Characteristics of tetrahydrofuran-based electrolytes with magnesium alkoxide additives for rechargeable magnesium batteries

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Abstract

The electrochemical behavior of magnesium (Mg) metal was investigated in tetrahydrofuran (THF)-based solutions containing magnesium bromide (MgBr_2) and/or magnesium ethoxide ($\text{Mg}(\text{OEt})_2$). THF solutions containing a single solute, MgBr_2 or $\text{Mg}(\text{OEt})_2$, show no visible faradaic current based on Mg deposition and/or dissolution. However, the electrolyte system containing both solutes, $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$, gives a reversible current response of Mg deposition and dissolution. The ionic structure of the electrolyte system containing the binary solute was examined by infrared (IR) spectroscopy and density functional theory (DFT) calculations. It was confirmed that MgBr_2 and $\text{Mg}(\text{OEt})_2$ are coordinated (solvated) with THF molecules to form an $\text{EtO-Mg-Br}\cdot 4\text{THF}$ complex. The DFT calculations also suggest the possible formation of μ -complexes for the $\text{MgBr}_2/\text{Mg}(\text{OEt})_2$ binary system in THF. The voltammetric responses at the Pt electrode indicate low overpotential and high coulombic efficiency for Mg deposition and dissolution in THF-based solutions containing suitable molar ratios of MgBr_2 and $\text{Mg}(\text{OEt})_2$. The constant-current charge-discharge cycling of Mg in $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$ electrolyte also shows low overpotential and good cyclability over 300 cycles.

Key words: Rechargeable magnesium battery, magnesium bromide, magnesium alkoxide, tetrahydrofuran, complex formation

1. Introduction

Rechargeable magnesium (Mg) batteries that use Mg metal negative electrodes (anodes) present a possible candidate for “post-lithium-ion batteries for large-scale applications such as electric vehicles and stationary energy-storage systems, because of their high electrical capacity, non-explosiveness and low cost. One of the key issues in developing a practical Mg battery is establishing an electrolyte composition that has a wide electrochemical window without the formation of a passivation layer on Mg metal during electrochemical deposition and dissolution. It is well-known that Mg metal shows good reversibility in various ethereal solutions of Grignard reagents (RMgX ; R= alkyl, aryl; X= halide) and $\text{Mg}(\text{AlCl}_{4-n}\text{R}_n)_2$ complexes [1-7]. Recently, solutions of oligo(ethylene glycol) dimethyl ethers, so-called “glymes”, containing Mg salts, typically magnesium bis(trifluoromethanesulfonyl)amide ($\text{Mg}(\text{TFSA})_2$), have been widely researched as Mg battery electrolytes. These glyme-based electrolytes, i.e., $\text{Mg}(\text{TFSA})_2$ in monoglyme + diglyme (G1 + G2) or triglyme (G3), enable Mg metal to be reversibly deposited and dissolved [8-10]. However, these glyme-based electrolytes also have problems such as high overpotential and low coulombic efficiency for electrochemical deposition and dissolution.

More recently, Abe et al. and Sakaguchi et al. have independently proposed electrolyte systems comprising magnesium halides and ethereal solvents, i.e., MgBr_2 or MgCl_2 in tetrahydrofuran (THF), 2-methyltetrahydrofuran or n-butyl methyl ether [11-13]. This type of electrolyte solution comprising a simple Mg salt in an ether solvent had been previously found to be inactive for the reversible deposition and dissolution of Mg. However, those authors found that the reversibility improved with good coulombic efficiency by adding magnesium ethoxide ($\text{Mg}(\text{OEt})_2$) to the electrolyte system. We have also reported the effects of alkoxide addition on the electrochemical deposition and dissolution of Mg in $\text{Mg}(\text{TFSA})_2/\text{G3}$ electrolyte [10]. The addition of magnesium alkoxide ($\text{Mg}(\text{OR})_2$; R = alkyl group) tends to shift the onset potential for both the cathodic deposition and anodic dissolution. Thus, the role of the alkoxide in the Mg deposition/dissolution process is very important.

