Polymer Bulletin 57, 115–120 (2006)
DOI 10.1007/s00289-006-0528-0

Polymer Bulletin

Thermally stable ion conductive polymer composites containing imide-anion-type zwitterions

Asako Narita, Wataru Shibayama, Masahiro Tamada, and Hiroyuki Ohno (✉)

Department of Biotechnology, Tokyo University of Agriculture and Technology
2-24-16 Naka-cho, Koganei, Tokyo, 184-8588, Japan

Received: 9 November 2005 / Revised version: 25 January 2006 / Accepted: 1 February 2006

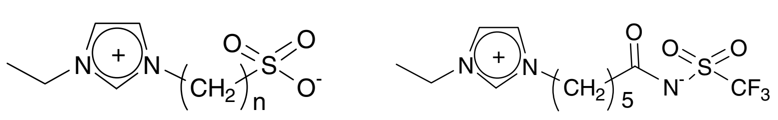
Summary

Zwitterion bearing highly dissociable imide anion (EIm5csI) was used as major component for stable polymer electrolytes. A polymerization of methyl acrylate in the presence of EIm5csI/LiTFSI mixture gave a flexible film with the ionic conductivity of 9.3 x 10^{-6} Scm^{-1} at 50 °C. Mixing of poly(lithium acrylate) and EIm5csI/LiTFSI mixture improved ionic conductivity (3.3 x 10^{-5} Scm^{-1} at room temperature), lithium transference number (0.44), and thermal stability.

Introduction

Ionic liquids (ILs) with low melting point are expected as important components for electrochemical energy devices because of their outstanding properties such as negligibly small vapour pressure, wide electrochemical potential window, and high ionic conductivity [1]. Usually, they are used as mixtures with salts or acids as carrier ion source. However, such mixtures of IL with salt or acid have difficulty in the target cation transport because component ions of IL also migrate under potential gradient. Therefore, functionalization of ILs for selective carrier ion transport is a strong request for practical use.

To suppress mobility of matrix ions, we have proposed zwitterions in which both anion-site and cation-site are covalently tethered [2]. For example, the structure of zwitterion 1-(1-ehtyl-3-imidazolio)propane-3-sulfonate (EIm3S), represented in Figure 1-a is the results of the tethering of alkylimidazolium cation and sulfonate anion [2]. Although sulfonate type zwitterions; EIm3S melts at 176 °C, it became a liquid when mixed with equimolar amount of lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) [2]. This liquidizaton is comprehensible



n = 3: EIm3S, **n** = 4: EIm4S
a. sulfonate-type-zwitterions

b. imide-anion-type zwitterion

Figure 1 Zwitterions used in this study for us as a formation of IL-like ion pair between imidazolium cation and the added TFSI anion. These mixtures of zwitterions and lithium salts are expected to be lithium cation transporting matrix because zwitterion and TFSI anion formed large triple ion-like complex. The mixture of imidazolium-sulfonate-type zwitterion and an equimolar amount of LiTFSI showed ionic conductivity of 10^{-5} Scm^{-1} at 50 ºC despite that pure zwitterion is an insulator.

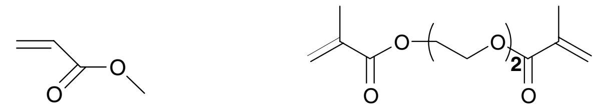
Furthermore, a mixture composed of EIm3S, LiTFSI, and poly(vinilydene fluoride-co-hexafluoropropylene) showed the transference number of lithium cation of 0.56 at room temperature [3]. This value strongly suggests that zwitterions are useful as ion conductive matrices, and they are also effective to prepare target ion transport pathway even when mixed with polymers. To prepare zwitterion-containing polymer electrolyte gel films, we examined polymerization of vinyl monomer, e.g., methyl acrylate in the presence of both zwitterion (e.g., 1-(1-ethyl-3-imidazolio)butane-4-sulfonate, EIm4S in Scheme 1-a) and LiTFSI [4]. The resulting gel showed the ionic conductivity of 8.3 x 10^{-6} Scm^{-1} at 50 ºC, and was stable up to 375 ºC. As these results, zwitterions are interesting materials to afford ion conductive matrices having excellent thermal stability and cation mobility.

Very recently, we have designed novel zwitterions, 1-(1-ethyl-3-imidazolio)hexane-6-(carbonyl)(trifluoromethylsulfonyl)imide (Figure 1-b, EIm5csI) that possesses highly dissociable asymmetric imide anion [5]. The equimolar mixture of EIm5csI with LiTFSI showed higher ionic conductivity than that of EIm4S / LiTFSI mixture. In the present work, highly ion conductive polymer composites containing this novel zwitterion was prepared, and basic characteristics have been studied.

