



Short communication

## Electrochemical co-deposition of magnesium with lithium from quaternary ammonium-based ionic liquid

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## ABSTRACT

Electrochemical deposition of magnesium (Mg) has been successfully achieved from an ionic liquid (IL) solution based on quaternary ammonium salt containing lithium (Li) salt. Irreversible electrochemical behavior was generally observed in the IL-based electrolytes containing simple Mg salt. In the IL-based electrolyte dissolving both Mg and Li salts, electrochemical reduction and oxidation of magnesium cation ( $Mg^{2+}$ ) have become detectable. Such reversible processes correspond respectively to cathodic deposition and anodic dissolution of metallic Mg, which are accompanied by the co-deposition/co-dissolution of Li. Potentiostatic electrolysis of IL dissolving binary Mg and Li salts gave metallic deposit consisting of both elements with total current efficiency of ca. 52%.

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### 1. Introduction

Metallic magnesium (Mg) is a possible candidate for a negative electrode of high energy density rechargeable batteries. It is well known, however, that a reversible process of electrochemical reduction and oxidation of Mg is hardly achieved, not only in aqueous but also in organic electrolyte solutions. This is because that Mg is easily oxidized by water (moisture) and even by other protonic solvents to form passivation films [1–3]. Conner and co-workers [4] have first reported the cathodic deposition of Mg from ether solutions dissolving  $MgBr_2$ . Liebenow [5] has demonstrated the possibility of reversible deposition and dissolution of Mg in ether-based solutions of Grignard reagents. Aurbach et al. [6–9] also reported reversible processes of Mg in electrolyte solutions based on organo-haloaluminate salts in THF or polyethers of glyme family. It is generally accepted that no compact passivation film covers the Mg surface in this type of ether-based solutions, which can enable reversible deposition and dissolution of Mg. However, as the ether solvents have, in general, high vapor pressure and are highly flammable, the above proposed electrolyte systems are still not practical from the viewpoint of safety and reliability of the system.

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. Thus, ILs are expected as promising components of novel electrolyte systems for rechargeable batteries, especially for lithium-ion batteries (LIB) [10]. Also, ILs can be used as the plating bath of various metals, especially for the metals that are difficult to deposit from aqueous solutions [11].

Recently some efforts have been published to develop electrolyte systems based on ILs in which Mg electrodes behave reversibly. For example, NuLi et al. [12,13] reported that the Mg can be electrodeposited from an IL, 1-butyl-3-methylimidazolium tetrafluoroborate ( $BMIImBF_4$ ), containing magnesium trifluoromethylsulfonate ( $Mg(CF_3SO_3)_2$ ). However, no concrete evidence has so far presented for the deposition of metallic Mg form such an IL-based electrolyte system. That is, Cheek et al. [14] and Amir et al. [15] have not been able to reproduce the electrodeposition of Mg under the same condition as that reported by NuLi et al. [12,13]. We also reported that  $Mg^{2+}$  forms an ion-pair, or strongly associates with anion, in an IL dissolving Mg salt [16]. Thus, it is now accepted that reversible deposition and dissolution of Mg is practically difficult in ILs containing simple Mg salts.

With respect to application of Mg in battery area, beside pure material, binary or ternary systems containing Mg species would be also useful as the negative electrode. In metal finishing area, some metal components that are hardly obtained in their pure forms by cathodic deposition can be obtained as composites from binary electrolyte systems. Therefore we have tried in the present work

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to obtain binary composite or alloy films consisting of Mg and Li by electrodeposition, where Li was chosen as the counter component because of their use in rechargeable battery systems. Cathodic deposition of Mg–Li composite was demonstrated from IL without conventional organic solvents.

