Phenoxyimine Ligand Molecular Structure Influence on Reversible Magnesium Electrode Reaction in a Magnesium Chloride Complex

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ABSTRACT

Non-aqueous electrolytes containing magnesium chloride complex in which magnesium is coordinated by synthesized phenoxyimine ligand have unique properties for magnesium deposition and dissolution. Those properties have been compared using ligands with different terminal groups. For electrochemical and Raman spectroscopic studies, mixed electrolytes were prepared by dissolving a phenoxyimine–magnesium-chloride complex with magnesium [bis(trifluoromethane sulfonfonyl)imide] in triglyme solvent. An electrolyte containing phenoxyimine with an n-butyl terminal group shows higher Coulombic efficiency of magnesium deposition than the electrolyte prepared with dimethylamine-terminated phenoxyimine, probably because of preferred formation of active triglyme–magnesium-chloride coordinated cations. By contrast, adding aluminum chloride to the electrolyte with n-butyl-terminated phenoxyimine adversely affected reversible magnesium deposition, probably because trapping of chloride occurred preferentially.

Keywords: Magnesium Batteries, Magnesium Chloride Electroyt, Phenoxyimine Ligand

1. Introduction

To meet increasing demands for alternative secondary batteries with safety, low cost, and high energy density, magnesium batteries have been investigated intensively during the past decade.1,2 High barriers against realization of commercially available magnesium batteries lie in the reversibility of magnesium negative electrodes.2,3-5

Apart from lithium, the magnesium electrode reaction and magnesium deposition and dissolution occur in only a few non-aqueous electrolyte systems. An ethereal solution of alkylmagnesium chloride complex, Grignard reagent, has received attention from the earliest stages of magnesium battery research because it provides reversible magnesium deposition–dissolution with small overpotential. In the first presented magnesium battery prototype, a stoichiometric mixture of alkylmagnesium chloride and a Lewis acid, Mg[AlCl4–R3N] (R: alkyl) was used.6 In such an electrolyte, multi-nuclear magnesium–chloride clusters such as μ-Mg2Cl64+ with coordinating solvent molecules are formed under some dissociation equilibrium including Schlenk equilibrium: they are assumed as active species to promote reversible magnesium deposition.6-11

According to assumptions about the active species, some probability exists of promoting reversible magnesium deposition also in solutions containing high concentrations of MgCl2. Indeed, reversible magnesium deposition has been reported in ethereal solutions of magnesium[bis(trifluoromethane sulfonfonyl)imide]–[Mg(TFSA)2] and MgCl2,12-14 and ethereal solutions of MgCl2 with AlCl3 or other Lewis acids.15-17 The chloride-containing species is expected to dissolve the passivation layer on the magnesium surface and to support smooth conversion from metallic magnesium to divalent ion.18-20 Such chloride-containing electrolytes are adversely affected by the possibility of corroding metallic components and by the low anodic limit.20 Recent progress on magnesium batteries has yielded several attractive magnesium salts based on boron-based weakly coordinated anions,21,22 which also promote reversible magnesium deposition with moderate overpotential and which have higher anodic stability than chloride-based systems. However, the chloride-containing electrolytes are still beneficial in terms of low preparation cost and low overpotential of magnesium deposition. Moreover, some reports have suggested that the existence of chloride ion in electrolyte is favorable for reactions on a positive electrode.23,24 Therefore, the authors believe that chloride-containing electrolytes are still powerful candidates for 2 V-class practical magnesium battery electrolytes with such positive electrodes as Chevrel phase or sulfur.

For these magnesium chloride-based electrolytes, the coordination state of magnesium influences the stability, Schlenk equilibrium, and solubility in various solvents. Some coordinator materials having an electron-withdrawing site, as do alkoxide and hexamethyldisilazide (HMDS), can improve the stability while retaining the reversibility of magnesium deposition via the formation of a complex cation with magnesium.25-28 The authors have proposed a phenoxyimine ligand having bi-dentate sites. The ligand is easily substituted to alkyl in alkylmagnesium halide, to which it provides a magnesium halide complex that is stable, even under ambient moisture. The mixed electrolyte in which the resulted magnesium chloride complex is dissolved in Mg(TFSA)2/triglyme improves the magnesium deposition–dissolution reversibility and overpotential.29,30 The phenoxyimine ligand delivers an ionic complex in which the ligand forms a complex anion against a multi-nuclear magnesium–chloride–solvent complex cation. Indeed, one benefit of such a ligand is the possibility of designing the molecular structure for tuning the properties of magnesium chloride complex and also the resultant electrolyte. Apart from practical battery usage, the present study is aimed to display two synthesized phenoxyimine ligands having different terminal groups, with intensive assessment of how the phenoxyimine molecular structure affects the magnesium electrode reaction.
2. Experimental

