Coordination Chemistry in magnesium battery electrolytes: how ligands affect their performance

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Magnesium battery is potentially a safe, cost-effective, and high energy density technology for large scale energy storage. However, the development of magnesium battery has been hindered by the limited performance and the lack of fundamental understandings of electrolytes. Here, we present a study in understanding coordination chemistry of Mg(BH$_4$)$_2$ in ethereal solvents. The O donor denticity, i.e. ligand strength of the ethereal solvents which act as ligands to form solvated Mg complexes, plays a significant role in enhancing coulombic efficiency of the corresponding solvated Mg complex electrolytes. A new electrolyte is developed based on Mg(BH$_4$)$_2$, diglyme and LiBH$_4$. The preliminary electrochemical test results show that the new electrolyte demonstrates a close to 100% coulombic efficiency, no dendrite formation, and stable cycling performance for Mg plating/stripping and Mg insertion/de-insertion in a model cathode material Mo$_6$S$_8$ Chevrel phase.

Low cost and safe battery technologies are critical to both transportation and grid energy storage applications$^{1-4}$. Significant efforts have been made in past years to investigate technologies beyond lithium-ion chemistry$^5$. Magnesium batteries could potentially provide high volumetric capacity due to the divalent nature of Mg$^{2+}$ (3832 mAh/cm$^3_{Mg}$ vs. 2062 mAh/cm$^3_{Li}$ and 1136 mAh/cm$^3_{Na}$), improved safety (dendrite-free Mg deposition$^6,7$), and low cost by using earth abundant Mg element$^8$. Significant progresses$^8-11$ have been made since Aurbach and coworkers$^{12}$ reported the first rechargeable Mg battery prototype. These include new electrolytes$^{10,13-17}$ and recent progresses in cathode$^{18-26}$ and anode materials$^{27}$.

Electrolytes play a pivotal role in all battery systems, particularly for Mg batteries. Conventional electrolytes by mixing Mg salts (e.g., Mg(ClO$_4$)$_2$) and nonaqueous solvents (e.g., propylene carbonate), a typical approach to preparing electrolytes for lithium batteries, do not produce reversible plating/stripping of Mg$^{28,29}$. This is usually attributed to the nonconductive layer that is formed on Mg surface in these conventional electrolytes. This nonconductive layer is similar to the so-called “solid electrolyte interphase” (SEI) in lithium batteries but could not conduct Mg$^{2+}$ probably due to the divalent nature of Mg cation$^{30}$. This is fundamentally different from Li$^+$ and Na$^+$ systems in which the SEI in fact enables Li or Na batteries.

There are only a limited number of electrolytes that show reversible Mg plating/stripping; but many of these electrolytes contain volatile solvents such as tetrahydrofuran (THF)$^{13,15,16}$ or dimethoxyethane (DME)$^{17}$. Electrolytes based on less volatile or nonvolatile solvents are desired$^{11,12}$ and recent progresses in cathode$^{18-26}$ and anode materials$^{27}$. It is believed that the solution coordination structures of Mg complexes in these electrolytes are critical for reversible Mg plating/stripping, but limited information is available in the literature$^{10,11}$.

