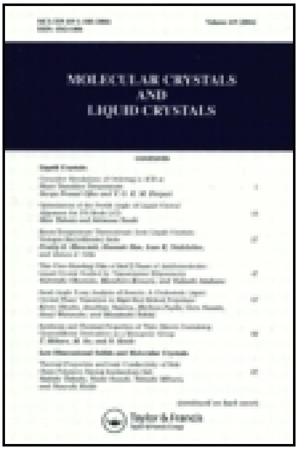

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Sol-Gel Preparation of Organic-Inorganic Hybrid Polymer Electrolytes and Their Electrochemical Characterizations

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SOL-GEL PREPARATION OF ORGANIC-INORGANIC HYBRID POLYMER ELECTROLYTES AND THEIR ELECTROCHEMICAL CHARACTERIZATIONS

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Abstract For the preparation of solid polymer electrolytes with high conductivity and good mechanical properties, organically modified ceramic electrolytes were prepared based on low molecular weight poly(ethylene glycol), lithium salt and an inorganic matrix produced by sol-gel process of tetraethoxysilane and a new poly(ethylene glycol)-modified sol-gel precursor which was synthesized by the reaction of mono-methoxy terminated poly(ethylene glycol) and 3-isocyanatopropyl triethoxysilane. Transparent and self-supporting films were obtained showing high ionic conductivities ($3.2 \times 10^{-6} \sim 1.4 \times 10^{-4}$ S/cm) at room temperature.

INTRODUCTION

Organically modified ceramic electrolytes (ORMOLYTEs) have been proposed as a solid electrolytes for the lithium secondary batteries and electrochromic displays.[1-3] These hybrid solid electrolytes are, however, quite susceptible to hydrolysis and/or difficult to obtain as a free-standing membrane along with the low conductivity at room temperature. This paper describes an approach to a new class of organically modified ceramic electrolytes which incorporated Li^+-solvating amorphous polymer (e.g. low molecular weight PEG) in sol-gel processed amorphous hybrid polymer networks. To prevent the phase separation of the low molecular weight PEG from the inorganic network, we have designed an inorganic matrix produced by sol-gel process of tetraethoxysilane and a new PEG-modified sol-gel precursor which was synthesized by the reaction of mono-methoxy terminated PEG (PEGMe) and 3-isocyanatopropyl triethoxysilane (IP-TEOS).

EXPERIMENTALS

The description of cell and the conductivity measurement system in this study was previously reported in the literature.[4]

To synthesize the PEG-modified sol-gel precursor, poly(ethylene glycol) monomethyl ether (PEGMe, Mw=350, 0.10 mole) was reacted with 3-isocyanatopropyl triethoxysilane (IP-TEOS, 0.12 mole) in the presence of di-n-butyltin dilaurate in THF at 70 °C for 8 h. The resulting solution was thoroughly washed with hexane to remove unreacted PEGMe. After evaporating solvent, a dynamic vacuum was applied at 70 °C for 48 h in order to remove the residual solvent and excess IP-TEOS. ω-Methoxy poly(ethylene glycol) 3-triethoxysilylpropylcarbamate (MPGSC), was obtained as a transparent liquid with 98 % yield. Sol-gel route was used to prepare the organic-inorganic hybrid electrolytes. Typical method of preparation was depicted as follows: The precursor solution was prepared by mixing 0.15 N HCl, ethanol, DMF, $LiCF_3SO_3$, TEOS, MPGSC and poly(ethylene glycol) (PEG, Mw=300) and stirring for 120 h at room temperature to form a homogeneous solution. After adjusting a viscosity by evaporating solvent, the solution was filtered using a Teflon syringe filter (0.45 μm) and the gel solution (50 ~ 80 μm thickness) was spin-coated (1000 ~ 2000 rpm, 60 s) on a indium/tin oxide (ITO) cell.[4] The resulting film was dried by standing at room temperature for 7 days and cured in a vacuum oven at 120 °C for 8 h. A solid electrolyte was obtained as a transparent flexible film with conductivities of $3.2 \times 10^{-6} \sim 1.4 \times 10^{-4}$ S/cm (25 °C).

RESULT AND DISCUSSIONS

To design a organic-inorganic hybrid electrolyte, it is reasonable to prevent the phase separation between organic and inorganic polymer chains unless those two chains are hybridized in a single molecular structure. Therefore, we designed a new hybrid solid polymer electrolytes composed of low molecular weight PEG, lithium salt and an inorganic polymer matrix (polysiloxane network from TEOS and MPGSC), where sol-gel processed polysiloxane network serves as a inorganic matrix and the low m.w. PEG complexed with lithium salt serves as an ionic conduction pathway.

