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<td>Author(s)</td>
<td>Kitada, Atsushi; Kang, Yuu; Matsumoto, Kazuhiko; Fukami, Kazuhiro; Hagiwara, Rika; Murase, Kuniaki</td>
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<tr>
<td>Citation</td>
<td>Journal of the Electrochemical Society (2015), 162(8): D389-D396</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2015-05-02</td>
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<tr>
<td>URL</td>
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Room Temperature Magnesium Electrodeposition from Glyme-Coordinated Ammonium Amide Electrolytes

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We prepared less volatile and halide-free electrolytes for room temperature non-dendritic magnesium (Mg) electrodeposition by mixing a Mg2+-amide-containing ionic liquid (IL) with equimolar glyme (Mg2+ : glyme = 1 : 1). Raman spectroscopy suggested that in the equimolar mixture most glyme molecules are coordinated to Mg2+ cations and/or IL cations, which is also supported by a single crystal X-ray diffraction study. The glyme-coordinated IL electrolytes showed sizable redox currents (order of mA cm–2), while aging deterioration of electrochemical properties was observed for the triglyme mixture due to partial bath decomposition. The tetraglyme-coordinated IL electrolyte enabled flat electrodeposition of Mg with a metallic luster and showed with very high anodic stability (ca. +4 V vs. Mg) because of decrease in uncoordinated glymes, which can be used for high-voltage Mg ion batteries.

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Manuscript submitted March 17, 2015; revised manuscript received May 11, 2015. Published June 3, 2015. This was Paper 65 presented at the Cancun, Mexico, Meeting of the Society, October 5–9, 2014.

In the last few decades elemental magnesium (Mg) has come to be viewed as one of the most interesting negative electrode materials for post lithium ion secondary batteries because of its high-theoretical capacity (3839 mA h cm–3), low electrode potential (–2.356 V vs. SHE), and natural abundance. The well-known electrolytes for electrodepositing Mg metal at room temperature are Grignard electrolytes comprised of an ether solvent tetrahydrofuran (THF) and alkylmagnesium halides RMgX (R = allyl or aryl groups; X = Cl, Br). Addition of AlCl3 makes more electroactive species of organo-halo-aluminates, giving larger current density and/or higher anodic stability.1–10 However, the highly volatile THF and the highly moisture sensitive (trifluoromethyl)sulfonyl or CF3SO2, have recently been reported to show successful electrodeposition of Mg metal.16–19 We have demonstrated that room temperature electrodeposition of Mg metal was successfully also reported an amide-containing glyme-IL solution with which (trifluoromethyl)sulfonylimidate was purchased from Kanto Chemical. Electrochemistry-grade diethylene glycol dimethyl ether (diglyme; G2) was also received from Kanto Chemical. Ethylenimagnesium bromide (EtMgBr) in THF (Kanto Chemical, 0.95 mol dm–3) was used for electrode of the reference electrode (described later). Triethylenglycol dimethyl ether (triethylene glycol) and tetraethyleneglycol dimethyl ether (tetruglyme; G4) were obtained from Tokyo Chemical Industry.

Experimental

Reagents.— All reagents were used as received. Battery-grade Mg(Tf2N)2 was purchased from Kishida Kagaku. An ionic liquid PP13-Tf2N (N-methyl-N-propylpiperidinium bis(trifluoromethyl) sulfonylimidate) was purchased from Kanto Chemical.

Electrochemistry-grade diethylene glycol dimethyl ether (diglyme; G2) was also received from Kanto Chemical. Ethylenimagnesium bromide (EtMgBr) in THF (Kanto Chemical, 0.95 mol dm–3) was used for electrolyte of the reference electrode (described later). Triethylenglycol dimethyl ether (triethylene glycol; G3) and tetraethyleneglycol dimethyl ether (tetruglyme; G4) were obtained from Tokyo Chemical Industry.