Back in 1950’s, Connor et al.$^{35}$ reported electrochemical deposition of Mg metal from Mg(BH$_4$)$_2$ ethereal solutions with 90% efficiency. Recently, Mohkadi et al.$^{37}$ reported reversible Mg plating/stripping in the mixed solution of Mg(BH$_4$)$_2$, LiBH$_4$ and DME, in which the coulombic efficiency of 94% for Mg plating/stripping was achieved. For a metal anode, 100% coulombic efficiency is desired but very difficult to achieve; a coulombic efficiency of lower than 100% may indicate that some plated Mg metal is not dissolved during the stripping process. The stripping problem could be related to the coordination structure of Mg complexes in the electrolyte$^{26}$. A stable Mg(BH$_4$)$_2$ coordination structure may be easier to form during Mg stripping, thus favors the stripping process and improves the coulombic efficiency. Furthermore, the stability of Mg(BH$_4$)$_2$ coordination structures
may be related to the ligands. In literature, it has been shown that the ligand displacement in the complex Mg(BH$_4$)$_2$·nL (L = ligand) is achieved according to the series Et$_2$O < THF < DME < DGM (diglyme)$^{15}$, which is consistent with the chelating effect$^{16-19}$. It is reported that the stability of the solvated Mg(BH$_4$)$_2$ complexes with those ligands increases with the denticity of the solvent ligands$^{19}$. Mohtadi et al.$^{17}$ showed a higher coulombic efficiency of Mg(BH$_4$)$_2$-based electrolyte in DME solvent (a bidentate ligand) than that in THF solvent (a monodentate ligand). These previous studies led us to think that alternative solvents like DGM (a tridentate ligand) could be a more donating ligand for magnesium to further improve the coulombic efficiency of Mg plating/stripping in Mg(BH$_4$)$_2$-based electrolyte close to 100%. More importantly, the Mg(BH$_4$)$_2$/glymes mixture is also a good model system in understanding the molecular structures in Mg complex electrolytes and study the structure-property relationship of Mg electrolytes.

As a result, a potentially safer electrolyte based on Mg(BH$_4$)$_2$ and DGM is developed (the boiling/flash points of DGM, DME, THF are 162 °C/57 °C, 85 °C/2 °C, 66 °C/−14 °C, respectively). LiBH$_4$ is also employed as an additive since it has been shown to further increase the performance in the case of Mg(BH$_4$)$_2$/DME$^{17}$. This electrolyte with 0.1 M Mg(BH$_4$)$_2$ and 1.5 M LiBH$_4$ in DGM demonstrates a close to 100% coulombic efficiency (CE) for reversible Mg plating/stripping under the preliminary electrochemical test condition — the Mg(BH$_4$)$_2$ concentration is limited by its solubility in DGM. A well-known Mg intercalation material Mo$_6$S$_8$ Chevrel phase$^{19}$ is used as a model cathode to evaluate the electrolyte which shows high reversibility and stability. More importantly, we focused on the fundamental understanding of the structure-property relationship for the Mg electrolyte through the spectroscopic study of the coordination chemistry of Mg$^{2+}$ with ligands (solvent and BH$_4^−$) in DGM and comparison with that in DME and THF. The performance of electrolytes was found to be strongly correlated with the coordination structures of the electrochemically active Mg$^{2+}$ species in the solutions.

**Results**

Figure 1a shows the cyclic voltammograms (CVs) of Mg electrochemical plating/stripping in electrolytes of Mg(BH$_4$)$_2$ dissolved in DGM, DME and THF respectively. The coulombic efficiencies which are calculated with a widely-used literature method$^{9,17}$ are 77%, 67%, 34% for DGM, DME and THF respectively (see Figure S1 for examples of how to calculate coulombic efficiency); The overpotential for Mg plating/stripping in DGM is the smallest; and the current density in DGM is the highest, followed by DME and then THF. Therefore, these experimental observations clearly show that solvents have significant effects on Mg electrochemistry. We notice that the purity of Mg(BH$_4$)$_2$ is 95%, the 5% impurities may also affect the electrochemical performance; however, since we use the same Mg(BH$_4$)$_2$, the trend of comparison between different electrolytes/solvents should not be affected.

The LiBH$_4$ additive also changes Mg electrochemistry dramatically$^{17}$. To take DGM as an example, Figure 1b shows the CVs of Mg electrochemistry in Mg(BH$_4$)$_2$-LiBH$_4$/DGM electrolytes with various LiBH$_4$ concentrations. Figure 1c summarizes the effect of solvents and LiBH$_4$ concentration on the coulombic efficiency of Mg plating/stripping. In Figure 1b, with increasing LiBH$_4$ concentration, the waves of both Mg plating and Mg stripping shift towards 0 V, and the peaks become narrower. This indicates enhanced reaction kinetics of both processes. The smallest voltage gap between Mg plating and stripping potentials is only ~ 0.2 V. The current density is also related to LiBH$_4$ concentration which shows the highest value at LiBH$_4$ concentration of 1.5 M (which is chosen for further investigation).