Experimental section

Preparation of EIm5csI/LiTFSI/polymer composites

LiTFSI (99.97%), donated from Sumitomo 3M, was used without further purification. Equimolar amount of EIm5csI and LiTFSI were dissolved in methanol. After stirring the solution, methanol was removed under reduced pressure. And then, the resulting liquid was dried in vacuum at 80 ºC for 2 days. The liquid was then mixed with a half molar amount of methyl acrylate (MA, Aldrich) (Figure 2-a) toward EIm5csI. Then, diethyleneglycol dimethacrylate (3mol% to MA, Figure 2-b) was added as a cross-linker. The mixture was stirred at room temperature under nitrogen atmosphere. AIBN 1mol % to MA was added as a radical polymerization initiator, and then the mixture was introduced into the space between two glass plates equipped with 0.5 mm Teflon® spacer. The mixture was kept at 70 ºC for 8 hours to afford a flexible gel supported by the polymerized MA (PMA). The obtained gel was dried under reduced pressure at 60 ºC for 24 hours. Both ^{1}H-NMR and FT-IR spectra indicated no C = C double bond remained.



a. Methyl acrylate (MA) **b**. Diethyleneglycol dimethacrylate

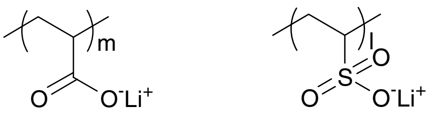
Figure 2 Vinyl monomer and cross-linker

Mixing of poly(anion) with EIm5csI and LiTFSI

Poly(sodium acrylate) 6.3 g (Aldrich, Mw 8000, 45wt% aqueous solution) was mixed with 60ml of cation-exchange resin (Aldrich, Amberlite IRA-120H). After the mixture was stirred for 6 hours, the resin was removed by filtration. The obtained acidic solution was added to a solution of 0.73g of lithium hydroxide (Wako) dissolved in 50ml of milli-Q water. After water was removed by evaporation, poly(lithium acrylate) (PLiAC, Figure 3-a) was obtained as a white powder.

Sodium vinylsulfonate (Nippon Kasei Chemical) 3.3g was passed through a column filled with 60ml of cation-exchange resin in milli-Q water. Obtained acid aqueous solution was mixed with 0.6g of lithium hydroxide dissolved in 50ml of milli-Q water. Then the solution was frozen with liquid nitrogen. Potassium persulfate (1.1g, 4mmol, Wako) powder was poured on the frozen solution. After the ice began to melt, the mixture was stirred at room temperature. After the mixture was stirred for 24 hours, most water was removed under reduced pressure, then the resulting polymer was washed with dry methanol. Poly(lithium vinylsulfonate) (PLiVS, Figure 3-b), was obtained as a white solid.

EIm5csI, LiTFSI, and PLiAC, or PLiVS were mixed in milli-Q water in the following mixing ratio. **1**; EIm5csI : PLiAC = 1 : 1 (mol), **2**; EIm5csI : PLiVS = 1 : 1 (mol), **3**; EIm5csI : PLiAC : LiTFSI = 2 : 1 : 1 (mol), **4**; EIm5csI : PLiVS : LiTFSI = 2 : 1 : 1 (mol). After the solutions were stirred for 1 hour, most of water was removed under reduced pressure. The resulting mixtures were dried in vacuum at 80 °C for 2-3 days.



a. poly(lithium acrylate) (PLiAC) **b**. poly(lithium vinylsulfonate) (PLiVS)

Figure 3 Polyanions used in this study

Measurements

The decomposition temperature (T_d) of samples was determined as the point for 5% weight loss by thermogravimeteric analysis (TG, SII TG/DTA220, Seiko Instruments). The glass transition temperature (T_g) and the melting point (T_m) were measured using differential scanning calorimetry (DSC, SII DSC EXSTAR6000, Seiko Instruments) over a range from -120 °C to 200 °C at the heating rate of 10 °C min^{-1}. Ionic conductivity was measured by complex impedance method using Impedance/Gain-phase analyzer (Solartron 1260, Schlumberger) under nitrogen gas over a range from 10 °C to 60 °C (for gel films) or from 30 °C to 120 °C (for poly(anion) composites) at the cooling process. The transference number of lithium cation (t_{Li^+}) was calculated by combination of AC impedance and DC polarization method (potential-static field: 10mV, lithium metal electrode, under argon atmosphere at room temperature) [6].

