Electromagnetic (Mg) is anticipated as a negative electrode material for post lithium-ion secondary batteries because of its high-theoretical capacity (3839 mAh cm\(^{-2}\)), high negative electrode potential (−2.356 V vs. SHE) and natural abundance. Because aqueous electrolytes are not available for electrodeposition of Mg, as is also the case for Li, the electrochemistry of magnesium has been studied in aprotic organic solvents since the early 1900’s. As Mg ion batteries attract increasing interest, electrodeposition of Mg has been investigated over the last thirty years by several groups, using mainly electrolytes consisting of an ether solvent tetrahydrofuran (THF) and alkylmagnesium halides. Aurbach et al. showed the Mg deposition/dissolution cycle of Mg with high coulombic efficiency in 2Me-Tf\(_2\)N-containing ILs, subsequent studies by other groups have not reproduced their results, indicating that their results of reversible deposition/dissolution are highly questionable.

In this paper, we studied the electrodeposition of Mg metal at room temperature from relatively safe electrolytes consisting of IL/diglyme mixture (1 : 4 by volume) dissolving a simple amide salt Mg(Tf\(_2\)N)\(_2\). Addition of an ionic liquid as supporting electrolyte resulted in increased conductivity by an order of magnitude (2.5 – 2.6 mS cm\(^{-1}\)) compared to the IL-free diglyme solution (0.50 mS cm\(^{-1}\)). Although certain flammability and volatility still exist in the glyme solution with an IL additive, this plating bath enabled the deposition of a thin and adherent film of elemental Mg with a metallic luster on Cu substrate.

**Experimental**

**Preparation of the baths.**—Trimethyl-n-hexylammonium bis[(trifluoromethyl)sulfonyl]amide (TMHAA-Tf\(_2\)N) was synthesized from TMHABr and LiTf\(_2\)N via metathesis as reported previously. N-methyl-N-propylpiperidinium bis[(trifluoromethyl)sulfonyl]amide (PP13-Tf\(_2\)N) and battery-grade diethylene glycol dimethylether i.e. diglyme (G2) were purchased from Kanto Chemical. Battery-grade Mg(Tf\(_2\)N)\(_2\) was purchased from Kishida Kagaku. First, we made 0.5 mol dm\(^{-3}\) Mg(Tf\(_2\)N)\(_2\)-containing ILs, and 0.5 mol dm\(^{-3}\) Mg(Tf\(_2\)N)\(_2\)/PP13-Tf\(_2\)N (molar ratio 1 : 7) by mixing under an inert atmosphere in a glove box, and then we mixed these IL solutions with diglyme (1 : 4 by volume or 1 : 56 by mole) in the glove box to make 0.1 mol dm\(^{-3}\) Mg\(^{2+}\)-containing IL/G2 solutions.

**Conductivity and viscosity measurements.**—The water content of each solution was about 200 – 400 ppm, determined by Karl Fischer titration. Conductivity measurements were performed at 25°C using Radiometer Analytical CDM230. Kinematic viscosity measurements were conducted using SEKONIC VM-10A and VP-1 G calibrated using a standard solution (NIPPON GREASE Co., Ltd.). The densities of 0.5 mol dm\(^{-3}\) Mg\(^{2+}\)-containing ILs were calculated to be 1.41 g cm\(^{-3}\) for TMHAA-Tf\(_2\)N and 1.46 g cm\(^{-3}\) for PP13-Tf\(_2\)N using the measured value of weight and volume, while those of G2-mixed solutions were assumed to be 1.03–1.04 g cm\(^{-3}\) for 0.1 mol dm\(^{-3}\) Mg(Tf\(_2\)N)\(_2\) in IL/G2 and 1.01 g cm\(^{-3}\) for 0.125 mol dm\(^{-3}\) Mg(Tf\(_2\)N)\(_2\) in G2 using the reported density of pure G2 (0.937 g cm\(^{-3}\)).

**Electrochemical measurements and characterization of deposits.**—Within an hour after bath preparation, 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 in an electrode cell. 

---

**Manuscript submitted November 6, 2013; revised manuscript received December 3, 2013. Published December 28, 2013. This was Paper 73 presented at the San Francisco, California, Meeting of the Society, October 27–November 1, 2013.**
of 20 cm$^3$ capacity where the planar dimension of WE was fixed to 7.5 mm$^2$ (Fig. 1a, EC Frontier, VM-2A). Potentiostatic electrolysis was conducted using a glass cell of 15 cm$^3$ capacity (Fig. 1b). Cu sheet (Nilaco, 99.9% purity) 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 some TF$_2$N-based ILs, as reference electrodes (RE) we used a Mg rod immersed in ethylmagnesium bromide (EtMgBr) in THF (Kanto Chemical, 0.95 mol dm$^{-3}$), separated from the main electrolyte by porous vycor glass (see Fig. 1). For CV measurements Cu sheets were washed with acetone, while for potentiostatic electrolysis they were first washed with acetone and then with about 1 mol dm$^{-3}$ nitric acid before use. Mg sheets were polished with emery paper (#800) before measurements. In the potentiostatic electrolysis, dihedral angle of WE was about 90° with a stirring speed of 300 rpm (see Fig. 1b). In order to characterize the deposits, X-ray diffraction (XRD) and scanning electron microscope (SEM) measurements were performed using RIGAKU RINT2200 and KEYENCE VE-7800, respectively.

