The electrolytes containing halide-free inorganic magnesium salt Mg(BH₄)₂ dissolved in ether solvents have shown reversible Mg deposition-dissolution performance. Herein, we improved the anodic stability of the electrolytes on non-inert stainless-steel electrode by mixing PP₄-TFSI ionic liquid with tetraglyme (TG) and dimethoxyethane (DME) ether solvents. The effect of mixing ratios and salt concentrations on the electrochemical behavior of the electrolyte was investigated. High anodic stability, good ionic conductivity, excellent cycling efficiency, feasibility of the preparation and good compatibility toward Mo₆S₈ and TiO₂ insertion cathode make the electrolytes promising for the potential application in rechargeable magnesium batteries.

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be overcome by lowering the ion solvation energies via the addition of high-polarity cosolvents.

Recently, pure alkoxy-ammonium based ILs and PEGylated-ILs (in which polyether chains are pendent from the organic pyrrolidinum cation of ILs) were designed and prepared to meet the coordination conditions required for Mg deposition/dissolution from the Mg(BH$_4$)$_2$ source. The presence of polyether chains in the ILs can displace TFSI$^-$ and BH$_4^-$ anions to coordinate with Mg$^{2+}$, thus facilitate reversible electrochemical deposition-dissolution of Mg. Herein, in order to simplify the preparation technology, develop IL and cosolvent system for promoting dissociation of Mg-containing ions, the electrochemical behavior of the electrolytes simply dissolving the Mg(BH$_4$)$_2$-LiBH$_4$ complex in TG, DME and PP$_14$TFSI mixed solvents with different ratios were investigated based on previous Mg(BH$_4$)$_2$-LiBH$_4$/TG electrolytes. In view of few reports about the compatibility of ILs-based magnesium electrolytes with cathodes, an appropriate electrolyte formulation for Mg batteries and hybrid Mg-Li batteries was further identified for practical application.

**Experimental**

**Chemicals and material synthesis.**—Magnesium borohydride (Mg(BH$_4$)$_2$, 95%) and magnesium ribbon (1 mm diameter) were purchased from Sigma-Aldrich. Lithium borohydride (LiBH$_4$, 95%) was purchased from K&J Scientific. Dimethoxyethane (DME) and tetraglyme (TG) purchased from Aladdin reagent and N-methyl-N-butyl-piperidinium bis(trifluoromethanesulfonylimide) (PP$_14$TFSI) from Lanzhou Institute of Chemical Physics were further dried using 3Å molecular sieve. Commercially available TiO$_2$ (Aladdin Industrial Corporation) was used without further treatment.

The synthetic work for the electrolytes were conducted in an argon-filled glove box (Mbraun, Unilab, Germany) containing less than 2 ppm water and O$_2$ by dissolving the predetermined amount of Mg(BH$_4$)$_2$ and LiBH$_4$ in solvents under stirring for at least 2 hours. Synthesis route of Mo$_6$S$_8$ followed the literature.

**Measurement procedures and apparatus.**—The conductivity of the electrolytes was measured using a DDB-303A conductivity meter (INESA INSTRUMENT). IR analysis of the solutions was run using a Spectrum 100 FT-IR spectrometer (Perkin Elmer, Inc., USA). X-ray Photoelectron Spectroscopy (XPS) measurements were conducted on a Kratos spectrometer (AXIS Ultra DLD). X-ray diffraction (XRD) analysis of the magnesium deposits was conducted on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu Kα radiation. The morphology of the deposits was observed using scanning electron microscope (SEM) on a FEI SIRION200 field-emission microscope. Before the analysis of the deposits, the sample deposited for 8 hour at −0.1 mA was washed in the glove box with drying THF solvent to remove soluble residue and then transferred out of the box and kept without exposure to the atmosphere.

