

Short communication

Ionic conductance behavior of polymeric gel electrolyte containing ionic liquid mixed with magnesium salt

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Abstract

A new polymeric gel electrolyte system conducting magnesium ion has been proposed. The gel electrolytes consisted of poly(ethylene oxide)-modified polymethacrylate (PEO-PMA) dissolving ionic liquid mixed with magnesium salt, $\text{Mg}[(\text{CF}_3\text{SO}_2)_2\text{N}]_2$. The polymeric gel films were self-standing, transparent and flexible with enough mechanical strength. The ionic conductance and the electrochemical properties of the gel films were investigated. Thermal analysis results showed that the polymeric gel is homogeneous and amorphous over a wide temperature range. The highest conductivity, $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature (20 °C), was obtained for the polymeric gel containing 50 wt.% of the ionic liquid in which the content of the magnesium salt was 20 mol%. The dc polarization of a Pt/Mg cell using the polymeric gel electrolyte proved that the magnesium ion (Mg^{2+}) is mobile in the present polymeric system.

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1. Introduction

Magnesium (Mg) is one of the ideal materials as the negative electrode of practical batteries because of its low electrochemical equivalence (12.15 g eq^{-1}) and low electrode potential (-2.3 V versus SHE). Despite of the practical use of primary and reserve batteries [1], development of rechargeable Mg batteries has been retarded mainly due to the irreversibility of the Mg negative electrode and the lack of proper Mg^{2+} -conducting nonaqueous electrolyte [2]. Thus, the development of Mg^{2+} -ion conductor, preferably at solid state, has been a key issue to realize the rechargeable Mg batteries.

On the analogy of the Li^+ -ion conductor, there have been some publications on the polymeric complexes of poly(ethylene oxide) (PEO) with inorganic Mg salts [3–5]. High conductivities ranging from 10^{-6} to $10^{-4} \text{ S cm}^{-1}$ were reported for PEO–Mg salt complexes in the temperature

range of 80–100 °C, but the transport number of Mg^{2+} was found to be very low in those systems [6]. Polymeric gel systems swollen with such aprotic solvents as propylene carbonate (PC) [7,8] and gel electrolytes based on PEO–Grignard [9] have also been proposed as Mg^{2+} -conductors with high ionic mobility. We also obtained high ionic conductivity for the gels containing Mg salts with mixed alkyl carbonates, ethylene carbonate (EC) and dimethyl carbonate (DMC), as a plasticizer [10], where we chose a cross-linked polymethacrylate with repeated ethylene oxide (EO) units as the solid polymer matrix reported previously [11]. Such a network polymer with polar functionalities dissolves a wide variety of inorganic salts of multivalent cations with high concentrations even at ambient temperature. However, those low molecular weight organic plasticizers would cause serious troubles when the gel will be applied to practical battery systems at a higher temperature range than their boiling or flash points.

Recently, air- and water-stable organic ionic liquids (also known as room temperature molten salts) have been proposed as non-volatile polar media in variety of electrochemical sys-

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tems. Especially, much attention has been directed to the combinations of imidazolium cations and specific organic anions [12,13], due to their unique characteristics of thermal stability, non-flammability and extremely high ionic conductivity. These ionic liquids can be used for polymeric gel electrolyte as not only the charge carrier but also the plasticizer [14–18].

In this work, we have applied the ionic liquid to polymeric solid (gel) electrolyte that conducts Mg^{2+} ion at ambient temperature. The system consists of poly(ethylene oxide)-modified poly(methacrylate) (PEO-PMA) as the polymer matrix and an ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), dissolving Mg salt, $\text{Mg}[(\text{CF}_3\text{SO}_2)_2\text{N}]_2$. The ionic conductance behavior of the resulting gel was investigated by ac impedance measurements in an ambient temperature range. The mobile species in the polymeric gel system was also examined by a dc polarization method using blocking and non-blocking electrodes.

2. Experimental

2.1. Materials

Poly(ethylene glycol) monomethacrylate (PEM) and poly(ethylene glycol) dimethacrylate (PED) (Shin-Nakamura Chemical, Scheme 1(a)) were used as prepolymers for the polymer matrix formation [19]. The prepolymers, PEM and PED, were dehydrated by molecular sieves prior to use, and then kept in a glove box filled with dry Ar. Reagent grade of 1-ethyl-3-methylimidazolium bromide (EMIBr; Acros Organics) was used as received. Salts of bis(trifluoromethylsulfonyl)imide, LiTFSI and $\text{Mg}(\text{TFSI})_2$, were also used without further purification.