Phenoxyimine molecules for ligands have been synthesized as described earlier in the literature, with addition of the corresponding imine to salicyl aldehyde. The structures of phenoxyimine ligands prepared for this study are presented in Fig. 1. Notations of these ligands are, as the figure shows, a Lx, with terminating moiety x, dimethylamine DMA, or n-butyl BU. The authors expected that the DMA terminating moiety also participates in the coordination to magnesium and somewhat stabilizes the coordination. The purity and the correspondence of the molecular structure of the product were assured by 1H-NMR. The phenoxyimine was then dissolved in Mg(TFSA)2 (battery grade; Kishida Pure Chemical Co. Ltd., Japan) as the concentration of the phenoxyimine was 1.0 mol dm⁻³. The water content of solvent was confirmed as lower than 30 ppm using a Karl–Fisher titrator (MKC-710; Kyoto Electronics Mfg. Co., Ltd., Japan). The magnesium halide complex was obtained by mixing the phenoxyimine/THF solution and an excess amount of methyl/magnesium chloride/THF solution (ca. 1.8–2.2 mol dm⁻³, Kanto Chemical Co. Ltd., Japan) during 4 days. The reaction is expected to occur between the phenol moiety (Ph-OH) in a Lx molecule and CH3MgCl as shown in following equation:

\[ \text{Ph-OH}(\text{L}_x) + \text{CH}_3\text{MgCl} \rightarrow \text{Ph-OMgCl} + \text{CH}_4 \uparrow \]  (1)

The reaction product has been checked to contain no residual methylmagnesium halide by 1H-NMR, of which spectra are shown in Fig. 2. The disappearance of phenolic hydrogen clearly indicates the relevance of the above reaction scheme. It is observed that the peak at ~0.67 ppm in the spectrum for the methyl in CH3MgCl completely disappears in the spectra for each reaction product. Also, the spectra region between 1.0 and 3.0 ppm indicates that the residual methylmagnesium halide reacts with the alpha-carbon of the imine to provide amino moiety. The magnesium halide complex was collected by evaporation of the THF solvent. The prescribed amount of the complex was dissolved in the corresponding solution of Mg(TFSA)2 (battery grade; Kishida Pure Chemical Co. Ltd., Japan) in triglyme (battery grade; Kanto Chemical Co. Ltd., Japan). The water content of the Mg(TFSA)2/triglyme solution was also checked as lower than 30 ppm. In some cases, aluminum chloride (AlCl3; Kanto Chemical Co. Ltd., Japan) was added to the MgCl2/Mg(TFSA)2/triglyme solution so that the content of AlCl3 was 0.1 mol dm⁻³. The solution structures were assessed using a laser Raman spectrometer (Agility; BecSpec Inc., Japan). The laser wavelength was 1064 nm, with lower energy than conventional green laser of 532 nm wavelength, thereby preventing decomposition of the complex by laser irradiation. Peak separation based on the Lorenzian–Gaussian model for the collected spectra was then conducted using Rapswin software.

Computational estimation of the structure of ligand coordination to magnesium chloride was conducted using Gaussian09 software. The method and basis function were, respectively, RB3LYP and 6-31+G.

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The electrochemical magnesium deposition was performed in a prepared electrolyte solution using commercial three-electrode cell (BAS Inc., Japan) with a gold plate (the Nilaco Corp., Japan) as a working electrode, a magnesium plate (The Nilaco Corp., Japan) attached with a platinum wire as a counter electrode, and a silver wire in AgNO₃/acetonitrile solution filled in a glass tube with a Vicor® glass as a reference electrode. After the cell was assembled in a glove box filled with argon gas, it was placed in a sealed container. The magnesium deposition–dissolution test was conducted by cyclic voltammetry using a potentiostat (Solartron 1286) under 5.0 mV s⁻¹ of scan rate, at potentials of −3.5 V and 1.0 V versus the reference electrode. The cell container was placed in a temperature chamber to be three cycles at 298 K.