Results and Discussion

Table I shows the conductivities and viscosity viscosities of pure TMHA-TF$_2$N and Mg(TF$_2$N)$_2$ solutions in TMHA-TF$_2$N and/or G2. The kinematic viscosity of 0.5 mol dm$^{-3}$ Mg(TF$_2$N)$_2$ in TMHA-TF$_2$N:G2 (6.35 $\times$ 10$^2$ mm$^2$ s$^{-1}$) became about five times higher than pure TMHA-TF$_2$N (1.31 $\times$ 10$^2$ mm$^2$ s$^{-1}$). By mixing with G2, the kinematic viscosity decreased by two orders of magnitude (2.19 mm$^2$ s$^{-1}$), which is comparable with that of the Mg$^{2+}$-G2 solution (1.31 mm$^2$ s$^{-1}$). The conductivity of the TMHA-TF$_2$N-G2 solutions improved by an order of magnitude (2.5 mS cm$^{-1}$) compared to the other Mg(TF$_2$N)$_2$ solutions and was only about half value for pure TMHA-TF$_2$N (4.9 mS cm$^{-1}$). Such dilution effect by adding G2 was also seen in the case of PP13-TF$_2$N (see Table II). The kinematic viscosity of 0.5 mol dm$^{-3}$ Mg(TF$_2$N)$_2$ in PP13-TF$_2$N (4.02 $\times$ 10$^2$ mm$^2$ s$^{-1}$) was about four times higher than pure PP13-TF$_2$N (1.16 $\times$ 10$^2$ mm$^2$ s$^{-1}$). By mixing with G2, the kinematic viscosity decreased by two orders of magnitude (2.23 mm$^2$ s$^{-1}$) from the case of 0.5 mol dm$^{-3}$ Mg(TF$_2$N)$_2$ in PP13-TF$_2$N (4.02 $\times$ 10$^2$ mm$^2$ s$^{-1}$) and the conductivity improved by an order of magnitude (2.6 mS cm$^{-1}$) compared to the IL solution (0.35 mS cm$^{-1}$) or the G2 solution (0.50 mS cm$^{-1}$). As a result, the IL-G2 mixture gave better results than the other Mg$^{2+}$-containing solutions.

**Table II.** Molar ratio, molar concentrations (C), conductivities (σ) and kinematic viscosities (η) of PP13-TF$_2$N and Mg(TF$_2$N)$_2$-containing PP13-TF$_2$N and/or G2 solutions measured at 25°C.

<table>
<thead>
<tr>
<th>Molar ratio of Mg(TF$_2$N)$_2$:PP13-TF$_2$N/G2</th>
<th>C (mol dm$^{-3}$)</th>
<th>σ (mS cm$^{-1}$)</th>
<th>η (mm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 : 1 : 0</td>
<td>-</td>
<td>5.6</td>
<td>1.16 x 10$^2$</td>
</tr>
<tr>
<td>1 : 7 : 0</td>
<td>0.5</td>
<td>0.35</td>
<td>6.35 x 10$^2$</td>
</tr>
<tr>
<td>1 : 7 : 56</td>
<td>0.1</td>
<td>2.5</td>
<td>2.19</td>
</tr>
<tr>
<td>1 : 0 : 56</td>
<td>0.125</td>
<td>0.50</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Cyclic Voltammetry.— Figure 2 shows the CVs measured in several electrolytes. As shown in Fig. 2a, 2b, before adding G2, the CVs show reduction currents of about –0.3 mA cm$^{-2}$ at –1.0 V vs. Mg and only a little oxidation currents. In contrast, mixing Mg-containing ILs with G2 caused a drastic increase in the current density (by an order of magnitude) and sizable decrease in the overpotentials (see Fig. 2c, 2d). These results can be mainly attributed to the following two reasons. The first is a dilution effect, where the mobility of Mg$^{2+}$ cations becomes much larger when glymes are added, as proposed in the case of Li$^+$. The second is the possible change in coordination geometry, where Mg$^{2+}$ cations are coordinated by G2 molecules instead of TF$_2$N$^-$ anions. It has been reported that some strong Lewis acids such as Li$^+$ and Zn$^{2+}$ are coordinated by TF$_2$N$^-$ anions in the ILs, and exist in the form of monovalent [Li(TF$_2$N)$_2$]$^-$ and [Zn(TF$_2$N)$_2$]$^+$ anions. Because the ionic radius of Mg$^{2+}$ (89 pm) is similar to that of Li$^+$ (92 pm), it would exist in the form of [Mg(TF$_2$N)$_2$]$^-$ in the IL solutions without glymes, while in the presence of glymes they would solvate and form Mg$^{2+}$-G2 complex cations (e.g. [Mg(G2)$_2$]$^{2+}$) like Li$^+$-glyme complexes. If Mg$^{2+}$-glyme complex cations were formed, they may more easily access the cathode surface compared to [Mg(TF$_2$N)$_2$]$^-$ because of the electrostatic attractions with cathode. Another possibility is that the complex of Mg$^{2+}$ and TF$_2$N$^-$ can hardly desolvate because of the electrostatic attraction, while glymes with neutral charge may more easily desolvate from Mg$^{2+}$, even though it should be thermodynamically disadvantageous compared to TF$_2$N$^-$ complex.