The coulombic efficiency increases with LiBH$_4$ concentration in all of the three solvents DGM, DME and THF (Figure 1c); for example, in DGM it increases from 77% for the electrolyte without LiBH$_4$ to 90% for 0.2 M LiBH$_4$, to 99% for 0.6 M LiBH$_4$ and close to 100% when LiBH$_4$ concentration increases to 1.0 M and beyond — we understand that more accurate and precise measurements are needed to confirm the exact coulombic efficiency$^{19}$; since we use the same method to calculate coulombic efficiency for each electrolyte$^{19}$, the trend should not be affected. More interestingly, the coulombic efficiency in DGM (with the same LiBH$_4$ concentration) is always higher than those in DME and THF, with THF being the lowest one, which is consistent with the results without LiBH$_4$ (Figure 1a). These indicate the significant effects of solvents and LiBH$_4$ additive on the coulombic efficiency. We measured the conductivity of the electrolytes, for example 3.27 mS/cm, 2.07 mS/cm, 2.61 mS/cm for DGM [0.1 M Mg(BH$_4$)$_2$ + 1.5 M LiBH$_4$], DME

![Figure 1](https://www.nature.com/scientificreports)

Figure 1 | (a) Cyclic voltammograms (20 mV/s) recorded on a Pt electrode in 0.01 M Mg(BH$_4$)$_2$ in DGM, DME and THF; (b) Cyclic voltammograms (20 mV/s) recorded on a Pt electrode in 0.1 M Mg(BH$_4$)$_2$/DGM with LiBH$_4$ of various concentrations; (c) The coulombic efficiency (CE) of Mg plating/stripping of investigated electrolytes: 0.1 M Mg(BH$_4$)$_2$ + LiBH$_4$ + solvent (solvent = DGM, DME, or THF), and the concentrations of LiBH$_4$ x = 0–2.0 M.
[0.1 M Mg(BH$_4$)$_2$ + 0.6 M LiBH$_4$, THF [0.1 M Mg(BH$_4$)$_2$ + 1.5 M LiBH$_4$], respectively, which are higher than or comparable to other Mg battery electrolytes$^{43,44}$ and are also close to lithium battery electrolytes$^{43,44}$. This also indicates that the difference in the electrolyte performance is not due to their conductivity since these three electrolytes have similar conductivity. As we will discuss later, both solvents and BH$_4^-$ coordinate with Mg as ligands which affects the structure of Mg complexes, thus their performance as an electrolyte.

It is well-known that for a metal anode in a battery, two factors are the most critical: morphology of plated metal (smooth, dendrite-free surface desired) and coulombic efficiency (100% desired). These two problems are major challenges for lithium batteries in that they lead to severe safety issues and short lifetime of a battery$^{45,46}$. Mg(BH$_4$)$_2$-LiBH$_4$-DGM electrolyte shows promise in these two aspects for Mg anode. The SEM image (Figure 2a) shows a smooth, dendrite-free morphology of Mg plated from Mg(BH$_4$)$_2$-LiBH$_4$-DGM electrolyte ([LiBH$_4$] = 1.5 M). We also further investigate the reversibility of Mg plating/stripping in Mg(BH$_4$)$_2$-LiBH$_4$-DGM electrolyte ([LiBH$_4$] = 1.5 M). The XPS spectra (Figure 2b, red trace) recorded after Mg plating on Pt electrode clearly show plated Mg, and Mg completely disappeared after stripping (Figure 2b, black trace). We did not observe any detectable boron (binding energy ~ 188 eV$^{47}$) or lithium (binding energy ~ 55 eV) in XPS spectra; oxygen signal (binding energy ~ 531 eV) was observed but very little carbon signal (binding energy ~ 285 eV) was observed in XPS spectra (Figure 2b). These indicate that no or very little electrolyte decomposition and no lithium deposition take place. It should be mentioned that Aurbach and coworkers have reported that ethers are stable against magnesium$^{48,49}$. XRD results confirm that the plated metal is Mg (Figure 2c) and EDS results reveal no carbon element indicating no electrolyte decomposition (Figure S3). These indicate that Mg plating/stripping is highly reversible, and the coulombic efficiency is close to 100% under the test condition. Of course, more efforts are needed to further study morphology evolution during long-term cycling of Mg plating/stripping and the exact values of coulombic efficiency. But this is beyond the focus of this paper. In this work, we focus on the structure-property relationship of the Mg electrolyte.

