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A novel composite polymer electrolyte: Effect of mesoporous SiO$_2$ on ionic conduction in poly(ethylene oxide)–LiCF$_3$SO$_3$ complex

Yoichi Tominaga [a], Shigeo Asai [a], Masao Sumita [a,*],
Stefania Panero [b,1], Bruno Scrosati [b,1,2]

[a] Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan
[b] Dipartimento di Chimica, Università "La Sapienza", Roma 00185, Italy

Abstract

Internal modified-mesoporous SiO$_2$ using ionic liquid (IL-MPSi) as one of the additives has been prepared and added to the poly(ethylene oxide) (PEO)-based solid electrolytes for improving the ionic conductivity. In this study, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) has been used as an ionic liquid. The conductivity was significantly improved by the addition of IL-MPSi, to be more than 10^{-5} S cm^{-1} at room temperature and at the filler contents of 15 wt.%, in the solid state. From the combination of dc polarization and ac impedance measurement for lithium cells, it was revealed that the addition of IL-MPSi increased the Li$^+$ transference number (t_+), because the EMImBF$_4$ used in this study possesses higher t_+ (approximately 0.5) than the PEO-salt simple mixture. This means that the MPSi domains can act as "bypass" for transport of carrier ions to the PEO matrix through the inside IL phase.
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1. Introduction

Ion-conductive polymers such as poly(ethylene oxide) (PEO) including metal salts [1] have an interest as solid-state alternatives to liquid electrolytes for electrochemical device applications [2–5], especially for lithium batteries [2,3]. These have recently been many studies on the macromolecular design of PEO-based polymers as electrolyte materials with mainly reduced degree of crystallinity, showing good electrochemical stability, and improvement in salt solubility [6,7]. However, these materials suffer from a relatively low ionic conductivity in the solid state compared with most liquid or ceramic electrolytes. For fast migration of ions, a technique that can modify the localized polar structure containing ions is needed.

On the other hand, Scrosati and co-workers have reported that the addition of nano-size ceramic particles can be effective for improving the conductivity with good mechanical strength [8–15]. The addition of fillers to the PEO-based electrolytes gives rise to the significant increase in the conductivity, the inhibition of polymer re-crystallization, the decrease in glass transition temperature (T_g), and the increase in the cation transport number. It is considered that the enhanced cationic conduction might be caused by the active interface between polymer and filler surface based on the Lewis acid–base interactions [13,14].

In this paper, we report the mesoporous silica (MPSi) which was internal modified by ionic liquid (IL) as a new kind of additives for PEO-based electrolytes. It is well known that the MPSi possess high-ordered organizations based on the hexagonal SiO$_2$ structure with high surface area [16]. On the other hand, the IL (e.g. imidazolium derivatives) has recently been recognized as excellent liquid electrolytes because it shows high conductivity with good chemical and thermal stability [17,18]. We expect that the IL-modified MPSi act

* Corresponding author. Tel.: +81 3 5734 2431; fax: +81 3 5734 2876.
  E-mail address: msumita@o.cc.titech.ac.jp (M. Sumita).
[1] Tel.: +39 06 4462866; fax: +39 06 491769.
[2] Electrochemical Society Active Member.

as a fast-ion conductive path through the mesopores or as an active interface into the polymer electrolytes.

