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Preparation of solutions of amidomagnesium chlorides in poly(ethylene oxide) and their characterization by conductivity measurements

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Abstract Polymer electrolyte systems were prepared for the first time by dissolution of amidomagnesium chlorides in poly(ethylene oxide), (PEO). For the preparation, solutions of (hexamethyldisilylamido)magnesium chloride, (dimethylpyrrolyl)magnesium chloride, (diisopropylamido)magnesium chloride, piperidinomagnesium chloride and morpholinomagnesium chloride were chosen. The composition of these polymer electrolyte systems corresponds to the general formula $R_2NMgCl \cdot P(EO)_n \cdot THF$. Most work has been done with the system (hexamethyldisilylamido)magnesium chloride in PEO, $(Me_3Si)_2NMgCl \cdot P(EO)_n \cdot THF$, with $n = 3, 4, 5$, or 7 . The electrolytes have a soft rubber-like consistency. At $30^\circ C$, electrical conductivities of 10^{-6} – 10^{-5} S/cm were found. The conductivities were measured in the temperature range 20 – $60^\circ C$. Within this temperature range a linear dependence of the logarithms of the conductivity on the inverse temperature was found and activation energies for the conducting process of 30 – 60 kJ/mol were calculated. Using those polymer electrolytes with a high content of the amidomagnesium compound, a reversible magnesium deposition takes place by cathodic reduction at potentials below -1.9 V vs. a Ag/AgCl reference electrode. These polymer electrolytes were found to be stable against oxidation up to about -0.3 V vs. Ag/AgCl.

Keywords Amidomagnesium halide · Electrical conductivity · Electrode potential · Magnesium · Polymer electrolyte

Introduction

The use of magnesium as a negative electrode in secondary batteries was found to be problematic on the anode as well as on the cathode side [1, 2]. However, the latest work done by the group of Aurbach resuscitates the idea of a secondary magnesium battery [3, 4]. This rekindled interest will also influence the field of polymer electrolytes. Yet the knowledge of polymer electrolyte systems showing conductivity based on magnesium ions is quite confined at the moment. Electrolytes prepared by dissolving common magnesium salts, such as magnesium perchlorate or magnesium halides, in poly(ethylene oxide) (PEO) show very low conductivity at room temperature [5, 6, 7]. Enhanced conductivity could be obtained by the addition of monomeric diethyl ether [8], as well as by the use of highly activated δ -MgCl₂ [9].

Recently, work has been done with plasticized polymer electrolytes. They were prepared by dissolution of magnesium salts in a photochemically networked polymer matrix, which contained polyether groups, in the presence of poly(ethylene glycol dimethyl ether) or dimethylformamide. At room temperature, electrical conductivity up to 10^{-4} S cm⁻¹ could be realized [10, 11]. Similar conductivities were also found in systems prepared by the absorption of magnesium salt solutions in aprotic solvents within a microporous membrane [12, 13]. However, the reversible electrochemical magnesium deposition turns out to be the main problem with all of these electrolytes, which therefore normally behave as a pure anionic conductor.

In a previous paper the electrochemical magnesium deposition and reoxidation from solutions of alkylmagnesium halides in polymeric ether was reported [14]. These electrolyte systems also show conductivities up to 10^{-4} S cm⁻¹ at $40^\circ C$. The maximum conductivity was found for samples with a P(EO)/Mg ratio of about four, meaning a high content of alkylmagnesium halides. However, any potential application of these

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novel types of electrolyte in a magnesium battery is excluded by their insufficient stability against irreversible oxidation. Therefore the organomagnesium component of these electrolyte systems should be substituted by compounds helping to depassivate the magnesium surface and assist the magnesium deposition process but are themselves not as easy to oxidize.

The chemical behaviour of amidomagnesium halides is known to be similar to organomagnesium halides [15]. However, compared with the magnesium-carbon bond the magnesium-nitrogen bond has a higher polarity. The amidomagnesium halides show lower reactivity versus electrophilic reagents and therefore have better stability against oxidation. This higher oxidation stability of amidomagnesium halides as well as reversible magnesium electrodeposition have already been demonstrated for liquid systems [16].

Within this paper the preparation of polymer electrolytes by dissolving amidomagnesium chlorides in PEO is described for the first time. For this preparation, some representative compounds with varying chemical and physical properties were selected from the wide group of available amidomagnesium halides. An acceptable electrolytic conductivity and improved stability versus oxidation has already been found for (liquid) solutions of (hexamethyldisilylamido)magnesium chloride $[(\text{Me}_3\text{Si})_2\text{NMgCl}]$ in THF [16]. Therefore polymer electrolytes containing this compound were predominantly investigated. Furthermore, solutions of (dimethylpyrrolyl)magnesium chloride, (diisopropylamido)magnesium chloride, piperidinomagnesium chloride and morpholinomagnesium chloride were chosen for preparation of polymer electrolyte systems.