In the present study, we have examined an electrolyte combination of MgBr_2 and $\text{Mg}(\text{OR})_2$

as the salt and the additive, respectively dissolved in THF, where R denotes a methyl, ethyl, or isopropyl group. These electrolytes, $\text{MgBr}_2 + \text{Mg}(\text{OR})_2/\text{THF}$, were examined to clarify the mechanistic details of the electrochemical deposition and dissolution of Mg in ether-based electrolytes. The influences of the concentration and molar ratio of the salt and the additive were investigated to optimize the electrolyte composition. Cyclic voltammetry and constant-current charge-discharge cycling tests were carried out for the optimized electrolyte solution to establish the basic cell performance and coulombic efficiency of the process.

2. Experimental

2.1. Preparation and characterization of the electrolyte solution

MgBr_2 (97%, Strem Chemical Inc.), $\text{Mg}(\text{OMe})_2$ (Me = CH_3 ; 99.3%, Kojundo Chemical), $\text{Mg}(\text{OEt})_2$ (Et = C_2H_5 ; 99.3%, Kojundo Chemical) and $\text{Mg}(\text{OiPr})_2$ (*i*Pr = CH_3CHCH_3 ; 99.9%, Kojundo Chemical) were used as the electrolyte salt and the additives. These reagents were used as-received. The solvent THF (99.5%, WAKO) was used after the pre-treatment to remove residual water by molecular sieves, until the water content was less than 100 ppm in the system. The electrolyte solutions were prepared and stored in an Ar-filled glove box (< 5 ppm of water and oxygen). The water content of the resulting electrolyte solution was also verified by Karl-Fischer titration and was found to be 100 to 300 ppm throughout the experiments. The solubility of each solute, MgBr_2 and $\text{Mg}(\text{OR})_2$, is low, < 0.3 mol dm^{-3} (M), in THF. However, their mixture has a higher solubility in THF. That is, MgBr_2 can be dissolved up to 2.0 M or higher in THF at room temperature when an equivalent amount of $\text{Mg}(\text{OR})_2$ is dissolved. The structure of the electrolyte solution was analyzed using an FTIR spectrometer (JASCO, FT/IR-6100). The molecular structures of EtOMgBr and $\text{Mg}_2(\mu\text{-EtO}_x\text{Br}_{3-x})$ (Grignard reagent-like metal complexes of MgBr_2 and $\text{Mg}(\text{OEt})_2$) in THF medium were simulated by density functional theory (DFT) calculations using the Gaussian09 suit of programs [14]. The geometry optimizations of EtOMgBr and $\text{Mg}_2(\mu\text{-EtO}_x\text{Br}_{3-x})$ in THF were carried out using the DFT method, where the B3PW91 [15,16] functional was used for the exchange-correlation term. Analytical vibrational frequency computations at the optimized structures were then performed to confirm that the optimized structures were at an

energy minimum. The 6-311+G(d) basis set was used for these calculations.

2.2. Electrochemical measurements

The ionic conductivity of the electrolyte solution was measured by an AC impedance method using a frequency response analyzer with an electrochemical interface (Hokuto Denko, HZ-7000). A frequency range of 10^5 Hz to 10 Hz and an amplitude of 10 mV_{p-p} were employed as the AC conditions. A beaker-type two-electrode cell equipped with two parallel Pt sheet electrodes was used for the measurements. The electrochemical deposition and dissolution processes of Mg in the electrolyte solution were investigated by cyclic voltammetry (CV) using a potentiostat/galvanostat (Bio-Logic Science Instruments, VSP-300) at ambient temperature (298 ± 3 K). A 3-electrode Swagelok type cell was used with a Mg sheet (0.78 cm²) as the working electrode. The counter electrode was a Mg sheet with large surface area (3.80 cm²), and a Mg rod was used as a quasi-reference electrode (Mg QRE). The surface of the Mg metal was pretreated in an Ar-filled glove box before use. It was mechanically polished with suitable grade of Emery paper, followed by wiping with fresh THF solvent to clean the surface. The potential scanning range and sweep rate for CV were -2.0 to +2.0 V (vs. Mg QRE) and 20 mV s⁻¹, respectively. The surface morphology of the Mg working electrode after the CV measurement was observed by a scanning electron microscope equipped with an energy dispersive X-ray spectroscopy unit (SEM-EDS: JEOL, JSM-7600F/JED-2300). Galvanostatic charge-discharge measurements were performed using a charge-discharge cycler (Scribner Associates Inc., 580 Battery Test System) under a constant current of 100 μ A cm⁻² for 300 cycles at ambient temperature (298 ± 3 K).