Bath preparation.— First, we made 0.5 mol dm–3 Mg(Tf2N)2/PP13-Tf2N (molar ratio 1 : 7) by mixing at 80 °C overnight under an inert atmosphere in a glove box. Then we mixed the IL solution with each glyme (Mg(Tf2N)2 : PP13-Tf2N : glyme = 1 : 7 : 8 by mole) with glass-coated stirrers for 30 min in a glove box to make 0.324 or 0.298 or 0.272 mol dm–3 Mg(Tf2N)2 in IL/G2 or IL/G3 or IL/G4 solution. The water content of each bath was less than 50 ppm, determined by Karl Fischer titration.

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Raman spectroscopy.— Raman spectra were obtained at room temperature by an integrated Raman system (B&W Tek, innoRam 785) comprising a semiconductor laser light source (785 nm), a holographic probehead, an axial transmissive spectrogaph, and a charge-coupled device (CCD) detector. The spectral acquisition time, i.e., exposure time of CCD and the number of exposures was varied for each sample so as to improve the signal-to-noise ratio of each spectrum.

Bath properties.— Conductivity measurements were performed at 25°C using a Radiometer Analytical CDM230. Viscosity measurements were conducted using SEKONIK VM-10A and VM-1G calibrated using a standard solution (NIPPON GREASE Co., Ltd.). The densities of the 0.5 mol dm–3 Mg2+--containing IL were calculated to be 1.46 g cm–3 using the measured values of weight and volume, while those of glyme-mixed solutions were assumed to be 1.28 g cm–3 for 0.324 mol dm–3 Mg(Tf2N)2 in IL/G2 and 1.27 g cm–3 for 0.298 mol dm–3 Mg(Tf2N)2 in IL/G3 and 1.25 g cm–3 for 0.272 mol dm–3 Mg(Tf2N)2 in IL/G4 using the reported density of pure glymes (G2: 0.937 g cm–3, G3: 0.986 g cm–3, G4: 1.009 g cm–3).

Electrochemical properties.— Electrochemical measurements were conducted in the glove box with a potentiostat/galvanostat (BAS, ALS ELECTROCHEMICAL ANALYZER 660C) at 30°C. Cyclic voltammetry (CV) was performed without stirring an electrode cell of 20 cm3 capacity with the planar dimension of WE fixed at 7.5 mm×7.5 mm (EC Frontier, VM-2A). Galvanostatic electrolysis was conducted using a glass cell of 15 cm3 capacity with agitation speed of 300 rpm. Pt sheet and Mg sheet or rod (Nilaco, 99.9% purity) were used as the working electrode (WE) and counter electrode (CE), respectively. Because the potential of Mg was not stable in IL,28 as reference electrodes (RE) we used a Mg rod immersed in EtMgBr in THF (0.95 mol dm–3). Galvanostatic electrolysis was conducted using a standard solution (NIPPON GREASE Co., Ltd.). The spectra for Mg/G4 and that for Mg/IL were determined using an appropriate riding model.

Characterization of electrodeposits.— For characterizing the electrodeposits, X-ray diffraction (XRD) measurements and scanning electron microscope (SEM) observations were performed using RIGAKU RINT2200 and KEYENCE VE-7800, respectively.

Single crystal growth of Mg(Tf2N)2-glyme complex.— Battery-grade G2, G3, G4 and Mg(Tf2N)2 from Kishida Kagaku were used as reagents. Each glyme of 1.5 cm3 and Mg(Tf2N)2 was mixed at a molar ratio of 3:1, heated to 90°C, and then slowly cooled to room temperature over 3 days. As a result, single crystals were successfully grown only from the G4 solution. The quality of crystals grown from the G2 solution was not sufficient to determine its crystal structure, and no single crystals were obtained from the G3 solution.

Single crystal X-ray diffraction.— Since the obtained glyme-Mg2+--amide crystal was deliquescent, a white crystal with approximate dimensions 0.10 × 0.40 × 0.40 mm3 was selected and transferred into a quartz capillary (0.5 mmϕ, dried under vacuum at 150°C) under a dry Ar atmosphere, and centered on the X-ray diffractometer (R-axis Rapid II, Rigaku controlled by the program RAPID AUTO 2.40)29 equipped with an imaging plate area detector and graphite-monochromatic Mo-Kα radiation (0.71073 Å). The end of capillary was filled with vacuum grease and then sealed using an oxygen burner. The measurement consisted of 20ω scans (130–190, 3/’/frame) at the fixed ϕ (30°) and χ (45°) angles and 54ω scans (0°–162°, 3/’/frame) at the fixed χ (180°) and χ (45°) angles. Data collection was performed at −160°C with an exposure time of 450 s deg–1. Integration, scaling and absorption corrections were performed using RAPID AUTO 2.40.29

The structure was solved using SIR-9232 and refined by SHELXL-9731 linked to WinGX.32 Anisotropic displacement factors were introduced for all atoms except for hydrogen and hydrogen atoms, which were determined using an appropriate riding model.

