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<th>Title</th>
<th>Room-Temperature Electrodeposition of Mg Metal from Amide Salts Dissolved in Glyme-Ionic Liquid Mixture</th>
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<tr>
<td>Citation</td>
<td>Journal of the Electrochemical Society (2013), 161(3): D102-D106</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2013-12-28</td>
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<tr>
<td>URL</td>
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<td>© 2013 The Electrochemical Society</td>
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<tr>
<td>Type</td>
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Kyoto University
Elemental magnesium (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 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 alkylimagnesium halides $\text{RMgX}$ ($R = \text{alkyl, aryl groups}; \ X = \text{Cl, Br}$), and some reports indicate that addition of $\text{AlCl}_3$ to form an organo-halo-aluminate is effective in Mg deposition and/or dissolution. 

However, THF is so volatile and alkylimagnesium halides react so vigorously with water that they cannot be used practically. Thus, both the solvents and solutes for Mg deposition baths should be altered in interests of safety.

Since ionic liquids (ILs) have attractive characteristics such as lower volatility, incombustibility, high ion conductivity, and electrochemical stability, several studies on the redox behaviors of metallic Mg using IL have been conducted. Some studies recommend decreasing the volatility and increasing conductivity by mixing ILs with THF solutions of $\text{RMgX}$, where reversible Mg deposition/dissolution at room temperature is reported. Cheek et al. demonstrated the reversible process of Mg deposition/dissolution in THF-free IL solutions of $\text{RMgX}$ at 150°C. Alternative solvents include glymes because they have boiling points and flash points above 100°C and relatively low volatilities. Aurbach et al. showed the Mg deposition/dissolution cycle with high coulomb efficiency in the tetraglyme-Grignard mixture. Nevertheless, these mixtures still remain dangerous for commercial use since they contain $\text{RMgX}$.

Deposition of elemental Mg without THF and/or $\text{RMgX}$ has been reported. Cheek et al. showed Mg deposition redox behavior at room temperature in an IL dissolving $\text{Mg(ClO}_4)_2$ or $\text{MgCl}_2$, although their reduction currents were significantly lower than that in $\text{RMgX}$-containing ILs. Abe et al. demonstrated the reversible deposition/dissolution cycle of Mg with high coulomb efficiency in 2Me-THF where $\text{MgBr}_2$ dissolved. In addition, they also showed that some kinds of glyme solution, where $\text{MgCl}_2$ and $\text{AlCl}_3$ were dissolved, gave reversible deposition/dissolution behavior at room temperature. Nevertheless, the abovementioned Mg salts contain halide anions, which can form halogen gas through anodic oxidation. Because halogen gases carry a high environmental burden, non-halide anion electrolytes such as $\text{Mg(Tf}_2\text{N)}_2$ are favorable. Although NuLi et al. reported the reversible deposition/dissolution cycle of Mg in $\text{Mg(Tf}_2\text{N)}_2$-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 $\text{Mg(Tf}_2\text{N)}_2$. 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 TMHAABr and LiTf$_2$N via metathesis as reported previously. N-methyl-$N$-propylpiperidinium bis[(trifluoromethyl)sulfonyl]amide (PP13-Tf$_2$N) and battery-grade diethyleneeglycol dimethylether i.e. diglyme (G2) were purchased from Kanto Chemical. Battery-grade Mg($\text{ClO}_4$)$_2$ was purchased from Kishida Kagaku. First, we made 0.5 mol dm$^{-3}$ $\text{Mg(Tf}_2\text{N)}_2$/TMHAA-Tf$_2$N and 0.5 mol dm$^{-3}$ Mg($\text{ClO}_4$)$_2$/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$^{-3}$ $\text{Mg(Tf}_2\text{N)}_2$-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 VM-1 G calibrated using a standard solution (NIPPON GREASE Co., Ltd.). The densities of 0.5 mol dm$^{-3}$ $\text{Mg(Tf}_2\text{N)}_2$-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($\text{ClO}_4$)$_2$ in IL/G2 and 1.01 g cm$^{-3}$ for 0.125 mol dm$^{-3}$ Mg($\text{ClO}_4$)$_2$ 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
of 20 cm³ capacity where the planar dimension of WE was fixed to 7.5 mmφ (Fig. 1a). Electrolysis was conducted using a glass cell of 15 cm³ capacity (Fig. 1b). Cu rod (Nilaco, 99.9% purity) or Mg sheet (Nilaco, 99.9% purity) was used as the working electrode (WE) and counter electrode (CE), respectively. Because the potential of Mg was not stable in some Tf₂N-based ILs, as reference electrodes (RE) we used a Mg sheet or rod (Nilaco, 99.9% purity) were first washed with acetone and then with about 1 mol dm⁻³ Mg(Tf₂N)₂ solution and was only about half value for pure TMHA-Tf₂N (4.9 mS cm⁻¹). Such dilution effect by adding G2 was also seen in the case of PP13-Tf₂N (see Table II). The kinematic viscosity of 0.5 mol dm⁻³ Mg(Tf₂N)₂ in PP13-Tf₂N (4.02 × 10² mm² s⁻¹) was about four times higher than pure PP13-Tf₂N (1.16 × 10² mm² s⁻¹). By mixing with G2, the kinematic viscosity decreased by two orders of magnitude (2.23 mm² s⁻¹) from the case of 0.5 mol dm⁻³ Mg(Tf₂N)₂ in PP13-Tf₂N (4.02 × 10² mm² 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 Mg²⁺-containing solutions.