3. Results and Discussion

3.1. Deposition/dissolution mechanism of the electrolyte composite

Fig. 1 shows the cyclic voltammograms of the Mg electrode in THF solutions containing 0.2 M MgBr₂, 0.2 M Mg(OEt)₂, or 0.2 M MgBr₂ mixed with 0.2 M Mg(OEt)₂. The systems containing only MgBr₂ or Mg(OEt)₂ showed practically no current response for Mg deposition and dissolution, as shown in Fig. 1, except for a very small current that was

observed in MgBr_2/THF , shown in the inset of Fig. 1. However, significant current responses were observed in the mixed electrolyte system, $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$, for both the anodic and the cathodic branches. This result suggests that the co-existence of MgBr_2 and $\text{Mg}(\text{OEt})_2$ can result in the formation of new active species in THF. It is well known that Grignard reagents, RMgX , work actively for the electrochemical deposition and dissolution of Mg in ethereal solutions [3,5,17,18]. Thus, we have assumed the evolution of a Grignard reagent-like metal complex in the $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$ system. That is, the following equilibrium reactions are assumed:

where Eqs. (1) and (2) are similar to the equations for the Schlenk equilibrium and the ionization equilibrium in Grignard systems, respectively [18], and the resulting MgOR^+ and/or ROMgX_2^- ions can act as active species for the Mg electrode reaction, as similarly to Grignard reagents.

Fig. 1 Cyclic voltammograms of the Mg electrode in 0.2 M MgBr_2/THF , 0.2 M $\text{Mg}(\text{OEt})_2/\text{THF}$, and 0.2 M $\text{MgBr}_2 + 0.2 \text{ M } \text{Mg}(\text{OEt})_2/\text{THF}$.

Regarding the active species in Grignard reagents, Sobata and Duda first reported the possibility of forming a μ -complex (binuclear complex) [19]. Sakamoto et al. investigated the constitution of the complex for an RMgCl/THF system by X-ray crystallography in the solid-state and by cold-spray ionization mass spectrometry [20]. Aurbach et al. also proposed

dimeric Mg ions for $\text{Mg}(\text{AlCl}_2\text{BuEt})_2/\text{THF}$ solutions by X-ray diffraction measurements [4, 6]. Similar studies have been performed by Kim et al. [21] and Muldoon et al. [22]. They confirmed the structure of μ -complex Mg ions in solutions of Lewis acid/base combination electrolytes, and they found that the electrochemical activity of those $\text{Mg}_2(\mu\text{-Cl})_3$ cation structures was as high as that of conventional Grignard reagents. Thus, in the present $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$ system, it may be possible to form a μ -complex containing bromide with the alkoxide, $\text{Mg}_2(\mu\text{-OEt}_x\text{Br}_{3-x})$.

Fig. 2 IR spectra of neat THF and THF dissolving 0.2 M MgBr_2 , 0.2 M $\text{Mg}(\text{OEt})_2$ and 1.0 M MgBr_2 mixed with 1.0 M $\text{Mg}(\text{OEt})_2$.

