



Short communication

## Mixed electrolyte consisting of ethylmagnesiumbromide with ionic liquid for rechargeable magnesium electrode

Nobuko Yoshimoto<sup>a,b</sup>, Mami Matsumoto<sup>a</sup>, Minato Egashia<sup>a</sup>, Masayuki Morita<sup>a,b,\*</sup><sup>a</sup> Department of Applied Chemistry, Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan<sup>b</sup> CREST, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi 332-0012, Japan

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## ABSTRACT

A novel electrolyte system for a rechargeable magnesium battery has been developed. The electrolyte consists of ethylmagnesiumbromide in tetrahydrofuran (EtMgBr/THF) with an ionic liquid (IL) of quaternary ammonium salt. The ionic conductivity of the electrolyte with the composition of EtMgBr/THF:IL being 3:1 in volume was  $7.44 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ . A reversible processes of cathodic deposition and anodic dissolution of magnesium has been successfully achieved in the mixed electrolyte system of EtMgBr/THF + IL at room temperature.

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### 1. Introduction

Magnesium (Mg) is an attractive candidate for the anode (negative electrode) material of high energy density batteries. However, it is generally difficult to establish a reversible process of electrochemical reduction and oxidation for Mg, not only in aqueous but also in organic electrolyte solutions, because Mg is easily oxidized by water and other protic solvents to form passivation films [1–3]. As to the possibility of Mg anode for rechargeable Mg batteries, Conner et al. [4] reported the cathodic deposition of Mg in ethereal solutions dissolving MgBr<sub>2</sub>. Liebenow [5] demonstrated the possibility of reversible deposition and dissolution of Mg in ethereal solutions of Grignard reagents (RMgX, where R = alkyl, aryl groups; X = Cl, Br). Aurbach et al. [6–9] also reported the reversible process of Mg in electrolyte solutions based on organo-haloaluminate salts: Mg(AlCl<sub>3</sub>R)<sub>2</sub> or Mg(AlCl<sub>2</sub>RR')<sub>2</sub>, where R and R' are alkyl groups, in THF or polyethers of glyme family. It is considered that, in these solutions, no compact passivating film covers the surface of Mg, for which reversible deposition/dissolution of Mg can occur with low overvoltage. Thus, Gregory et al. [3] and Aurbach's group [8] have separately presented rechargeable Mg battery systems using intercalation compound cathodes (positive electrode) with non-

aqueous ether-based electrolytes. In general, however, as ether solvents have high vapor pressure and strong flammability, the proposed battery systems still have practical problems of safety and reliability.

Ionic liquids (ILs), also known as room temperature molten salts, possess many advantages such as high ionic conductivity, wide electrochemical window, good thermal and chemical stability, non-flammability, and non-volatility. Therefore, ILs are expected as the promising components of novel electrolyte systems for rechargeable batteries, especially for lithium-ion batteries. The present authors previously reported that Mg can be co-deposited with Li in quaternary ammonium salt based ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium-bis(trifluoromethanesulfonyl)imide (DEMETFSI) dissolving LiTFSI and Mg(TFSI)<sub>2</sub> [10]. The salts of DEME<sup>+</sup> cation have wide electrochemical window (ca. 6.0V) and good stability for cathodic reduction [11]. Cheek et al. [12] have investigated the electrodeposition of Mg in imidazolium-based ionic liquids containing a Grignard reagent, and reported reversible deposition and dissolution of Mg in the system consisting of 1:2 mixture of the Grignard reagent and the ionic liquids at  $150^\circ\text{C}$ .

In the present work, we have developed a novel electrolyte system consisting of Grignard reagent (ethylmagnesiumbromide in THF, EtMgBr/THF) and an IL of quaternary ammonium salt (DEMETFSI) for rechargeable magnesium batteries working at ambient temperature. Reversibility of Mg deposition and dissolution has been investigated in such a mixed electrolyte system. Then, the applicability of the present electrolyte system to rechargeable Mg batteries is briefly demonstrated.

\* Corresponding author at: Department of Applied Chemistry, Graduate School of Science and Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube 755-8611, Japan. Tel.: +81 836 85 9211; fax: +81 836 85 9201.

