



Short communication

Fire-retardant solid polymer electrolyte films prepared from oxetane derivative with dimethyl phosphate ester group

Ryo Shibutani, Hiromori Tsutsumi*

Applied Molecular Bioscience, Graduate School of Medicine, Yamaguchi University, 2-16-1, Tokiwa, Ube 755-8611, Japan

ARTICLE INFO

Article history:

Received 26 September 2011

Received in revised form 2 November 2011

Accepted 15 November 2011

Available online 25 November 2011

Keywords:

Poly(oxetane)

Fire retardant

Self-extinguishable polymer

Lithium battery

Solid polymer electrolyte

ABSTRACT

Fire-retardant polymer electrolytes are key materials for safer operation of lithium secondary batteries and other large-size batteries than the batteries with organic liquid electrolyte. Solid polymer electrolyte systems with fire-retardant polymer matrixes have been investigated in only few cases. We prepare an oxetane derivative with dimethyl phosphate ester group (DPOX). The cross-linked poly(oxetane) matrixes for solid polymer electrolytes are prepared from DPOX and oxetane-based cross-linker (DDOE). DDOE has two oxetane rings at both of the ends of oligo-ethylene oxide chain. Conductivities in the range of $10^{-5} \text{ S cm}^{-1}$ have been obtained for self-extinguishing, ion-conductive cross-linked poly(oxetane) matrix with DPOX and DDOE monomers. Polarization behavior of a lithium electrode in the cross-linked poly(oxetane)-based electrolyte films is also investigated. The polarization curves show some hysteresis character with potential steps, however, deposition and stripping of lithium on the lithium electrode are observed.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Improvements in safety of lithium-ion and lithium batteries are very important to construct large-sized secondary batteries for electric vehicles and load leveling systems. Large-sized batteries have large amounts of electrolyte and active materials, anode and cathode. Non-flammability of the electrolyte in the large-sized batteries is an important point for their safe operation. To decrease flammability of the electrolyte systems the fire-retardant reagents are added into them. Organic phosphorous compounds have been used as additives for their flame-retardant properties [1]. Some organic phosphorous compounds, tris(2,2,2-trifluoroethyl) phosphite [2], trimethyl phosphite [3], dimethyl methyl phosphonate [4,5], tributyl phosphate [6], triphenyl phosphate [6–8], tris(trifluoroethyl) phosphate [8], and cresyl diphenyl phosphate [9] were used as solvents or additives into the liquid electrolytes for lithium-ion and lithium batteries. Addition of the organic phosphorous compounds provides non-flammability of the electrolytes and affects battery performance, discharge capacity, life time, and so on. Some of them tend to decrease the overall efficiency of the battery systems.

Solid polymer electrolyte systems are promising candidates for construction of non-flammable batteries. Polymer is non-volatile and more stable thermally than normal organic solvents. Polymer

electrolyte systems with fire retardant property have been investigated about poly(acrylonitrile)-based gel systems [10–12] or poly(vinylidene fluoride-co-hexafluoropropylene)-based [13,14] gel electrolyte systems with organic phosphorus compounds, and poly(ethylene oxide)-based electrolyte system mixed with middle molecular weight organic phosphate compound [15]. Solid polymer electrolyte systems prepared from fire retardant polymer matrix have been very few cases as far as we know.

Fig. 1(a) shows the monomer structure, oxetane derivative with dimethyl phosphate group (DPOX). This molecule has two characteristic moieties. One is dimethyl phosphate group and another is oxetane ring. Its dimethyl phosphate group acts as a radical scavenger at the combustion reaction and a promoter of carbon char layers by dehydration reaction caused with phosphoric acid [1]. Oxetane ring structure provides us trimethylene oxide chains from ring-opening polymerization. The poly(trimethylene oxide) derivatives have flexible back bone and low glass transition temperature, like ethylene oxide-based polymer [16–22].

In this paper we report preparation of solvent-free cross-linked poly(oxetane)-based electrolyte films from photo-initiated polymerization of DPOX and DDOE monomer (in Fig. 1(b)), and their flammability and performance as solid polymer electrolytes, conductivity and polarization behavior of a lithium electrode.

