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Dynamics of the Coordination Complexes in a Solid-State Mg Electrolyte

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Abstract

Coordination complexes of magnesium borohydride show promising properties as solid electrolytes for magnesium ion batteries and warrant a thorough microscopic description of factors governing their mobility properties. Here, the dynamics of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ on the atomic level are investigated by means of quasielastic neutron scattering (QENS) supported by DFT calculations, IR and NMR spectroscopy. Employing deuterium labeling we can unambiguously separate all the hydrogen containing electrolyte components, which facilitate Mg^{2+} transport, and provide a detailed analytical description of their motions on the picosecond time scale. The planar diglyme chain coordinating the central Mg atom appears to be flexible, while two dynamically different groups of $[\text{BH}_4]^-$ anions undergo reorientations. The latter has important implications for the thermal stability and conductivity of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ and demonstrates that the presence of excess $\text{Mg}(\text{BH}_4)_2$ units in partially chelated Mg complexes may improve the overall performance of related solid-state electrolytes.

Graphical TOC Entry

Keywords

Magnesium borohydride, diglyme, quasielastic neutron scattering, diffusion on a sphere, Gaussian diffusion, jump reorientation, solid-state magnesium electrolyte

The success of Li-ion battery technology is undoubtful nowadays, but globally growing demand for energy motivates further search for safer and cheaper alternatives, which would prove even higher energy density and power. Magnesium batteries could be potentially a reasonable solution for today's and future energy challenges.¹⁻⁴ The main advantages of Mg as an anode material are its high volumetric capacity ($3833 \text{ mAh}\cdot\text{cm}^{-3}$ compared to $2036 \text{ mAh}\cdot\text{cm}^{-3}$ for Li), negative redox potential of -2.36 V vs. SHE, abundance and, finally, it does not tend to develop a dendritic structure upon battery cycling. Still magnesium-ion batteries are not yet a mature technology and there are many challenges to overcome. One of the hurdles is the design of a practical magnesium electrolyte with a good conductivity, oxidative stability, and high transference numbers for the magnesium-containing cation.⁴ Safety concerns should also be considered. Particularly the latter issue determines research activities in the field of solid-state magnesium conductors.

Low-ionic conductivities in a practically relevant temperature range are a major drawback of the known solid-state Mg electrolytes.⁵⁻⁷ The highest magnesium conductivities at ambient temperature have been reported by Aubrey et al.⁸ in a metal-organic framework (MOF) (0.25 mS/cm) and by Song⁹ et al. in a composite polymer electrolyte (0.54 mS/cm). However, the performance of these electrolytes in full electrochemical cells have not been evaluated and the design work on other groups of materials is being continued. For example, the high reductive stability of the $[\text{BH}_4]^-$ anion,¹⁰ popular in liquid electrolyte systems,^{11,12} motivated the development of solid-state conductors based on $\text{Mg}(\text{BH}_4)_2$.

Recently our group has investigated coordination complexes of ethylenediamine with $\text{Mg}(\text{BH}_4)_2$ as a potential solid-state magnesium electrolyte.¹³ Although the obtained conductivity and oxidative stability should be improved, the studied example has demonstrated a promising strategy for development of new $\text{Mg}(\text{BH}_4)_2$ -based solid-state conductors. Therefore, we have tested other organic ligands (dimethoxyethane, tetramethylethylenediamine, and diglyme), which can coordinate Mg^{2+} ions and, thus, render them more mobile. The most promising candidate with respect to the high thermal stability and overall high ion

conductivity ($\sigma = 2 \cdot 10^{-5}$ S/cm at 350 K) appeared to be $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ (for Analytical and Reference Data see the Supporting Information). Although the previously described $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{1.0}$ ^{14,15} showed initially a better conductivity value at room temperature, it tended to lose diglyme over time with a concurrent decrease in conductivity. To understand the reason for the different behavior of these related materials, a thorough microscopic description of dynamics and transport mechanism is required, which we aimed to obtain in this work by using quasielastic neutron scattering (QENS) supported by density functional theory (DFT) calculations, solid-state nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy.