E-mail address: [morita@yamaguchi-u.ac.jp](mailto:morita@yamaguchi-u.ac.jp) (M. Morita).

**Table 1**  
Ionic conductivity of the electrolyte solution.

Electrolyte	Ionic conductivity ( $\times 10^{-3} \text{ S cm}^{-1}$ )
EtMgBr/THF	0.33
EtMgBr/THF:DEMETFSl (3:1 by volume ratio)	7.44
DEMETFSl	2.73

## 2. Experimental

The ionic liquid used in this work was DEMETFSl (purchased from Kanto Chemical). A Grignard reagent,  $1.0 \text{ mol dm}^{-3}$  (M) EtMgBr/THF (purchased from Kanto Chemical) was used as an Mg source. These reagents were used as received, but stored in a grove box filled with dry Ar before use. Proper volume ratios of DEMETFSl and EtMgBr/THF were mixed to obtain the electrolyte solution.

The ionic conductivity of the electrolytes was measured by an ac impedance technique (Solartron 1260 coupled with Electrochemical Interface) at  $25^\circ\text{C}$  using a laboratory-made sealed glass cell with platinum indicating electrodes.

The cathodic deposition/anodic dissolution process of Mg in Grignard reagent or mixed electrolyte containing Grignard reagent and DEMETFSl was investigated by cyclic voltammetry (CV) using a three-electrode beaker cell. The working electrode (substrate) was an Au wire, and Ag wire and Pt sheet were used as the quasi-reference electrode (QRE) and the counter-electrode, respectively.

Constant-potential electrodeposition was conducted by using the same cell as CV measurements, except for the size of Au working electrode. The deposit on an Au sheet after constant-potential electrodeposition was analyzed by an X-ray diffractometer (XRD: Shimadzu, XD-D1, Cu K $\alpha$  radiation).

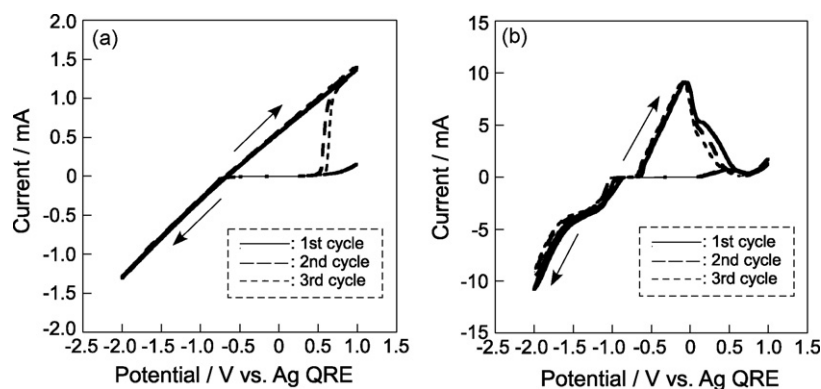
Charge (deposition) and discharge (dissolution) characteristics were examined under constant-current conditions using the same three-electrode beaker cell as used in CV measurements. The cell was cycled with a current density of  $5 \text{ mA cm}^{-2}$  and the cut off condition of 120 s for charge and 0.7 V (vs. Ag QRE) for discharge. These electrochemical experiments including electrolyte preparation were carried out under a dry Ar atmosphere at room temperature ( $22 \pm 3^\circ\text{C}$ ).

## 3. Results and discussion

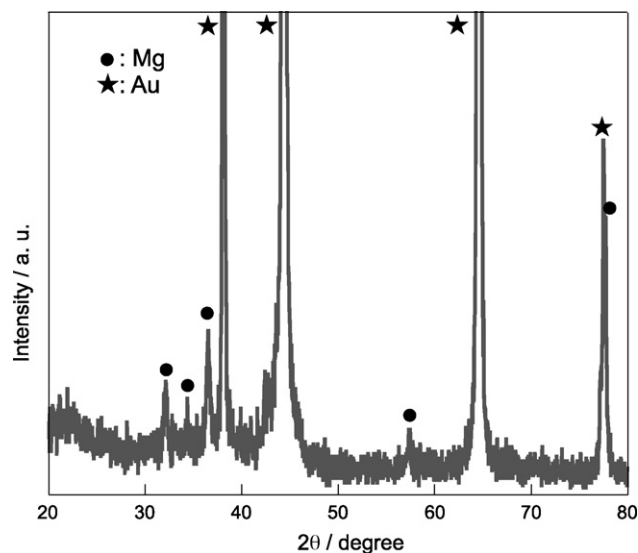
The ionic conductivity of the mixed electrolyte consisting of 3:1 (by volume) mixture of Grignard reagent (EtMgBr/THF) and DEMETFSl was measured at  $25^\circ\text{C}$ . The result is shown in Table 1, compared with those of EtMgBr/THF and neat DEMETFSl. The mixed electrolyte containing EtMgBr/THF and DEMETFSl showed higher ionic conductivity,  $7.44 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ , than that of neat

