Nanocomposite polymer electrolyte for rechargeable magnesium batteries

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Abstract
Nanocomposite polymer electrolytes present new opportunities for rechargeable magnesium batteries. However, few polymer electrolytes have demonstrated reversible Mg deposition/dissolution and those that have still contain volatile liquids such as tetrahydrofuran (THF). In this work, we report a nanocomposite polymer electrolyte based on poly(ethylene oxide) (PEO), Mg(BH\(_4\))\(_2\) and MgO nanoparticles for rechargeable Mg batteries. Cells with this electrolyte have a high coulombic efficiency of 98\% for Mg plating/stripping and a high cycling stability. Through combined experiment-modeling investigations, a correlation between improved solvation of the salt and solvent chain length, chelation and oxygen denticity is established. Following the same trend, the nanocomposite polymer electrolyte is inferred to enhance the dissociation of the salt.

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Introduction

Magnesium batteries have attracted increasing attention as a potentially low-cost, safe technology for large scale applications such as transportation and grid storage [1,2]. Magnesium—a divalent charge carrier—exhibits several intrinsic advantages for battery applications over other metals such as Li or Na. Mg metal is much less reactive in air than both Li and Na which makes it safer to handle; it has a significantly higher volumetric capacity (i.e., 3832 mAh cm\(^{-3}\), 2062 mAh cm\(^{-3}\) and 1136 mAh cm\(^{-3}\)); and smooth, dendrite-free Mg deposition [3,4] and close to a 100% coulombic efficiency (CE) for plating/stripping [5] have been demonstrated in selected electrolytes. These findings are potentially transformative since dendrite formation and low CE have been historic obstacles for Li metal battery development [6-8]. Finally, Mg is both abundant and inexpensive.

Over the past few years, extensive progress has been made in the rechargeable Mg battery field, especially with regard to electrolyte design and development [5,9-22]. Magnesium forms a “truly” passivating film in contact with oxygen or conventional electrolytes (i.e., mixtures of simple Mg salts and aprotic solvents, analogous to those in Li-ion batteries [23]), which impedes Mg\(^{2+}\) transfer [24-26]. Hence, a rechargeable Mg battery requires electrolytes in which no “solid electrolyte interphase” (SEI) or a weakened passivation layer is formed on the Mg metal surface to enable highly reversible Mg plating/stripping [2,21,27-31]. This design metric is in contrast to Li-ion batteries in which a stable, but Li\(^{+}\) conductive SEI is formed [32]. To date, functional electrolytes for a rechargeable Mg battery consist of complicated Mg complexes which possess a partial organometallic character [2,5,11,13,21,33]. These electrolytes usually also contain volatile solvents such as THF [2,21,34-36], which present a safety concern. The search for Mg electrolytes with solvents exhibiting higher boiling points, including ionic liquids [37,38], has been performed [39-41]. However, even though electrochemical Mg plating/stripping behavior has been reported in systems using ILS [42,43] and glymes [41], the reproducibility and truly reversible Mg plating/stripping in these systems still need to be confirmed [28,35], as large overpotentials and low CEs are observed [41,44-46].

Solid-state batteries (mostly based upon Li or Na chemistries [47-49]) provide great advantages such as flexibility in dimensions/geometry, ease of fabrication, a potentially high energy density, and most importantly high safety [49,50]. Solid-state electrolytes for battery applications can be roughly classified into two categories: inorganic and polymer-based. Recently, it has been reported [40] that a Mg(BH\(_4\))(NH\(_2\))\(_2\) solid-state electrolyte can enable reversible Mg plating/stripping (but with a CE of less than 50% and conductivity of 10\(^{-6}\) S/cm at 150 °C). There is also a recent report using metal-organic frameworks as a solid Mg electrolyte, but no electrochemical data have been demonstrated [51].