Cyclic voltamograms (CVs) were conducted in three-electrode cells inside an argon-filled glove box using an electrochemical instrument of CHI604A Electrochemical Workstation (Shanghai, China). The working electrode was a stainless steel (type 316), platinum or aluminum disk (geometric area = 3.14 × 10$^{-2}$ cm$^2$), which was polished with a corundum suspension and rinsed with dry acetone before use, and magnesium ribbon (99.5%, 0.15 mm thickness, Sigma-Aldrich), which was polished by metallocraphic abrasive paper (800Cw) and then cleaned up using tissues, as counter and reference electrodes. Mg ribbon can be used directly as a pseudo reference electrode, simplifying the experiments. Electrochemical magnesium deposition-dissolution cycles were examined with CR2016 experimental coin cells on a land battery measurement system (Wuhan, China). Stainless steel foil (12 mm, type 316, 25 μm thickness, Shenda Metals Co., Ltd.) was served as the working electrode (substrate). Mg ribbon as the counter electrode. An Entek PE separator (ET 20–60, 37% porosity, 20 μm thickness) and a fiber membrane as the separator.

The cells were assembled in the glove box. Magnesium was deposited onto the stainless steel substrate for fixed periods of 30 min followed by stripping to a fixed potential limit of 0.8 V vs. Mg at a constant current density of 0.1 mA. There was a 30 second rest between deposition and dissolution. The magnesium deposition and dissolution on the substrate were referred to as the discharge and charge process, respectively. The time of charge divided by the time of discharge was defined as the deposition-dissolution efficiency.

Cathode electrode slurry was prepared by mixing 80 wt% active material, 10 wt% super-P carbon powder (Timcal) and 10 wt% poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidinone. The electrodes were formed by coating the slurry onto stainless steel foil current collectors, drying at 80°C for 1 hour, pressing at 2 MPa, and drying again at 80°C for at least 12 hours under vacuum. The electrode, with a diameter of 12 mm, contains 0.5~0.7 mg active material, and the typical thickness of the active layer is 100 μm. Electrochemical behavior was examined via CR2016 coin cells with a magnesium counter electrode, an Entek PE membrane separator. The cells were assembled in an argon-filled glove box. Galvanostatic discharge-charge measurements were conducted at ambient temperature on a Land battery measurement system (Wuhan, China).

**Results and Discussion**

Fig. 1a shows typical CVs of the electrochemical Mg deposition-dissolution from the electrolytes of 0.5 mol L$^{-1}$ Mg(BH$_4$)$_2$/PP$_14$TFSI, 0.5 mol L$^{-1}$ Mg(BH$_4$)$_2$/PP$_14$TFSI + TG (2:1 volume ratio), and 0.5 mol L$^{-1}$ Mg(BH$_4$)$_2$+1.5 mol L$^{-1}$ LiBH$_4$/PP$_14$TFSI+TG (2:1) at 50 mV s$^{-1}$. Stainless steel (SS), an important component in coin-cell casing and current collector, was used as a working electrode. Typical voltammetric response was observed in the solutions at the second cycle and after it. Compared with that from Mg(BH$_4$)$_2$/PP$_14$TFSI solution, the addition of TG improves the reversibility of Mg deposition-dissolution. The cathodic current increase from approximately −0.8 V (vs. Mg/Mg$^{2+}$) corresponds to Mg deposition at the SS substrate, and the anodic peak at around 0.3 V is derived from the electrochemical dissolution of deposited Mg. It has been reported that O$_2$ (in the air) can react with magnesium electrode to form MgO and Mg(OH)$_2$. The cathodic current peak at ca. 0.3 V corresponds to the oxygen reduction reaction (ORR), which is a side reaction that occurs in the Mg/Li battery when the Mg anode is in contact with the electrolyte. The ORR produces MgO and H$_2$O, which can react further to form Mg(OH)$_2$. The Mg(OH)$_2$ can then react with the Mg anode to form Mg$_2$CO$_3$, which is a solid product that can block the Mg electrode and prevent further Mg deposition.

