristic values of (NH₂)⁻ anion close to Mg²⁺ and it must be noticed that no band is visible around 3150-3200 cm⁻¹, thus confirming the absence of imide (NH)₂⁻ moieties. Interestingly, in the 1000-1600 cm⁻¹ range, it can be observed that the B-H bending
bands are split into two compared to the spectrum of Mg(BH₄)(NH₂), which agrees well with the XRD refinement showing two different Wyckoff positions for the B atoms (vs. only one position in the case of Mg(BH₄)(NH₂)).

The thermal stability of Mg₃(BH₄)₄(NH₂)₂ was evaluated by Thermogravimetric Analysis (TGA) coupled with Differential Thermal Analysis (DTA) measurements (cf. Figure S3). Very importantly, no mass loss or exo/endothermic phenomenon was observed up to 190°C under argon. Only a slight decrease of the mass (less than 0.1 %) can be observed starting around 190°C, which is probably related to the beginning of the compound decomposition. Above 200°C, the compound readily decomposes forming a foamy material due to gas releases (a mixture of H₂ and NH₃). Nevertheless, the fact that Mg₃(BH₄)₄(NH₂)₂ remains stable at temperatures up to 190°C is very interesting, especially when compared to the recently reported compounds obtained by the addition of a neutral molecule to Mg(BH₄)₂ (molecules such as en = C₂H₄(NH₂)₂, NH₃, or NH₃BH₃). These compounds are indeed clearly less thermally stable than Mg₃(BH₄)₄(NH₂)₂: Mg(en)₁(BH₄)₂ has a phase transition at 75°C and starts to be decomposed at 100°C, Mg(BH₄)₂-NH₃ is decomposed at 138°C,²⁶ whereas Mg(BH₄)₂(NH₃BH₃)₂ melts at 48°C and starts to be decomposed at 85°C.²⁷ Even, Mg(BH₄)(NH₂), the only other compound reported in the Mg(BH₄)₂-Mg(NH₂)₂ phase diagram, becomes amorphous around 150°C and starts to be decomposed at 200°C (cf. Figure S1).

Owing to the good thermal stability of Mg₃(BH₄)₄(NH₂)₂, its ionic conductivity was measured on pellets by Electrochemical Impedance Spectroscopy (EIS) as a function of temperature. All Nyquist plots show the same shape as the one recorded at 100°C (cf. Figure 2a) i.e. only one semicircle at high frequency, that is attributed to the ionic conduction in the material, followed by a straight line at low frequency, that is the capacitance caused by the ion blocking electrodes placed on both sides of the pelletized sample. The ionic conductivity increases from 6.2x10⁻⁷ S.cm⁻¹ at 50°C to 4.1x10⁻⁵ S.cm⁻¹ at 100°C (cf. Figure 2b). These values
are among the highest recorded for a purely inorganic Mg$^{2+}$ solid ionic conductor at such low
temperatures. We can notice that the conductivity values remain exactly the same upon cooling
(and upon the subsequent heating/cooling cycles not shown here) confirming that the sample
does not undergo any thermal degradation. Actually, the impedance spectroscopy
measurements were performed up to 100°C, a much lower temperature than the degradation
temperature of above 190°C previously determined by TGA/DTA.

It is interesting to compare the high conductivity of 4.1x10^{-5} S.cm^{-1} at 100°C with the one
of 3x10^{-6} S.cm^{-1} that we have previously obtained at the same temperature for a Mg(BH$_4$)(NH$_2$) glass-ceramic material. Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ compound has undoubtedly an improved ionic
conductivity and a higher thermal stability. The activation energy for the ionic conduction of
Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ was found to be 0.84 eV from the plot of ln(σ.T) as a function of 1/T. This activation energy is low, indicating a high mobility of the Mg$^{2+}$ cations. Indeed, Ea extracted
from the plot of ln(σ.T) as a function of 1/T is the addition of the energy needed to form the
mobile charge carrier (E$_f$) and the energy barrier for its migration (E$_m$). If Ea is low, then the
Mg$^{2+}$ cations are easily formed and/or have a favourable path and low energy barrier to migrate.
In both cases, the low activation energy (0.84 eV) means a better mobility of the Mg$^{2+}$ cations
compared to similar compounds with higher activation energies.

The lowest activation energies reported in inorganic solid Mg$^{2+}$ electrolytes were 0.83-0.88 eV in MgZr$_4$(PO$_4$)$_6$ and related materials. The activation energy of Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$
is also much lower than the ones measured for other Mg(BH$_4$)$_2$-based solid electrolytes: 1.2,
1.47, 1.6, and 2.0 eV for Mg(BH$_4$)(NH$_2$), Mg(BH$_4$)$_2$(NH$_3$BH$_3$)$_2$, Mg(en)$_1$(BH$_4$)$_2$, and
Mg(BH$_4$)$_2$-NH$_3$, respectively. The good mobility of Mg$^{2+}$ in Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ is not fully understood yet but it might be linked to its unique crystal structure in which Mg$^{2+}$ cations
occupied mixed sites between tetrahedra made of four (BH$_4$)$^-$ anions and others made of two
(BH$_4$)$^-$ anions and two (NH$_2$)$^-$ anions, and the role of the dihydrogen bonds (of 2.11 and 2.23 Å
in the DFT-optimized structure). Deeper structural characterizations, if possible on single crystals, could be also useful to check the possible formation of vacancies, especially on the N crystallographic sites, which could promote largely the Mg$^{2+}$ mobility.