Significant efforts have been devoted to polymer-based (such as poly(ethylene oxide), PEO) solid-state rechargeable Mg batteries [50,52-57]. However, most of the polymeric solid-state Mg electrolytes in the literature are based on simple Mg salts such as magnesium triflate Mg(SO\(_3\)CF\(_3\))\(_2\) [58] and magnesium(II) bis(trifluoromethanesulfonylimide Mg(N(SO\(_2\)CF\(_3\))\(_2\) (or Mg(TFSI))\(_2\) [59], similar to those for solid-state lithium electrolytes [60]. These salts are known to be incompatible with the Mg metal anode (i.e., unable to produce reversible Mg plating/stripping) [30,35]; furthermore, it has been reported that the electrolytes based upon polymers and simple Mg salts are principally anion conductors (the transport number of Mg\(^{2+}\) being very low if not zero) because of the double charge and small size of Mg\(^{2+}\) [61-63]. There have been some efforts to increase the Mg\(^{2+}\) transference number, but no electrochemical properties—especially those pertaining to reversible Mg plating/stripping—have been reported [64,65]. Finally, there is one interesting report on solid-state Mg polymer electrolytes, consisting of PEO or PVDF and organometallic Mg complex salts, such as Mg(AIEBuC\(_2\))\(_2\)/THF or tetracylglyme, by Aurbach and coworkers [50] demonstrating reversible Mg plating/stripping.

To the best of our knowledge, there has been no report yet on Mg polymer electrolytes without flammable plasticizers that enable reversible Mg plating/stripping. More significantly, there is little fundamental understanding available on solid-state electrolytes for rechargeable Mg batteries. In this work, we report a new nanocomposite electrolyte based on PEO-Mg(BH\(_4\))\(_2\) for reversible Mg plating/stripping with a high CE and stable cycling. A design metric leading to this electrolyte chemistry has been elucidated using combined nuclear magnetic resonance (NMR) spectroscopy and theoretical molecular dynamics (MD) simulations.

Materials and methods

Chemicals

Magnesium borohydride (Mg(BH\(_4\))\(_2\), 95%), magnesium ribbon (99.5%), MgO nanoparticles, polyethylene oxide (PEO, MW 600,000), and anhydrous tetrahydrofuran (THF) were purchased from Sigma-Aldrich. Magnesium bis(trifluoromethylsulfonylimide (Mg(TFSI))\(_2\) was purchased from SOLVIONIC (France). Battery grade dimethoxyethane (DME), diglyme, triglyme, tetraglyme were obtained from Novolyte Technologies, Inc. The solvents were further dried over 3 Å molecular sieve, PEO was dried under vacuum at 60 °C for 24 h, and MgO nanoparticles were dried under vacuum at 300 °C for 24 h before use.
Nanocomposite polymer electrolyte preparation

The nanocomposite Mg polymer electrolyte was prepared using literature methods as used for constructing solid-state lithium battery electrolytes: hot-press [66] or solution casting [67] methods. In brief, for the hot-press method, PEO, Mg (BH4)2, and MgO nanoparticles with a specified composition were sealed in an airtight plastic bottle and mixed by ball-milling for at least 24 h to obtain a homogeneous mixture of the powders. The mass ratio of Mg(BH4)2/MgO/PEO is 1:1:8 which corresponds to the ratio Mg/EO = 1:10 (the ratio is 1:20 for the Mg(TFSI)2/PEO). The mixture was then hot-pressed in a specially designed die at a temperature ranging from 80 to 120 °C for 10–30 min. After cooling, it forms a semi-transparent thin film (Figure 1a, inset) which was then stored in an argon-filled glovebox. All processing was conducted without exposure to air. MgO nanoparticles were added to improve the conductivity and mechanical stability of the solid-state electrolytes [49,68]. For the solution casting method, in a typical procedure, a mixture containing appropriate amount of PEO, Mg(BH4)2, and MgO was dissolved in THF and the resulting solution was poured into a Teflon dish. A free-standing electrolyte film was formed when the THF was slowly evaporated at room temperature. Again, all processing was conducted without exposure to air.

Electrochemistry and cell test

Cyclic voltammetry measurements using a CHI660 workstation were conducted in a standard three-electrode cell with a Mg metal ribbon used as the reference/counter electrodes. The working electrodes were Pt wire, glass carbon, or stainless steel 316. The electrolytes were prepared by dissolving Mg(BH4)2 in glyme solvents. All the electrochemical tests were conducted in an argon-filled glovebox. The CE was calculated by dividing the charge of Mg obtained during stripping over the charge for Mg plating. The solid-state Mg cells were assembled using commercial coin cell parts (standard 2030 parts from NRC Canada) and tested using an Arbin Battery Tester, a CHI660 workstation (for CV test) and a Solartron electrochemical test setup (Model 1287A Potentiostat/Galvanostat plus Model 1260A Impedance/Gain-phase Analyzer).