2. Experimental

All reagents were used as received unless otherwise described. Cross-linking reagent, 1,9-bis(3-ethyl-3-oxetanyl)-2,5,

* Corresponding author. Tel.: +81 836 85 9282; fax: +81 836 85 9201.
E-mail address: tsutsumi@yamaguchi-u.ac.jp (H. Tsutsumi).

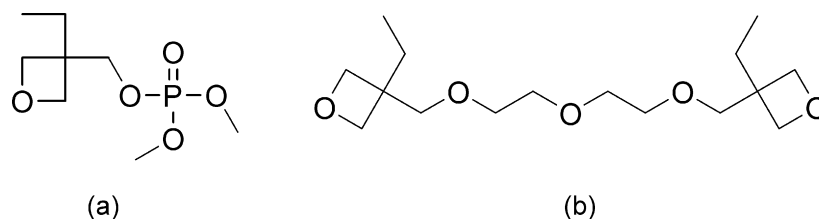


Fig. 1. Structures of oxetane derivatives, (a) DPOX and (b) DDOE (cross-linker).

8-trioxanonane (DDOE, Fig. 1(b)) was prepared as the reported route in our previous papers [18–20].

2.1. Preparation of monomer

Oxetane derivative, (DPOX, Fig. 1(a)) was prepared by coupling reaction between 3-ethyl-3-hydroxymethyloxetane (EHOX, Aldrich) and dimethylchlorophosphate (Aldrich). Typical preparation procedure of DPOX is as follows: EHOX (4.40 mL, 38.6 mmol) and *N*-methylimidazole (4.27 mL, 54.1 mmol, Tokyo Kasei) were dissolved into dichloromethane (50 mL) in the three-necked flask (200 mL) equipped with a reflux condenser and a dropping funnel. The dichloromethane solution (15 mL) with dimethylchlorophosphate (5 mL, 46.4 mmol) was added into the dropping funnel. The dichloromethane solution in the funnel was added into the EHOX solution, slowly, to prevent the violent reaction. After addition of all of the dimethylchlorophosphate solution, the mixture was stirred at room temperature (about 298 K) for 24 h. The reaction mixture was added into the ice-cooled ammonium chloride saturated aqueous solution. The mixture was washed with water (100 mL, 3 times) to remove the water-soluble byproducts and the starting reagents. Some amount of magnesium sulfate was added into the water-washed dichloromethane solution to remove water. The dichloromethane and unreacted materials in the dried solution were removed under reduced pressure (423 K, 133 Pa). The structure and purity (over 98%) of residue was checked by ^1H NMR and FTIR measurements. Yield: 7.1 g, 82%.

The structure of DPOX was confirmed by ^1H -NMR and FTIR measurements.

^1H NMR (CDCl_3 , ppm) 0.93 (3H, t, $J = 7.6$ Hz, CH_3CH_2-), 1.78 (2H, q, $J = 7.6$ Hz, CH_3CH_2-), 3.80 (6H, d, $J = 10.9$ Hz, $\text{CH}_3-\text{O}-\text{P}$), 4.19 (2H, d, $J = 5.3$ Hz, $\text{C}-\text{CH}_2-\text{O}-\text{P}$), 4.45 (4H, dd, $J = 19.7$, 5.9 Hz, $\text{O}-\text{CH}_2-\text{C}$ in oxetane ring).

FTIR (neat, cm^{-1}) 848 (oxetane ring's $\text{C}-\text{O}-\text{C}$), 1273 ($(\text{RO})_2\text{PO}$), 2863, 2961 (CH_2 , CH_3).

2.2. Preparation of cross-linked electrolyte films by using cationic photo-initiator

The electrolyte films were prepared by photo-initiating cationic polymerization. We used diphenyliodonium hexafluorophosphate (DPIHFP, Tokyo Kasei) as a cationic photo-initiator. Typical preparation procedure is as follows: the mixture of DPOX (0.1726 g, 0.76 mmol), DDOE (0.2480 g, 0.78 mmol), LiBF_4 (0.0729 g, 0.77 mmol), and DPIHFP (0.0196 g, 0.05 mmol) was stirred at room temperature for 2 h in the dark. The resulted homogeneous solution was pored into an aluminum foil dish and then irradiated for 2 h at room temperature with a high-pressure mercury lamp (250 W, average energy was 12.78 J cm^{-2}), (Optical Module X, USHIO). The resulted film was flexible and free-standing. Other electrolyte films were also prepared under similar procedure. The resulted electrolyte film is presented as $(\text{DPOX})_1(\text{DDOE})_1(\text{LiBF}_4)_1$ film. This means that the molar ratio of DPOX, DDOE, and LiBF_4 is 1:1:1. The electrolyte films containing other lithium salt,

lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) was also prepared under similar procedure.