## 2. Experimental

The ionic liquid used in this work was *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethylsulfonyl)imide (DEMETFSI) (purchased from Kanto Chemical), which was chosen because of its wide electrochemical window (ca. 6.0V) and excellent stability under cathodic polarization [17]. As the purity of DEMETFSI was enough high to work as “solvent”, it was used as received, but stored in a glove box filled with dry Ar before use. Magnesium bis(trifluoromethylsulfonyl)imide ( $\text{Mg}[(\text{CF}_3\text{SO}_2)_2\text{N}]_2$ ,  $\text{Mg}(\text{TFSI})_2$ , supplied from Central Glass Co.) and lithium bis(trifluoromethylsulfonyl)imide ( $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$ , LiTFSI, supplied from 3 M, Japan) were used as an electrolytic salt. These salts were dried under a vacuum at 120 °C for 24 h, and stored in a glove box filled with dry Ar before use. The proper amount (mol%) of  $\text{Mg}(\text{TFSI})_2$  and/or LiTFSI were dissolved in DEMETFSI to obtain the electrolyte solution with a designed composition. The residual water contents in the resulting solutions were determined by Karl-Fisher titration, and found to be less than 120 ppm.

The electrochemical behavior of Mg and/or Li in DEMETFSI was investigated by cyclic voltammetry (CV) using a conventional 3-electrode beaker cell. The working electrode was an Au wire, and the counter and quasi-reference electrodes (QRE) were a Pt sheet and an Ag wire, respectively. All electrochemical experiments including the electrolyte preparation were carried out under a dry Ar atmosphere at room temperature ( $22 \pm 3$  °C).

Potentiostatic electrolysis (electrodeposition under controlled potential) was conducted by using the same cell as the CV measurement, except for the working (substrate) electrode, an Au sheet instead of the wire. The deposit on the Au sheet was wrapped with polyethylene film under an inert atmosphere, and then analyzed by X-ray diffractometry (XRD: Shimadzu, XD-D1, Cu K $\alpha$  radiation). The chemical composition of the deposit was analyzed by ICP Atomic Emission Spectrometer (Shimadzu, ICPE-9000), after dissolving it in a hydrochloric acid solution.

## 3. Results and discussion

Fig. 1 shows the cyclic voltammograms (CVs) obtained for an Au wire working electrode in different compositions of IL-based electrolytes; neat DEMETFSI, IL dissolving 20 mol% LiTFSI, IL dissolving 20 mol%  $\text{Mg}(\text{TFSI})_2$ , and IL dissolving mixed 10 mol% LiTFSI and 10 mol%  $\text{Mg}(\text{TFSI})_2$ . In the case of DEMETFSI without the metal salts, only cathodic current was observed at about  $-2.5$  V (vs. Ag QRE) or below, which suggests some reductive decomposition of DEMETFSI itself. In the electrolyte containing 20 mol%  $\text{Mg}(\text{TFSI})_2$ , the cathodic current at  $-2.5$  V or below decreased significantly, but no visible current attributable to the redox process of  $\text{Mg}^{2+}$  was detected. On the other hand, the electrolyte system containing 20 mol% LiTFSI gave a clear couple of cathodic and anodic currents at around  $-3.0$  V, which corresponds to Li deposition and dissolution in this IL-based system. The redox response was also obtained in the IL-based electrolyte containing both LiTFSI and  $\text{Mg}(\text{TFSI})_2$ , where the current density was lower than that observed in IL dissolving Li salt only. These suggest that the addition of the Mg salt can suppress such cathodic processes as Li-deposition and DEMETFSI decomposition. However, we can observe the reversible deposition and dissolution of Li even in the IL-based electrolyte containing Mg salt. In Fig. 2, CVs in DEMETFSI-based electrolytes with differ-