Characterization

All of the NMR experiments were carried out on a Varian-Agilent 900 MHz NMR spectrometer at a magnetic field of 21.1 T. The 25Mg NMR spectra were referenced to 1.0 M MgCl2 (0 ppm), while 11B MAS NMR spectra were referenced to neat F3B∙O(CH2CH3)2 (0 ppm) using 0.1 M B(OH)3 in D2O as a secondary reference at 19.6 ppm. 1H NMR was referenced to TMS (0 ppm). The transmittance FTIR experiment was carried out on a Bruker IFS 66/S instrument with a mercury-cadmium-telluride (MCT) detector. X-Ray diffraction (XRD) patterns were obtained using a Philips Xpert X-ray diffractometer with Cu Kα radiation at λ = 1.54 Å. Samples were sealed in a special XRD sample holder which prevents oxygen and moisture from contacting the samples. Scanning electron microscope (SEM) images were collected on a JEOL SEM images of the Mg(BH4)2–MgO–PEO nanocomposite electrolyte. (a, b) Surface top view images. (c, d) Cross sectional images. (e–h) Element mapping of the Mg(BH4)2–MgO–PEO solid-state electrolyte.
5900 scanning electron microscope equipped with an EDAX energy dispersive X-ray spectroscopy (EDS) system.

Density functional theory (DFT) calculations

Computational modeling was carried out using the Amsterdam Density Functional (ADF-2013) package. The generalized gradient approximation (GGA) based Becke-Lee-Yang-Parr function [69,70] with dispersion correction (BLYP-D) [71] is employed for geometry optimization. All of the calculations were carried out using the TZ2P basis set (triple Z, 2 polarization functions, all-electron) with the Slater type functional [72] implemented in the ADF program. NMR calculation was performed based on the geometry optimized structures at the same level of the theory and with the same basis set to evaluate the chemical shielding tensors for each atom. For $^{25}$Mg, the chemical shift was referenced with respect to an H$_2$O solvated magnesium ion (i.e., Mg$^{2+}$·6H$_2$O at 0 ppm). The calculated absolute isotropic chemical shift of Mg$^{2+}$·6H$_2$O is −565 ppm. The calculated absolute isotropic chemical shift is converted to the observed ppm with reference to Mg$^{2+}$·6H$_2$O according to $\delta_{\text{iso}}$(obs) = $\delta_{\text{iso}}$(cal) − (−565) = $\delta_{\text{iso}}$(cal) + 565 ppm.

Molecular dynamics simulations

We performed classical molecular dynamics (MD) simulations using GROMACS MD simulation package version 4.5.3 [73]. The initial configurations were obtained by packing the molecules into a cubic box using PACKMOL [74]. The simulation box was made periodic in the xyz directions. The simulations were first performed in an isothermal-isobaric (constant NPT) ensemble for 2 ns to get the right density and then the production runs of 10 ns were obtained from a canonical (constant NVT) ensemble. The systems were energy minimized using the steepest descent followed by conjugated-gradient energy minimization schemes to relax the strained contacts between the ions and molecules in the initial configurations. A Berendsen barostat with time constant 2 ps was used to maintain the pressure of 1 bar and a velocity rescaling thermostat was used to control the temperature at 298 K with a time constant of 0.1 ps. A Verlet leapfrog integration algorithm was used with a time step of 1 fs. The long-range electrostatic interactions were truncated using the particle-mesh Ewald (PME) method at a cut-off distance of 1.2 nm and the Lennard-Jones interactions were truncated at 1.0 nm. We used non-polarizable force fields for all the ions and molecules. The force field parameters for Mg$^{2+}$ is taken from the OPLSAA force field developed by Jorgensen [75]. The force fields for BH$_4^-$ and glymes were developed by using a combination of electronic structure calculations and parameters from generalized Amber force fields (GAFF) [76]. Bulk simulations at 0.01 M contain 6Mg$^{2+}$ and 12BH$_4^-$ with 5799 DME, 3854 diglyme, 3330 triglyme or 2773 tetraglyme, respectively, for the different glymes. The simulation box lengths were approximately 10 nm.