In order to understand coordination structures of Mg(BH$_4$)$_2$ in these solvents and correlate the structure with its performance, DGM and DME solvated Mg(BH$_4$)$_2$ complexes were isolated and characterized by $^1$H NMR and $^{11}$B NMR spectroscopies in non-coordinating CD$_2$Cl$_2$, which does not interrupt the structures of the solvated Mg(BH$_4$)$_2$. Figure 3 shows $^1$H NMR spectra of the solvated Mg(BH$_4$)$_2$ complexes with DGM and DME respectively.

In the $^1$H NMR spectrum (Figure 3a), DGM solvated Mg(BH$_4$)$_2$ species shows proton resonances at 3.96 ppm (CH$_2$), 3.85 ppm (CH$_2$) and 3.61 ppm (CH$_3$) for the coordinating DGM. As expected for the shielding effect of DGM metalation, the proton resonances of the coordinating DGM are downfield shifted in comparison to those of free DGM in CD$_2$Cl$_2$ (3.56, 3.49 and 3.33 ppm respectively). Due to different coupling interactions with $^1$B (I = 3/2) and $^{10}$B (I = 3) isotopes, two sets of hydride signals, a major quartet ($J_{BH} = 80$ Hz) and a minor septet ($J_{BH} = 30$ Hz) were observed at the same chemical shift, −0.36 ppm (Figure 3a, inset). Integrals of proton resonances give 1:2 ratio of DMG versus BH$_4^-$ (Figure 3a), which leads to a ratio of Mg(BH$_4$)$_2$:DGM = 1:1. Thus, Mg(BH$_4$)$_2$ in DGM is formulated as seven coordinated Mg(BH$_4$)$_2$DGM (Figure 4a), which is consistent with the previously reported solid state structure determined by single crystal X-ray diffraction$^{40}$. In Mg(BH$_4$)$_2$DGM, DGM is a tridentate pincer ligand and each BH$_4^-$ anion coordinates with Mg via two hydrides. According to integrals of proton resonances (Figure 3b), the composition of Mg(BH$_4$)$_2$ complex in DME can be identified as Mg$_2$(BH$_4$)$_2$DME$_3$ by considering coordination geometry of Mg(BH$_4$)$_2$DGM and Mg(BH$_4$)$_2$:THF$^{35}$, Mg(BH$_4$)$_2$ in DME is assigned as a dimeric Mg species, Mg$_2$(BH$_4$)$_2$(DME)$_3$ (Figure 4b). In Mg$_2$(BH$_4$)$_2$(DME)$_3$, each Mg has two BH$_4^-$ anions, a bidentate DME ligand and a monodentate DME ligand bridging to the other Mg. In the $^{11}$B NMR spectrum (Figure S4), Mg(BH$_4$)$_2$:DGM and Mg$_2$(BH$_4$)$_2$(DME)$_3$ display the characteristic pentet ($J_{BH} = 80$ Hz) at −42.46 and −40.37 ppm respectively. Consistent with the above structural assignments for Mg(BH$_4$)$_2$:DGM and Mg$_2$(BH$_4$)$_2$(DME)$_3$, previous single crystal X-ray diffraction established THF solvated Mg(BH$_4$)$_2$ as Mg(BH$_4$)$_2$(THF)$_3$ with a similar coordination geometry (Figure 4c)$^{40}$.