EtMgBr/THF or DEMETFSl. The viscosity of the mixed electrolyte consisting of EtMgBr/THF with DEMETFSl is higher than that of the Grignard reagent without IL, but lower than that of neat DEMETFSl. On the other hand, the number of charge carrier in the mixed electrolyte solution will be higher than not only the Grignard reagent alone but also the neat IL, because the ionic dissociation of EtMgBr/THF will be accelerated in the IL with higher permittivity. These are possible causes that the present mixed Grignard reagent + IL system showed higher ionic conductivity than those of their components.

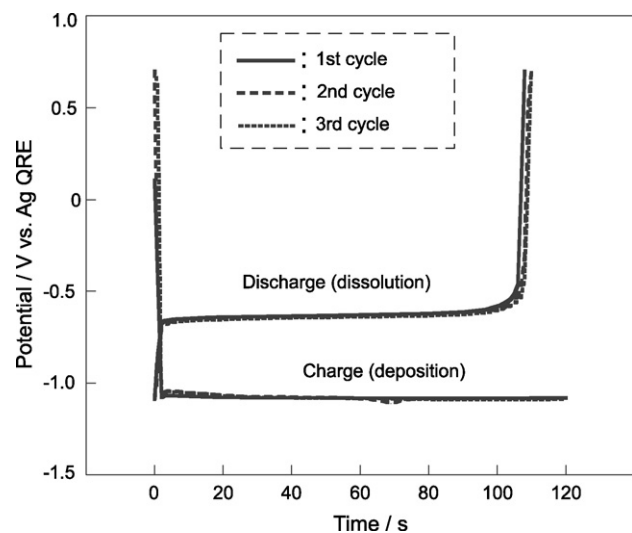
Fig. 1(a) shows the cyclic voltammogram (CV) of Au electrode in the neat Grignard reagent, EtMgBr/THF, with the scan rate of  $10 \text{ mV s}^{-1}$ . As already reported [5], cathodic deposition and anodic dissolution of Mg are observed in the neat Grignard reagent. However, the current–potential relation suggests that the system is controlled by ohmic polarization. That is, low ionic conductivity of EtMgBr/THF, as shown in Table 1, determines the almost linear response in the current–potential curve and relatively low current values even at highly polarized potentials. Fig. 1(b) shows the CV of Au electrode in EtMgBr/THF mixed with DEMETFSl (3:1 by volume ratio) under the same scan rate as in Fig. 1(a). The cathodic current increased below ca.  $-1.0 \text{ V}$ , and the anodic current increased over ca.  $-0.6 \text{ V}$ , which respectively correspond to the cathodic deposition and the anodic dissolution of Mg. The currents for reduction and oxidation are higher than those observed in EtMgBr/THF alone (Fig. 1(a)). This behaviour itself is quite similar to that reported previously [7]. However, rather high current responses were obtained in the present electrolyte system, compared with those shown in the system previously reported [7]. One of the important features of the present system is that the reversibility of the current response was kept with repeated cycles. The CV response in the mixed electrolyte using 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSl) [13], instead of DEMETFSl in the present work, as the IL component showed only the cathodic peak attributed to the decomposition of EMITFSl. The present result proves that the reversible deposition and dissolution of Mg can occur only in ILs having a good stability under the cathodically polarized conditions. No reversible process of cathodic deposition and anodic dissolution for Mg was achieved in mixed electrolyte system using propylene carbonate (PC) or ethylene carbonate (EC), which is normally used for Li-ion batteries as the electrolyte solvent, instead of DEMETFSl [13]. Consequently, in the present electrolyte solution, the IL DEMETFSl works as not only the solvent but also the supporting electrolyte. Thus, reversible deposition/dissolution process of Mg was obtained in the mixed electrolyte containing EtMgBr/THF and DEMETFSl. In addition, we found that the high volatility of THF solvent was partly suppressed by mixing the non-volatile component, DEMETFSl, due to so-called “dilution effect”.