Results and Discussion

Gel film using PMA as a host

The obtained film (EIm5csI / LiTFSI /PMA = 2 : 2 : 1 (mol)) was transparent rubbery film that was stable under air up to 293 °C. The T_d was slightly lower than that of EIm5csI/LiTFSI mixture (306 ºC). The ionic conductivity of the film (9.3 x 10^{-6} Scm^{-1} at 50 ºC) was higher than that of EIm4S/LiTFSI/PMA film [4] (Figure 4), possibly because of lower T_g of the film (EIm5csI/LiTFSI/PMA = 2:2:1 mol, T_g: -10 ºC [4]). The glass transition temperature of both composite films containing PMA was only slightly higher than that EIm5csI/LiTFSI or EIm4S/LiTFSI mixtures (-35 ºC and -16 ºC [4], respectively). Consequently, the ionic conductivity of these films was lower than that of liquid zwitterion/LiTFSI mixture. However, these solid films still maintained ionic conductivity around 10^{-6} Scm^{-1} at 50 ºC. On the other hand, t_{Li}^+ of EIm5csI/LiTFSI/PMA was not particularly high (0.2) compared with that of ordinary IL systems. To improve the t_{Li}^+, poly(anion)s were used instead of both PMA and LiTFSI. No anions were expected in the zwitterions/poly(anion) mixed system.

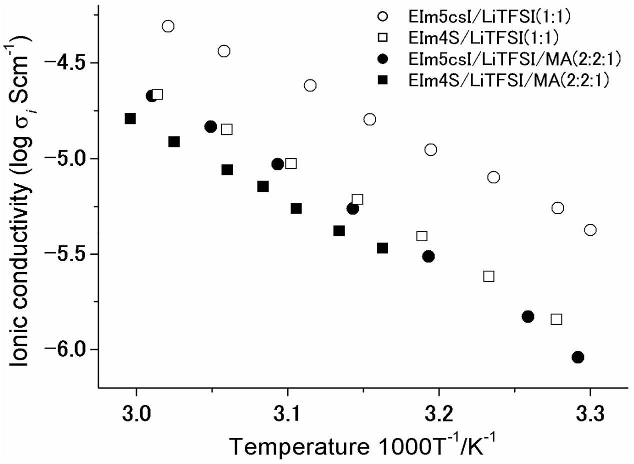


Figure 4 Ionic conductivity of zwitterion/LiTFSI mixture and their polymer composites. (○: ref.[5], □ and ■: ref.[4])

Poly(anion) composites

Four types of poly(anion) composites were prepared as depicted in Table 1 (composites **1** - **4** are defined therein). The Arrhenius plots of their ionic conductivity are shown in Figure 5.

Table 1 Thermal properties of poly(anion) composites containing EIm5csI.

	molar ratio				phase transition temperature (ºC)		
#	EIm5csI	LiTFSI	PLiAC	PLiVS	T_d	T_m	T_g
1	1	0	1	0	312	101	-21
2	1	0	0	1	311	101	-5
3	2	1	1	0	319	-	-42
4	2	1	0	1	321	-	-21
ref [5]	1	1	0	0	306	-	-35

- : not observed

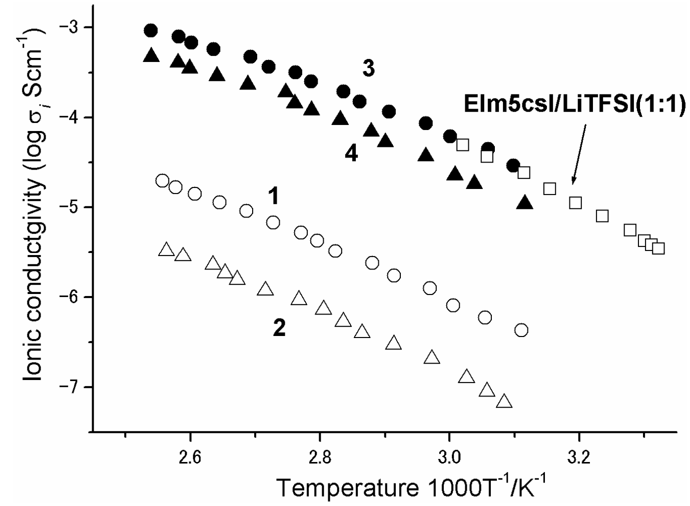


Figure 5 Ionic conductivity of poly(anion) composites containing EIm5csI.
(□: equimolar mixture of EIm5csI/LiTFSI, ref.[4])

Composites **1** and **2** are brittle white solid with T_m of 101 °C. To lower the T_g of matrices and improve the ionic conductivity, the use of poly(lithium acrylate) (PLiAC) was confirmed to be better than that of poly(lithium vinylsulfonate) (PLiVS). The ionic conductivity of both **1** and **2** was of course lower than that of liquid EIm5csI/LiTFSI mixture (ref. in Table 1). However, very high t_{Li}^+ (0.98) was observed for sample **1** attributable to the restriction of anion mobility. Then we added LiTFSI to these composites to elevate the ionic conductivity.