3. Results and Discussion

Cyclic voltammograms are shown in Figs. 3(a–c) for magnesium deposition–dissolution in (a) 1.5 mol dm⁻³ Mg(TFSA)2/triglyme, the mixed electrolytes of (b) 0.5 mol dm⁻³ of LDMA/MgCl and 1.0 mol dm⁻³ Mg(TFSA)2, and (c) the substituted electrolyte of LBU/MgCl to LDMA/MgCl. The Mg(TFSA)2/triglyme electrolyte provides ca. 1.3 V of overpotential between the onset potential.
The deposition of magnesium in the electrolytes containing LDMAMgCl and LBUMgCl is markedly lower than those in Mg(TFSA)2 because of the insufficiency of Cl− containing active species.

The coexistence of LxMgCl in Mg(TFSA)2/triglyme electrolyte improved the Coulombic efficiency of magnesium deposition and dissolution. The extent of the positive effect depends on the ligand structure. Although the Coulombic efficiency of magnesium deposition–dissolution in Mg(TFSA)2/triglyme is as low as 10%, the Coulombic efficiency values of magnesium deposition–dissolution in the electrolytes containing LxMgCl and LDMAMgCl calculated respectively from these voltammograms are 43% and 88%. It is noteworthy that these values are apparent ones because the oxidation current includes the contribution of anodic decomposition of the electrolyte, which would not isolate from the deposition current of magnesium.

The reduction current at −2.2 V in the LBUMgCl/Mg(TFSA)2/triglyme is markedly lower than those in Mg(TFSA)2/triglyme and LDMAMgCl/Mg(TFSA)2/triglyme. Such low current suggests that the mobility of magnesium species is low in the LBUMgCl-containing electrolyte. The Arrenius-manner temperature dependences of the conductivities of the LxMgCl/Mg(TFSA)2/triglyme electrolytes with (a) 0.5 mol dm−3, (b) 1.0 mol dm−3 for the concentration of LxMgCl (total Mg concentration 1.5 mol dm−3) are shown in Fig. 4. When the concentration of LxMgCl is 0.5 mol dm−3, conductivities at 298 K for the both ternary electrolytes are similar because the main salt in these electrolytes are Mg(TFSA)2. From the low temperature conductivities of 0.5
Table 1. Some values obtained from molecular orbital calculations.

|                  | L_{DMA}MgCl | L_{BU}MgCl |
|------------------|-------------|------------|
| Mg-O distance/nm | 0.1914      | 0.1898     |
| Mg-Cl distance/nm| 0.2296      | 0.2330     |
| Mulliken charge on Mg\(^{2+}\) | +0.600   | +0.845     |
| Mulliken charge on Cl\(^{-}\) | −0.517   | −0.542     |

Raman spectra of 0.5 mol dm\(^{-3}\) L_{DMA}MgCl/1.0 mol dm\(^{-3}\) Mg(TFSA)\(_2\)/triglyme at a selected region of 700–950 cm\(^{-1}\) without the addition of AlCl\(_3\) are presented in Fig. 6(a). In this region, the electrolyte, irrespective of the ligand, delivered peaks for asymmetric deformation of −CF\(_3\) from TFSA\(^{-}\), and C–O–C stretching at 741 cm\(^{-1}\) and around 800–900 cm\(^{-1}\), respectively. The peak at 741 cm\(^{-1}\) has only a negligible split at higher wavenumber, and thus TFSA\(^{-}\) is suggested to exist as a free ion without coordinating with Mg\(^{2+}\). The C–O–C peak has two marked splits at 860 and 875 cm\(^{-1}\). The peaks of these fractions differ because of the added L_{BU}MgCl complex: The L_{BU}MgCl delivers a larger peak at 875 cm\(^{-1}\) than with the L_{DMA}MgCl analogue. According to detailed spectroscopic studies for electrolyte containing magnesium chloride,\(^{13,52,53}\) the peak at 860 cm\(^{-1}\) is assigned to the −CH\(_2\)−O−CH\(_2\)− coordinated with Mg\(^{2+}\). The peak at 875 cm\(^{-1}\) is assigned to triglymes coordinated in Mg\(^{2+}\) with TFSA\(^{-}\) and chloride ion in Mg(TFSA)\(_2\)/MgCl\(_2\)/triglyme concentrated solution (rigorously, other band than 860 cm\(^{-1}\)). In any case, the latter peak includes the contribution of some Cl−Mg–triglyme coordination and suggests the existence of expected active species for magnesium deposition in magnesium chloride-based electrolytes. The L_{BU}MgCl containing electrolyte includes a more significant amount of Cl−Mg–triglyme coordination than the L_{DMA}MgCl analogue, where the coordination of Mg\(^{2+}\)–triglyme might be preferred.