**Fig. 1.** Cyclic voltammograms of Au substrate in (a) 1.0 M EtMgBr/THF and in (b) the mixed electrolyte consisting of EtMgBr/THF with DEMETFSl (3:1 by volume ratio). Surface area:  $0.26 \text{ cm}^2$ ; scan rate:  $10 \text{ mV s}^{-1}$ .



**Fig. 2.** XRD pattern of the electrodeposit on an Au substrate in the mixed electrolyte consisting of EtMgBr/THF with DEMETFSI (3:1 by volume ratio) at  $-2.0$  V vs. Ag QRE for 180 s.



**Fig. 3.** Charge–discharge curves for Mg on an Au substrate in the mixed electrolyte consisting of EtMgBr/THF with DEMETFSI (3:1 by volume ratio). Current density:  $5 \text{ mA cm}^{-2}$ ; charge: 120 s; discharge: to 0.7 V vs. Ag QRE.

Constant-potential electrodeposition was conducted in the mixed electrolyte consisting of EtMgBr/THF with DEMETFSI (3:1 by volume ratio) by using an Au sheet substrate at  $-2.0$  V vs. Ag QRE for 180 s. A grayish uniform deposit was detected on the Au substrate. The XRD pattern of the resulting electrodeposit is shown in Fig. 2. The diffraction peaks based on the Au substrate were observed at  $2\theta = 38.1^\circ$ ,  $44.3^\circ$ ,  $64.5^\circ$ , and  $77.5^\circ$  (black star), due to

small amount of the deposited film on the Au substrate. Other diffraction peaks, namely  $2\theta = 32.2^\circ$ ,  $34.4^\circ$ ,  $36.6^\circ$ ,  $57.4^\circ$ , and  $77.8^\circ$  (closed circle), were assigned to hexagonal Mg–metal from the database of JCPDS. Thus, the results of the XRD experiments confirm that the cathodic process on Au in the mixed EtMgBr/THF with DEMETFSI consists mainly of the deposition of metallic Mg.

The constant-current deposition and dissolution characteristics of Mg were investigated to examine the applicability of the present mixed electrolyte system to rechargeable Mg batteries. Fig. 3 shows the charge (deposition) and discharge (dissolution) profiles of Mg on the Au substrate in the solution consisting of EtMgBr/THF with DEMETFSI (3:1 by volume ratio). Here, we use the term “charge” for the Mg deposition on Au substrate and the term “discharge” for the Mg dissolution from Au. The potential plateaus were observed at about  $-1.1$  V vs. Ag QRE for charge and about  $-0.7$  V for discharge. From the potential difference between charge and discharge profiles, the overvoltage of each process was estimated to be about  $0.2$  V ( $\{-0.7 - (-1.1)\}/2$ ) under the cycling current of  $5 \text{ mA cm}^{-2}$ . The coulombic efficiency for each cycle was about 93%. The long term cycleability and the detail of the deposition/dissolution mechanism of Mg in the mixed electrolyte of EtMgBr/THF with DEMETFSI are now under investigation.

#### 4. Conclusions

Rechargeability of metal Mg electrode was investigated in a novel electrolyte system of Grignard reagent (EtMgBr/THF) mixed with ionic liquid (DEMETFSI). High ionic conductivity of  $7.44 \text{ mS cm}^{-1}$  (at  $25^\circ\text{C}$ ) was obtained in the 3:1 mixture (by volume) of EtMgBr/THF and DEMETFSI. The ionic liquid DEMETFSI works as not only the solvent but also the supporting electrolyte in the present electrolyte system. A reversible process of cathodic deposition and anodic dissolution of Mg has been successfully achieved in the present mixed electrolyte system at room temperature.

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