Characterization by means of QENS¹⁶ has proved to be very informative for solid hydrides and resulted in many examples of the apparent connection between anion reorientational motions and cation diffusion.^{17–21} One of the main strengths of the method is the simultaneous access to both time and spatial parameters of relaxation processes. Thus, jump rates, diffusion coefficients for long-range and localized diffusion, jump lengths, mechanisms of rotations (isotropical, uniaxial) can be evaluated, providing a detailed picture of stochastic molecular motions. QENS spectra are sensitive to hydrogen, making it challenging to separate different contributions in mixed compounds such as, for example, $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$. Because the neutron scattering cross section of deuterium is significantly less than that of hydrogen, we used isotope substitution to mask all hydrogens in diglyme and compared $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ with its partially deuterated analogue $\text{Mg}(\text{BH}_4)_2\text{-(diglyme-D)}_{0.5}$ to perform a more sophisticated analysis.

The synthesis and characterization of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ are presented in the Supporting Information. In brief, $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ is partially crystalline with substantial structural disorder and amorphous contribution (Figure S3). The major Bragg peaks can be attributed to the known structure of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{1.0}$,¹⁴ the minor contribution remains unassigned. To resolve the crystal structure, single-crystal spectra would be required, but so far they are not available. The sample undergoes a phase transition with the onset tem-

perature at $T_m = 330$ K and the peak temperature at $T_p = 345$ K (Figure S1), upon which the minor reflections disappear. The sample is thermally stable up to 520 K in contrast to $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{1.0}$, which starts decomposing at 303 K by releasing the organic ligand (Figure S2).

QENS measurements were conducted on the cold neutron time-of-flight spectrometer FOCUS at Paul Scherrer Institute in Villigen, Switzerland²² with the wavelength of incident neutrons of $\lambda=4.0$ Å. This setting allowed us to simultaneously characterize reorientational dynamics of the $[\text{BH}_4]^-$ anions and localized motions of the diglyme flexible chain in the quasielastic energy transfer range ($|E| \lesssim 1.5$ meV), as well as collective excitation seen in the inelastic range of the spectrum ($|E| \gtrsim 2.0$ meV). Modeling of QENS spectra of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ can be performed taking into account only the incoherent part of the dynamic structure factor $S(Q, E)$ dominated by hydrogen scattering (Table S1). Since correlation effects are negligible, the scattering functions of the hydrogenated and partially deuterated samples can be expressed in the following way:

$$S_{\text{prot}}(Q, E) = \frac{7}{15}S_{\text{digl}}(Q, E) + \frac{8}{15}S_{\text{BH}_4}(Q, E) \quad (1a)$$

$$S_{\text{deut}}(Q, E) = \frac{7\sigma_D}{7\sigma_D + 8\sigma_H}S_{\text{digl}}(Q, E) + \frac{8\sigma_H}{7\sigma_D + 8\sigma_H}S_{\text{BH}_4}(Q, E) \quad (1b)$$

where the $[\text{BH}_4]^-$ and diglyme contributions, $S_{\text{BH}_4}(Q, E)$ and $S_{\text{digl}}(Q, E)$, are weighted with respect to the total number of hydrogen atoms in each species. The neutron incoherent scattering cross sections of hydrogen and deuterium are denoted as σ_H and σ_D , respectively. The complete analytical form of the dynamic structure factors $S_{\text{BH}_4}(Q, E)$ and $S_{\text{digl}}(Q, E)$ can be found in the Supporting Information (eq S1–S7), whereas here we will focus on the physical meaning of the underlying models (Figure 1).

Both $S_{\text{BH}_4}(Q, E)$ and $S_{\text{digl}}(Q, E)$ have a low-energy (vibrational) inelastic broad band (Figure 2a) typical for amorphous systems and glasses and usually referred to as the “boson peak”.^{23–25} In the case of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ the vibrational frequency distribution is both

Figure 1: Model dynamic structure factors $S_{\text{digl}}(Q, E)$ and $S_{\text{BH4}}(Q, E)$ at $Q=1.5 \text{ \AA}^{-1}$. Green areas represent inelastic (vibrational) contributions to the spectra. The quasielastic component of the diglyme is described in terms of the Gaussian model taking into account segmental motions and rotations of the end methyl groups. The blue area of $S_{\text{BH4}}(Q, E)$ corresponds to the slowly rotating population of the $[\text{BH}_4]^-$ anions, whereas the $[\text{BH}_4]^-$ groups performing fast tumbling C2/C3 motions account for the orange area.