Figure 2 Electrochemical performance of the nanocomposite electrolyte Mg(BH$_4$)$_2$–MgO–PEO. (a) CV (20 mV s$^{-1}$) of Mg plating/stripping on a stainless steel (ss) electrode. (b) CV (0.05 mV s$^{-1}$) of Mg intercalation/deintercalation in Mo$_6$S$_8$. (c) Discharge/charge curve. (d) Cycling stability of a solid-state Mg cell. All electrochemical tests were done in coin cells at 100 °C. Cell architecture: (a) ss/Mg(BH$_4$)$_2$–MgO–PEO/Mg, (b–d) Mo$_6$S$_8$·Mg(BH$_4$)$_2$·MgO–PEO/Mg.
Results

SEM characterization

The nanocomposite polymer electrolyte consists of PEO (MW 600,000), Mg(BH$_4$)$_2$ and MgO nanoparticles. From the SEM images of the nanocomposite, the surface was smooth (Figure 1a) and the MgO nanoparticles were uniformly dispersed in PEO (Figure 1b). From the cross-section images, the thickness of the film is estimated to be 200 μm (Figure 1c)—the thickness is tunable through the amount of materials; and a dense and uniform structure is revealed in the SEM images (Figure 1c and 1d). The element mapping (Figure 1e-1h), showing uniformity for the Mg, B, C and O elements, indicates that the salt Mg(BH$_4$)$_2$ and nanoparticles MgO are uniformly dispersed in PEO, consistent with the SEM images.

Electrochemical properties

Figure 2 shows the electrochemical performance of the Mg cell at 100 °C with the nanocomposite electrolyte Mg(BH$_4$)$_2$-MgO-PEO. A reversible Mg plating/stripping is achieved and the CE is calculated to be 98% via dividing the electric charge for Mg stripping by the electric charge for Mg plating. A polymer electrolyte enabled reversible Mg plating/stripping with high efficiency is a key feature for solid-state rechargeable Mg batteries. The voltage gap between the onset potential for Mg plating and Mg stripping is only 0.2 V (note that this was in a two-electrode cell with Mg used as both the reference and counter electrodes), indicating high reversibility and fast kinetics. The current density is higher than for other polymer electrolytes [50] and solid-state electrolytes [40] reported in the literature. Reversible Mg intercalation/de-intercalation in the cathode Mo$_6$S$_8$ is also shown in Figure 2b. The charge/discharge curves (Figure 2c) show very flat plateaus and the cell using the nanocomposite electrolyte exhibits very high cycling stability for at least 150 cycles (Figure 2d). The Chevrel phase Mo$_6$S$_8$ is selected here to demonstrate the compatibility of the nanocomposite electrolyte with potential cathode materials because it is the most widely studied rechargeable Mg cathode material [77] even though its capacity is low. Higher performance is expected using higher capacity cathode materials.