In order to support the above discussion, we performed FTIR measurements for the THF solutions containing Mg species. Fig. 2 shows typical FTIR spectra of 0.2 M MgBr_2 , 0.2 M $\text{Mg}(\text{OEt})_2$ and 1.0 M $\text{MgBr}_2 + 1.0$ M $\text{Mg}(\text{OEt})_2$ dissolved in THF. For comparison, neat THF solvent without any salts was also measured. The absorption peaks at around 905 cm^{-1} and 1065 cm^{-1} observed in the THF spectra are very consistent with the data shown in the literature [18, 23-25], where the former is attributed to the C-O ring deformation and the latter to the C-O stretching vibration of THF molecule, respectively. The THF solution containing mixed MgBr_2 and $\text{Mg}(\text{OEt})_2$ gave additional absorption peaks at 880 cm^{-1} and 1025 cm^{-1} which are believed to result from the “red-shift” of $\delta(\text{C-C-O})\text{THF}$ (905 cm^{-1}) and $\nu(\text{C-O})\text{THF}$ (1065 cm^{-1}), respectively. These peaks observed at lower wavenumbers are attributed to the “bound” THF. The solution containing MgBr_2 (MgBr_2/THF) also showed absorption peaks at

lower wavenumbers; however, their peak shifts were less significant than in the mixed MgBr_2 and $\text{Mg}(\text{OEt})_2$ solution. On the other hand, no wavenumber shift was observed in $\text{Mg}(\text{OEt})_2/\text{THF}$, which indicates very weak or no interaction between Mg and O in this system. These results strongly suggest that Mg-containing complexes, EtOMgBr and/or $\text{Mg}_2(\mu\text{-OEt}_x\text{Br}_{3-x})$, are formed by strong coordination of the THF molecules in mixed MgBr_2 and $\text{Mg}(\text{OEt})_2$ solution in THF.

Fig. 3 Optimized structures of $\text{EtO-Mg-Br} \cdot 4\text{THF}$ (a), $\text{Mg}_2(\mu\text{-OEt}_2\text{Br}) \cdot 6\text{THF}$ (b), and $\text{Mg}_2(\mu\text{-OEtBr}_2) \cdot 6\text{THF}$ (c) complexes.

We performed DFT calculations for the EtOMgBr and $\text{Mg}_2(\mu\text{-OEt}_x\text{Br}_{3-x})$ complexes, arising from the dissolution of MgBr_2 and $\text{Mg}(\text{OEt})_2$, which will occur a “red-shift” of THF. The resulting optimized geometries are given in Fig. 3; as can be seen, three types of complexes, in which four or six molecules of THF are coordinated to the Mg center, can be formed. Fig. 3a shows the optimized structure of the simple mononuclear complex, $\text{EtO-Mg-Br} \cdot 4\text{THF}$. A portion of the $\text{EtOMgBr} \cdot 4\text{THF}$ complex can be ionized to EtOMg^+ and/or EtOMgBr_2^- in THF, and these become possible active species, as in Grignard reagent systems. The inter-atomic distances in the resulting complex system are listed in Table 1. The estimated inter-atomic distance, or bond length, of Mg-Br is 2.632 Å, which is the longest among the bonds. This also suggests that the binding energy of Mg-Br is much weaker than those of the other Mg-O bonds. In Figs. 3b and 3c, the optimized geometries for $\text{Mg}_2(\mu\text{-OEt}_x\text{Br}_{3-x})$ complexes with six molecules of THF are shown, where ionized Mg-containing species can evolve. From the DFT calculations, therefore, it is reasonable to

assume that the EtOMgBr and/or $\text{Mg}_2(\mu\text{-OEt}_x\text{Br}_{3-x})$ complexes in THF can behave similarly to conventional Grignard reagents. The mixture of MgX_2 and Mg(OR)_2 in THF can be called “quasi-Grignard reagent.” In the present study, however, we could not conclude which species is the most probable active species for the electrochemical Mg deposition/dissolution processes. Both the spectroscopic data and the DFT calculations indicate the possibility of contributions from each species to the electrochemical activity.

Table 1 Inter-atomic distance of the Br-Mg-OEt·4THF system calculated by DFT method.