Results and Discussion

Raman spectroscopy.— In Raman spectroscopy the CH2 rocking and C-O-C symmetric stretching vibration area ranged between 900 cm–1 and 780 cm–1. Figure 1 displays the Raman spectra for pure IL, pure G4, and G4 and/or IL solutions of Mg(Tf2N)2. It is known that C-O-C vibrations in ethers are usually seen in the regions between 890–850 cm–1 on Raman measurements. In the case of free ethers, which are not coordinated by alkaline metal cations, the Raman band is observed at around 855 cm–1.33 Therefore, the Raman band at 852 cm–1 is assignable to free G4, which is seen both in pure G4 and in G4 solution with Mg2+. G4 = 1.8 by mole. The spectra for the IL/G4 mixture with Mg2+:IL/G4 = 1:7:8 by mole can be viewed as a combination of the spectrum for Mg/G4 and that for Mg/IL. This takes into account that the profiles of Mg/IL and Mg/IL/G4 between 870 and 830 cm–1 are quite similar except around 852 cm–1. Since no phase separation was observed for the 1:7:8 mixed solution, the rest glymes should weakly coordinate IL cations through hydrogen bonding,21 and the number of free (or uncoordinated) glymes should decrease. In the case of ethers coordinated by alkaline metal cations, the Raman band is seen at around 880 cm–1 for mononuclear complex and at 890 cm–1 for binuclear complex.34,35 For Mg2+, however, the binuclear complex would not exist due to high coulomb repulsive forces between the two Mg2+. Therefore, we assign the band at 891 cm–1 to mononuclear complex cations. The spectra for IL/G2 and IL/G3 resemble those for IL/G4 in appearance (see Fig. 2).

Table I lists the vibrational frequencies of pure glyme and the Mg-glyme complex corresponding to the combination of CH2 rocking and C-O-C stretching modes, the values of which are close regardless of glymes. Consequently, it is strongly indicated that sizable amount of specific peaks centered at 891, 852, 752, and 741 cm–1.

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Raman shift (cm–1)</th>
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<tr>
<td>G2</td>
<td>854</td>
</tr>
<tr>
<td>G3</td>
<td>885</td>
</tr>
<tr>
<td>G4</td>
<td>891</td>
</tr>
<tr>
<td>[Mg(G2)2]+</td>
<td>889</td>
</tr>
<tr>
<td>[Mg(G3)2]+</td>
<td>885</td>
</tr>
<tr>
<td>[Mg(G4)2]+</td>
<td>891</td>
</tr>
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</table>

In other spectrum regions, Raman spectra for TF2N− anions are specifically seen as h(CF3) vibration between 760 and 720 cm–1.
Figure 2. Raman spectra in the range of 900 cm\(^{-1}\) and 780 cm\(^{-1}\) for Mg(Tf\(_2\)N\(_2\))\(_2\):PP13-Tf\(_2\)N:glyme = 1:7:8, during 7 days after bath preparation: (a) G2, (b) G3, and (c) G4 mixture. No aging variation was observed.

Figure 3. Raman spectra in the range of 800 cm\(^{-1}\) and 720 cm\(^{-1}\) for Mg(Tf\(_2\)N\(_2\))\(_2\):PP13-Tf\(_2\)N:glyme = 1:7:8, during 7 days after bath preparation: (a) G2, (b) G3, and (c) G4 mixture. No aging variation was observed.