2.3. Fire retardant test of samples

Fire retardant test of the electrolyte films was performed with a Bunsen gas burner as an ignition source. A sample film (about $3\text{--}5 \text{ mm}^2$) picked up with a pair of tweezers was set on the gas flame of the burner. The distance between sample film and the top of the flame of the gas burner was 2 cm. The period for the sample ignition (T_i) was recorded. After the sample ignition, the ignition source was removed and the flame on the sample was timed until it self-extinguished.

2.4. Measurements

Infrared spectra of samples were recorded with an FTIR spectrophotometer (IRPresatge-21, Shimadzu). ^1H -NMR spectra of the oxetane monomer were obtained on an NMR spectrophotometer (EX-270, JEOL). XRD patterns of the composites films were recorded with an X-ray diffraction meter (XD-D1, Shimadzu, $\text{CuK}\alpha$, $\lambda = 0.1542 \text{ nm}$). DSC measurements of the samples were performed with a differential scanning calorimeter (DSC5100S, Bruker AXS); heating rate was 10 K min^{-1} .

Conductivity of the prepared electrolyte films was measured by using an LCR meter. An electrolyte film was sandwiched with two stainless steel plates (13 mm in diameter). Conductivity of the electrolyte film was measured with an LCR meter (HIOKI 3532-80 chemical impedance meter, $100 \text{ mV}_{\text{p-p}}$, 10–100 kHz) under various temperature conditions from 293 K to 353 K.

Electrochemical characterization of the solid polymer electrolyte films was performed with polarization measurement of lithium electrode in the polymer electrolyte film. Detail cell configuration for electrochemical measurements was reported in our previous papers [21,22]. Electrochemical measurements were performed with a computer-controlled potentiogalvanostat (HZ-5000, Hokuto Denko) under Ar atmosphere (dew point was at 203 K) at 328 K.

3. Results and discussion

3.1. Fire retardant property of poly(oxetane)-based electrolyte films

Structure of the poly(oxetane)-based electrolyte films prepared from DPOX and DDOE was confirmed from FTIR spectra of the films. Disappearance of the peaks attributed to the oxetane structure was established, which indicates that the oxetane rings in the monomers are opened by the photo-initiator. The resulted electrolyte films were flexible and free-standing. The XRD patterns of the poly(oxetane)-based films prepared from DPOX and DDOE with and without lithium salts had very broad peaks. The results suggest that the poly(oxetane)-based films are amorphous and the polymer matrixes can dissolve the lithium salts in themselves. The glass