To clarify the influence of TG on coordination with Mg$^{2+}$ ions, Fourier transform infrared (FTIR) analyses were performed. Fig. 1b shows a disparity between TG, PP$_14$TFSI and PP$_14$TFSI+TG (2:1) solvents and Mg(BH$_4$)$_2$/PP$_14$TFSI. After adding TG, the peak density of 850 cm$^{-1}$ concerned with CH$_2$ rocking vibration with C−O stretching, and those of 1028, 1100 and 1247 cm$^{-1}$ related to C−O−C stretching decrease. New shoulder peaks at 862 and 1259 cm$^{-1}$, which arise from the coordination between the C−O group and the Mg$^{2+}$ ions, appear. The ion-dipole interaction between the TG moiety and the Mg$^{2+}$ ions affects the stretching vibration mode.

Fig. 1c shows the CVs of Mg electrochemical deposition-dissolution on Pt disk electrode from three solutions. There is still few magnesium deposition-dissolution from Mg(BH$_4$)$_2$/PP$_14$TFSI solution when the electrode is changed from stain steel to platinum, and the addition of TG improves the reversibility. Although the solution shows high reversibility on Pt electrode due to an apparent limitation of SS electrode to intermediate efficiencies of Mg deposition-dissolution, a higher anodic stability is obtained on SS electrode (shown in inset of Fig. 1c). A similar trend was also observed in the
electrolytes without PP14TFSI.\textsuperscript{25} The thermodynamic stability limit of the electrolyte should be independent of electrode material.\textsuperscript{24} The difference probably reflects the varying kinetics due to different properties of electrode/electrolyte interface.

LiBH\textsubscript{4} was further added in the solution since it has been shown to have a remarkable effect to Mg(BH\textsubscript{4})\textsubscript{2}/THF, Mg(BH\textsubscript{4})\textsubscript{2}/DGM and Mg(BH\textsubscript{4})\textsubscript{2}/TG solutions due to the improved ionic conductivity as a result of increasing Mg(BH\textsubscript{4})\textsubscript{2} dissociation in the solution.\textsuperscript{26–27} Herein, the deposition-dissolution currents decrease after adding LiBH\textsubscript{4}, which is resulted from the larger turbidity of the solution as shown in Fig. 1d, thus lower ionic conductivity (1.33 and 0.38 mS cm\textsuperscript{-1}, respectively). The anodic stability improves and reaches nearly 3.0 V (vs. Mg/Mg\textsuperscript{2+}) on SS electrode (Fig. 1a), probably related to the change of electronic structure of the Mg complexes in the solutions.

In order to keep the anodic satiability and improve the Mg deposition-dissolution currents, the effect of salt concentrations on the electrochemical performance was further investigated. Figs. 2a and 2b compare CVs of Mg deposition-dissolution on SS electrode from the solutions of 0.5 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}/LiBH\textsubscript{4}/PP\textsubscript{14TFSI} and Mg(BH\textsubscript{4})\textsubscript{2}/PP\textsubscript{14TFSI}+TG solution (2:1) and 0.25 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}/LiBH\textsubscript{4}/PP\textsubscript{14TFSI}+TG (2:1) with different concentrations of LiBH\textsubscript{4}, respectively. The electrochemical window changes little, and maintains at approximately 3.0 V (vs. Mg/Mg\textsuperscript{2+}). However, the deposition-dissolution currents change with the different concentrations of magnesium and lithium salts, which are probably related to the difference of the ionic conductivity (shown in Table 1). The higher concentration obviously increases the viscosity of the solutions and decreases the ionic conductivity. 0.25 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}+0.25 mol L\textsuperscript{-1} LiBH\textsubscript{4}/PP\textsubscript{14TFSI}+TG (2:1) solution has a high currents for Mg deposition and dissolution. Further decreasing the concentration may lead to the limited rate performance of Mg batteries for practical application. With increasing LiBH\textsubscript{4} concentration, the peak potentials of Mg dissolution shift toward 0 V, indicating enhanced reaction kinetics. This means that the difference in the electrolyte performance is not just due to their conductivity. Both solvents and BH\textsubscript{4}– can coordinate with Mg\textsuperscript{2+} as ligands which affect the structure of Mg complexes, thus the performance of the electrolyte. Acting as the second coordination ligand, the addition of LiBH\textsubscript{4} and its increased concentration can speed up the stripping process at electrode surface from the kinetics viewpoint.\textsuperscript{28}