Figure 1b shows the Raman spectra obtained between 800 and 720 cm\(^{-1}\). The Raman profile of the 1:7:8 Mg/IL/G4 mixture with a single peak centered at 741 cm\(^{-1}\) is fairly similar to those of Mg-G4 and pure IL, which is different from that of Mg\(^{2+}\)-containing IL in that a shoulder peak was seen at 752 cm\(^{-1}\) like the case of other divalent metal cations;\(^{36}\) in a similar Tf\(_2\)N-based IL, metal(II) cations are coordinated by three Tf\(_2\)N\(^-\)anions or six-O-coordinated complexes with the valence of –1. Thus we predict that without glymes Mg\(^{2+}\) would exist in the form of [Mg(Tf\(_2\)N\(_3\))]\(^-\) in the IL solutions, while in the presence of glymes the coordination of Tf\(_2\)N\(^-\) to Mg\(^{2+}\) was significantly loosened and all Tf\(_2\)N\(^-\) anions become free. The spectra in this range for IL/G2 and IL/G3 also resemble those for IL/G4 in appearance (see Fig. 3). Therefore, when glymes and ILs are mixed the coordination environment should change from [Mg(Tf\(_2\)N\(_3\))]\(^-\) to [Mg(glyme)\(_n\)]\(^{2+}\). We also noted that within 7 days after bath preparation, there were no distinguishable changes in Raman spectra as displayed in Figs. 2 and 3.

Single crystal structures of glyme-Mg(Tf\(_2\)N\(_2\)) complex.— Table II lists crystallographic data for the G4-Mg(Tf\(_2\)N\(_2\)) complex. The fractional coordinates of each atom are listed in Table S1 (Supplemental Material). The crystal obtained from the 3:1 solution of G4 and Mg(Tf\(_2\)N\(_2\)) crystallized into a monoclinic space group \(P2_1/\text{c}\), and was found to be their 1:1 complex. While the Li\(^+\) analogue of 1:1 complex of G4 and LiTf\(_2\)N is liquid at room temperature,\(^{20}\) the Mg\(^{2+}\)-complex was solid due to its relatively high charge density. Figure 4 shows the packing diagram of [Mg(G4)](Tf\(_2\)N\(_2\)): structure viewed along the \(b\) axis. The structure is a quasi-two dimensional system, consisting of the Mg layer (represented by the blue Mg) with the G4 molecules and O atoms in the anion and fluorous layer (represented by green F). Figure 5 shows the coordination environment around Mg\(^{2+}\). Mg\(^{2+}\) was surrounded by five equatorial oxygen atoms of G4 and two axial oxygen atoms in two Tf\(_2\)N\(^-\) anions to form a pentagonal bipyramid in [Mg(G4)](Tf\(_2\)N\(_2\)). The observed glyme coordination in the solid form supports the Raman results from which we suggest the formation of [Mg(glyme)]\(^{2+}\) in the glyme/IL solution. The equatorial oxygen atoms have longer Mg···O distances (2.1614(17) Å).

\[ R_1 = \Sigma |F_o| - |F_c|/\Sigma |F_o|, \]
\[ wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}. \]

| Table II. Crystallographic data for [Mg(G4)](Tf\(_2\)N\(_2\)). |
|-----------------|-----------------|
| formula        | C\(_{14}\)H\(_{22}\)N\(_2\)O\(_3\)F\(_{12}\)MgS\(_4\) |
| fw             | 806.89          |
| \( T \)/ K     | 113             |
| crys system     | Monoclinic      |
| space group     | \(P2_1/\text{c}\) |
| \( a \)/ Å     | 10.1447(4)      |
| \( b \)/ Å     | 8.3961(3)       |
| \( c \)/ Å     | 35.3953(11)     |
| \( \beta \)^\circ | 96.6300(10)     |
| \( V \)/ Å\(^3\) | 2994.67(18)     |
| \( Z \)        | 4               |
| \( \rho_{calc} \)/ g cm\(^{-3}\) | 1.790 |
| \( \mu \)/ mm\(^{-1}\) | 0.474 |
| \( R_1 \)^a   | 0.0392          |
| \( wR_2 \)^b   | 0.0899          |
| \( \text{cryst size} / \text{mm}^3 \) | 0.10 \times 0.40 \times 0.40 |

\(^a R_1 = \Sigma |F_o| - |F_c|/\Sigma |F_o|, \]
\(^b wR_2 = (\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}. \)
Figure 4. Schematic crystal structure of [Mg(G4)](Tf2N)2 viewed along the b-axis. Mg: blue, O: red, F: green, C: black, N: cyan, S: yellow. Hydrogen atoms are omitted for clarity. Unit cell is shown with blue dashed lines. The arrow shows direction of layer stacking.