2.2. Preparation of ionic liquid and polymeric gel electrolytes

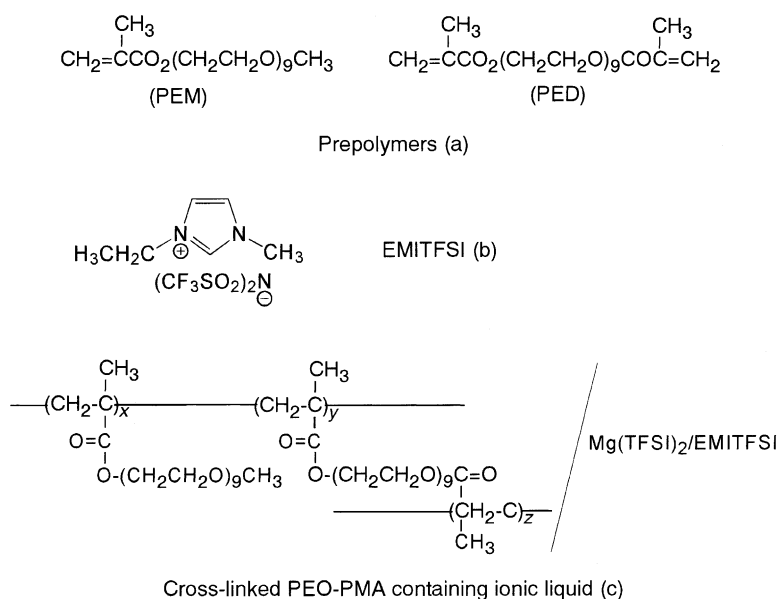
The ionic liquid, EMITFSI (Scheme 1(b)) was synthesized by an anion exchange reaction of LiTFSI and EMIBr according to the literature [20]. The reaction product was purified by rinsing with distilled water, and then thoroughly dried by heating under a vacuum. The obtained ionic liquid was identified by ^1H NMR and IR spectra.

A proper amount (mol%) of $\text{Mg}(\text{TFSI})_2$ was dissolved in EMITFSI at room temperature. A mixture of PEM/PED (9:1 by molar ratio) containing a small amount of a radical initiator, 2,2-dimethoxy-2-phenylacetophenone (Aldrich, 99% purity), was added to the ionic liquid solution of $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$. The resulting homogeneous solution was solidified by photo-induced radical polymerization. In this paper, the composition of the polymeric gel electrolyte is formulated as (PEO-PMA)- a mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ (x - y), where a denotes the mol% of $\text{Mg}(\text{TFSI})_2$ in EMITFSI ionic liquid and x - y the ratio (wt.%) of the polymer matrix to the liquid component $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$. The overall preparation procedure was carried out under a dry Ar atmosphere.

2.3. Measurements

Thermal properties of the polymeric gel were analyzed using a differential scanning calorimeter (DSC: DSC-50Q, Shimadzu). The measurement was performed in the temperature range from 123 to 573 K (–150 to 300 °C) at a heating rate of 10 K min^{-1} .

The ionic conductivity of the polymeric gel was measured by an ac impedance technique using an electrochemical impedance analyzer (S-5720C, NF electronics), where the ac



Scheme 1. Chemical structure of the prepolymers (a), ionic liquid (b), and cross-linked PEO-PMA (c) containing ionic liquid as a plasticizer.

frequency was scanned from 100 kHz to 1 Hz. A film of the polymeric gel (13 mm diameter, 0.5–1.0 mm thick) was sandwiched between two stainless steel blocking electrodes in a sealed Teflon cell case. The ac impedance was measured in the temperature range from 298 to 333 K (20–60 °C).

Electrochemical polarization measurements were carried out using the same apparatus as used in the ionic conductivity measurements, except for the electrode material. Metal sheets of Pt and Mg were used as blocking and non-blocking electrodes, respectively. The polarization (electrolysis) was conducted under a constant voltage condition (1.0 V versus rest potential).

3. Results and discussion

3.1. Thermal properties

The polymeric gel was obtained as a self-standing transparent film with sufficient mechanical strength, as shown in Fig. 1. The thermal properties of the polymer matrix generally determine the ion-transport behavior of the resulting polymeric gel electrolyte. Fig. 2 shows typical DSC profiles of the polymeric systems. As shown in curve a, phase transition behavior was observed at about -70°C (203 K) for the polymer matrix, PEO-PMA. This is attributed to the glass transition of the repeated EO units involved in the cross-linked and side chains of the polymer structure [11]. The temperature of the phase transition (T_g) shifted to higher one when the system contains the ionic liquid, EMITFSI. For the complex containing the mixed salt, $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$, the T_g value shifted further to higher temperature than that of the system containing neat EMITFSI. This suggests that the interaction between the polymer matrix and Mg salt is stronger than that of the polymer matrix with EMITFSI. In other words, partial crystallization of the repeated EO units would be promoted by the interaction of EO with Mg^{2+} ion.