For purpose of practical applications, preliminary electrochemical tests are carried out to study the electrolyte (Mg(BH$_4$)$_2$-LiBH$_4$-DGM, [LiBH$_4$] = 1.5 M). The preliminary cycling test tells that this electrolyte is stable for Mg plating/stripping (Figure 5a); the coulombic efficiency retains close to 100% during cycling and the electric charge for Mg plating/stripping, which corresponds to the electrode capacity at such a cycling condition, increases slightly during cycling (Figure 5a).

A well-known Mg intercalation material Mo$_6$S$_8$ Chevrel phase$^{19,52}$ is used as a model cathode to evaluate the new electrolyte for Mg$^{2+}$ insertion/de-insertion reaction. Cyclic voltammogram in Figure 5b
shows reversible Mg insertion (peak at 1.25 V) and de-insertion (peak at 1.43 V) in Mo\textsubscript{6}S\textsubscript{8} Chevrel phase cathode. The Mg cell which consists of Mg metal anode, the new electrolyte and Mo\textsubscript{6}S\textsubscript{8} cathode delivers an initial capacity of 99.5 mAh/g (based on Mo\textsubscript{6}S\textsubscript{8} only) at a C/10 rate (Mo\textsubscript{6}S\textsubscript{8} theoretical capacity is 128.8 mAh/g); the capacity drops slightly for the first a few cycles and then is stabilized for the remaining cycles with a 89.7% capacity retention for 300 cycles (Figure 5c). These indicate the new Mg(BH\textsubscript{4})\textsubscript{2}-LiBH\textsubscript{4}-DGM electrolyte is able to support reversible Mg\textsuperscript{2+} insertion/de-insertion in cathode material and the cycling is stable.

Discussion
We believe that the performance of the electrolyte is closely related with the solution structure of Mg ions in solvents. The better performance of the new Mg(BH\textsubscript{4})\textsubscript{2}-LiBH\textsubscript{4}-DGM electrolyte could be explained by the coordination chemistry in the electrolytes. In terms of denticity and donating strength, these coordinating solvent molecules (DGM, DME and THF) could impose different kinetic and thermodynamic influences on the Mg electrochemical process, which is essentially related with coulombic efficiency. Several aspects are rationalized below. In terms of the entropy effect, DGM as a tridentate solvent ligand, is more thermodynamically favorable than DME (and THF) in the complexion of Mg\textsuperscript{2+} during 2 electron oxidation. This is consistent with the stability of these complexes that long-chain glymes lead to more stable complex\textsuperscript{36,37,41,53}. In addition, DGM complexion is also kinetically favorable since only one DGM is involved in the stripping process in comparison to 1.5 molecules of DME and 3 molecules of THF. As for the additive of LiBH\textsubscript{4} which acts as the second coordination ligand (BH\textsubscript{4}\textsuperscript{2-}), from the kinetics viewpoint, its increased concentration can also speed up the stripping process at electrode surface. In brief, chelating solvent and increased BH\textsubscript{4}\textsuperscript{2-} concentration can significantly improve the stripping process through the synergetic effects as discussed above, which accounts for the enhanced coulombic efficiency. Other factors may also contribute to the enhanced performance. For example, the solubility of Mg(BH\textsubscript{4})\textsubscript{2} increases with the addition of LiBH\textsubscript{4}. This could

![Figure 3](https://example.com/figure3.png)

**Figure 3** | 'H NMR spectra of Mg(BH\textsubscript{4})\textsubscript{2}DGM (a) and Mg\textsubscript{2}(BH\textsubscript{4})\textsubscript{4}(DME)\textsubscript{3} (b) recorded at 22°C in CD\textsubscript{2}Cl\textsubscript{2}. Insets are the hydride resonances. Chemical shift values and integrals are labeled at the top and the bottom of resonances respectively.