$^{25}$Mg solid-state NMR

The high performance of the Mg(BH$_4$)$_2$-MgO-PEO nanocomposite polymer electrolyte inspired us to explore the mechanism for why this nanocomposite electrolyte exhibits excellent performance in contrast to many other solid polymer electrolytes. For example, we found that the corresponding Mg(TFSI)$_2$-MgO-PEO nanocomposite does not produce reversible Mg plating/stripping (Supplementary Figure S1). Hence, solid-state NMR measurements were conducted to understand the Mg chemical environment in the solid PEO matrix, i.e., the interaction between Mg ions and PEO. The $^{25}$Mg solid-state NMR spectrum (Figure 3) obtained from pure Mg(BH$_4$)$_2$ shows a typical second order quadrupolar powder pattern from the central transition (m = +1/2 ↔ −1/2) of a quadrupolar nucleus $^{25}$Mg with nuclear spin number I = 5/2 [78]. This characteristic second-order powder pattern disappears in Mg(BH$_4$)$_2$-PEO (MgO is not included in the NMR study in order to facilitate the analysis) which indicates a strong interaction between the Mg$^{2+}$ cations and the oxygen atoms in the PEO chains (the XRD powder pattern shows the loss of crystallinity of Mg (BH$_4$)$_2$ in the Mg(BH$_4$)$_2$-PEO polymer electrolyte, see Supplementary Figure S2). However, in contrast to the $^{25}$Mg NMR spectra of the Mg(TFSI)$_2$-PEO polymer electrolyte (Figure S1), the $^{25}$Mg spectrum of Mg(BH$_4$)$_2$-PEO does not show the resonance peaks at 26.7 ppm or −165.5 ppm which indicates an absence of the hexagonal Mg-O coordination (MgO$_6$) and its sideband [78] which are due to the coordination of the Mg$^{2+}$ cations and the oxygen atoms from PEO, and also perhaps from some of the oxygen atoms of the TFSI$^-$ anions (for the Mg(TFSI)$_2$-PEO polymer electrolyte) [38]. However, it has been reported [79] that there are no ion pairs in Mg(TFSI)$_2$-PEO electrolytes when the ratio between the repeating EO units (−CH$_2$−O−) and Mg$^{2+}$ cations is larger than 9 and the usual coordination number for Mg$^{2+}$ cations is six. In our Mg(TFSI)$_2$-PEO electrolyte, the EO/Mg$^{2+}$ ratio is 20. In related LiX-PEO polymer electrolytes with weakly coordinating anions such as TFSI$^-$, Li-O coordination by ether oxygens alone occurs if the EO/Li$^+$ ratio is high enough [80–82]. Due to the similar cation size, Mg$^{2+}$-PEO mixtures may have a comparable coordination environment to Li$^+$-PEO mixtures. Therefore, the Mg$^{2+}$ cations in Mg(TFSI)$_2$/PEO may be strongly coordinated by six oxygen atoms and their mobility thus limited which perhaps explains, in part, why the Mg(TFSI)$_2$-PEO electrolyte does not produce reversible Mg plating/stripping and its Mg$^{2+}$ transport number is close to zero [61-63].

The $^{25}$Mg NMR resonance obtained from the Mg(BH$_4$)$_2$-PEO electrolyte is rather broad at 25 °C, whereas that at higher temperature (80 °C) can be fitted to both narrow and broad components (Figure 3). The fast motion of the Mg$^{2+}$ cations averages out anisotropic components that would otherwise appear in the $^{25}$Mg spectrum, resulting in a narrower line width, via so-called motional narrowing [83]. This suggests that the amounts of fast moving Mg$^{2+}$ cations, which corresponds to the relative peak area of the narrow component, is significantly enhanced with increasing temperature, likely due to the enhancement of chain

Figure 3 $^{25}$Mg solid-state NMR spectra of Mg(BH$_4$)$_2$ at 25 °C and Mg(BH$_4$)$_2$-PEO at 25 °C and 80 °C.
fluctuations, which is similar to the enhancement of Li⁺ cation mobility in polymer electrolytes with dissolved LiX salts [84,85]. The mobility enhancement of the Mg²⁺ cations at elevated temperature is also observed from the $^{11}$B and $^1$H NMR spectrum (Supplementary Figure S3) where both the $^{11}$B and $^1$H resonances become narrower in the Mg{(BH$_4$)$_2$}-PEO electrolyte. These results represent the first NMR study of solid-state electrolytes for rechargeable Mg battery applications.

Discussion

Model system study

In order to further understand how the coordination interactions affect the electrochemical properties, we chose smaller glyme model molecules (DME, diglyme, triglyme and tetruglyme) which have a similar structure to PEO. This makes the characterization and theoretical modeling easier since PEO is a large molecule without a well-defined molecular weight.

Figure 4a shows the cyclic voltammograms (CVs) of Mg plating/stripping in the four solutions: Mg{(BH$_4$)$_2$}-DME, Mg{(BH$_4$)$_2$}-diglyme, Mg{(BH$_4$)$_2$}-triglyme and Mg{(BH$_4$)$_2$}-tetraglyme (0.01 M Mg{(BH$_4$)$_2$} was used due to the limited solubility of Mg{(BH$_4$)$_2$} in glymes [39]). The CE for Mg plating/stripping is also shown. As is evident, the CE (and the current density) increases in the order of tetraglyme > triglyme > diglyme > DME (i.e., the efficiency increases with increasing chain length of the glymes). Thus, we infer that longer chain glymes favor the electrochemical processes of Mg plating/stripping.