Bond	Length (distance) / Å
Mg-Br	2.632
Mg-OEt	1.951
Mg-O1 (THF)	2.255
Mg-O2 (THF)	2.215
Mg-O3 (THF)	2.207
Mg-O4 (THF)	2.200

3.2. Optimization of the composite electrolyte solution

Fig. 4 shows the cyclic voltammograms of the Mg electrode in 0.2 M MgBr_2 /THF solutions containing 0.2 M Mg(OMe)_2 , 0.2 M Mg(OEt)_2 , or 0.2 M Mg(OiPr)_2 as the additive. The Mg electrode was active in MgBr_2 /THF solution containing Mg(OMe)_2 ; however, its current response was lower than in the system containing Mg(OEt)_2 . A much lower current response was observed for the system containing Mg(OiPr)_2 . As the solubility of Mg(OiPr)_2 was rather low in THF, decreased ROMgBr complex formation and/or lower activity of the complex are possible reasons for the low current response in the solution containing Mg(OiPr)_2 . Among the three alkoxides, Mg(OEt)_2 showed the highest current response and hence the highest activity for Mg deposition and dissolution.

The influences of the electrolyte composition on the Mg electrode process were further examined by CV measurements in bromide/alkoxide/THF systems with different

compositions. Fig. 5 shows a comparison of the CV responses obtained in solutions with different $\text{MgBr}_2/\text{Mg}(\text{OEt})_2$ molar ratios, i.e., bromide/alkoxide concentration ($M = \text{mol dm}^{-3}$) was 0.5/0.5, 0.5/1.0, 0.5/1.5, 1.0/0.5, or 1.0/1.0. As is clearly shown, the highest current response was observed in the solution containing 1.0 M MgBr_2 and 1.0 M $\text{Mg}(\text{OEt})_2$, and the magnitude of the current response depended on the amount of the Mg species whose concentration was lower than (or equal to) that of the other. Thus, the results shown in Fig. 5 also support that the formation of a 1:1 complex from MgBr_2 and $\text{Mg}(\text{OEt})_2$ should create an active species for reversible Mg deposition and dissolution in THF.

Fig. 4 Cyclic voltammograms of the Mg electrode in 0.2 M MgBr_2 + 0.2 M $\text{Mg}(\text{OMe})_2/\text{THF}$, 0.2 M MgBr_2 + 0.2 M $\text{Mg}(\text{OEt})_2/\text{THF}$, and 0.2 M MgBr_2 + 0.2 M $\text{Mg}(\text{OiPr})_2/\text{THF}$.

Fig. 5 Cyclic voltammograms of the Mg electrode in THF-based electrolytes containing different molar ratios of MgBr_2 and $\text{Mg}(\text{OEt})_2$.

In Fig. 6, the influences of the concentration of the Mg species on the ionic conductivity of $\text{MgBr}_2/\text{Mg}(\text{OEt})_2/\text{THF}$ solution (Fig. 6a) and the current response in CV (Fig. 6b) are shown; the molar ratio of the bromide/alkoxide in THF was kept constant at 1/1. The ionic conductivity increased with increasing Mg salt concentration up to 1.0 M and then decreased again with increasing concentration to 2.0 M. This behavior is caused by the balance of changes in the salt concentration and the viscosity of the system. That is, the increase in the charge-carrier (ion) concentration mainly contributes to the increase in conductivity in the salt concentration range of 0.2 to 1.0 M, and the increase in the viscosity of the solution at salt concentrations higher than 1.0 M predominantly influences the decrease in conductivity in the system.

Fig. 6 Temperature dependence of the ionic conductivity (a), and cyclic voltamograms of $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$ electrolytes with different salt concentrations, the molar ratio of $\text{MgBr}_2/\text{Mg}(\text{OEt})_2$ kept 1:1 in each system (b).

The maximum ionic conductivity of 4.1 mS cm^{-1} was obtained for the $1.0 \text{ M MgBr}_2 + 1.0 \text{ M Mg(OEt)}_2/\text{THF}$ solution at 293 K (20°C). This value was 10 times higher than that of conventional Grignard reagent electrolyte [26]. The temperature dependence of the ionic conductivity showed fairly different profiles between the salt concentrations. This was possibly caused by changes in the equilibrium composition, determined by Eqs. (1) and (2), which would depend both on the temperature and the salt concentration.