![Figure 1](image-url) Schematic illustration of the cell configuration for (a) cyclic voltammetry and (b) potentiostatic electrolysis.


D103
Figure 2. Cyclic voltammograms measured for 0.5 mol dm$^{-3}$ Mg(Tf$_2$N)$_2$ in (a) TMHA-Tf$_2$N, (b) PP13-Tf$_2$N, and 0.1 mol dm$^{-3}$ Mg(Tf$_2$N)$_2$ in (c) TMHA-Tf$_2$N/G2 and (d) PP13-Tf$_2$N/G2. Sweep rate: 20 mV s$^{-1}$.

Figure 3. CV (from 0 V to $-1.5$ V to $+3$ V to 0 V; 20 mV s$^{-1}$) showing the electrochemical window for Mg$^{2+}$-free PP13-Tf$_2$N/G2, where Cu was used as WE, Mg in THF solution of EtMgBr was used as RE, and glassy carbon was used as CE.

Figure 4. (a) I-t curve for the cathodic deposition at $-1.0$ V in the PP13-Tf$_2$N/G2 mixture. The cathodic current density at the beginning was as high as about 7.5 mA cm$^{-2}$ and became higher with time, reaching the order of 10 mA cm$^{-2}$ after 30 min. This implies that the effective surface area for deposition became larger and larger with time. Shown in Fig. 4b is a photograph of the Cu WE and Mg CE after electrolysis at $-1.0$ V; the WE Cu sheet is coated by silver-colored material with a metallic deposit.

Potentiostatic electrodeposition.—Figure 4a shows the I-t curve for bath decomposition and anodic dissolution of Cu WE at ca. +2.4 V, respectively. These results strongly indicate that the observed reduction and oxidation current in Fig. 2d strongly indicate deposition and dissolution of Mg metal. Therefore we attempted electrodeposition of Mg metal from the PP13-Tf$_2$N/G2 mixture that showed the largest current density and the smallest overpotential of Mg electrodeposition.

Potentiostatic electrodeposition.—Figure 4a shows the I-t curve for the cathodic deposition at $-1.0$ V in the PP13-Tf$_2$N/G2 mixture. The cathodic current density at the beginning was as high as about 7.5 mA cm$^{-2}$ and became higher with time, reaching the order of 10 mA cm$^{-2}$ after 30 min. This implies that the effective surface area for deposition became larger and larger with time. Shown in Fig. 4b is a photograph of the Cu WE and Mg CE after electrolysis at $-1.0$ V; the WE Cu sheet is coated by silver-colored material with a metallic deposit.

Downloaded on 2014-03-05 to IP 130.54.130.67 address. Redistribution subject to ECS terms of use (see ecsdl.org/site/terms_use) unless CC License in place (see abstract).
luster and the immersed area of the CE Mg sheet became brighter than before, strongly indicating success in electrodeposition of Mg at the WE and anodic dissolution of Mg at the CE. The coulombic efficiency for deposition at −1.0 V was calculated to be about 100% from the mass change when we used a polished Mg sheet as WE. In general, at higher potentials or lower cathodic currents, more flat deposition can be obtained. However, as shown in Figure 5, the observed nonuniform deposition suggests that nucleation of Mg on Cu is much more difficult at the lower potentials, while the deposition at −1.0 V enabled non-localized Mg nucleation on Cu substrate. As a result, relatively flat electrodeposition of Mg at a high growth rate was achieved.

Characterization of deposits.— Figure 6 shows SEM images of the Mg deposits; they are round in shape, different from a typical dendritic morphology, similar to those obtained from Grignard electrolytes. Shown in Fig. 7 is the XRD pattern of WE after electrodeposition, which confirms that the deposits consisted of elemental Mg without any Mg–Cu alloy formation or sizable impurities; notably, however, the intensity ratio of the 002 peak was much weaker than the standard one.

Conclusions

In this work, we demonstrated electrodeposition of Mg metal from Mg(Tf2N)2 in an IL-glyme mixture at room temperature. We revealed that addition of an IL to glyme considerably increased the conductivity, and is very effective for increasing the reduction current. It is likely suggested that the IL-glyme mixture can perform fast and flat deposition of Mg negative electrode at room temperature. diglyme solution can possibly be used for battery application. Moreover, in charging process, the electrolyte is advantageous in that one can perform fast and flat deposition of Mg negative electrode at room temperature.

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 Grants-in-Aid for Scientific Research (A) (No. 25249106) from the Japan Society for the Promotion of Science (JSPS).

References