![Figure 4](https://example.com/figure4.png)

**Figure 4** | Coordination structures of Mg(BH\textsubscript{4})\textsubscript{2} in DGM (diglyme), DME and THF (the structure in THF is from Ref. 50,51).
are consistent with the solid structures from single crystal X-ray diffraction in the literature. Mg(BH₄)₂ forms coordination structures of Mg(BH₄)₂ DMG, Mg(BH₄)₂ (DME)₃, Mg(BH₄)₂ (THF)₃ in DMG, DME and THF respectively. DMG complexation is thermodynamically and kinetically favorable; LiBH₄ additive acts as the second coordination ligand (BH₄⁻) and its increased concentration can also speed up the stripping kinetics at electrode surface. In brief, chelating solvent and increased BH₄⁻ concentration can significantly improve the stripping process through synergistic effects, thus improve the coulombic efficiency. This structure–property relationship will help to design new electrolytes for Mg battery. For future Mg battery development, there are still significant challenges in electrolyte and electrode materials. New electrolytes using scalable chemical processes with large electrochemical window, less volatility and new cathodes using earth abundant materials with high voltage and high capacity are needed. These are under development and will be reported later.

Methods

Chemicals and material synthesis. Magnesium borohydride (Mg(BH₄)₂, 95%) lithium borohydride (LiBH₄, 95%), anhydrous tetrathiafulvalene (THF), magnesium ribbon (99.5%) were purchased from Sigma-Aldrich. THF was distilled from LiBH₄ using 3 Å molecular sieve. Battery grade dimethoxethane (DME) and diglyme (DGM) were obtained from Novolyme Technologies, Inc. (Cleveland, US).

Chevrel phase Mo₆S₈ was synthesized using the molten salt synthesis method as reported in the literature by Aurbach and coworkers. Mo₆S₈ (99% Aldrich), CuS (99.5%), and Mo (99%) were obtained from Aldrich, all in powder form. The XRD patterns of in-house made CuMo₆S₈ and Mo₆S₈ are shown in Figure S5.

Electrochemistry. Cyclic voltammetry was conducted in a standard three-electrode cell with fresh polished Mg ribbon as reference and counter electrodes which are controlled by a CHI660D workstation (CH instruments). The working electrodes are Pt, glass carbon, or stainless steel 316. The electrolytes were prepared by dissolving Mg(BH₄)₂ and LiBH₄ in solvents. LiBH₄ is soluble in diglyme (4.25 M⁻¹) and DME (0.60 M), while Mg(BH₄)₂ is slightly soluble. Both LiBH₄ and Mg(BH₄)₂ are highly soluble in THF. The solubility of Mg(BH₄)₂ in diglyme and DME was measured by slowly adding Mg(BH₄)₂ into diglyme or DME, which is ~ 0.1 M/0.01 M with/without LiBH₄ respectively. The electrolyte conductivity was measured using WP CP650 conductivity meter (OA KONT Instruments). The electrochemical testing was conducted in an argon filled glovebox with O₂ and H₂O below 0.1 ppm. The coulombic efficiency (CE) was calculated by dividing the total amount of charge for Mg stripping over the total amount of charge for Mg plating (see examples in Figure S1), which is a widely-used method for CE measurement in literature.

Prototype rechargeable Mg batteries comprising a fresh polished Mg disk anode, a Mo₆S₈-carbon composite cathode and a separator (glass fiber B) soaked in the electrolyte solution, were tested in coin type cells (standard 2030 parts from NRC Canada). The Mo₆S₈-carbon composite electrode slurry was prepared by mixing Mg(BH₄)₂, diglyme and optimized concentration of LiBH₄. This LiBH₄-DGM electrolyte ([LiBH₄] = 0.6 M) for reversible Mg plating/stripping; (b) Cyclic voltammogram (0.05 mV/s) of Mg insertion/de-insertion on the Mo₆S₈ Chevrel phase at 22°C. 1H NMR (CD₂Cl₂, ppm): 3.96 (m, 4 H, CH₂); 11B NMR (CD₂Cl₂, ppm): -42.46 (pentet, JHH = 80 Hz). The preparation for Mg(BH₄)₂(DME) complex was conducted in a similar manner. 1H NMR (CD₂Cl₂, ppm): 3.81 (s, 12 H, CH₂), 3.59 (s, 18 H, CH₂), -0.33 (quartet, JHH = 80 Hz), 16 H, BH₄⁻; 11B NMR (CD₂Cl₂, ppm): 40.37 (pentet, JHH = 80 Hz).