Fig. 2c compares CVs of the electrochemical Mg deposition-dissolution from the solutions of 0.25 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}+0.25 mol L\textsuperscript{-1} LiBH\textsubscript{4}/PP\textsubscript{14TFSI}+TG with different volume ratios of PP\textsubscript{14TFSI} and TG (2:1, 1:1 and 1:2). The solution with 2:1 volume ratio of PP\textsubscript{14TFSI}+TG shows no appreciable anodic current up to 3.0 V (vs. Mg/Mg\textsuperscript{2+}) and an obvious increase of the anodic current at approximately 3.2 V (vs. Mg/Mg\textsuperscript{2+}) on SS electrode. In order to ensure further the anodic stability of the electrolyte, chronamperometry measurements at different voltage hold of 2.8 V and 3.0 V were conducted on SS electrode from 0.25 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}+0.25 mol L\textsuperscript{-1} LiBH\textsubscript{4}/PP\textsubscript{14TFSI}+TG (2:1) solution. As shown in Fig. 2d, the negligible current density in chronamperometric experiments confirms 3.0 V anodic stability of the solution. As shown in Fig. 2c, the anodic stability of the solutions decreases with increasing the amount of the TG. The voltammetric response in the composition of 2:1 volume ratio of PP\textsubscript{14TFSI}+TG leads to the lower peak currents, however, a higher anodic stability. The former is related to the lower electric conductivity (1.44, 1.96 and 2.18 mS cm\textsuperscript{-1}), respectively, and the latter is probably because the solution composition has a preferable ionic structure.

In our previous report, the heating-treatment process for the preparation of 0.5 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}+1.5 mol L\textsuperscript{-1} LiBH\textsubscript{4}/TG is a key issue to improve the electrochemical window due to a lower electron cloud density of the radical group after heating treatment.\textsuperscript{27} The influence of heating treatment for 0.25 mol L\textsuperscript{-1} Mg(BH\textsubscript{4})\textsubscript{2}+0.25 mol L\textsuperscript{-1} LiBH\textsubscript{4}/PP\textsubscript{14TFSI}+TG (2:1 volume ratio) on the Mg deposition-dissolution performance is shown in Fig. 3a. The electrochemical window changes...
little, maintains at approximately 3.0 V (vs. Mg/Mg\(^{2+}\)). The currents for Mg deposition-dissolution increases and the overpotential decreases a little with the increase of heating temperatures. Considering the simplification of operation, unheated process, that is, stirring ensures the existence of MgO.\(^{47}\) XRD measurement was further conducted to ensure the component of the deposit and the pattern is shown in Fig. 3d. The diffraction peaks observed at 2\(\theta\) = 32.2, 34.4, 36.6, 47.8, 57.4, 63.1 and 68.6\(^{\circ}\) are attributed to metallic Mg (JCPDS file 35–0821), suggesting that deposition of pure metal Mg was obtained from the solution. No peaks are observed for the surface oxide state. It has been reported that metallic Mg is highly reactive to O\(_2\) even under a very high vacuum (\(\sim\)10\(^{-8}\) Torr) and therefore thin films prepared under different background pressures must exhibit the surface characteristics of the oxides in their respective XPS results.\(^{45}\) Ley et al.\(^{46}\) have studied the XPS of pure Mg films in the pressure range 3 \times 10\(^{-10}\)–6 \times 10\(^{-11}\) Torr and the positions of the peaks in the core electron spectra were 49.4 eV and 88.55 eV for the Mg 2p and Mg 2s levels, respectively. Herein, the peak shifts for Mg on oxidation are 1.2 eV and 1.05 eV for the Mg 2p and Mg 2s levels, respectively. The O 1s spectrum shows a peak at 531.6 eV (inset of Fig. 3c), further ensuring the existence of MgO.\(^{46}\) XRD measurement was further conducted to ensure the component of the deposit and the pattern is shown in Fig. 3d. The diffraction peaks observed at 2\(\theta\) = 32.2, 34.4, 36.6, 47.8, 57.4, 63.1 and 68.6\(^{\circ}\) are attributed to metallic Mg (JCPDS file 35–0821), suggesting that deposition of pure metal Mg was obtained from the solution. No peaks are observed for the signals associated to magnesium oxide. It indicates the surface oxide layer is extremely thin and cannot be detected by XRD measurement. Surface SEM image shows the deposit layer is compact and uniform.

