Influence of Halide Species on Magnesium Deposition Properties in Electrolyte Containing Phenoxyimine–Magnesium Halide Complex

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ABSTRACT
This study evaluated the influence of halide anion of phenoxyimine–magnesium halide complex on magnesium deposition–dissolution in Mg(TFSA)2/triglyme electrolyte containing the magnesium halide complex. The chloride complex provides rather high Coulombic efficiency of reversible magnesium deposition compared with bromide analogue. This difference appears to be in relation to the different complexation equilibrium by Mg2+, Cl−, and solvent molecules.

1. Introduction
Secondary batteries with magnesium metal as a negative electrode have attracted interest in the battery research field because of the resource abundance, the high volumetric theoretical capacity, the potential safety by virtue of non-dendritic deposition of magnesium.1–3 However, the practical application of magnesium batteries has been hindered by the paucity of non-aqueous electrolytes that are compatible with magnesium negative electrode processes, magnesium deposition, and dissolution without overpotential, except for very recent researches.4–11 An ethereal solution of alkylmagnesium halide, Grignard reagent, and its derivatives have been investigated as electrolytes where reversible magnesium deposition and dissolution are conducted without overpotential.5–8 However, it is somewhat difficult to use an electrolyte of this kind for practical systems because of instability of the alkylmagnesium halide complex. Such a non-aqueous solution containing magnesium cation and halide anion provides numerous Mg–Cl multinuclear complex ions. One such complex, Mg2X3(solvent)6 where X = halide, denoted as μ-complex, has been proposed as an active species for reversible magnesium deposition.8–11 The multiple modes of such complex ions including Mg2+, X−, solvent species and ligands under equilibrium is a key factor for the reversible magnesium deposition in electrolytes of this kind.9,12 Therefore, the combinations of inorganic salts such as magnesium bis(trifluoromethane sulfonyl) amide (Mg(TFSA)2) with magnesium chloride and magnesium chloride with aluminum chloride, have also been proposed to provide magnesium–halogen complex active species with improved stability,11,13 even though the solubility of an inorganic halide in non-aqueous solvent is limited. Alternative way to enhance the chemical stability of soluble Mg–X complex can be enhanced by the exchange of ligand from alkyl to an electron rich group.14,15 Further stabilization is expected to be achieved by a multi-dentate ligand, such as a phenoxyimine ligand (Supporting Information I) proposed in the previous study.16 The ligand-Mg–Cl complex obtained by exchange reaction from CH3MgCl with a ligand molecule has moderate solubility in non-aqueous solvent even at ambient temperature. The mixed salt electrolyte of Mg(TFSA)2 and the complex conducts rather improved magnesium deposition with low overpotential. In this kind of novel magnesium complex for electrolyte, the expected active species is again a multinuclear Mg–X complex. The association equilibrium of Mg–X in the phenoxyimine–MgX complex is expected to be influenced by the component of the complex, ligand structure, and halide X−. The influence of the ligand structure will be discussed elsewhere. Here the electrolyte properties containing chloride or bromide complex have been compared and the influence of halide is estimated.

2. Experimental
A functionalized phenoxyimine molecule for a ligand has been synthesized as described in an earlier report.16 The purity and the correspondence of the molecular structure of the product were confirmed using 1H-NMR. The phenoxyimine was then dissolved in tetrahydrofuran (THF; organic synthesis grade; Kanto Chemical Co. Ltd., Japan) such that the phenoxyimine concentration was 1.0 mol dm−3. The magnesium halide complex was obtained by mixing the phenoxyimine/THF solution and a double volume of 1.0 mol dm−3 CH3MgX/THF solution (Kanto Chemical). The excess CH3MgX reacts with the α-carbon of the imine to provide amine. The reaction product was confirmed to include no residual CH3MgX by 1H-NMR. The resulted complex, hereinafter denoted as L1MgX, was collected by the evaporation of THF solvent. The prescribed amount of the complex was dissolved in the corresponding solution of Mg(TFSA)2 (battery grade; Kishida Chemical Co. Ltd., Japan) in triglyme (G3; battery grade; Kanto Chemical). The solution structures were assessed using a laser Raman spectrometer (Agility; Bayspec Inc., United States) with laser wavelength of 1064 nm to avoid fluorescence emission. The peak separation based on a Lorentzian–Gaussian model was then conducted using RapsWin software (HT SoftLab, Japan).