X-ray photoelectron spectroscopy (XPS) was measured on a Physical Electronics Quantum 2000 Scanning ESCA Microprobe with a 16 element multichannel detector. This system uses a focused monochromatic Al Kα X-ray (1486.7 eV) source and a spherical section analyzer. The X-ray beam used was a 100 W, 100 μm diameter beam that was rastered over a 1.3 mm × 0.2 mm rectangle on the sample. The X-ray beam is incident normal to the sample and the photoelectron detector was at 45° off-normal using an analyzer angular acceptance width of 20° × 20°. Wide-scan data were collected using a pass energy of 117.4 eV. For the Ag3d₅/₂ line, these conditions produce FWHM of better than 1.6 eV. High energy resolution spectra were collected using a pass energy of 80 Hz.

In summary, we have developed a new electrolyte based on Mg(BH₄)₂, diglyme and optimized concentration of LiBH₄. This new electrolyte demonstrates a close to 100% coulombic efficiency, stable cycling performance, and no dendrite formation; and the new electrolyte is able to support reversible Mg⁺⁺ insertion/de-insertion in a well-known Mg battery cathode Mo₆S₈ Chevrel phase. In comparison, electrolytes comprising Mg(BH₄)₂ in DME and THF show lower coulombic efficiencies. The solution structures of Mg(BH₄)₂ in different solvents are investigated and identified using NMR, which increase the concentration of active species and the conductivity of the electrolyte, thus enhances the electrochemical performance. It should be point out that the limited concentration of Mg(BH₄)₂ (0.1 M) may lead to limited rate performance of Mg batteries for practical applications. But the finding of the structure-property relationship will help the discovery of new electrolytes. We are working on high concentration Mg(BH₄)₂ electrolytes and will report the results later.

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Figure 5 | (a) Cycling stability of Mg(BH₄)₂-LiBH₄-DGM ([LiBH₄] = 1.5 M) for reversible Mg plating/stripping; (b) Cyclic voltammogram (0.05 mV/s) of Mg insertion/de-insertion on the Mo₆S₈ Chevrel phase cathode in Mg(BH₄)₂-LiBH₄-DGM electrolyte ([LiBH₄] = 1.5 M); (c) Discharge/charge profiles of an Mg-Mo₆S₈ cell using the Mg(BH₄)₂-LiBH₄-DGM electrolyte ([LiBH₄] = 1.5 M) (inset: cycling stability).

The physicochemical characterization. Nuclear magnetic resonance (NMR). Excess Mg(BH₄)₂ was added to 2 mL DGM (diglyme) to prepare a saturated solution. After filtering off insoluble Mg(BH₄)₂, the clean solution was stirred for 30 min and then mixed with 30 mL pentane to precipitate Mg(BH₄)₂ DGM complex as white powder. The white powder was washed with pentane (10 mL) three times and then dried by vacuum. The white powder was dissolved in CDCl₃ to record NMR spectra. 1H and 11B NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for 1H, 162 MHz for 11B) at 22°C. 1H NMR (CDCl₃, ppm): 3.96 (m, 4 H, CH₂); 11B NMR (CDCl₃, ppm): -42.46 (pentet, JHH = 80 Hz). The preparation for Mg(BH₄)₂(DME) complex was conducted in a similar manner. 1H NMR (CDCl₃, ppm): 3.81 (s, 12 H, CH₂), 3.59 (s, 18 H, CH₂), -0.33 (quartet, JHH = 80 Hz), 16 H, BH₄⁻; 11B NMR (CDCl₃, ppm): 40.37 (pentet, JHH = 80 Hz).
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Author contributions
Y.Y.S. and J.L. conceived and designed this work. Y.Y.S., T.B.L., G.S.L., M.G., Z.M.N., M.E., D.P.L. and C.M.W. performed the experiment, acquired and analyzed the data. Y.Y.S., T.B.L. and J.L. wrote the paper. G.S.L., J.X., C.M.W. and J.G.Z. revised the manuscript, and all authors participated in the discussion of this work.

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