2. Experimental section

2.1. Sample preparations

The mesoporous silica (MPSi) was synthesized by simple sol–gel method using non-ionic surfactant ($EO_{20}PO_{70}EO_{20}$ block copolymer, $M_w = 5800$, Aldrich Co.) as template molecules for the formation of high-ordered structures [16]. The synthesis procedure of the MPSi was followed by the same process written in a previous report [19]. From small angle X-ray scattering (SAXS) measurement, the long period, SiO_2 wall thickness, and pore size of neat MPSi used in this study were estimated as 9.7, 2.6, and 7.1 nm, respectively [19]. For the internal modification of neat MPSi, 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMImBF_4$, Aldrich Co.) was used as ionic liquid. The preparation process was also followed by our previous study [19]. The schematic images of MPSi domain structure and the $EMImBF_4$-modified mesopore are shown in Fig. 1. From the elemental analysis and SAXS measurement, it was revealed that more than 60 wt.% of $EMImBF_4$ molecules are filled into inside the mesopores without the destruction of high-ordered structure [19]. The PEO (Aldrich Co., $M_w = 100,000$), battery-grade $LiCF_3SO_3$ (LiTf, Aldrich Co.), and the fillers were mixed by using the solvent-free method [15]. These materials were introduced into a polyethylene bottle with small glass balls and it was rolled by ball-milling system for at least 24 h. Resulting homogeneous powder was compression-molded into an approximately 130 μm-thick film at 80 °C for 20 min under argon. The PEO–LiTf composition of all samples is specified as 5 mol% (OE:Li = 20:1), which gives the ratio of the number of oxyethylene (OE) units to the number of Li cations.
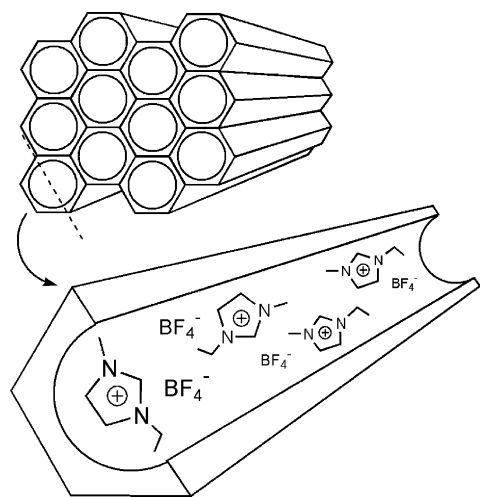

Fig. 1. Structural images of neat MPSi domain (up) and $EMImBF_4$ phase in the mesopore (down).

The composite samples with the filler contents from 1.7 to 27.8 wt.% have been prepared in this study.

2.2. Measurements

The ionic conductivity of all the samples was measured by a complex ac impedance method using a Solatron 1250 Impedance Analyzer in the frequency range from 1 to 100 kHz. The measurement was carried out in an oil bath where the temperature was controlled from 90 to 30 °C to hold constant every 10 °C interval for at least 8 h. The sample was sandwiched between two stainless electrodes with a 110 μm-thick Teflon® spacer. A measurement cell was introduced into a coffee-bag and it was placed into the oil bath.

The DSC measurement was carried out using a Mettler Toledo Co. system consisting of a DSC-822e. The temperature was increased from −100 to 200 °C at a heating rate of 10 °C min^{-1}.

The Li transference number t_+ was determined by using a combination method of dc polarization and ac impedance measurement, which has been reported by Evans et al. [20]. The equation is shown as follows,

$$t_+ = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)} \tag{1}$$

where I is the dc current and R the electron-transfer resistance between electrode and electrolyte. Both of the subscripts 0 and s means initial and steady state. The current and resistance were measured from a multi-channel potentiostat VMP1 and a Solatron 1260 Impedance analyzer. The sample was sandwiched between two stainless disks with the 0.5 mm-thick Li foils as non-blocking electrodes. A Li|electrolyte film|Li cell was introduced into a coffee-bag. The entire process was carried out in an argon gas-filled glove box (MBRAUN Lab Master 130) which was controlled the pressure inside and the contents of water and oxygen below 1 ppm. Finally, it was placed into an outside oven, which was held the temperature at 90 °C.

3. Results and discussion

3.1. ac conductivity measurement

Temperature dependence of ionic conductivity for original $PEO_{20}LiTf$ and the composite electrolytes filled with neat and IL-MPSi is shown in Fig. 2. An original sample had a low conductivity, of the order of 10^{-7} S cm^{-1} at room temperature, because of a transition at approximately 60 °C corresponding to the melting of crystalline PEO domains. Above the transition point, the conductivity increases linearly with temperature and the temperature dependence essentially follows an Arrhenius-type equation. The conductivity of the neat MPSi composite was higher than the original one at low temperatures because the addition of filler gives rise to the decrease in the PEO crylstalline phase. However, there are almost no dif-

Table 1
Glass transition temperature (T_g), melting point (T_m), and heat of fusion (ΔH) for the original and the composite electrolytes obtained from DSC

Sample	T_m (°C, peak)	ΔH (J g^{-1})	T_g (°C)	σ_i (S cm^{-1})
Pure PEO	76	155	−58	−
PEO$_{20}$LiTf	62	103	−48	7.1×10^{-8}
+neat MPSi 5 wt.%	72	99	−49	6.5×10^{-7}
+neat MPSi 10 wt.%	70	92	−53	1.6×10^{-6}
+neat MPSi 15 wt.%	68	82	−50	8.9×10^{-7}
+IL-MPSi 5 wt.%	68	108	−45	3.2×10^{-6}
+IL-MPSi 10 wt.%	72	116	−50	1.1×10^{-5}
+IL-MPSi 15 wt.%	72	117	−50	3.8×10^{-5}
Pure EMImBF$_4$[a]	14	84	−110	6.3×10^{-3}

The conductivities (σ_i) at 40 °C are also shown.