temperature- and Q -independent for $280 \text{ K} < T < 365 \text{ K}$ and, hence, can be reliably separated from the quasielastic contribution overlapping at $|E| \lesssim 1.5 \text{ meV}$ for elevated temperatures (Figure 2a). In a phenomenological approach, the boson peak in $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ can be adequately modeled with the well-known damped harmonic oscillator (DHO) function²⁶ (DHO frequency $\Omega = 4.9 \text{ meV}$, damping constant $\Gamma = 11.1 \text{ meV}$, see Supporting Information for details), while the Q -dependence of the DHO intensity permits calculation of the mean square displacement $\sqrt{\langle u^2 \rangle}$ associated with the confined vibrational modes of the $[\text{BH}_4]^-$ anions and diglyme (Figure 2b).

Diglyme molecules are not supposed to freely rotate in the solid phase, but segmental motions and end methyl group reorientations may lead to a quasielastic contribution observed in addition to the broad inelastic broad band (Figure 1). However, these localized dynamics

Figure 2: **a)** Inelastic part of the $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ spectra measured at different temperatures and divided by the Bose-phonon population factor $n(E, T)$ for a mean wave vector transfer $\langle Q \rangle = 1.5 \text{ \AA}^{-1}$. At elevated temperatures the inelastic bump significantly overlaps with the quasielastic contribution at low $|E|$ values.

b) Temperature dependence of the mean square displacement $\sqrt{\langle u^2 \rangle}$ of the vibrational modes. The step like increase of both the diglyme and $[\text{BH}_4]^-$ contributions is related to the phase transition of the sample

do not change the major conformation of the diglyme as can be seen from the low frequency part of the IR spectra (Figure S5). The diglyme bands in the region below 1000 cm^{-1} are conformationally sensitive, but the patterns of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ and $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{1.0}$ are almost identical, suggesting the same planar geometry of the molecule in both samples, where the three oxygen atoms coordinate the central Mg^{2+} , while two $[\text{BH}_4]^-$ anions are bound to Mg^{2+} through double borohydride bridges $\text{Mg-H}_2\text{-B}$.^{14,15} The Gaussian model²⁷ can be used to fit the quasielastic region of $S_{\text{digl}}(Q, E)$. The model considers particles diffusing in a confinement with soft boundaries and has been successfully applied for the characterization of the flexibility of alkyl substituents in ionic liquids.²⁸ Thus, the ethereal chain contribution can be fully described by the two parameters D_G and σ , which stand for the diffusion coefficient for localized motions and the radius of the confinement (Figure 3).

Figure 3: Temperature dependence of the diffusion coefficient for localized motions, D_G , and the size of the confinement, σ , describing the spatially restricted dynamics of the diglyme ligands. The vertical dashed line corresponds to the onset temperature of the phase transition at $T=330\text{ K}$.

The dynamic structure factor of the borohydride units, $S_{\text{BH}_4}(Q, E)$, appears to contain two quasielastic components (Figure 1). This implies that either all $[\text{BH}_4]^-$ anions exhibit