In the Mg{(BH$_4$)$_2$}-glyme solutions, since the complete dissociation of Mg{(BH$_4$)$_2$} is unlikely [14,86], we propose the following simplified equilibrium to describe the dissociation of Mg{(BH$_4$)$_2$}:

\[
[Mg{(BH}_4)_2]_x \rightleftharpoons [Mg{(BH}_4)]^x + BH_4^- \rightleftharpoons [Mg]^{2x} + 2BH_4^- \quad (1)
\]

with the overall Mg$^{2+}$ coordination number to anions and/or ether oxygens likely to be constant at five-six. This dissociation equilibrium will be influenced by the solvent structure (in the case of glymes, they can be considered to be ligands) which provide a driving force for the salt dissociation. Stronger coordination between the Mg$^{2+}$ cations and solvent will lead to a higher degree of dissociation of the Mg$^{2+}$ cations and BH$_4^-$ anions. For electrolytes with lithium salts, fully ion dissociation (i.e., full cation solvation) is desirable as this generally improves the electrochemical properties of the electrolyte as well-solvated charge carriers usually correlate with improved charge transfer—both in the bulk electrolyte and at the electrode interface. But, importantly, this may not be the case for Mg$^{2+}$-based electrolytes, as exemplified by the poor performance of electrolytes with the weakly coordinating TFSI⁻ anion. Full solvation (i.e., [Mg$^{2+}$])—by either one or two polyether chains—may result in immobilized Mg$^{2+}$ cations due to the stronger coordinate bonds formed between the cations and ether oxygens than for Li$^+$ cations. Extensive ionic association (i.e., [Mg{(BH$_4$)$_2$}]_x aggregate clusters of cations and anions) is also undesirable as the mobility of the Mg$^{2+}$ cations will again be strongly restricted. Instead, some form of intermediate association (i.e., [Mg{(BH$_4$)}$^x$]) in which the cations are only partially solvated by one or two polyether chains may lead to the most favorable mobility of the cations.

Glymes are considered to be very effective at coordinating cations due to both the strong donor character of the ether oxygen electron lone pairs and to the flexibility of the ethylene oxide segments [87]. Therefore, in the Mg{(BH$_4$)$_2$}-glyme mixtures, the coordination interactions between the Mg$^{2+}$ cations and glymes originates from the coordination by the ether oxygens. Stronger interactions (i.e., increased electron donation) would increase the shielding of the Mg nuclei, thus lowering the $^{25}$Mg NMR chemical shift. This is shown in $^{25}$Mg NMR spectra of these solutions in Figure 4b. It is evident that the $^{25}$Mg chemical shift moves to lower values from DME through diglyme to triglyme. This indicates that the coordination interactions increase with chain length, which is consistent with the known literature [88-91]. However, interestingly, the $^{25}$Mg chemical shift in tetruglyme falls between that of triglyme and diglyme.
To aid in identifying the origin for the exception of tetraglyme from the length-dependent trend observed for the other species, DFT calculations were carried out. Based upon our previous report [39] and the coordination structures of Mg$^{2+}$ cations with ethers and glymes [88,92,93], the Mg(BH$_{4}$)$_{2}$ coordination structures in different glymes were assigned to be: [Mg(BH$_{4}$)$_{2}$]$_{2}$: DME, Mg(BH$_{4}$)$_{2}$: diglyme, Mg(BH$_{4}$)$_{2}$: triglyme, and Mg(BH$_{4}$)$_{2}$: tetraglyme. The DFT calculated $^{25}$Mg NMR chemical shift trend was found to be (Supplementary Table S1):

$$[\text{Mg(BH}_{4})_{2}]_{2} \rightarrow \text{DME} \rightarrow \text{Mg(BH}_{4})_{2} \rightarrow \text{diglyme} \rightarrow \text{Mg(BH}_{4})_{2} \rightarrow \text{triglyme} \rightarrow \text{Mg(BH}_{4})_{2} \rightarrow \text{tetraglyme}$$