Experimental

Preparation of the electrolytes

Liquid solutions of amidomagnesium chlorides in THF were prepared reacting by ethylmagnesium chloride with the respective secondary amine [17, 18] and the exact concentration of the solutions, which were generally about one molar, was determined by complexometric (magnesium) and argentometric (chloride) titration. The polymer electrolyte systems were prepared by intensive mixing of the respective amidomagnesium chloride dissolved in THF with a stoichiometric amount of PEO (Aldrich, MW 200,000) followed by evaporation of the THF under vacuum at an elevated temperature (50 °C).

After this preparation procedure, the magnesium as well as the chloride content of the polymer electrolytes was determined by complexometric and argentometric titration and from these values the amount of amidomagnesium chloride in the polymer could be calculated.

The stoichiometric ratio n of the $\text{C}_2\text{H}_4\text{O}$ units to magnesium ions of the polymer electrolyte systems was calculated from the amount of PEO which had been weighed and the amount of amidomagnesium chloride. It was assumed that the THF content corresponds to the mass difference between the overall mass of the polymer electrolyte and the sum of the mass of PEO plus the mass of the amidomagnesium chloride in the system. In this way the overall composition of the electrolyte systems could be determined.

Electrochemical characterization

For conductivity measurements, samples of the polymeric substances (area 1.5 cm^2 , thickness 0.25 or 0.50 mm) were placed between two gold electrodes. The space between the electrodes was kept constant by a distance ring (polyethylene). Impedance diagrams were measured within the frequency range of 65 kHz down to 10 Hz and the conductivity of the electrolytes was calculated from the resistance, which was taken from the high-frequency intercept of the impedance data with the abscissa (real part) of the Nyquist plot.

The cyclic voltammogram was measured using a three-electrode cell, which contained a nickel working electrode, a magnesium counter electrode and a Ag/AgCl reference electrode. The reference electrode was separated from the polymeric electrolyte by a thin layer of a KCl-P(EO)₁₀ polymer electrolyte to prevent the reduction of silver ions by the amidomagnesium compounds. The temperature of the cell was kept at 60 °C to achieve sufficient conductivity of the polymer electrolyte layers. For the electrochemical experiments, a frequency response analyser in combination with an electrochemical interface (Solartron, FRA 1255 and ECI 1286) were used.

As the electrolytes showed a marked reactivity towards moisture, all operations were carried out in an argon atmosphere.

Results and discussions

The kind of the polymer electrolytes which are described within this paper represent a novel type of polymer electrolyte and, besides the results of a first electrochemical characterization, some remarks on the composition as well as on the appearance of the electrolytes should be given. It was found that under the conditions described in the experimental part there always remains about 1.0–1.3 molecules of the monomeric ether THF per magnesium atom in the polymer electrolyte system. That means that its overall composition can be described by the general formula $\text{R}_2\text{NMgCl}\cdot\text{P}(\text{EO})_n\cdot 1.0\text{--}1.3\text{THF}$. For the electrolyte systems containing (dimethylpyrrolyl)magnesium chloride, (diisopropylamido)magnesium chloride, piperidinomagnesium chloride and morpholinomagnesium chloride, a P(EO)/Mg ratio of 4 was chosen, corresponding to the overall composition $\text{R}_2\text{NMgCl}\cdot\text{P}(\text{EO})_4\cdot\text{THF}$. In the case of the (hexamethyldisilylamido)magnesium chloride-containing system, electrolytes with the P(EO)/Mg ratio n of 3, 4, 5 and 7 were prepared.

Within this composition range the polymer electrolytes have a soft rubber-like consistency. At lower magnesium contents, rather solid materials were obtained. As the conductivity decreases drastically with increasing the ratio n , compounds with a lower magnesium content were not further investigated.