The DSC profiles of the polymeric gel electrolyte did not give any peaks corresponding to the decomposition or

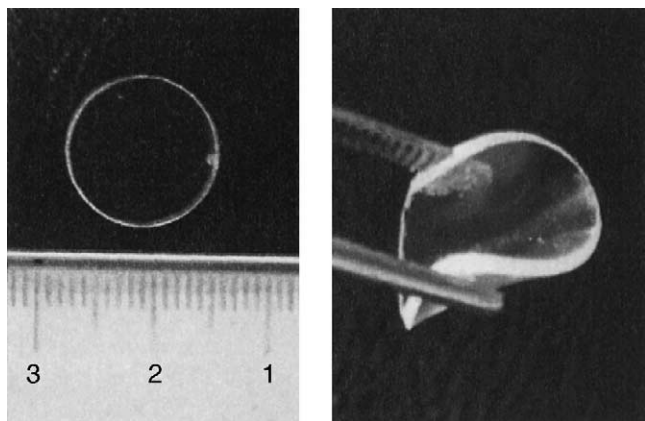


Fig. 1. Photographs of polymeric gel electrolyte film: (PEO-PMA)-20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ (50–50).

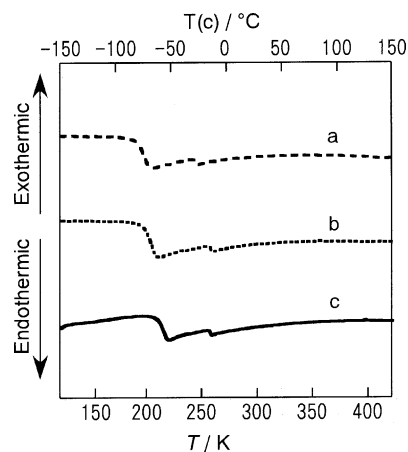


Fig. 2. DSC curves for PEO-PMA-based complexes: (a) PEO-PMA matrix; (b) (PEO-PMA)/EMITFSI; (c) (PEO-PMA)-20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ (50–50).

evaporation of the gel electrolyte components in the temperature range from -150 to 300°C . Thus, we conclude that the present polymeric gel electrolyte system is stable over a wide temperature range.

3.2. Ionic conductivity

The temperature dependence of the ionic conductivity measured by the ac method is shown in Fig. 3. In this case, the films of (PEO-PMA)-20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ (x - y) were used, where the y value, the content (wt.%) of the 20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ component was changed from 10 to 50. Every $\log \sigma$ versus T^{-1} plot showed slightly positive deviation from a linear Arrhenius relation, similar to conventional polymeric gel electrolyte system [11]. The ionic conductivity increased with the increase in the content of the ionic liquid component. As the concentration of $\text{Mg}(\text{TFSI})_2$ in the ionic liquid was kept 20 mol% throughout the mea-

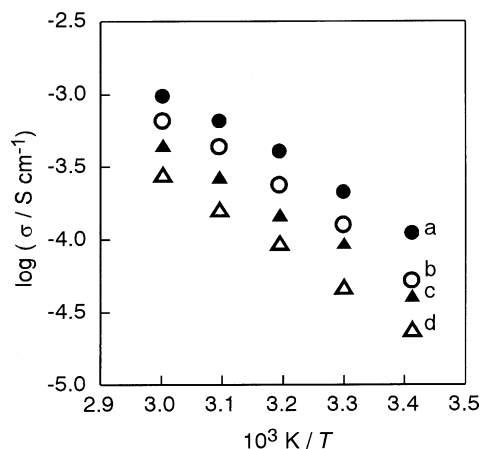


Fig. 3. Temperature dependence of ionic conductivity for gel electrolytes containing 20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$: (a) (PEO-PMA)-20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ = 50–50 (by wt.%), (b) 60–40, (c) 70–30, and (d) 80–20.

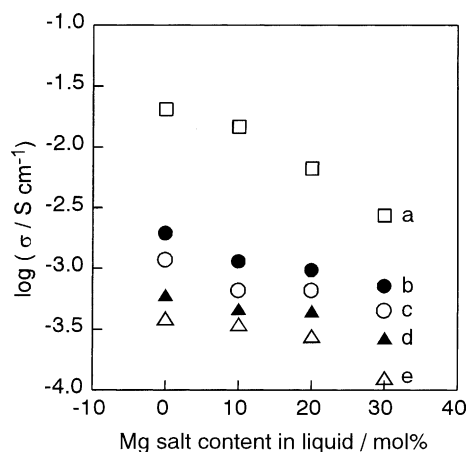


Fig. 4. Ionic conductivity as a function of $\text{Mg}(\text{TFSI})_2$ concentration in solution for electrolytes and polymeric gel electrolytes at 60°C : (a) solution, (b) (PEO-PMA)- a mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI} = 50-50$ (by wt.%), (c) 60–40, (d) 70–30, and (e) 80–20.

surements, the higher conductivity in the polymeric gel with the content of ionic liquid means that the number of charge carriers increases with the content of the ionic liquid in the polymeric gel.