[a] The conductivity has been measured using a cell for liquid electrolytes with the same impedance system.

ferences in the conductivity between these samples at higher temperatures. The composite sample including 15 wt.% of neat MPSi showed a little lower conductivity than the original one at high temperature range. On the other hand, the conductivities of the IL-MPSi composites are higher at the entire measurement temperature. Especially, the sample including 15 wt.% of IL-MPSi shows more than 10-fold higher conductivities than the original and the neat MPSi composite samples. Fig. 3 summarizes the relation between the conductivity at 40 and 90 °C and the filler contents for the composite electrolytes. The data of composite samples, which were filled with nano-particle SiO$_2$, are also shown as reference [15]. The conductivities for some composite samples are also summarized in Table 1. The conductivity at 40 °C for the neat MPSi composite samples shows a maximum at approximately 10 wt.% filler contents. This behavior of the PEO-based simple composite systems is well known as reported by Scrosati et al. [8]. At high contents above 10 wt.%, the conductivity decreases gradually with increasing the filler contents at

both temperatures. The conductivity of the composites shows lower than that of the original and particle SiO$_2$ composites at 90 °C. This may be due to the aggregation of filler domains as insulator, which prevents the segmental motion of local PEO chains and the ionic conduction in the amorphous phase. By contrast, the composites including IL-MPSi showed different conduction behavior. The conductivity has significantly been improved by the addition of IL-MPSi. The composite including IL-MPSi of 15 wt.% (the amount of MPSi in IL-MPSi can be estimated to be 9.2 wt.%) shows the maximum conductivity, of an approximately 4×10^{-5} S cm^{-1} at 40 °C. The composites show the highest conductivities of all the composites and the original sample. Moreover, the composite samples including IL-MPSi of more than 15 wt.% still maintain the enhanced conductivities. The enhancement might be caused by the fast migration of ions in the IL phase or ion exchange between the PEO phase and IL phase inside
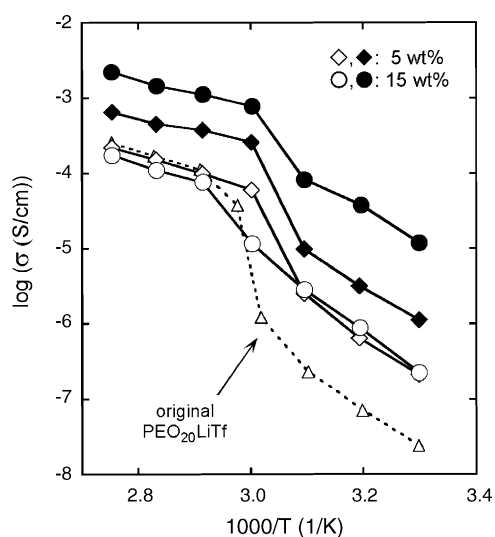

Fig. 2. Temperature dependence of ionic conductivity for original PEO$_{20}$LiTf and the composite electrolytes filled with neat (open plots) and with IL-MPSi (close plots).
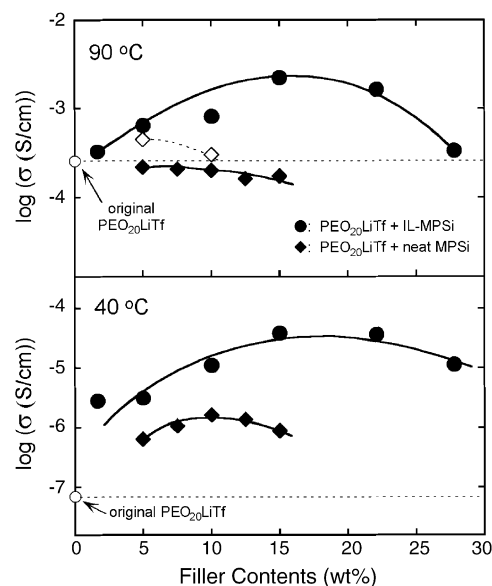

Fig. 3. Relation between ionic conductivity at 40 and 90 °C and filler contents for PEO$_{20}$LiTf composite electrolytes. The PEO$_{20}$LiTf composites filled with nano-particle SiO$_2$ (open square plots, at 90 °C) are shown as reference data [15].