Within the first electrochemical characterization of these electrolytes, attention was focused on the electrical conductivity σ and its dependence on the kind of amidomagnesium chloride that was used for the preparation, the composition and the temperature. In Table 1 the electrical conductivity for electrolytes containing different amidomagnesium chlorides are shown. At 40 °C, conductivities in the range 2–9 $\mu\text{S}/\text{cm}$ were measured for the different systems, showing that the

Table 1 Electrical conductivity of electrolytes containing different amidomagnesium chlorides at 30 °C and 40 °C

	σ at 30 °C (S/cm)	σ at 40 °C (S/cm)	Activation parameter (kJ/mol)
(Hexamethyldisilylamido)MgCl·P(EO) ₄ ·THF	5.2×10^{-6}	9.5×10^{-6}	47.1
(Dimethylpyrrolyl)MgCl·P(EO) ₄ ·THF	–	2.1×10^{-6}	–
(Diisopropylamido)MgCl·P(EO) ₄ ·THF	1.5×10^{-6}	2.2×10^{-6}	31.6
(Piperidino)MgCl·P(EO) ₄ ·THF	5.0×10^{-6}	7.0×10^{-6}	25.4

kind of organic component of the amidomagnesium chloride has a rather small influence on the conductivity. This corresponds to the similarity of the chemical behaviour of the various amidomagnesium chlorides, especially to the presence of the same kind of anions (chloride ions) which is supposed to account for a great part of the electrical conductivity in all systems.

The exception in this respect was the very low electrical conductivity (below 10^{-6} S/cm at 40 °C) of the polymer compounds containing morpholinomagnesium chloride (not listed in the table). In this case, probably the additional oxygen in the morpholino ring (compared with the piperidino ring) causes a strong interaction among the magnesium ion-containing complex cations inside the polymer matrix.

For the system $(\text{Me}_3\text{Si})_2\text{NMgCl}\cdot\text{P}(\text{EO})_n\cdot\text{THF}$, the dependence of the electrical conductivity on the P(EO)/Mg ratio n was investigated for samples with a high content of amidomagnesium halide. The conductivity values measured for the samples with a P(EO)/Mg ratio n of 3, 4, 5 and 7 are plotted in Fig. 1, demonstrating that the highest conductivity (at room temperature) was found for the electrolyte with a P(EO)/Mg ratio of 5. For this substance the electrical conductivity at 30 °C amounts to 3.5×10^{-5} S/cm. Such a maximum conductivity for a high content of organomagnesium compounds was also found for the solutions of alkylmagnesium halides in a polymeric ether [14].

It has to be mentioned that a certain dispersion (up to about 1 $\mu\text{S/cm}$) was found for the conductivity values

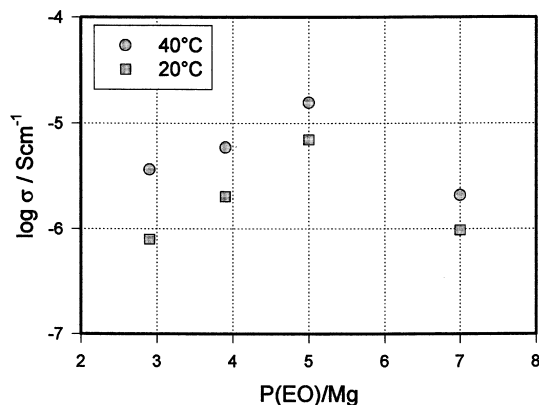


Fig. 1 Dependence of the electrical conductivity on the P(EO)/Mg ratio n for the system $(\text{Me}_3\text{Si})_2\text{NMgCl}\cdot\text{P}(\text{EO})_n\cdot\text{THF}$ (temperature: 20 °C and 40 °C)

measured on different samples of the same overall composition. This could be caused mainly by irregularities of composition within the bulk of the samples, which could not be excluded. Especially the content of the monomeric ether (THF) strongly influences the electrical conductivity, as was found for systems containing alkylmagnesium halides instead of amidomagnesium halides [19]. The values, given in Table 1 as well as in Figs. 1 and 2, were measured on samples which showed typical behaviour.

For the electrolytes of the composition $(\text{Me}_3\text{Si})_2\text{NMgCl}\cdot\text{P}(\text{EO})_n\cdot\text{THF}$ with a P(EO)/Mg ratio of $n=3, 4$ and 5, the conductivity was measured in the temperature range from 20 °C to 60 °C. At higher temperatures, problems with long-term stability arose, as the resistances of the electrolytes drifted with time. In Fig. 2 the logarithm of the electrical conductivity σ is plotted versus the inverse temperature for three electrolyte samples. A linear dependence was found, at least in this narrow temperature range, and an overall activation energy for the conduction process of 30–58 kJ mol⁻¹ could be calculated from the slope of the Arrhenius plot. These values correspond to the activation energies which were found for systems containing other amidomagnesium chlorides (see Table 1). However, it was not yet possible from the experimental data to ascribe this

