Electrochemical Behavior of Magnesium in Mixed Solutions Consisting of Ionic Liquid and Alkylmagnesiumbromides with Different Alkyl-Chains

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ABSTRACT

Electrochemical deposition and dissolution of magnesium have been investigated in organic solutions consisting of alkylmagnesiumbromides/tetrahydrofuran (RMgBr/THF) having different alkyl-chains mixed with an ionic liquid. Coulombic efficiency for cathodic deposition and anodic dissolution of magnesium, obtained from voltammetric responses, decreased with the increase in the alkyl-chain length of the magnesium complex. The highest current response was observed in the electrolyte system consisting of CH₃MgBr/THF with a quaternary ammonium salt-based ionic liquid.

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Keywords : Rechargeable Magnesium Battery, Alkylmagnesiumbromide, Ionic Liquid, Electrodeposition of Magnesium

1. Introduction

Rechargeable magnesium (Mg) battery that uses metal Mg as the negative electrode is a potential candidate of the next-generation power sources for electric vehicles (EV) and other large scale applications due to high energy density, low cost, easiness to handle, and environment-friendly nature of Mg.^{1,2} One of the key technologies for developing practical rechargeable Mg batteries is to establish a reversible redox process (deposition and dissolution) of Mg. However, not like lithium (Li) metal whose surface is covered with a Li⁺-conducting film, the surface of Mg metal in organic electrolyte solutions generally consists of compact passivation films that are produced by reactions with solvent molecules and/or electrolyte anion.³ Thus, it has generally accepted that reversible Mg deposition and dissolution do not occur in usual organic electrolyte solutions dissolving conventional Mg salts. As the possibility of Mg anode (negative electrode) for rechargeable batteries, Liebenow⁴ first reported the reversible deposition and dissolution of Mg in ether solutions of so-called Grignard reagents. It is considered that no compact passivation film covers the Mg surface and hence the reversible deposition and dissolution of Mg occur with low overvoltage in those systems. Since then, similar organo-magnesium complexes in ethereal solvents have widely been examined as the electrolytes for rechargeable Mg batteries.^{1,5–7} Because of high vapor pressure and strong flammability of the ether solvents, however, the battery systems so far proposed have still practical problems in safety and reliability. In the previous paper, we have reported that Mg can be deposited and dissolved in a mixed electrolyte system consisting of an ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium-bis-(trifluoromethanesulfonyl)imide (DEMETFSI), with ethyl magnesium bromide (C₂H₅MgBr) dissolved in tetrahydrofuran (THF).⁸ In this mixed solution, the ionic liquid, DEMETFSI, works not only as non-volatile solvent but also as a supporting electrolyte to enhance the ionic conductivity. We confirmed that the high vapor pressure caused by the volatile component of THF was partly suppressed by mixing the non-volatile component, DEMETFSI, due to so-called “dilution effect”.

In the present work, we have examined an optimum chain length of the alkyl group in the organo-magnesium complex,

RMgBr, for electrochemical deposition and dissolution of Mg in the DEMETFSI-based electrolyte. That is, the effects of the chemistry of RMgBr on the electrochemical behavior of Mg were investigated in the mixed electrolyte solutions consisting of RMgBr/THF with DEMETFSI.

2. Experimental

The ionic liquid used in this work, DEMETFSI, purchased from Kanto Chemical, was chosen because of its wide electrochemical window (ca. 6.0 V) and excellent stability under cathodic polarization.⁹ Five kinds of commercially available alkylmagnesiumbromides dissolved in tetrahydrofuran (RMgBr/THF, R = CH₃, C₂H₅, *n*-C₃H₇, C₃H₁₁, *n*-C₈H₁₇) were used as Mg sources. The concentration of RMgBr dissolved in THF was 1.0 mol dm⁻³ (M), except for C₂H₅MgBr/THF (0.9 M). These reagents were used as received, but stored in a glove box filled with dry Ar before use. Proper amounts of DEMETFSI and RMgBr/THF were mixed to obtain the electrolyte solutions with the molar ratio of 1:1 in RMgBr/DEMETFSI.

The ionic conductivity of the electrolyte solution was measured at 25°C by an ac impedance method (Solartoron 1260 coupled with an electrochemical interface) using a laboratory-made sealed glass cell with platinum indicating electrodes. The viscosity of the mixed solution was measured using an Ostwald viscometer in the Ar-filled glove box at room temperature (25 ± 2°C). The density of the mixed solution was determined by measuring the mass (weight) of the constant volume of the solution at the same temperature.