Figure 5. Coordination environment of Mg atom in [Mg(G4)](Tf2N)2 with ORTEP plot (50% thermal probability ellipsoids) of Mg (gray), O (red), C (white), S (orange), N (blue), F (green) with H (open spheres). Mg...O coordination is represented as dashed sticks, consisting of five equatorial oxygen atoms of tetraglyme and two axial oxygen atoms of two Tf2N–.

same coordination number. Given the seven oxygen coordination for Mg in the glyme amide complex and monodentate coordination of Tf2N–, one glyme (G2 or G3) and two Tf2N– cannot donate seven oxygen ligands, and thus the number of conformation in the G2- or G3-Mg(Tf2N)2 complexes should be further increased compared to the G4 complex. This should be related to the fact that the G4 complex was obtained as a highly crystalline sample while the G2 complex was poorly crystalline and the G3 complex could not be obtained as a solid.

Bath properties.— Table III shows the conductivities and viscosities of Mg(Tf2N)2 solutions of PP13-Tf2N-glyme mixture. As the molecular weight of glyme increased, the conductivities decreased and the viscosities increased monotonically. The viscosity of each glyme mixture is about 25–26 mPa s, one order of magnitude higher than that of the previously reported glyme-rich mixture (2.32 mPa s; Mg2+:IL:G2 = 1:7:56 by mole).16 However, the conductivities shown in Table III (2.6–3.8 mS cm–1) are comparable to the previous values for glyme-rich mixtures (2.6 mS cm–1 for Mg2+:IL:G2 = 1:7:56, 2.52 mS cm–1 for Mg2+:G2 = 1:11, and 3 mS cm–1 for Mg2+:G3 = 1:7 by mole),16,17,19 although slightly smaller than typical lithium-ion conductive electrolyte solutions. Notably, the bulk bath properties were fairly similar within 7 days for each IL/glyme mixture (see Fig. 6), which was consistent with the Raman results.

Table III. Molar ratio, molar concentrations, conductivities and viscosities of the glyme mixture with molar ratio of Mg(Tf2N)2:PP13-Tf2N:glyme = 1:7:8 measured at 25°C 1 day after bath preparation.

<table>
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<tr>
<th>Electrolyte</th>
<th>Concentration (mol dm–3)</th>
<th>Conductivity (mS cm–1)</th>
<th>Viscosity (mPa s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2 mixture</td>
<td>0.324</td>
<td>3.8</td>
<td>25.2</td>
</tr>
<tr>
<td>G3 mixture</td>
<td>0.298</td>
<td>3.3</td>
<td>25.9</td>
</tr>
<tr>
<td>G4 mixture</td>
<td>0.272</td>
<td>2.6</td>
<td>26.0</td>
</tr>
</tbody>
</table>

Cyclic voltammetry.— Figures 7a–7c shows the CVs for IL/glymes measured just after bath preparation. As shown in Fig. 7a, at –1.0 V vs. Mg the CV for G2 mixture showed sizable reduction currents up to about 6 mA cm–2, 1.5 times larger than the previous report on diglyme-rich mixture.16 Because the Mg complexes as cationic species in the solution which was revealed by the Raman results, they can more easily access the cathode surface due to the electrostatic attractions to 2.2402(17) Å than those for the apical oxygen atoms (2.0385(17) and 2.0555(16) Å) (see Table S2, Supplemental Material), and thus the Mg ions have stronger interaction with the two Tf2N– anions than with the G4 in solid, while in the solution Mg2+ ions have less interaction with Tf2N– as indicated by the Raman results. The bond valence (v) of each Mg···O interaction was calculated by the equation

\[ v = \exp\left(\frac{R - R_0}{B}\right) \]

where \( R \) is Mg···O distance, \( R_0 = 1.693 \) Å, and \( B = 0.37 \) Å.