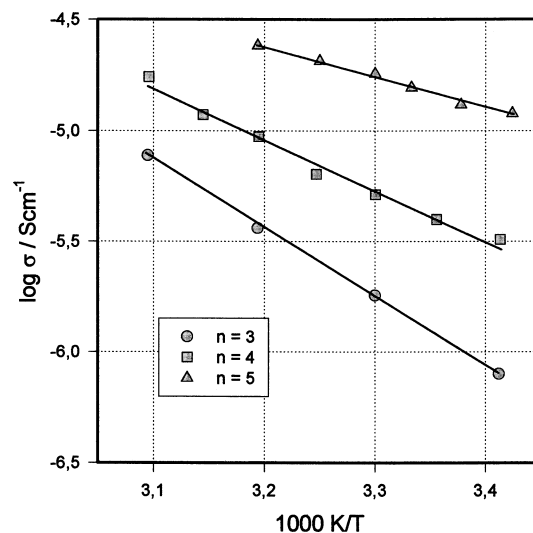


Fig. 2 Temperature dependence of the conductivity of the electrolyte system $(\text{Me}_3\text{Si})_2\text{NMgCl}\cdot\text{P}(\text{EO})_n\cdot\text{THF}$ with $n=3, 4$ and 5

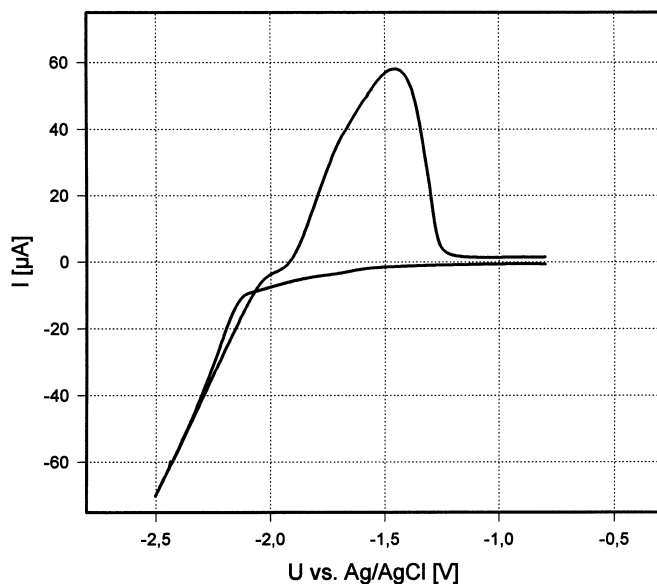


Fig. 3 Cyclic voltammogram of the system $(\text{Me}_3\text{Si})_2\text{NMgCl}\cdot\text{P}(\text{EO})_4\cdot\text{THF}$ at $60\text{ }^\circ\text{C}$; scan rate 1 mV/s , working electrode nickel (area: 0.2 cm^2), counter electrode magnesium, reference electrode Ag/AgCl

activation energy to a certain step of the conduction process.

Working with electrolytes containing magnesium ions, the occurrence of magnesium electrodeposition is always a decisive question. As is demonstrated in Fig. 3, a reversible electrodeposition could be observed in the cyclic voltammogram measured on electrolytes with a high content of amidomagnesium chloride at potentials less than -1.9 V vs. a Ag/AgCl reference electrode.

With lower contents of amidomagnesium chloride within the electrolyte system, the magnesium deposition turns out to be impeded and no deposition could be obtained using the electrolyte with a $\text{P}(\text{EO})/\text{magnesium}$ ratio of 7.

As was expected from the experience with liquid systems [16], the polymer electrolyte systems containing (hexamethylsilylamido)magnesium chloride show a remarkably high oxidation stability, as was found for polymer electrolyte systems containing other organomagnesium compounds [14]. The irreversible oxidation of the organic component $[(\text{Me}_3\text{Si})_2\text{N}^-]$ was found for potentials above -0.3 V vs. the Ag/AgCl electrode. With reference to the potential of the magnesium electrode in contact with this electrolyte, it gives a window of electrochemical stability higher than 1.6 V .

Conclusions

The aim of this study was to give a first electrochemical characterization of polymer electrolytes prepared by

dissolution of amidomagnesium halides in polymeric ether. Distinct conductivity at temperatures slightly above room temperature could be proven for these substances. Their ability for reversible magnesium electrodeposition as well as their oxidation stability up to about 1.6 V with reference to a magnesium electrode makes them an interesting new group of polymer electrolytes.

The polymeric ether used for the electrolyte preparation was a common PEO. A considerable improvement of the electrochemical and mechanical properties should be obtainable by using a polymer component which has been optimized with regard to the preparation of this kind of electrolyte, e.g. by networking or copolymerization. Other potential ways of finding more optimized systems are the variation of the amidomagnesium halide as well as of the monomeric ether.

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