The cathodic deposition and anodic dissolution processes of Mg in the mixed electrolyte containing RMgBr/THF with DEMETFSI were investigated by cyclic voltammetry (CV) using a conventional three-electrode beaker cell. The working (substrate) electrode was a nickel (Ni) disk, which was chosen from reasons that Ni has less catalytic activity for cathodic decomposition of the solvent components (THF and DEMETFSI) and does not form alloys with deposited Mg. A Pt sheet and a piece of Mg wire were used as the counter and the quasi-reference electrodes (QRE), respectively. In the CV measurements, the electrode potential was first scanned to cathodic direction for deposition of Mg on the Ni substrate.

Figure 1. Ionic conductivity and viscosity of the mixed solutions consisting of RMgBr/THF with DEMETFSI (1:1 by mol) at room temperature ($25 \pm 2^\circ\text{C}$).

Charge (deposition) and discharge (dissolution) characteristics were examined under constant-current conditions using the same three-electrode cell as used in CV measurements. The cell was cycled with a current density of 5 mA cm^{-2} and cut-off conditions of 180 s for charge and 1.5 V (vs. Mg QRE) for discharge. These electrochemical experiments including electrolyte preparation were carried out under a dry Ar atmosphere at room temperature.

3. Results and Discussion

Figure 1 shows the ionic conductivity and viscosity of the mixed solutions consisting of RMgBr/THF with DEMETFSI (1:1 by mol) at room temperature, as a function of the alkyl-chain length of the Mg complex. The ionic conductivity generally decreased with an increase in the alkyl-chain length of RMgBr. Contrary, the viscosity of the mixed electrolyte solution increased with the increase in the alkyl-chain length, where the exceptionally low viscosity of $\text{C}_2\text{H}_5\text{MgBr}$ system seems to be due to lower concentration of the commercially available Grignard reagent ($0.9 \text{ M C}_2\text{H}_5\text{MgBr/THF}$) in the mixed electrolyte system than those in the other systems (1.0 M RMgBr/THF). On the other hand, the density of the mixed solution, whose values were needed to determine the solution viscosity, did not change significantly with the alkyl-chain length: i.e., 0.435, 0.398, 0.437, 0.451, and 0.483 g cm^{-3} for CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, C_5H_{11} , and $n\text{-C}_8\text{H}_{17}$ of R in RMgBr, respectively. Thus, such viscosity increase with the increase in the alkyl-chain length is probably analogous to that observed for conventional concentrated organic solution systems. In Grignard reagents, which contain high concentration of alkyl groups, thermal motion of the alkyl-chain will become inhibited with increasing the chain length. Thus, higher viscosity of the Grignard reagent (RMgBr/THF) with longer alkyl-chain will reflect on the higher viscosity of the resulting solution with the ionic liquid containing longer alkyl-chain of RMgBr. As the ionic conductivity of the RMgBr/THF/DEMETFSI solution is found to be determined mainly by its viscosity, we can conclude that there would be no significant differences in the ionic structure of the electrolyte system among the RMgBr complexes with different alkyl-chain lengths. The highest ionic conductivity of 8.24 mS cm^{-1} at 25°C was obtained for the system consisting of $\text{CH}_3\text{MgBr/THF}$ with DEMETFSI.

Electrochemical behavior of Mg in the mixed electrolyte solution consisting of RMgBr/THF with DEMETFSI was investigated by cyclic voltammetry (CV). Figure 2 compares the voltammetric responses of the third cycle obtained for a Ni disk working electrode. In all electrolyte solutions, the current increases during the cathodic polarization and the reverse current peaks for the anodic

Figure 2. Cyclic voltammograms of Ni substrate in the mixed electrolyte solutions consisting of RMgBr/THF with DEMETFSI (1:1 by mol). Scan rate: 10 mV s^{-1} .

Table 1. Coulombic efficiency for Mg deposition and dissolution calculated from the electricity passed in CV.