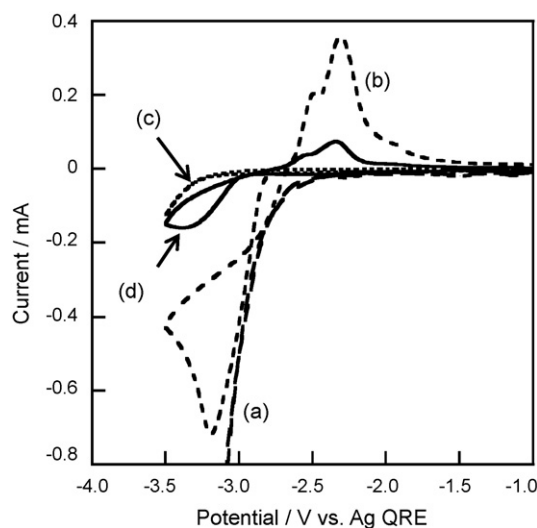


Fig. 1. Cyclic voltammograms of Au electrode in (a) DEMETFSI, (b) DEMETFSI dissolving 20 mol% LiTFSI, (c) DEMETFSI dissolving 20 mol%  $\text{Mg}(\text{TFSI})_2$ , and (d) DEMETFSI dissolving mixed 10 mol% LiTFSI and 10 mol%  $\text{Mg}(\text{TFSI})_2$ .

ent contents of metal salts are compared. The current response in the electrolyte containing 20 mol% LiTFSI with 10 mol% Mg salt is smaller than that obtained in the electrolyte dissolving the same content of LiTFSI without the Mg salt. This result also reveals that the Mg salt suppresses the redox process of Li deposition and dissolution in IL. However, we can still expect that the co-deposition of Mg will proceed in the mixed salt electrolyte.

Potentiostatic electrolysis was carried out using an Au sheet to analyze the cathodic deposition process in IL dissolving mixed Li and Mg salts. The electrolysis was done for 5 h at  $-3.5$  V (vs. QRE) in DEMETFSI containing 10 mol% LiTFSI and 10 mol%  $\text{Mg}(\text{TFSI})_2$ . The total amount of the electricity passed was 1.55 C for 5 h. After the electrolysis, black deposit was observed on the Au sheet. Fig. 3 shows an X-ray diffraction pattern of the deposit on the Au substrate, where the diffraction data for metallic Mg, Li and Au are included as references. Besides sharp diffraction peaks attributed to the substrate Au ( $2\theta = 44.4^\circ$ ,  $64.6^\circ$ , and  $77.6^\circ$ ), we can observe a broad diffraction peak at around  $2\theta = 32^\circ$ , which corresponds to (100) plane of the hexagonal lattice of metallic Mg. However,

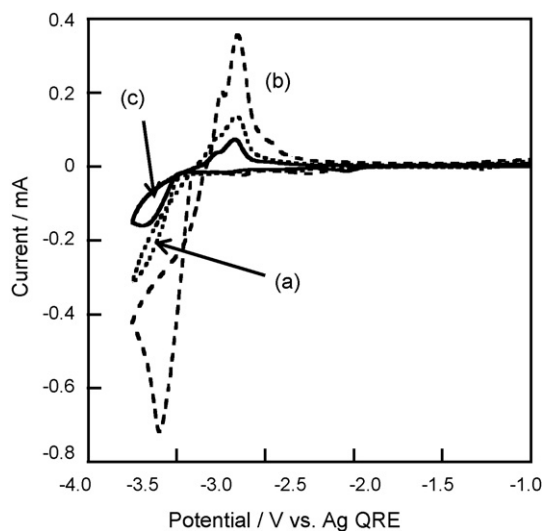


Fig. 2. Cyclic voltammograms of Au electrode in (a) DEMETFSI dissolving 20 mol% LiTFSI with 10 mol%  $\text{Mg}(\text{TFSI})_2$ , (b) DEMETFSI dissolving 20 mol% LiTFSI, and (c) DEMETFSI dissolving mixed 10 mol% LiTFSI and 10 mol%  $\text{Mg}(\text{TFSI})_2$ .