### Table I. The ionic conductivities of the electrolytes with different concentrations of Mg(BH\(_4\))\(_2\) and LiBH\(_4\), and different volume ratios of PP\(_{14}\)TFSI, TG and DME.

| PP\(_{14}\)TFSI | TG | DME | Mg(BH\(_4\))\(_2\) (mol L\(^{-1}\)) | LiBH\(_4\) (mol L\(^{-1}\)) | Ionic conductivity (mS cm\(^{-1}\)) at 15\(^{\circ}\)C |
|---------------|----|-----|------------------|-----------------|---------------------|
| 1             | 0  | 0   | 0.50             | 0               | 0.65                |
| 2             | 1  | 0   | 0.50             | 0               | 1.33                |
| 2             | 1  | 0   | 1.50             | 0               | 0.38                |
| 2             | 1  | 0   | 0.50             | 0.25            | 1.32                |
| 2             | 1  | 0   | 0.25             | 0.50            | 1.17                |
| 2             | 1  | 0   | 0.25             | 0.25            | 1.44                |
| 1             | 1  | 0   | 0.25             | 0.25            | 1.96                |
| 1             | 2  | 0   | 0.25             | 0.25            | 2.18                |
| 2             | 0  | 1   | 0.25             | 0.25            | 3.64                |
| 2             | 0.5| 0.5 | 0.25             | 0.25            | 2.68                |
| 2             | 1  | 1   | 0.25             | 0.25            | 3.01                |

Figure 2. Typical CVs of Mg electrochemical deposition-dissolution on SS disk electrode at 50 mV s\(^{-1}\) from the solutions consisting of (a) 0.5 mol L\(^{-1}\) Mg(BH\(_4\))\(_2\)+LiBH\(_4\)/PP\(_{14}\)TFSI+TG (2:1) and (b) 0.25 mol L\(^{-1}\) Mg(BH\(_4\))\(_2\)+LiBH\(_4\)/PP\(_{14}\)TFSI+TG (2:1) with different concentrations of LiBH\(_4\); (c) 0.25 mol L\(^{-1}\) Mg(BH\(_4\))\(_2\)+0.25 mol L\(^{-1}\) LiBH\(_4\)/PP\(_{14}\)+TG with different volume ratios of PP\(_{14}\)TFSI and TG (2:1, 1:1, 1:2), inset shows enlarged section near the upper voltage limit, (d) The chronoamperometry curves on SS electrode from 0.25 mol L\(^{-1}\) Mg(BH\(_4\))\(_2\)+0.25 mol L\(^{-1}\) LiBH\(_4\)/PP\(_{14}\)TFSI+TG (2:1).
Figure 3. (a) Typical CVs of Mg electrochemical deposition-dissolution on SS electrode at 50 mV s$^{-1}$ from 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$+0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI+TG (2:1) solutions with different heating temperatures. (b) (c) XPS spectrum, and (d) XRD result of deposits from 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$+0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI+TG (2:1), inset of (d) is the SEM image of the electrodeposits obtained at 2.55 C cm$^{-2}$ charge.