$\text{C}_n\text{H}_{2n+1}\text{MgBr/THF}$ with DEMETFSI	Coulombic efficiency (%)
$n = 1$ (CH_3)	84
2 (C_2H_5)	75
3 ($n\text{-C}_3\text{H}_7$)	78
5 (C_5H_{11})	76
8 ($n\text{-C}_8\text{H}_{17}$)	63

polarization respectively indicate the cathodic deposition and anodic dissolution of Mg. In the case of $\text{CH}_3\text{MgBr/THF}$ with DEMETFSI solution, the redox current response was higher than that observed in the other systems. In addition, the overpotential between Mg deposition and dissolution was smaller in the $\text{CH}_3\text{MgBr/THF/DEMETFSI}$ system than that in the other systems. The coulombic efficiency for Mg deposition and dissolution calculated from the electricity passed in CV is summarized in Table 1. The highest efficiency of ca. 84% was obtained in the system consisting of $\text{CH}_3\text{MgBr/THF}$ with DEMETFSI. These results correspond well to the observation that the electrolyte system of $\text{CH}_3\text{MgBr/THF/DEMETFSI}$ showed the lower viscosity and hence the higher ionic conductivity than the others. That is, the electrode reaction in the mixed electrolyte consisting of RMgBr/THF with DEMETFSI would be diffusion-controlled. On the other hand, the coulombic efficiency of ca. 84% in $\text{CH}_3\text{MgBr/THF/DEMETFSI}$ is still not sufficiently high in its use in a practical battery system. The observed efficiency lower than 100% is probably due to undesired side reactions such as reductive decomposition of the mixed electrolyte solution, because a rather low potential limit ($-1.2 \text{ V vs. Mg QRE}$) was adopted for CV in the present work. In fact, when the potential range of CV was changed to -0.5 to 0.5 V vs. Mg QRE , the coulombic efficiency for Mg deposition and dissolution was improved to ca. 94% in $\text{CH}_3\text{MgBr/THF/DEMETFSI}$.¹⁰ From these results, we conclude that the solution containing $\text{CH}_3\text{MgBr/THF}$ is the most promising of the systems examined, as the electrolyte solution for the rechargeable Mg electrode.

The long term cycleability of Mg deposition and dissolution was investigated by constant-current charge and discharge measurements. Figure 3 shows the charge and discharge profiles of Mg on the Ni substrate in the mixed electrolyte consisting of $\text{CH}_3\text{MgBr/THF}$ with DEMETFSI (1:1 by mol). Potential plateaus were observed at about $-0.3 \text{ V vs. Mg QRE}$ for charge and about 0.1 V

Figure 3. Charge-discharge curves for Mg on Ni substrate in the mixed electrolyte solutions consisting of $\text{CH}_3\text{MgBr}/\text{THF}$ with DEMETFSI (1:1 by mol). Current density: 5 mA cm^{-2} , Charge: for 180 s, Discharge: to 1.5 V vs. Mg QRE.

for discharge in the 1st cycle. The potential difference between charge and discharge tended to increase with the repeated cycles. Variations in the coulombic efficiency with the repeated cycle in the $\text{CH}_3\text{MgBr}/\text{THF}/\text{DEMETFSI}$ and $n\text{-C}_8\text{H}_{17}\text{MgBr}/\text{THF}/\text{DEMETFSI}$ systems are compared in Fig. 4. The efficiency in the system containing $n\text{-C}_8\text{H}_{17}\text{MgBr}/\text{THF}$ was about 70% for initial cycles and gradually decreased with cycle repetition. On the other hand, the coulombic efficiency in the system consisting of $\text{CH}_3\text{MgBr}/\text{THF}$ with DEMETFSI kept a higher value of ca. 85% over the repeated cycles.

4. Conclusion

Electrochemical behavior of Mg was investigated in the mixed electrolyte consisting of alkylmagnesiumbromide having different alkyl-chain length (RMgBr) with an ionic liquid, DEMETFSI. High ionic conductivity of 8.24 mS cm^{-1} and low viscosity of 0.88 cP were obtained in the 1:1 mixture of $\text{CH}_3\text{MgBr}/\text{THF}$ and DEMETFSI at 25°C . Highly reversible behavior was observed for

Figure 4. Variations in coulombic efficiency with the cycle number of Mg deposition/dissolution on Ni substrate in the mixed electrolyte solutions consisting of RMgBr/THF with DEMETFSI (1:1 by mol).

cathodic deposition and anodic dissolution of Mg, and the highest coulombic efficiency was achieved for the constant-current cycling in the system consisting of $\text{CH}_3\text{MgBr}/\text{THF}$ with DEMETFSI.

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