Figure 2. a) Nyquist plot obtained by EIS at 100°C for Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ and b) the ionic conductivity as a function of 1/T.

As Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ is among the compound with the highest Mg$^{2+}$ ionic conductivity, it was important to prove that reversible Mg deposition/stripping is possible and that its use as electrolyte in all solid-state Mg-ion batteries could be realized. In order to determine the Electrochemical Stability Window (ESW), cyclic voltammetry measurements were done at 100°C on a composite working electrode (WE) made by mixing Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ with 10 wt.% of carbon black, the latter needed to bring electrons in the material and, thus, to really evaluate its electrochemical stability. This composite WE was separated from the Mg counter electrode by a layer of pure Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$.

When starting the cyclic voltammetry with a sweep towards low potentials first, a strong reduction peak assigned to Mg deposition is clearly visible below 0 V vs. Mg$^{2+}$/Mg (cf. Figure 3). This phenomenon is partially reversible as the corresponding Mg stripping occurs
upon oxidation. The coulombic efficiency at this first cycle is about 20 %, which might be improved by a better mixing of the carbon with the solid electrolyte (here simply made with an agate mortar). No reduction peak other than the Mg deposition occurred so the Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ solid electrolyte is stable at low potentials. This result is interesting because solid electrolytes often react with a metallic anode. On the other side, the oxidation of the Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ solid electrolyte is unfortunately observed with an onset potential of about 1.48 V vs Mg$^{2+}$/Mg. This oxidation is irreversible and the exact reaction occurring is not fully identified, but it is most probably related to the oxidation of the (NH$_2$)$^-$ moieties. It is noteworthy that the coulombic efficiency of the Mg deposition/stripping remains around 20 % for the first 5 cycles meaning that the decomposition products formed upon oxidation do not affect this process. The ESW of Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ ranges from 0 to 1.48 V vs. Mg$^{2+}$/Mg which is similar to the ESWs previously reported for Mg(en)$_2$(BH$_4$)$_2$ and Mg(BH$_4$)$_2$(NH$_3$BH$_3$)$_2$ (i.e. 0 to 1.2 V vs. Mg$^{2+}$/Mg for both of them).

![Cyclic voltammetry measurement](image.png)

**Figure 3.** Cyclic voltammetry measurement at 100°C and 0.05 mV.s$^{-1}$ of a cell made of Mg / Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ / Mg$_3$(BH$_4$)$_4$(NH$_2$)$_2$ + carbon (90:10 wt.%).
In conclusion, a compound with the Mg₃(BH₄)₄(NH₂)₂ stoichiometry was synthesized when exploring the Mg(BH₄)₂-Mg(NH₂)₂ binary phase diagram. The crystal structure of Mg₃(BH₄)₄(NH₂)₂ was solved in a tetragonal unit cell with the I-4 space group, where the Mg²⁺ cations occupy three different Wyckoff sites in distorted tetrahedra. Interestingly, the Mg₃(BH₄)₄(NH₂)₂ compound has a thermal stability up to 190°C, which is higher than those of the compounds recently reported, based on addition of neutral molecules to Mg(BH₄)₂. The ionic conductivity of Mg₃(BH₄)₄(NH₂)₂ is among the highest ever measured at low temperatures for a purely inorganic Mg²⁺ ionic conductor with a value of 4.1×10⁻⁵ S.cm⁻¹ at 100°C and a low activation energy (0.84 eV). Its electrochemical stability window was determined as ranging from 0 to 1.48 V vs. Mg²⁺/Mg, which are common voltages for Mg-(BH₄)-(NH₂) based solid electrolytes. The reversible Mg deposition/stripping was demonstrated at 100°C and Mg₃(BH₄)₄(NH₂)₂ is indeed a very interesting Mg²⁺ ionic conductor that could help to develop better rechargeable Mg-ion batteries.

Acknowledgements

The RS2E (French network on electrochemical energy storage) is acknowledged for the PhD funding of Ronan Le Ruyet (STORE-EX Labex Project ANR-10-LABX-76-01) and the Communauté Française de Belgique for the support under grant ARC 18/23-093. Matthieu Courty (LRCS, UPJV, Amiens) is also thanked for the thermal analysis measurements. The present research benefited from computational resources made available on the Tier-1 supercomputer of the Fédération Wallonie-Bruxelles, infrastructure funded by the Walloon Region under grant agreement n°1117545.
Supporting Information Available

Experimental section including conditions for material synthesis, characterizations and electrochemical measurements; Table listing the parameters for the experimentally solved and the DFT-optimized structures of the new \( \text{Mg}_3(\text{BH}_4)_4(\text{NH}_2)_2 \) compound; computational methods. Figures showing the experimentally determined \( \text{Mg}(\text{BH}_4)_2-\text{Mg}(\text{NH}_2)_2 \) binary phase diagram, the infrared spectra of \( \text{Mg}(\text{BH}_4)_2, \text{Mg}(\text{NH}_2)_2, \text{Mg}(\text{BH}_4)(\text{NH}_2) \) and \( \text{Mg}_3(\text{BH}_4)_4(\text{NH}_2)_2 \) and, the thermal stability of the \( \text{Mg}_3(\text{BH}_4)_4(\text{NH}_2)_2 \) compound.

References


(25) Dimitrievska, M.; White, J. L.; Zhou, W.; Stavila, V.; Klebanoff, L. E.; Udovic, T. J. Structure-Dependent Vibrational Dynamics of Mg(BH₄)$_2$ Polymorphs Probed with Neutron


$Mg_3(BH_4)_4(NH_2)_2$

$E_a = 0.84$ eV