The bond valence sum of 2.00 for Mg2+ in this structure is in excellent agreement with the ideal valence of 2+. This seven-coordination by oxygen atoms is in contrast to the five coordination for the lithium amide complex of G3 or G4, where one oxygen from Tf2N– and four oxygen atoms from a glyme molecule coordinate. The larger coordination number in the Mg2+ complex comes from its stronger Lewis acidity than Li2+-complexes.

Considering that both the G3- and G4-Li+ complexes have five-coordination of oxygen atoms, and that the bond valence sum of Mg in the G4-Mg2+ complex closely matches the ideal valence, it can be deduced that other glyme-Mg2+ complexes (G2 and G3) have the
Figure 6. Conductivities and viscosities of the Mg(Tf₂N)₂:PP13-Tf₂N:G2 = 1:7:8, aged 0 day (within 1 h), 1 day, 3 days, and 7 days after bath preparation, showing that those values are independent of aging time.

Figure 7. Cyclic voltammograms measured for the Mg(Tf₂N)₂-containing (a) PP13-Tf₂N/G2, (b) PP13-Tf₂N/G3, and (c) PP13-Tf₂N/G4 0 day (within 1 h) after bath preparation, and (d) PP13-Tf₂N/G2, (e) PP13-Tf₂N/G3, and (f) PP13-Tf₂N/G4 1 day after preparation. Aging variation was clearly seen for the G3 mixture. Sweep rate: 20 mV s⁻¹.

Figure 8. Photographs of the IL/glyme baths stored in a drybox for 7 days after preparation, where the IL/G3 mixture decomposed to became yellowish.

with cathode, giving the large current densities. Compared to the case of Ref. 16 the concentration of Mg²⁺ is three times larger and the viscosity is about ten times larger while the conductivity is almost the same. Thus the present electrolyte has larger mobility of Mg²⁺. By contrast, the redox currents for IL/G3 shown in Fig. 7b were five times smaller than those in 0.5 mol dm⁻³ Mg²⁺ in G3 solution. Although the viscosity of the pure G3 solution is not presented, the viscosity can be one order of magnitude lower than the IL/G3 mixed solution, and both the concentration and conductivity are similar to those of the IL/G3. Thus similar mobility of Mg²⁺ should be present in the pure G3 and the IL/G3 solutions.

Figures 7d–7f show CVs of the IL/glyme mixtures, aged for 1 day after mixing. Among them the G3 mixture has order-of-magnitude smaller redox currents than the others, while its bath properties are similar to the other glyme solutions. Without ILs, the G3 solution of Mg(Tf₂N)₂ shows as large current density as IL/G2 or IL/G4 mixture. Moreover, the IL/G3 sample kept in a glove box for 7 days after mixing changed to yellowish from colorless while the others remained fairly colorless (see Fig. 8). Thus it is strongly indicated that the G3 mixture decomposed to some extent, affecting not its bulk properties (see Fig. 6) but its redox behavior. Consequently, among these Mg²⁺-containing baths, PP13-Tf₂N/G4 showed relatively large reduction and oxidation currents and did not decay up to the 10th cycle (see Fig. 7f).

Regardless of the time since bath preparation, oxidation currents are clearly seen above +0.6 V vs. Mg. A similar anodic overpotential of 0.6 V has been reported in a pure G3 solution of Mg(Tf₂N)₂. Dissolution of Mg is prohibited in these amide-based electrolytes because the Tf₂N⁻ anions developed passivation films on the deposited Mg.

Anodic stability of IL/glyme mixtures.— Figure 9 shows the linear sweep voltammogram of the Pt electrode obtained with a sweep rate of 1 mV s⁻¹. Comparison of Figs. 9a and 9b shows that aging variation was not seen except in the G2 mixture. The potentials for electrolyte decomposition were defined as the potential at which \( i > 20 \mu A \) cm⁻² was +3.70 V for the IL/G2, +3.95 V for the IL/G3, and above +4 V for the IL/G4 in Fig. 9b. According to the above definition, the decomposition potential of the 0.5 mol dm⁻³ Mg(Tf₂N)₂/G3 solution locates at around +3.4 V vs. Mg QRE with the same sweep rate. Such an improvement in anodic stability due to a lack of free glymes has also been reported in LiTf₂N/glyme solution. Therefore, it is concluded that the IL/glyme mixtures have higher anodic stability than the IL-free Mg(Tf₂N)₂/G3 solution. It is also notable that as the number of ether oxygens increased the anodic stability...
became higher, due to the stronger chelating ability of the longer-chain polyethers.