Fig. 4 shows the dependence of the ionic conductivity on the content of $\text{Mg}(\text{TFSI})_2$ (a mol%) in $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ for the (PEO-PMA)- $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$ gels with different mass ratio of the polymer and ionic liquid measured at 60°C . The data for the ionic liquid, $\text{Mg}(\text{TFSI})_2/\text{EMITFSI}$, are also shown for comparison. The ionic conductivity of the gel decreased with the increase in the $\text{Mg}(\text{TFSI})_2$ content in the liquid component. However, the tendency of the decrease in the ionic conductivity was smaller for the polymeric gel than that for the ionic liquid itself. The viscosity of the ionic liquid increased with the increase in the $\text{Mg}(\text{TFSI})_2$ content. This is the main reason that the ionic conductivity decreases with the increase in the Mg salt content for the mixed ionic liquid. In the polymeric gel system, the ionic interaction between Mg^{2+} and the polymer matrix is rather strong, as shown in the DSC results. Thus, the tendency of the conductivity decreasing with the Mg salt content may be lowered in the polymeric gel system.

3.3. Mobile species in the gel

The mobile species in the polymeric gel system was identified by a dc polarization method [21–23]. Polarization curves of Pt/Mg, Pt/Pt and Mg/Pt cells using (PEO-PMA)-20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI} (50-50)$ as the electrolyte are shown in Fig. 5. Here, the positive electrode of Mg and Pt act as non-blocking and blocking sources for Mg^{2+} , respectively. For the Pt/Pt and Mg/Pt cells, the polarization current steeply decreased in the initial stage, and reached a steady-state value after sufficient polarization time. Particularly, the current for the Mg/Pt cell showed the continuous decrease throughout the polarization. This behavior was attributed to the increasing

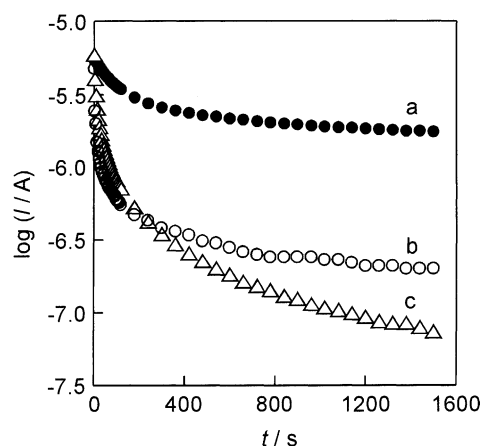


Fig. 5. Polarization curves for (a) Pt/polymeric gel electrolyte (PGL)/Mg, (b) Pt/PGL/Pt and Mg/PGL/Pt cells at 60°C . Polymeric gel electrolyte: (PEO-PMA)-20 mol% $\text{Mg}(\text{TFSI})_2/\text{EMITFSI} (50-50)$.

interfacial resistance between the Mg negative electrode and the polymeric gel electrolyte with the polarization time. On the other hand, the Pt/Mg cell using the polymeric electrolyte showed higher polarization current over the whole polarization time scale, even under the same applied voltage (1.0 V). If the electrolyte is absolutely anion-conducting or only EMI cation-conducting, the three cells will show essentially the same polarization behavior. The result shown in Fig. 5, the higher steady-state current observed for Pt/Mg cell, confirms the fact that the Mg^{2+} ion is supplied from the Mg anode and migrates in the polymeric electrolyte under a bias. Although we could not determine the actual value of the ionic mobility for the Mg^{2+} species in the gel, it was clearly proved from the polarization experiments that the Mg^{2+} is a mobile species in the present polymeric system. The way to estimate the ionic mobility in the present gel system has still been examined. The application of the polymeric gel conducting Mg^{2+} ion to a rechargeable battery system is also under investigation.

4. Conclusions

Polymeric gel electrolytes consisting of a PEO-PMA matrix with EMITFSI dissolving $\text{Mg}(\text{TFSI})_2$ were synthesized, and their ionic conductance behavior has been investigated as solid electrolyte for rechargeable Mg batteries. The results are summarized as follows:

1. The polymeric gel electrolyte is flexible and self-standing with proper mechanical strength.
2. The ionic conductivity depended on the content of the ionic liquid containing $\text{Mg}(\text{TFSI})_2$. The highest conductivity of the gel examined was $1.1 \times 10^{-4} \text{ S cm}^{-1}$ (at 20°C) for the composition of 50 wt.% of EMITFSI dissolving 20 mol% $\text{Mg}(\text{TFSI})_2$.
3. The polarization experiments of Pt/Mg, Pt/Pt and Mg/Pt cells using the polymeric gel electrolyte proved that Mg^{2+} is mobile in the present polymeric system.

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