Therefore, organic-inorganic hybrid polymer films were prepared by sol-gel process as summarized in Table 1. Transparent, flexible and self-supporting films were obtainable in most cases. Conductivities of those films ranged from 3.2 x 10^{-6} to 1.4 x 10^{-4} S/cm (25 °C) depending on the process condition. In these hybrid polymer electrolytes, the siloxane polymer network from the polycondensation of TEOS and MPGSC provides a good mechanical properties and the high compatibility is granted from the PEG moiety in the modified precursor, MPGSC.

TABLE 1. Preparing Conditions for Various Sol-Gel Processed Electrolytes

Sample Code	MPGSC (M)	TEOS (M)	PEG (M)	$LiCF_3SO_3$ ([Li]/[EO])
SV01~SV07	1.0	2.0	0.4	varied
TV01~TV07	1.0	varied	0.4	0.067
PV01~PV11	1.0	2.0	varied	0.067
MP01~MP10	varied	2.0	0.4	0.067

In Figure 1, log(σ)s of polymer electrolyte samples were plotted against varied compositions. In every cases, a maximum in conductivity was found as varying composition was increased and then σ decreased afterwards. In the case of SV series (Fig. 1a), a sharp maximum was found at [Li]/[EO] = 0.067. Similar maxima in σ have been reported for many organic polymer electrolytes with slightly lower [Li]/[EO].[5,6] This was presumably attributed by the interaction between Li^+ ion and oxygen in the polysiloxane. The maximum of σ can be rationalized by that the increase in T_g restricts segmental motion of polymer chains resulting in the decreased carrier mobility. In some cases, a phase separation between the inorganic sol-gel matrix and PEG as obviously noticed by

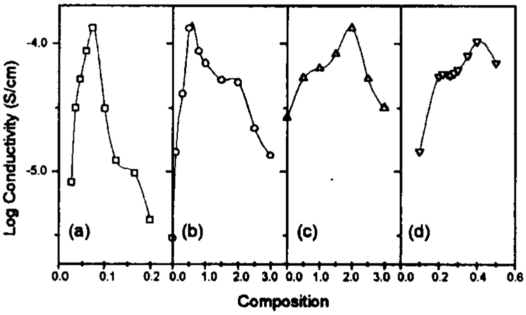

FIGURE 1. Plots of log(σ)'s of polymer electrolyte samples vs. (a) [EO]/[Li], (b) MPGSC, (c) TEOS, and (d) PEG at 25 °C

AFM on the electrolyte surface or a formation of ion-pair[7,8] seemed to be responsible for the decrease in conductivity after the maximum. In order to elucidate the conduction mechanism further in relation with the composition, the temperature dependence of the conductivity was investigated. By fitting log(σ) vs. 1/T curves with respect to [Li]/[EO], [TEOS], [PEG] and [MPGSC] using VTF equation[9], VTF coefficients were realized empirically and depicted in Figure 2, which clearly showed a sharp decrease in the number of charge carrier after a certain maximum.

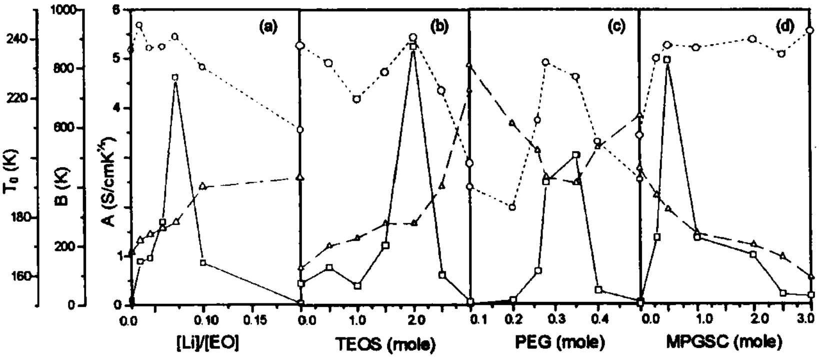

FIGURE 2. Plots of VTF coefficients with varied compositions, A : (□); B : (○); T_0 : (△). Coefficients were calculated by fitting log(σ) vs. 1/T curves with VTF equations.

Further studies including the temperature dependence of ionic conductivities in relation with compositions will be reported elsewhere.

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