Electrolysis.— As mentioned above, the IL/G4 mixture (aged 1 day) showed good redox behaviors and high anodic stability. In addition, G4 has higher boiling and flash points than G2 and G3, indicating that crystal growth became dominant rather than electrolyte decomposition as well as Mg nucleation. The potential gradually increased from –0.8 V vs. Mg and became almost constant at –0.6 V within 10 s or 0.003 h. We suggest that the change in effective surface area is very little during electrolysis because nucleation of Mg crystal was accelerated at such a high current density. In fact, relatively flat electrodeposits with metallic luster were obtained (see Fig. 10), and the SEM image shows that Mg deposits were densely packed with relatively uniform grain size (2–5 μm; see Fig. 12b), because fine nuclei were largely produced. The current efficiency of electrodeposition at 1.5 mA cm$^{-2}$ was calculated to be about as high as 95.3% from the mass change of WE, although there were small deposits exfoliated from Pt WE.

The electrodeposition at 0.5 mA cm$^{-2}$ gave sparse deposits (see Fig. 10). We speculate that nucleation of Mg occurred at relatively low rate, which caused about an order-of-magnitude larger grain size compared to electrolyte together with Mg electrodeposition, because the system is unable to catch up with the total current flowing the electrochemical cell.

In Fig. 11, taking into account that the intensities for Pt substrate are very strong in the case of 1.5 mA cm$^{-2}$ while those at 0.5 and 2.5 mA cm$^{-2}$ are weak. Therefore, the observed XRD intensities are in good agreement with the cover area of Mg deposits. Besides, for electrodeposition using Grignard solutions, preferred orientation of [100] plane parallel to the substrate was observed only above 2 mA cm$^{-2}$. By contrast, in each XRD pattern the intensity ratio of the 002 reflection was rather weak compared to the standard one even in the case of 0.5 mA cm$^{-2}$. Furthermore, for the galvanostatic electrodeposition at 0.5 mA cm$^{-2}$ in the IL-free 0.5 mol dm$^{-3} \text{Mg(Tf}_2\text{N)}_2$ bath, the XRD pattern was quite similar to the standard one. Thus it is suggested that the tendency to orient toward the [100] is more remarkable in the IL-containing baths.
Conclusions

By mixing an Mg(Tf$_2$N)$_2$-containing IL with glyme solutions, we prepared a safe electrolyte without highly volatile solvents or free halide anions. We revealed that the equimolar mixture of glymes and Mg$^{2+}$-containing ILs caused a decrease in the number of free or uncoordinated glymes, which show sizable redox currents and high electrochemical stabilities toward oxidation. It was also indicated that [Mg(glyme)$_n$]$^{2+}$ cation is the Mg dissolved species in the IL/glyme mixture. Aging variation in electrochemical properties were observed especially for the triglyme solution, while the physicochemical properties (viscosity and conductivity) were almost unchanged. Flat electrodeposition of Mg metal with a metallic luster was demonstrated at room temperature using the PP13-Tf$_2$N/tetraglyme mixture. Although a large anodic overpotential for dissolving Mg metal is still observed, the glyme-coordinated amide-type-IL electrolytes may open-up new options for Mg-ion secondary battery electrolytes. Further studies on IL/glyme electrolytes with other mixing ratios are of special interest in terms of electrolyte improvements.

Acknowledgments

This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology Agency (JST). The work was also partly supported by Grant-in-Aid for Scientific Research (A) (No. 25249106) and Grant-in-Aid for Young Scientists (B) (No. 15K18253) from the Japan Society for the Promotion of Science (JSPS), and by the Kyoto University Global Frontier Project for Young Professionals (the John-Mung Advanced Program).

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