Raman spectra for the AlCl\(_3\)-added electrolytes containing L_{DMA}MgCl or L_{BU}MgCl shown in Fig. 6(b) indicate different features. The CF\(_3\)-peak at 741 cm\(^{-1}\) splits into several fractions. The main peak becomes smaller. The change in the C–O–C peak might be readily apparent. The split at 860 cm\(^{-1}\) is greater for the L_{BU}MgCl-containing electrolyte than with the L_{DMA}MgCl analogue.
In these cases, the ion pair contact Mg$^{2+}$–TFSA$^-$ appears to increase for both L$_2$ ligands. Furthermore, the Mg$^{2+}$–triglyme complex coordination appears to be greater than the active Cl–Mg–triglyme coordination in the L$_{al}$MgCl-containing electrolyte. Under the existence of the L$_{al}$ ligand, the addition of AlCl$_3$ accelerates the formation of Mg$^{2+}$–TFSA–triglyme type contact ion pairs more than it accelerates Cl–Mg–triglyme coordination. This change in coordinating equilibrium in the solution might correspond to the lack of a marked effect of the AlCl$_3$ addition on magnesium deposition–dissolution. By contrast, the addition of AlCl$_3$ equilibrates the formation of the Mg–Cl–triglyme complexes because of the existence of the L$_{al}$MgCl as reported for many Cl-containing electrolytes.

The electrochemical behavior, Raman results, and molecular orbital calculations all indicate that the L$_{al}$ ligand might change the Schlenk-type equilibrium and might thereby accelerate the formation of some active triglyme–Mg–Cl coordination. That formation might include multi-nuclear complex ions such as μ-Mg$_2$Cl$_3$ or μ-Mg$_2$Cl$_{2+}$ (with coordination by solvent molecules) by its polarized structure by raising the equilibrium concentration of chloride. The increase of active triglyme–Mg–Cl coordination aids the dissolution of deposited magnesium. However, the effect of AlCl$_3$ addition is not strong in the L$_{al}$MgCl-containing electrolyte, for reasons that remain unclear. AlCl$_3$ might act as a trap for chloride ions through the following reaction.

$$\text{Cl}^- + \text{AlCl}_3 \rightleftharpoons \text{AlCl}_4^-$$

(2)

If AlCl$_4^-$ complex ion is somewhat stabilized, then the equilibrium concentration of chloride ion might decrease. As a result, the Mg$^{2+}$–TFSA$^-$–triglyme contact ion pair might become favorable, thereby decreasing the electrolyte activity. In the cases presented herein, AlCl$_3$ is added only in small and insufficient amounts such that AlCl$_4^-$ might act as a stable ion, not as a sink of chloride ion, in particular for the L$_{al}$MgCl-based electrolyte. Increasing the AlCl$_3$ amount might improve the formation of triglyme–Mg–Cl coordination and improve the Coulombic efficiency for magnesium somewhat, but the high viscosity of the mixed electrolyte would allow only slow AlCl$_3$ dissolution. Little information exists to elucidate changes of AlCl$_3$ in the L$_{al}$MgCl-containing electrolyte. Therefore, further discussion must be undertaken to reveal the effects of AlCl$_3$.

4. Conclusion

The deposition–dissolution behavior of magnesium in the mixed electrolyte containing phenoxime-imino-coordinated magnesium chloride is influenced by the terminal group structure of the phenoxime ligand. The ligand with an n-butyl terminal in the mixed electrolyte provides higher Coulombic efficiency than that of the phenoxime ligand with dimethylamine terminal, although the coexistence of coordinated magnesium chloride improves the magnesium dissolution of Mg(TFSA)$_2$/triglyme electrolyte, irrespective of the terminal group. Molecular orbital calculation results suggest that the n-butyl terminal ligand is more polar than the other ligand, and that changes occur in the equilibrium of the magnesium–chloride–triglyme system to form active triglyme–magnesium–chloride coordinated species. By contrast, adding a small amount of AlCl$_3$ is ineffective for improving magnesium reversibility in this electrolyte, probably because of chloride ion trapping and the decrease of active species. Molecular design of a ligand for this electrolyte system is possible, but the influence of ligand structure on the solution and electrochemical properties are difficult to predict directly from the ligand molecular structure.

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