Table 2
Initial and steady state electrode resistance (R_0, R_s), direct current (I_0, I_s), and calculated Li$^+$ transference numbers (t_+) for original PEO$_{20}$LiTf and the composite samples

Sample	R_0 (Ω)	R_s (Ω)	I_0 (μA)	I_s (μA)	t_+
PEO$_{20}$LiTf	142.6	154.0	136.3	28.2	0.35
+neat MPSi 5 wt.%	37.6	36.1	78.2	42.8	0.47
+IL-MPSi 5 wt.%					
[Phase I]	25.5	29.7	50.9	30.3	0.57
[Phase II]	122.5	103.4			0.33

the MPSi. It means that the added MPSi domains can act as fast ion-conduction "bypass" between the amorphous PEO phases.

3.2. Thermal properties

On the other hand, the thermal data, which have been obtained from the DSC measurement, show peculiar behaviors in the MPSi composite electrolytes (Table 1). The pure PEO decreases in the T_m and ΔH by the addition of the salt, because the PEO crystal phase decreased. The addition also gives rise to the significant increase in the T_g. This is due to the strong interactions between dissolved Li ions and dipoles of ether oxygens [4,5,7]. Adding the neat MPSi, the ΔH gradually decreases with increasing the filler contents, in spite of the increase in the T_m. The decrease in ΔH and the increase in T_m might be caused by the decrease in the crystallinity of PEO and the increase in the crystal size. The increase in the conductivity at low temperatures is due to the decrease in the crystallinity by the addition of neat MPSi. The addition also gives rise to the slightly decrease in the T_g. From these results, it seems that the neat MPSi can disperse into the PEO matrix to some extent. By contrast, the ΔH of IL-MPSi composites slightly increases with increasing the filler contents, in spite that the conductivities have been largely improved by the addition, as seen in Figs. 2 and 3. The increase in the ΔH might be related to the crystal phase of IL inside the mesopores. However, the peaks at around the T_m of PEO, which have been observed from DSC curves, become broad with increasing the filler contents. It probably means that the addition of IL-MPSi gives rise to the disordered structure of PEO crystal phase.

3.3. dc polarization and Li$^+$ transport numbers

For understanding the species of carrier ions where the enhancement of the conductivity occurs, it is important to reveal the cation transference numbers (t_+) in the composite electrolytes. Bruce and co-workers have reported a technique in which a combination of dc and ac electrical polarizations is used to enable the t_+ to be determined [20]. Elapsed time (t) dependence of dc polarization current for the original and the composite samples under constant voltage of 10 mV is shown in Fig. 4. The initial and steady state currents, I_0 and I_s, are also summarized in Table 2. The I_0 drop immediately
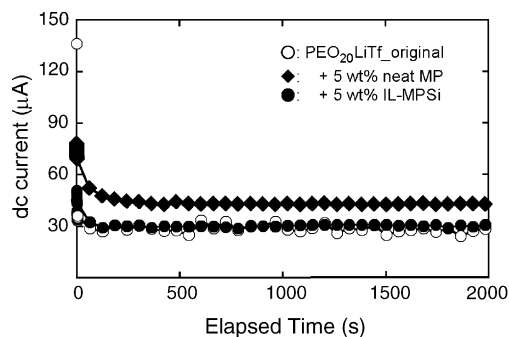

Fig. 4. Elapsed time dependence of direct current for Li|electrolyte|Li cells under the constant voltage of 10 mV.