Electrochemical magnesium deposition in a prepared electrolyte solution was performed using commercial three-electrode cell (BAS Inc., Japan) with a gold plate (The Nilaco Corp., Japan) as a working electrode, a magnesium plate (Nilaco) as a counter electrode, and a Ag/Ag+ reference electrode (BAS). The cell was assembled in a glove box filled with argon gas, and placed in a home-made sealed container. The magnesium deposition–dissolution test was conducted using cyclic voltammetry with a potentiostat (1286; Solartron Analytical) under a 5.0 mV s−1 scan rate at a potential range of −4.0 V and 1.0 V versus the Ag/Ag+ reference. Measurements were taken for 3 cycles at 298 K.
and dissolution is as low as 11 mol dm$^{-3}$ Mg(TFSA)$_2$ irrespective of halides. The Mg-Br complex can exhibit good reagent-based electrolytes, magnesium deposition similarly occurs contrast to the case of the L1MgCl. For conventional Grignard dissolution of L1MgBr decreases the Coulombic efficiency for the same contents of the complex. In addition, the further containing electrolyte is lower than the L1MgCl-containing electrolyte. By coordination with the L1 ligand, the equilibrium of the Mg-Br system might not be adequate for the formation of active species. The solution structures of the solutions containing L1MgCl and L1MgBr are mutually compared using spectroscopic methods.

The $^1$H-NMR spectra of the L1MgCl and the L1MgBr have been compared (Supporting Information II). The peak around 5 ppm, assigned to $\beta$-hydrogen of amine moiety, is different for these spectra, suggesting a difference in the interaction mode between magnesium and the second coordination site of L1 molecule. The Raman spectra of the G3 electrolytes containing 1.0 mol dm$^{-3}$ Mg(TFSA)$_2$/G3 solution in Fig. 2(a). All peaks found in the figure are assigned to triglyme and TFSA$^-$, and characteristic peaks for L1MgCl and L1MgBr might be hindered in this region. In particular, peaks at 850 cm$^{-1}$ for the electrolyte containing L1MgBr and 844 cm$^{-1}$ for the electrolyte containing L1MgCl, assigned to the second coordination site of L1 molecule. The solution structures of the solutions containing L1MgCl and L1MgBr are compared (Supporting Information II). The peak around 5 ppm, assigned to $\beta$-hydrogen of amine moiety, is different for these spectra, suggesting a difference in the interaction mode between magnesium and the second coordination site of L1 molecule.

3. Results and Discussion

The cyclic voltammogram for magnesium deposition–dissolution in the 1.5 mol dm$^{-3}$ Mg(TFSA)$_2$/G3 electrolytes is shown in Fig. 1(a). A reduction current flows from $-2.2$ V vs. Ag/Ag$^+$ at a negative scan and an oxidation current from $-1.0$ V at a positive scan. The reduction and oxidation currents respectively correspond to the deposition and dissolution of magnesium: the overpotential efficiency by coordination with the L1 ligand, the equilibrium of the Mg-Br system might not be adequate for the formation of active species. The solution structures of the solutions containing L1MgCl and L1MgBr are mutually compared using spectroscopic methods. The $^1$H-NMR spectra of the L1MgCl and the L1MgBr have been compared (Supporting Information II). The peak around 5 ppm, assigned to $\beta$-hydrogen of amine moiety, is different for these spectra, suggesting a difference in the interaction mode between magnesium and the second coordination site of L1 molecule. The Raman spectra of the G3 electrolytes containing 1.0 mol dm$^{-3}$ Mg(TFSA)$_2$/G3 solution in Fig. 2(a). All peaks found in the figure are assigned to triglyme and TFSA$^-$, and characteristic peaks for L1MgCl and L1MgBr might be hindered in this region. In particular, peaks at 850 cm$^{-1}$ for the electrolyte containing L1MgBr and 844 cm$^{-1}$ for the electrolyte containing L1MgCl, assigned to the second coordination site of L1 molecule. The solution structures of the solutions containing L1MgCl and L1MgBr are compared (Supporting Information II). The peak around 5 ppm, assigned to $\beta$-hydrogen of amine moiety, is different for these spectra, suggesting a difference in the interaction mode between magnesium and the second coordination site of L1 molecule.

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containing electrolyte. As various coordination modes of Mg\(^{2+}\) with triglyme have been reported for Mg(TFSA)\(_2\)/triglyme electrolyte,\(^{17}\) ion association is similarly important for the halide-containing electrolytes. Such a difference in the complexation equilibrium is considered to be provided by different Lewis basicity and hardness between Cl\(^-\) and Br\(^-\).

4. Conclusion

The magnesium electrode properties of the mixed electrolyte of Mg(TFSA)\(_2\)/triglyme with phenoxyimine–magnesium halide complex are influenced by the kind of halide. The electrolyte containing chloride complex exhibits higher Coulombic efficiency and lower overpotential for magnesium deposition compared with the bromide analogue. The equilibrium among the complex ion formation including Mg\(^{2+}\), halide, and solvent molecule differs by the halide species. The coordination state of Mg\(^{2+}\) is also influenced by the halide species. The halide ion might contribute to such solution characteristics and might therefore affect the magnesium deposition process. This is the first report to describe the influence of the halide on the complex formation, because the different magnesium deposition behavior by halide species is delivered by the tuned coordination with L1 ligand Mg-X complex.

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