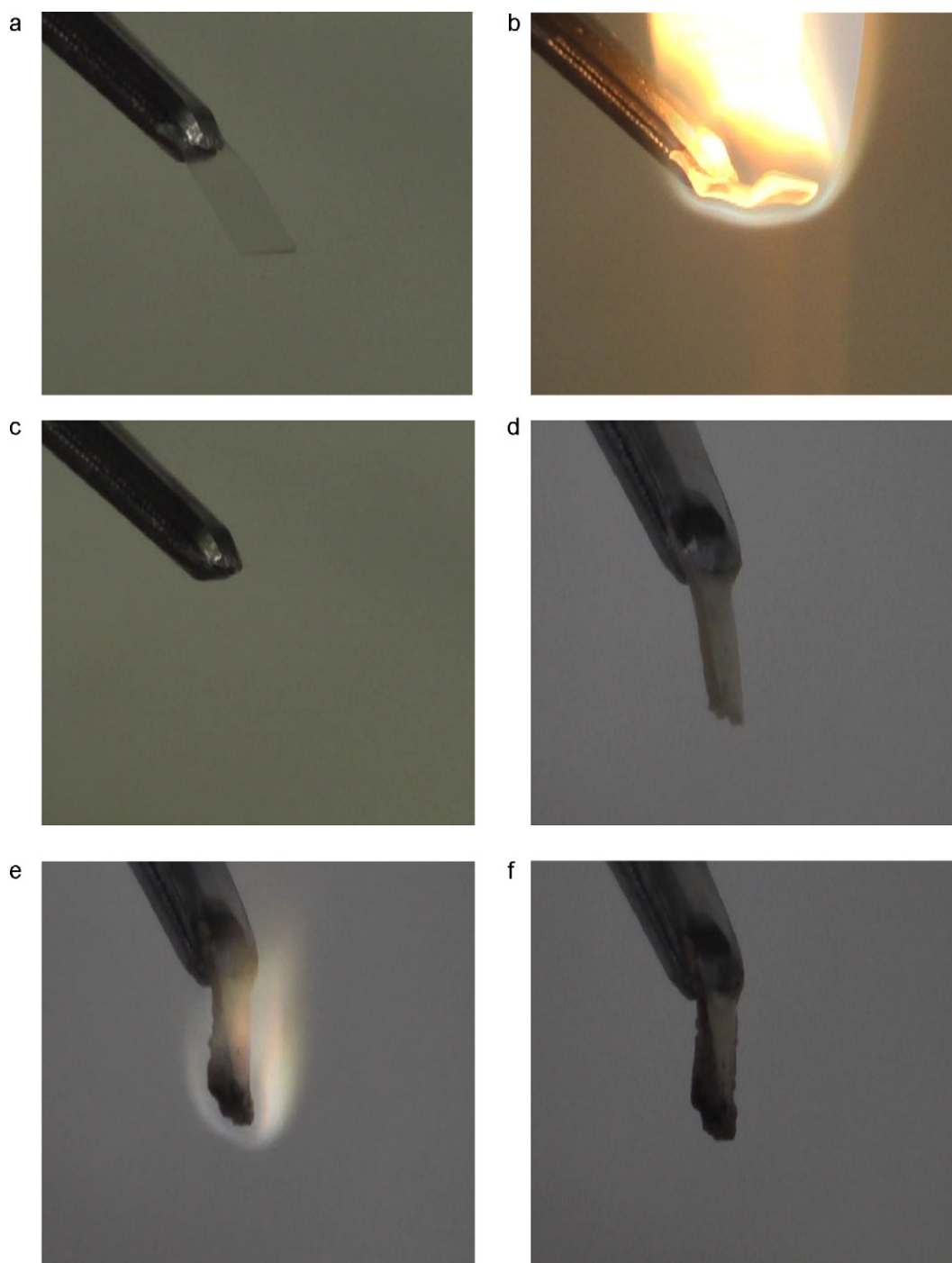


Fig. 2. Flammability test of samples, P(DDOE) matrix, (a) 0 s, (b) 4 s (ignition of sample) and (c) 10 s (burn out of sample), and (DPOX)1(DDOE)1(LiBF₄)1 electrolyte film, (d) 0 s, (e) 60 s (ignition of sample), and (f) self-extinguished sample film.

transition temperature (T_g) of the films is listed in Table 1. The T_g of (DPOX)1(DDOE)1 film (lithium salt-free film) is 248 K. Addition of LiBF₄ in the film elevated the T_g of the film to 277 K. Addition of LiTFSI did not increase the T_g of the matrix, considerably. Thus,

Table 1
Glass transition temperature of (DPOX)1(DDOE)1(X)*n* films.

X	<i>n</i>	T_g (K)
–	–	248
LiBF ₄	1	277
LiTFSI	1	256
LiTFSI	2	251

anion of lithium salt will affect the mobility of polymer chains in the oxetane-based matrix.

Flammability of the DPOX-based electrolyte film was compared with that of the DDOE-based film without DPOX, P(DDOE). The P(DDOE) film was prepared from DDOE (cross-linker) and DPIHFP (photo-initiator). Fig. 2(a) shows the P(DDOE) film on the flame of the gas burner (the ignition source). After 4 s later, the sample ignited as shown Fig. 2(b), $T_i = 4$ s. Removing the ignition source did not affect the combustion status of the P(DDOE) film. After 10 s later, the P(DDOE) film burned away as shown in Fig. 2(c). The results suggest that the P(DDOE) film is flammable and not self-extinguishable.