Figure 4. (a), (b) The cycling curves and (c) cycling efficiency of Mg deposition-dissolution on SS substrate at 0.1 mA, and (d) CVs of Mg electrochemical deposition-dissolution on SS electrode at 50 mV S$^{-1}$ from 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$+0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI+TG+DME with different volume ratio of PP$_{14}$TFSI, TG and DME. Inset of (d) show a typical CV curve on Al disk electrode at 50 mV s$^{-1}$ from 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$+0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI+TG+DME (2:1:1).
Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME solutions with different volume ratios of PP$_{14}$TFSI:TG:DME. Note that the electrolytes with mixed solvents show a greatly reduced potential barrier for Mg deposition during the first cathodic scan, decreasing obviously compared with the solution without DME (Fig. 4a). Moreover, overpotentials appear and maintain at ~0.25 V and 0.25 V during the subsequent cathodic and anodic scans, indicating low ohmic resistance for Mg deposition-dissolution on the SS electrode. Compared with the electrolyte with 2:0.5:0.5 PP$_{14}$TFSI:TG:DME mixed solvent, 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME (2:1:1) shows lower Mg deposition-dissolution overpotentials, which is related to a higher ionic conductivity (Table I). Fig. 4c shows the Mg deposition-dissolution cycling efficiencies, which are calculated according to the ratios of the charge amounts of magnesium dissolution to those of magnesium deposition. 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME (2:1:1) shows better cycling efficiencies. The coulombic efficiencies increase gradually from initial 79.9% with the progressive cycle numbers and reach to 91.5% after 3 cycles and are stable at above 92% gradually from initial 79.9% with the progressive cycle numbers, showing better cycling efficiencies. The coulombic efficiencies increase slightly at the initial several cycles and is stabilized at approximately 92% after 20 cycles. The electrolyte with Mg-complex/IL systems exhibits higher anodic stability$^{33-36}$ and more stable Mg deposition-dissolution efficiencies$^{36}$ than Grignard reagent/IL systems. However, higher efficiencies are necessary for the purpose of practical applications. Thus, we believe that further optimization of the ionic structure of Mg(BH$_4$)$_2$ + LiBH$_4$/PP$_{14}$TFSI + TG + DME system will realize a promising electrolyte system for rechargeable Mg battery. Fig. 4d compares the CVs of Mg electrochemical deposition-dissolution on SS electrode from 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME solutions with different volume ratios of PP$_{14}$TFSI:TG:DME. The anodic stability of the solution with 2:1:1 ratio on SS electrode can maintain at approximately 3.0 V with higher current densities. The improved Mg deposition-dissolution performance seems to be partly due to the improved ionic conductivity (Table I). However, the electrolyte with PP$_{14}$TFSI + DME (2:1) solvent does not exhibit the highest current density even if having the highest ionic conductivity among four solutions (Fig. 4d). It means that the CV properties of Mg deposition-dissolution of electrolytes are also influenced by other factors, for example, electrolyte viscosity, the solution structure of Mg ions in solvents, action intensity of solvents to salts and interfacial properties of electrolytes with electrode. The inset of Fig. 4d shows CVs on Al disk electrode at 50 mV s$^{-1}$ from 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME (2:1:1). The electrolyte exhibits much lower Mg deposition-dissolution current and anodic stability on Al than those on SS, indicating slow deposition-dissolution speed on Al and the existence of Al corrosion in the electrolyte. Mg$^{2+}$ insertion material Mo$_6$S$_8$ (128.8 