If, however, one of the BH$_{4}^{-}$ anions is removed from the Mg(BH$_{4}$)$_{2}$·tetraglyme complex (i.e., Mg(BH$_{4}$)$_{2}$ dissociates), the DFT calculated $^{25}$Mg NMR chemical shift trend is instead:

$$[\text{Mg(BH}_{4})_{2}]_{2} \rightarrow \text{DME} \rightarrow \text{Mg(BH}_{4})_{2} \rightarrow \text{diglyme} \rightarrow [\text{Mg(BH}_{4})_{2}]^{+} \cdot \text{tetraglyme} \rightarrow \text{Mg(BH}_{4})_{2} \rightarrow \text{triglyme}$$

which is in excellent agreement with the trend shown in Figure 4b. This result indicates that higher Mg(BH$_{4}$)$_{2}$ dissociation may perhaps be expected in tetraglyme.

The $^{25}$Mg NMR peak shapes is also informative regarding the dissociation of Mg(BH$_{4}$)$_{2}$ in the series of glymes. The line width—measured through the full-width-at-half-maximum ($\Delta \nu _{1/2}$)—increases from DME (85 Hz), diglyme (128 Hz), triglyme (327.62 Hz) to tetraglyme (527.67 Hz) (Figure 2), indicating the enhancement of diversity of the coordination environment surrounding the Mg$^{2+}$ cations in long chain glymes. Based upon the above Mg(BH$_{4}$)$_{2}$ dissociation equilibrium (Eq. 1), we infer that the $^{25}$Mg NMR peak is the overall averaged signal of solvated [Mg(BH$_{4}$)$_{2}$], [Mg(BH$_{4}$)$_{2}$]$^{+}$, and [Mg]$^{2+}$ solvate species. The narrow peaks for DME and diglyme likely originate from these solvents forming complexes in which all of the solvent ether oxygens are coordinated to the Mg$^{2+}$ cations. For example, this occurs in crystalline solvate structures for (DME)$_{2}$:Ca(BH$_{4}$)$_{2}$ and (diglyme)$_{2}$:Mg(BH$_{4}$)$_{2}$ [93,94]. The longer triglyme and tetraglyme, with more ether oxygens and conformation flexibility, may instead adopt more numerous modes of coordination to the cations, with some or all of the ether oxygens from one or two glyme molecules coordinated,

which may vary the local environment of the Mg$^{2+}$ cations to a greater extent (for both the solvent and anion coordination due to steric factors) thus explaining the broad peak widths observed for the solutions with these glymes.

This is also confirmed from the transmittance FTIR spectra. The spectrum in the range of 2500-2100 cm$^{-1}$ is shown in Figure 4c. A comparison of the B–H stretching from Mg(BH$_{4}$)$_{2}$ dissolved in DME, diglyme, triglyme and tetraglyme shows a vibration band around 2170 cm$^{-1}$, which is not present in the pure solvents, which is assigned as the B–H stretching feature. The red-shift of the $\sim$2170 cm$^{-1}$ peak is clearly evidenced by changing the solvent from DME to tetraglyme (Figure 4c), indicating the presence of more uncoordinated BH$_{4}^{-}$ anions in the solutions with longer chain glymes [14]. This is consistent with the NMR results showing that longer glymes promote the dissociation of Mg(BH$_{4}$)$_{2}$ to a greater extent. It should be noted that the vibration features from the solvent molecules (e.g., peaks at $\sim$2400, 2350, 2240, 2130 cm$^{-1}$) are even stronger than for the B–H stretching from Mg(BH$_{4}$)$_{2}$, and the very low concentration of Mg(BH$_{4}$)$_{2}$ due to its poor solubility further decreases the intensity of the B–H peaks.