within 200 s and show the I_s versus t for more than 3 h. Especially, a significant drop in the current has been observed for the Li|original PEO$_{20}$LiTf|Li cell. It is due to the polarization at the Li cathode based on the migration of mainly CF$_3$SO$_3$ anions. On the other hand, a charge transfer reaction between the electrode and electrolyte interface can be observed from the ac impedance measurement. The impedance response for the three Li cells at the initial state ($t = 0$) is shown in Fig. 5. The initial and steady state resistances, R_0 and R_s, are also summarized in Table 2. In the above figure, the arcs represent the charge transfer resistance (R_0) at the interface between Li electrode and electrolyte based on the double-layer capacitance (C_e). The equivalent circuit consists of a series of the bulk and the charge transfer components is represented as seen in the above figure. The R_0 of the original PEO$_{20}$LiTf is more than two-fold larger than the electrolyte bulk resistance, R_b, because of the anionic polarization at the cathode
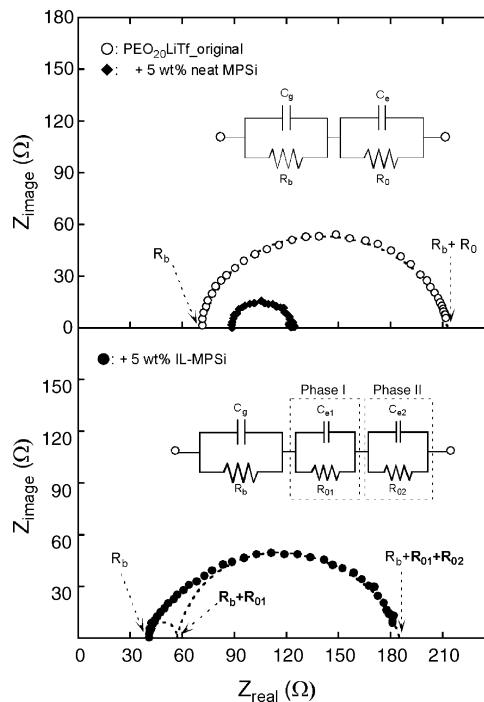

Fig. 5. Cole–Cole plots for Li|electrolyte|Li cells at the initial state ($t = 0$) and 90 °C. The equivalent circuit models are also shown.

interface. The composite sample including neat MPSi shows quite small R_0 and R_s compared with that of the original. It means that the interfacial stability between electrode and electrolyte, which is related to the passivation layers prepared on the Li electrodes, has been highly maintained by the addition of inorganic fillers. According to the previous report, the preparation process of the layers is kinetically rapid compared with the filler-free system [9]. On the other hand, we have analyzed that the impedance response of an IL-MPSi composite includes two arcs, which can be separated as each charge transfer component. One is due to the IL phase I (R_{01}), and the other is due to the bulk PEO phase II (R_{02}). Probably, this is due to the phase separation between the PEO matrix and the IL phase. From the above combination measurement, the t_+ of the original and the composite electrolytes have been calculated using an Eq. (1) as summarized in the Table 2. It is well known that the PEO-salt simple mixtures are the anion-conducting system, because the t_+ is lower than 0.5 [4,5]. In the neat MPSi composite system, the t_+ has been enhanced, to be almost of 0.5. This behavior has already been explained that the improvement of t_+ is due to the increase of interactions between the surface groups such as hydroxyl and the anions or polyether oxygens, which is based on the Lewis acid–base nature [13,14]. From the phase I and II in the IL-MPSi composite, the t_+ has been calculated as 0.57 and 0.33, respectively. The higher t_+ in the phase I is attributable to the IL inside the mesopores, because the t_+ of $EMImBF_4$ has been estimated to be 0.5 from the diffusion coefficient measurement using PGSE-NMR [21]. It is thought that the lower t_+ is attributable to the separated PEO-salt complex phase. In fact, the phase II shows almost the same t_+ of the above original $PEO_{20}LiTf$. From these results, it is certain that the increase in the t_+ of IL-MPSi composite is due to the cationic conduction in the IL phase inside the mesopores or the exchange of carrier ions at the active of the MPSi domains. Therefore, we can say that the MPSi domains functioned as "bypass", which can transport carrier ions rapidly through the IL-tunnels in the PEO matrix.

4. Conclusion

We have prepared the ionic liquid-modified-mesoporous silica (IL-MPSi) as one of the additives for improving the ionic conductivity of PEO-based polymer electrolytes in solid state. The conductivity was significantly improved by the addition of IL-MPSi, to be more than $10^{-5}\,\mathrm{S\,cm^{-1}}$ at room temperature and at the filler contents of 15 wt.%. It has been shown from the DSC measurement that the heat of fusion based on the crystal PEO phase increased with increasing the IL-MPSi contents, whereas the conductivity at $40\,^\circ$C increased. This might be caused by the crystalline IL phase inside the mesopores. From the combination consists of dc polarization and ac impedance measurement for Li cells, it was revealed that the addition of IL-MPSi increases in the Li^+ transference number. It indicates that the MPSi domains can act as "bypass", which transports mainly Li^+ cations through the IL-tunnels.

Acknowledgments

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