two distinct relaxation processes or that there are two dynamically different populations of $[\text{BH}_4]^-$. Because QENS allows evaluation of both spatial and time characteristics at the same time, the choice between the two variants can be unambiguously made based on the geometrical parameters of the supposed processes. For example, the assumption about two relaxations inherent to all anions results in an unreasonably small and temperature dependent B-H bond length and, hence, can be ruled out. The second case with two dynamically different $[\text{BH}_4]^-$ groups, on the contrary, allows to keep the B-H distance equal to 1.22 Å in the whole investigated temperature range, which is in a good agreement with other studies.²⁹ The fraction of the slowly or fast rotating $[\text{BH}_4]^-$ groups is an additional parameter, which has to be introduced in the latter model. The QENS analysis alone provides only a rough estimate of this quantity ($p_{\text{fast}} = 1 - p_{\text{slow}} = 0.50 \pm 0.15$). Interestingly, the solid-state ^{11}B magic-angle spinning (MAS) NMR spectra also reveal the presence of two distinct $[\text{BH}_4]^-$ sites, as observed by the narrow resonances at -41.0 and -42.8 ppm (Figure S6). The quantitative evaluation of the center band areas results in $p_i = 0.50 \pm 0.05$ for both types of the $[\text{BH}_4]^-$ anions in both complexes $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$ and $\text{Mg}(\text{BH}_4)_2\text{-(diglyme-D)}_{0.5}$. For this reason, for all further calculations we assume the ratio between the nonequivalent boron sites equal to 1:1. Moreover, we found that, compared to $\text{Mg}(\text{BH}_4)_2$, the NMR resonances of the magnesium borohydride-diglymates were considerably narrower, indicating enhanced mobility of the $[\text{BH}_4]^-$ anions.

The quasielastic linewidth of the faster $[\text{BH}_4]^-$ groups is equal to 125 μeV at ambient temperature and is almost independent of Q . Both this fact and the previously discussed geometrical constrained posed by the uniform B-H bond length strongly suggest that the $[\text{BH}_4]^-$ anions undergo isotropic jump reorientations around their C2- or/and C3-axes of symmetry with the characteristic jump rate of $1/\tau_0$.^{21,30} It is much harder to determine the rotation mechanism for the slower reorienting group of $[\text{BH}_4]^-$, because the characteristic linewidths are at the limit of the instrumental resolution ($\sim 10 \mu\text{eV}$ at $T=300 \text{ K}$). Nevertheless, the gradual increase of the linewidths with Q indicates that the continuous diffusion

Figure 4: Temperature dependence of the characteristic relaxation times of the two $[\text{BH}_4]^-$ populations. The fast $[\text{BH}_4]^-$ group performs C2/C3-reorientations with the jump rate $1/\tau_0$, the mechanism of the slow $[\text{BH}_4]^-$ rotation is modeled by the rotational diffusion with the relaxation time τ_{rot} . The vertical dashed line corresponds to the onset temperature of the phase transition at $T=330$ K.

on the surface of a sphere could be a possible model description.¹⁶ The radius of this sphere equals the length of the B-H bond, the corresponding relaxation time will be further denoted as τ_{rot} .

To answer the question about the origin of the two distinct populations of $[\text{BH}_4]^-$, it is helpful to consider the temperature dependence of the evaluated parameters in the frame of the proposed model. The studied temperature range includes the phase transition, upon which some minor unassigned peaks of the powder XRD pattern disappear, while the Bragg peaks corresponding to the molar ratio 1:1 are preserved (Figure S3). At the same time the linewidths in the ^1H and ^{11}B MAS NMR spectra (Figure S7) do not change between 313 and 373 K, confirming that the material does not convert into a liquid in the studied temperature range. Generally, the ^{11}B MAS NMR resonances are very narrow for a solid similar to a highly conductive material presented in an earlier study.³¹ The QENS analysis

shows that the phase transition is accompanied with the significant acceleration of the slow $[\text{BH}_4]^-$ groups at 330 K (Figure 4), while the localized vibrations of the borohydride anions are intensified as can be observed from a step-like increase of the associated mean square displacement (Figure 2b). Thus, the thermal energy initially seems to weaken the coordination of the slow group of the $[\text{BH}_4]^-$ anions first. The temperature effect on the confined vibrational modes of the diglyme is seen with a delay at 345 K, while the parameters describing segmental dynamics of the ethereal chain show a step-like increase corresponding to an enhanced flexibility (Figure 3). Still the σ -values considerably lower than 1 Å indicate that the diglyme conformation does not completely change, which is also proved by the IR spectra (Figure S5). The motion of the rapidly tumbling anions is affected to a lesser degree. Nevertheless, the fast reorientations become gradually more disordered above 345 K, which was proved by introducing the rotational diffusion model instead of the C2/C3-jump model into the complete dynamic structure factor. To sum up, the phase transition is accompanied by the dynamical changes in all four contributions resolved in our QENS analysis (vibrational part, quasielastic parts of the diglyme, the slowly and fast reorienting populations of the borohydride anions). This implies that $\text{Mg}(\text{BH}_4)_2$ -diglyme_{0.5} cannot be simply considered just as a mixture of the known 1:1 phase with some contributions of amorphous $\text{Mg}(\text{BH}_4)_2$. The sub-phase, which undergoes a phase transition at 330–345 K, consists of both the diglyme and $\text{Mg}(\text{BH}_4)_2$, but the molar ratio of the components may not coincide with the stoichiometry of the mixture. The existence of the two dynamically different populations cannot be explained solely by existence of the minor and 1:1 phases either. In the latter case only one group of the $[\text{BH}_4]^-$ anions would exhibit an abrupt change of the parameters upon the phase transition. Taking into account that the composition and the structure of the amorphous phase also remain unknown, the further discussion can be based only on the consideration of possible coordination complexes.