In Fig. 6b, voltammetric current responses for the electrochemical deposition and dissolution of Mg are compared among the solutions containing different salt concentrations. The highest current was observed for the solution containing $1.0 \text{ M MgBr}_2 + 1.0 \text{ M Mg(OEt)}_2$, which showed the highest ionic conductivity, as shown in Fig. 6a. This result suggests that the concentration of the electrochemically active species increases with the salt concentration and that the current response is partly controlled by the viscosity of the electrolyte solution.

3.3. Cycle performance of Mg deposition/dissolution

The electrochemical deposition/dissolution of Mg in the $\text{MgBr}_2/\text{Mg(OEt)}_2/\text{THF}$ electrolyte system was further investigated as the negative electrode process of a rechargeable Mg battery. The variations in the voltammetric response with repeated cycles are shown in Fig. 7a, where a Pt sheet and $1.0 \text{ M MgBr}_2 + 1.0 \text{ M Mg(OEt)}_2$ composition were used as the substrate electrode and the electrolyte, respectively. The current response showed good reversibility for Mg deposition and dissolution with a small overpotential between the onset potentials for deposition and dissolution. This behavior is similar to the Mg deposition and dissolution on Pt in conventional Grignard reagent electrolytes [4, 26, 27]. The coulombic efficiency for each dissolution/deposition cycle was calculated from the voltammetric current (quantity of the electricity passed) and is shown in the inset of Fig. 7a as a function of the cycle. The efficiency increased with each cycle from ca. 80% (3rd cycle) to ca. 90% (20th cycle).

The surface of the Pt electrode after the CV measurements was observed by SEM-EDS. The SEM image and the EDS mapping of the Pt surface after 20 cycles in $1.0 \text{ M MgBr}_2 + 1.0 \text{ M Mg(OEt)}_2/\text{THF}$ are shown in Fig. 7b. It was confirmed that the Pt surface was covered with an inhomogeneous film of the deposit. The EDS images suggest that the deposit comprise Mg

with MgO (or MgOH), the latter of which would probably form in atmospheric conditions after the CV measurements. The intensity levels of Br and C elements were very low. Hence no side reactions other than the deposition/dissolution of Mg occurred during the CV measurements in this potential region between -2 V and +2.5 V vs. Mg QRE.

Fig. 7 Cyclic voltammograms of the Pt electrode in 1.0 M MgBr_2 + 1.0 M $\text{Mg}(\text{OEt})_2/\text{THF}$ (a) and SEM image with EDS mapping of the Pt surface after the voltammetric measurements (b); Inset figure in (a) indicating the variation of the coulombic efficiency with the cycle.

Galvanostatic charge and discharge cycling was carried out for the Mg electrode in 1.0 M

MgBr₂ + 1.0 M Mg(OEt)₂/THF electrolyte. Fig. 8 shows the potential profiles at the 1st, 10th, 100th, and 300th cycles under a constant current of 0.1 mA cm⁻² for 1 h. The thickness, d , of the Mg layer deposited or dissolved during the constant-current polarization was estimated using Eq. (3),

$$d = (q \times W_{\text{Mg}}) / (2 \times F \times \rho_{\text{Mg}}) \quad (3)$$

where, q , W_{Mg} , F and ρ_{Mg} denote the quantity of electricity passed during the charge (or discharge), the atomic weight (mass) of Mg, the Faraday constant, and the density of Mg metal, respectively. Assuming that the process does not involve any side reactions that consume electricity, the total quantity of electricity passed (282 mC) leads to an amount of Mg deposited or dissolved with a thickness of 260 nm. The overpotential, defined as the potential difference between the cathodic deposition and the anodic dissolution of Mg, decreased with repeated cycles, from ca. 0.4 V (1st) to ca. 0.2 V (10th). After several tens of cycles, it remained almost constant up to the 200th cycle. The cathodic polarization gave a higher overvoltage (difference between the operating and the rest potentials) than the anodic polarization, especially after 100 cycles. This tendency is probably caused by surface inhomogeneity during the cathodic deposition, as shown in Fig. 7b.