mAh g$^{-1}$ theoretical capacity) and Li$^+$ insertion material TiO$_2$ (168.0 mAh g$^{-1}$ theoretical capacity) were chosen as cathode to test the compatibility with the electrolyte. The coin cell was constructed using 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME (2:1:1) solution as the electrolyte, Mo$_6$S$_8$ and TiO$_2$ as the cathode, and Mg as the anode. As shown in Fig. 5a, the cell with Mo$_6$S$_8$ cathode delivers 74.3 mAh g$^{-1}$ discharge capacity and 57.3 mAh g$^{-1}$ charge capacity at 0.05 C rate. At the second and third cycles, the cell delivers 54.8 mAh g$^{-1}$ and 54.4 mA g$^{-1}$ discharge capacity, respectively. The plateau at approximately 1.35 V in the first discharge curve, which disappears in subsequent discharge curves, relates to ion intercalation in inner sites with more difficulty upon subsequent cycles and that at 1.1 V relates to that in outer ones.$^7$ The plateaus at approximately 1.3 V and 1.45 V (which is unconspicuous but always existent, as shown in inset of Fig. 5a) in charge curves are concerned with the de-intercalation from outer ones and inner sites, respectively. The discharge capacity increase slightly at the initial several cycles and is stabilized at approximately 55 mAh g$^{-1}$ for the remaining 55 cycles (Fig. 5b), indicating the electrolyte is compatible with Mg$^{2+}$ intercalation material. Fig. 5c shows the voltage profiles of the TiO$_2$ Mg coin cell with 0.25 mol L$^{-1}$ Mg(BH$_4$)$_2$ + 0.25 mol L$^{-1}$ LiBH$_4$/PP$_{14}$TFSI + TG + DME (2:1:1) electrolyte between 0.5 and 1.7 V at a rate of 0.2 C. During the first discharge, TiO$_2$ exhibits a well-defined plateau at approximately 0.72 V, corresponding to the Li$^+$ intercalation. The first charge plateau is observed at a slightly higher potential of 1.11 V. In the 5th and 10th cycles, the discharge platform moves up slightly to about 0.8 V, and the charge platform remains almost the same at 1.1 V, meaning a lower polarization. The first discharge capacity is 128.6 mAh g$^{-1}$, and the corresponding charge capacity is 124.1 mAh g$^{-1}$. There is a...
little increase in the 5th and 10th cycles, with the discharge capacities being 133.3 mAh g⁻¹ and 133.2 mAh g⁻¹, respectively. The activation process during the initial cycles is related to the slow infiltration of electrolyte in electrode. Fig. 5d displays the discharge and charge capacities with respect to cycle number at 0.2 C and 2 C over 200 cycles. The close match between the discharge and charge capacities manifests an excellent reversibility. The reversible specific capacity remains at the quite considerable value of ~120 and 85 mAh g⁻¹ for all of the cycles, demonstrating good cycling stability. It is worth noting that the electrochemical performance of two intercalation materials in the electrolyte with PP14TFSI ionic liquid is worse than those in the electrolyte without the ionic liquid, which is probably resulted from slow penetration of the electrolyte between the cathode particles, poor contact property of electrode/electrolyte interface, and low ion diffusion rate in the electrolyte.

Conclusions

We proposed a ternary solvent system consisting tetracylme (TG) and dimethoxyethane (DME) ether solvents and PP14TFSI ionic liquid for Mg(BH₄)₂ based Mg electrolytes and investigated the effects of the solvent ratios and salt concentrations on the electrochemical behavior. The electrolyte 0.25 mol L⁻¹ Mg(BH₄)₂+0.25 mol L⁻¹ LiBH₄/PP14TFSI+DME (2:1:1) shows good ionic conductivity, high reversibility for Mg deposition-dissolution and 3.0 V (vs. Li⁺/Li) anodic stability on non-inert stainless steel. Furthermore, good compatibility with Mg₂⁺ insertion material Mo₆S₈ and Li⁺ insertion material TiO₂ indicates that the solution could be used as a potential electrolyte in rechargeable Mg battery system.

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