**Molecular dynamics simulations**

Classical MD simulations of the electrolyte system were performed to obtain a better understanding of the effects of ligands on the ionic coordination in the glyme solutions. Figure 5a shows the obtained average radial distribution function (RDF) for the Mg$^{2+}$ cation interaction with specific atoms in the anion and tetraglyme (similar RDFs are obtained for Mg(BH$_{4}$)$_{2}$ in DME, diglyme and triglyme). The first coordination shell originates from Mg–H (from BH$_{4}^{-}$) and manifests around 1.9 Å followed by another strong peak from Mg–B (from BH$_{4}^{-}$) at 2.3 Å, indicating a very strong and rigid interaction between the salt cation and anion and arguing for the formation of ion-pairs and/or aggregates in the liquid electrolytes. The peak for Mg–O (from tetraglyme) is observed at 2.1 Å, while the Mg–C (from tetraglyme) peak occurs at 3.1 Å, consistent with the solvent as a secondary ligand. These RDF results are consistent with the literature in that the coordination between the Mg$^{2+}$ and BH$_{4}^{-}$ ions is

![Figure 5](image-url)
through the Mg-H bond (instead of Mg-B bond) [39] and between Mg2+ and the glymes through the Mg-O bond [39,87]. Figure S5b shows the RDF of Mg-O (from glyme) for the different glymes, where we observe a shift in the peak position to a shorter distance with an increase in the chain length from DME to tetraglyme which signifies the enhanced coordination between the Mg2+ cation and oxygens of glymes with the increase in chain length. Also, we find that the coordination numbers of BH4- in the first coordination shell of the Mg2+ cations falls quite dramatically from 1.969 in DME to 0.628 in tetraglyme, supporting the conclusions regarding a higher dissociative tendency (i.e., less ionic association) for the long-chain glymes (Supplementary Figure S5).

The above analysis implies that even higher dissociation of Mg(BH4)2 may be expected in PEO [88]; but due to the absence of the polygonal Mg-O coordination (MgO6) in Mg(BH4)2-PEO, the complete dissociation of Mg(BH4)2 is unlikely. Therefore, it is possible that many of the [BH4-]2- anions are dissociated from the divalent Mg2+ cations resulting in solvated [MgBH4]+ ion pairs; thus, the solvated [MgBH4]+ cation complexes may function as the main Mg2+ charge carrier in the nanocomposite polymer electrolytes. More experimental and theoretical simulation work is needed, however, to further delineate the solvation and ionic association interactions within such electrolytes.

Conclusions

In summary, a nanocomposite polymer electrolyte consisting of PEO, Mg(BH4)2 and MgO nanoparticles has been developed for rechargeable Mg batteries. It results in a high coulombic efficiency of 98% for Mg plating/stripping, high cycling stability, and highly efficient Mg intercalation/de-intercalation in Mo6S8. A fundamental combined experiment-modeling investigation has been conducted to understand the mechanisms behind the enhanced performance. Mg(BH4)2-glyme electrolytes have been utilized to aid in elucidating the effects of ligand structure on the electrochemical properties of Mg electrolytes. Longer-chain glymes demonstrate a stronger coordinating capability to the Mg2+ cations through their increased electron donor and chelating ability. An even more enhanced dissociation of the salt Mg(BH4)2 is thus expected in PEO and, if following the same trend as for the glymes, improved electrochemical performance. The reason that reversible Mg plating/stripping was observed in Mg(BH4)2-MgO-PEO nanocomposite polymer electrolytes but not in Mg(TFSI)2-MgO-PEO is probably that it forms solvated [MgBH4]+ cation complexes in the former. The understanding and design metrics obtained from the Mg(BH4)2/PEO nanocomposite system may be further developed and utilized in nanocomposite solid electrolytes for other multivalent chemistry.

Author contribution

Y.Y. Shao and J. Liu conceived and designed this work. Y.Y. Shao conducted the electrochemistry work; J.Z. Hu, T.B. Liu, M.Y. Hu, X.C. Deng, and S.C. Xu acquired the NMR data; Y.Y. Shao, J.Z. Hu, T.B. Liu, K.S. Han, and K. T. Mueller analyzed the NMR data; Z.H. Wei and Y. Wang acquired and analyzed the IR data; Y.Y. Shao and J.L. Wang fabricated and tested the nanocomposite electrolytes; M. Gu and C.M. Wang carried out the electron microscopy characterization; Z.M. Nie acquired and analyzed the XRD data; G.S. Li provided the cathode material; N.N. Rajput and K. Persson performed the MD simulations; Y.Y. Shao, N.N. Rajput, K. Persson and J. Liu wrote the paper; K.R. Zavadil, W.A. Henderson and T.B. Liu contributed significantly to the preparation of the manuscript. All authors participated in the discussion of the work.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nano.2014.12.028.

References

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