Fig. 8 Potential variations of the Mg electrode under constant-current (0.1 mA cm⁻²) charge-discharge cycling in 1.0 M MgBr₂ + 1.0 M Mg(OEt)₂/THF

4. Conclusions

Electrochemical Mg deposition and dissolution was examined for a THF-based electrolyte system containing MgBr_2 and $\text{Mg}(\text{OEt})_2$. The $\text{MgBr}_2/\text{Mg}(\text{OEt})_2$ mixture with a 1:1 molar ratio showed reversible Mg deposition and dissolution behavior similar to that observed in conventional Grignard reagents. The FTIR spectra and the DFT calculation results strongly suggest that quasi-Grignard complexes, $\text{EtOMgBr} \cdot 4\text{THF}$ and/or $\text{Mg}_2(\mu\text{-OEt}_x\text{Br}_{3-x})$, are formed in the 1:1 molar ratio mixture in THF. The electrolyte system has high ionic conductivity at room temperature and shows low overpotential and high coulombic efficiency for Mg deposition and dissolution compared with conventional Grignard reagents. Constant-current charge-discharge cycling tests revealed good performance at the rechargeable Mg negative electrode for 300 cycles. This $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$ system is a good potential candidate as a rechargeable Mg battery electrolyte.

Acknowledgments

This work was partly supported by the Advanced Low Carbon Technology Research and Development Program-Specially Promoted Research for Innovative Next Generation Batteries (ALCA-SPRING) from Japan Science and Technology Agency (JST). The authors would like to thank Enago for the English language review.

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Figure captions

Fig. 1 Cyclic voltamograms of the Mg electrode in 0.2 M MgBr_2/THF , 0.2 M $\text{Mg}(\text{OEt})_2/\text{THF}$, and 0.2 M $\text{MgBr}_2 + 0.2 \text{ M Mg}(\text{OEt})_2/\text{THF}$.

Fig. 2 IR spectra of neat THF and THF dissolving 0.2 M MgBr_2 , 0.2 M $\text{Mg}(\text{OEt})_2$ and 1.0 M MgBr_2 mixed with 1.0 M $\text{Mg}(\text{OEt})_2$.

Fig. 3 Optimized structures of $\text{EtO-Mg-Br} \cdot 4\text{THF}$ (a), $\text{Mg}_2(\mu\text{-OEt}_2\text{Br}) \cdot 6\text{THF}$ (b), and $\text{Mg}_2(\mu\text{-OEtBr}_2) \cdot 6\text{THF}$ (c) complexes.

Fig. 4 Cyclic voltamograms of the Mg electrode in 0.2 M $\text{MgBr}_2 + 0.2 \text{ M Mg}(\text{OMe})_2/\text{THF}$, 0.2 M $\text{MgBr}_2 + 0.2 \text{ M Mg}(\text{OEt})_2/\text{THF}$, and 0.2 M $\text{MgBr}_2 + 0.2 \text{ M Mg}(\text{OiPr})_2/\text{THF}$.

Fig. 5 Cyclic voltamograms of the Mg electrode in THF-based electrolytes containing different molar ratios of MgBr_2 and $\text{Mg}(\text{OEt})_2$.

Fig. 6 Temperature dependence of the ionic conductivity (a), and cyclic voltamograms of $\text{MgBr}_2 + \text{Mg}(\text{OEt})_2/\text{THF}$ electrolytes with different salt concentrations, the molar ratio of $\text{MgBr}_2/\text{Mg}(\text{OEt})_2$ kept 1:1 in each system (b).

Fig. 7 Cyclic voltamograms of the Pt electrode in 1.0 M $\text{MgBr}_2 + 1.0 \text{ M Mg}(\text{OEt})_2/\text{THF}$ (a) and SEM image with EDS mapping of the Pt surface after the voltammetric measurements (b); Inset figure in (a) indicating the variation of the coulombic efficiency with the cycle.

Fig. 8 Potential variations of the Mg electrode under constant-current (0.1 mA cm^{-2}) charge-discharge cycling in 1.0 M $\text{MgBr}_2 + 1.0 \text{ M Mg}(\text{OEt})_2/\text{THF}$.