The interaction between Mg^{2+} and $[\text{BH}_4]^-$ is known to be highly directional.^{14,15,17,32} Several $[\text{BH}_4]^-$ units can form the coordination environment of Mg^{2+} , two of the four hy-

drogen atoms being directed to the nearest metal atom.^{15,32,33} It is thus conceivable that the probability of clusters formed by Mg-BH₄-Mg blocks increases in the presence of the excess Mg(BH₄)₂. Possible structures of such extended coordination complexes were calculated with the use of the GGA-PBE³⁴ exchange correlation functional, with further details provided in the Supporting Information (Figure S11, Table S4). [BH₄][−] anions connecting two Mg²⁺ serve as bridging ligands, whereas there are terminal [BH₄][−] groups coordinating to only one Mg²⁺. The mobility of the terminal borohydride units is presumably enhanced as compared to the bridging ligands, because any reorientations of the latter induce additional Mg-H bond breaking. Consequently, terminal and bridging borohydrides could give origin to the two dynamically different populations appearing in the QENS analysis. Although faster anion dynamics are more favorable for the Mg conductivity, but the coordination complexes may become unstable resulting in the loss of diglyme as observed in the case of Mg(BH₄)₂-diglyme_{1.0}. We assume that the slowly reorienting population of the [BH₄][−] anions may account for the significantly better thermal stability of Mg(BH₄)₂-diglyme_{0.5}.

In summary, Mg(BH₄)₂-diglyme_{0.5} represents a class of promising magnesium solid-state electrolytes, where high Mg²⁺ conductivity is achieved through the chelating ability of diglyme. The presence of excess Mg(BH₄)₂, which are not solvated by the organic ligand, reduces the conductivity insignificantly, whereas it has a benign effect on the thermal stability of the electrolyte. To characterize the cation-anion and cation-diglyme interactions influencing transport and stability properties, we have developed a comprehensive model description of molecular motions employing the QENS analysis supported by DFT simulations, IR and NMR spectroscopy. The observed localized motions of the ethereal chain point out to its internal flexibility, while the major planar configuration coordinating one Mg²⁺ cation is retained. The two dynamically distinct groups of the [BH₄][−] anions have been revealed and tentatively ascribed to terminal (fast reorienting) and bridging (slowly reorienting) borohydride units. Inhibited dynamics of the [BH₄][−] anions are beneficial for balancing magnesium-diglyme complexes and might be an explanation for the enhanced thermal sta-

bility of $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$. Thus, a powerful combination of the spectroscopic techniques and DFT calculations, indispensable for the analysis of such complex systems as $\text{Mg}(\text{BH}_4)_2\text{-diglyme}_{0.5}$, provides valuable information on molecular level for rational design of improved multivalent solid-state electrolytes.

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Supporting Information Available

The following files are available free of charge.

- $\text{MgBH}_4\text{diglyme_suppmat.pdf}$: material and methods section (DSC and conductivity characterization, IR, XRD, and solid-state MAS NMR spectra, QENS experiment, data analysis, and DFT calculations)
- molA.xyz , molB.xyz : structures of the proposed complexes

This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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$D_G \times 10^9 \text{ m}^2/\text{s}$

$\sigma [\text{\AA}]$

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