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, 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 Mg²⁺ 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 Mg²⁺ cations are coordinated by G2 molecules instead of Tf₂N⁻ anions. It has been reported that some strong Lewis acids such as Li⁺ and Zn⁺ are coordinated by Tf₂N⁻ anions in the ILs, and exist in the form of [Mg(G₂)₉]⁻ and [Zn(Tf₂N)₉]⁻ anions with anion TMHA-Tf₂N and Mg(Tf₂N)₂ in PP13-Tf₂N and/or G2 solutions measured at 25°C.

Table II. Molar ratio, molar concentrations (C), conductivities (σ) and kinematic viscosities (η) of PP13-Tf₂N and Mg(Tf₂N)₂-containing PP13-Tf₂N and/or G2 solutions measured at 25°C.

<table>
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<tr>
<th>Molar ratio of Mg(Tf₂N)₂: PP13-Tf₂N/G2</th>
<th>C (mol dm⁻³)</th>
<th>σ (mS cm⁻¹)</th>
<th>η (mm² s⁻¹)</th>
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<tr>
<td>0 : 1 : 0</td>
<td>-</td>
<td>5.6</td>
<td>1.16 × 10²</td>
</tr>
<tr>
<td>1 : 7 : 0</td>
<td>0.5</td>
<td>0.35</td>
<td>6.35 × 10²</td>
</tr>
<tr>
<td>1 : 7 : 56</td>
<td>0.1</td>
<td>2.6</td>
<td>2.23</td>
</tr>
<tr>
<td>1 : 0 : 56</td>
<td>0.125</td>
<td>0.50</td>
<td>1.31</td>
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in TMHA-Tf₂N (6.35 × 10² mm² s⁻¹) became about five times higher than pure TMHA-Tf₂N (1.31 × 10² mm² s⁻¹). By mixing with G2, the kinematic viscosity decreased by two orders of magnitude (2.19 mm² s⁻¹), which is comparable with that of the Mg²⁺-G2 solution (1.31 mm² s⁻¹). The conductivity of the TMHA-Tf₂N-G2 solutions improved by an order of magnitude (2.5 mS cm⁻¹) compared to the other Mg(Tf₂N)₂ solutions and was only about half value for pure TMHA-Tf₂N (4.9 mS cm⁻¹). Such dilution effect by adding G2 was also seen in the case of PP13-Tf₂N (see Table II). The kinematic viscosity of 0.5 mol dm⁻³ Mg(Tf₂N)₂ in PP13-Tf₂N (4.02 × 10² mm² s⁻¹) was about four times higher than pure PP13-Tf₂N (1.16 × 10² mm² s⁻¹). By mixing with G2, the kinematic viscosity decreased by two orders of magnitude (2.23 mm² s⁻¹) from the case of 0.5 mol dm⁻³ Mg(Tf₂N)₂ in PP13-Tf₂N (4.02 × 10² mm² 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 Mg²⁺-containing solutions.
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 immersed area.

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 immersed area.
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, potentiostatic electrolysis at higher than –1.0 V, i.e. –0.8 V, –0.6 V, and –0.4 V did not result in flat deposition. 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. Matsui discussed the orientation of Mg deposits obtained in Grignard solutions, where (100) orientation was observed at a high deposition rate of 2 mA cm⁻², probably due to the different crystal growth rate in the hexagonal structure. Because the deposition current in the glyme-IL solution was as high as about 10 mA cm⁻², our result is consistent with Ref. 38.

Possibility for battery application.— Here we remark whether the PP13-Tf₂N/G2 mixture could be used for Mg ion secondary batteries. Consistent with Ref. 38, glyme-IL solution was as high as about 10 mA cm⁻², 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. Matsui discussed the orientation of Mg deposits obtained in Grignard solutions, where (100) orientation was observed at a high deposition rate of 2 mA cm⁻², probably due to the different crystal growth rate in the hexagonal structure. Because the deposition current in the glyme-IL solution was as high as about 10 mA cm⁻², our result is consistent with Ref. 38.

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 that addition of an IL to glyme considerably increased the conductivity, and is very effective for increasing the reduction current. Addition of an IL to glyme considerably increased the conductivity, and is very effective for increasing the reduction current. Moreover, in charging process, the electrolyte is advantageous in that one can perform fast and flat deposition of Mg negative electrode at room temperature.

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 that addition of an IL to glyme considerably increased the conductivity, and is very effective for increasing the reduction current. 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