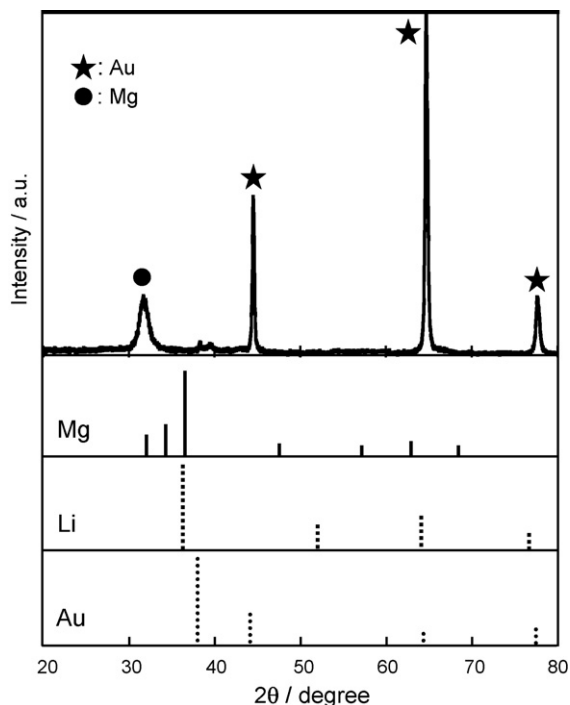


Fig. 3. XRD pattern of the electrodeposit on Au substrate in DEMETFSI dissolving mixed 10 mol% LiTFSI and 10 mol% Mg(TFSI)<sub>2</sub> at  $-3.5$  V vs. Ag QRE for 5 h.

Table 1  
Results of chemical analysis of the electrodeposit.

	Amount of deposit ( $\times 10^{-6}$ mol)	Current efficiency (%)
Mg	2.31	28.8
Li	3.93	24.6

no other diffraction peaks than the hexagonal (100) plane of Mg were observed, which suggests that the Mg deposit has grown in some orientation. Also we could not detect any peaks that can be assignable to Li or Li–Mg alloys (e.g. Li<sub>6.46</sub>Mg;  $2\theta = 33.8^\circ$ ,  $35.5^\circ$ ,  $38.8^\circ$ ,  $59.6^\circ$ ,  $71.3^\circ$ , and  $74.9^\circ$ , from the JCPDS database) in the diffraction pattern of the deposit.

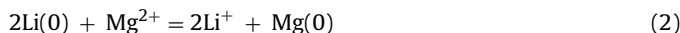
The composition of the deposit was chemically analyzed by ICP-AES, and the results are shown in Table 1. Both Li and Mg were found in the deposit, and their amounts were equivalent to the coulombic efficiency of 24.6% for Li and 28.8% for Mg, if the deposition from the present IL-based electrolyte is assumed to occur through following electrochemical processes.



The total current efficiency of ca. 52% is rather reasonable because such side reactions as cathodic reduction of impurity components and/or decomposition of IL itself would be included during the potentiostatic electrolysis. As both metallic Li and Mg are chemically active, some parts of the deposit might be lost during the

rinsing the surface of the deposit by the solvent IL before the chemical analysis.

Judging from the voltammetric response of Au in Mg(TFSI)<sub>2</sub>/DEMETFSI (Fig. 1), the simple cathodic reduction of Mg (Eq. (1b)) will be hard to proceed in the present electrolyte system. The experimental result that metallic Mg was obtained by the potentiostatic electrolysis in the electrolyte containing mixed salt of LiTFSI and Mg(TFSI)<sub>2</sub> can be explained by a kind of “induced deposition” for binary metal deposition process [18,19]. Another possibility is also considered, eg., redox reaction between Mg<sup>2+</sup> in the liquid and Li metal deposited on the Au substrate, as follows.



In the latter case, some of deposited Li will be lost to dissolve as ionic species in the electrolyte. Even in the case, the remaining Li would not exist as crystal Li nor Li–Mg alloy, as shown in XRD result. Thus, the deposit will be a composite that consists of amorphous phase of Li containing metallic Mg with hexagonal crystal. We can expect that the deposit works as an active material of negative electrode for rechargeable battery, whose performances are now under investigation.

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