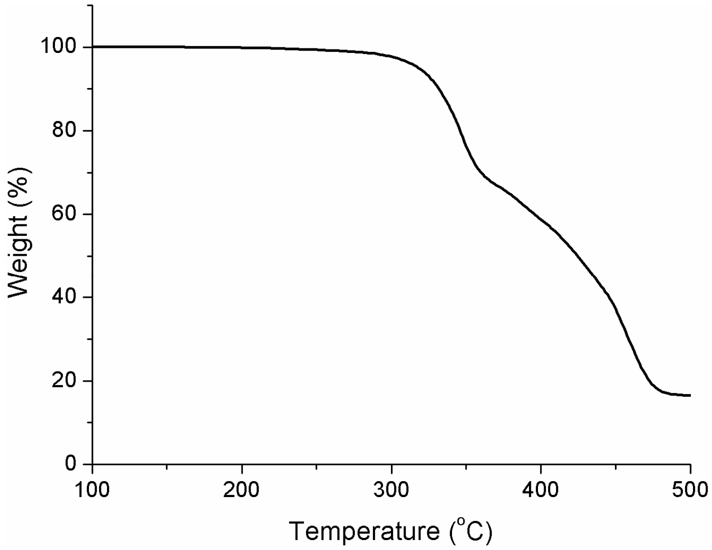


Figure 6 Thermogravimetric profile of composite **3**

Since the polyanion needs the equimolar amount of zwitterions to raise the degree of dissociation, zwitterions equimolar to both polyanion and LiTFSI were added. Ionic conductivity increased by the addition of EIm5csI/LiTFSI mixture. The temperature dependence of ionic conductivity for **3** and **4** is represented in Figure 5. When ratio of EIm5csI : LiTFSI : poly(anion) was 2 : 1 : 1 by mol in Table 1, run **3** and **4**, the composite showed much improved ionic conductivity. The contribution of the addition of EIm5csI/LiTFSI mixture is obvious by comparing results in Figure 5 (**1** vs. **3**, and **2** vs. **4**). Composites **3** and **4** were white paste, showing slightly higher T_d than EIm5csI / LiTFSI mixture (Figure 6). The ionic conductivity of **3** (3.3 x 10^{-5} Scm^{-1} at 50 ºC) was almost the same as that of liquid EIm5csI/LiTFSI mixture. The ionic conductivity of **4** was 1.1 x 10^{-5} Scm^{-1} at 50 ºC. Furthermore, t_{Li}^+ of **3** was 0.44, which was lower than that of composite **1** due to the contribution of TFSI anions, but higher than those for not only EIm5csI/LiTFSI mixture (0.2) but also other polymer composites containing typical ILs (t_{Li}^+ = 0.2 – 0.3 [7]). Comparing the equimolar mixture of EIm5csI/LiTFSI, the use of poly(anion) increased significantly the number of lithium ions.

In conclusion, polymer composites containing zwitterion with asymmetric imide-anion-site were prepared. EIm5csI/LiTFSI/MA (2 : 2 : 1 by mol) composite was rubbery solid which was stable up to 293 ºC. The ionic conductivity and t_{Li}^+ of the solid was found to be 1.0 x 10^{-6} Scm^{-1} and 0.2 at room temperature, respectively. EIm5cs/LiTFSI/PLiAC (2 : 1 : 1 by mol) composite exhibited further improved both ion conductive characteristics and thermal stability. The composite showed ionic conductivity of 3.3 x 10^{-5} Scm^{-1} at 50 ºC, and t_{Li}^+ of 0.44 at room temperature. Zwitterions are indispensable component to improve ionic conductivity of polymer electrolytes without elevating the glass transition temperature.

Acknowledgements. The financial support for this study by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports Science and Technology, Japan (No. 17205020 and 17073005) is gratefully acknowledged. LiTFSI was a gift from Sumitomo 3M. The present study has been carried out under the 21st Century COE program of Future Nano-Materials.

References

1. Ed: Ohno H (2005) Electrochemical Aspects of Ionic Liquids: Wiley-Interscience
2. Yoshizawa M, Hirao M, Ito-Akita K and Ohno H (2001) J Mater Chem 11: 1057
3. Ohno H, Yoshizawa M, Ogihara W (2003) Electrochim Acta 48: 2079
4. Tamada M, Yoshizawa M, Ohno H (2006) Proceedings of 206th ECS Annual meeting: in press
5. Narita A, Shibayama W, Ohno H (2006) J. Mater Chem: in press
6. Kato Y, Watanabe M, Sanui K, and Ogata N (1990) Solid State Ionics 40/41: 632
7. Shin J-H, Henderson WA, Passerini S (2003) Electrochem Commun 5: 1016