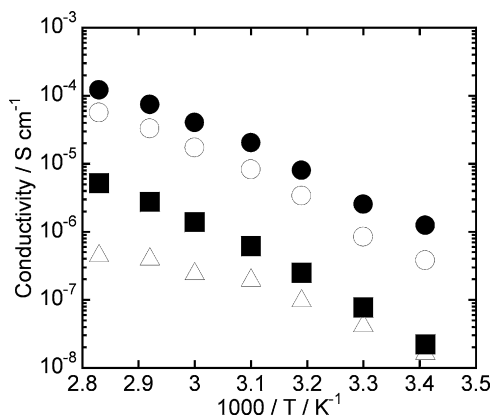


Fig. 3. Temperature dependence of conductivity of the cross-linked poly(oxetane)-based electrolyte films. Closed circle, (DPOX)1(DDOE)1(LiTFSl)2; open circle, (DPOX)1(DDOE)1(LiTFSl)1; closed square, (DPOX)1(DDOE)1(LiBF₄)1; and open triangle, (DPOX)1(DDOE)1 matrix.

The similar flammability test was applied to the (DPOX)1(DDOE)1(LiBF₄)1 film. Fig. 2(d) shows the (DPOX)1(DDOE)1(LiBF₄)1 film on the flame of the ignition source. After 60 s later, the sample ignited as shown Fig. 2(e), $T_i = 60$ s. After removing the ignition source the flame on the film was immediately disappeared as shown in Fig. 2(f). This suggested that the (DPOX)1(DDOE)1(LiBF₄)1 film is self-extinguishable. Char layer (containing carbonaceous compounds) was found on the surface of the self-extinguished film as shown in Fig. 2(f). The self-extinguishable property of the (DPOX)1(DDOE)1(LiBF₄)1 is induced by the char production as similar fire-retardant mechanism of the organic phosphorous compounds [1]. Other cross-linked DPOX- and DDOE-based electrolytes with LiTFSl and without lithium salt also show similar fire retardant behavior and self-extinguishable property. The DPOX-based films have fire-retardant and self-extinguishable properties based on the DPOX unit with the alkyl phosphate group.

3.2. Conductivity of poly(oxetane)-based electrolyte films

Temperature dependence of conductivity for poly(oxetane)-based electrolyte films are shown in Fig. 3. Conductivity of the lithium salt-free film (open triangle in Fig. 3) was $0.49 \mu\text{S cm}^{-1}$ at 353 K. The charge carriers in the lithium ion-free film are produced by decomposition of the photo-initiator, DPIHFP. The estimated charge carriers from DPIHFP and its photo-reacted products are PF₆ anion, diphenyliodonium cation, phenyliodonium cation, and so on [23,24]. Conductivity of the electrolyte films with lithium salt is one to three orders of magnitude higher than that of the lithium ion-free film. Conductivity at 353 K of the (DPOX)1(DDOE)1(LiX)_n was $5.15 \mu\text{S cm}^{-1}$ ($X = \text{BF}_4$, $n = 1$) and $56.1 \mu\text{S cm}^{-1}$ ($X = \text{TFSl}$, $n = 1$), and 0.122 mS cm^{-1} ($X = \text{TFSl}$, $n = 2$). The temperature dependence curves of conductivity for the electrolyte films are slightly convex. The curves are best fitted to an expression of the Eq. (1):

$$\sigma = AT^{-1/2} \exp \left[\frac{-B}{R(T - T_0)} \right] \quad (1)$$

where σ is conductivity, A is pre-exponential factor, which is proportional to the number of charge carriers, B is estimated activation energy for conduction, R is gas constant, T is absolute temperature, and T_0 is normally called the equilibrium glass-transition temperature [25,26]. T_0 is set for 50 K lower than T_g . Fig. 4 shows the VTF plots for the electrolyte films and the lithium salt-free film. All plots show the linear relationships. The estimated parameters, A and B , are listed in Table 2. The estimated activation energy of the lithium salt-free film is 7.14 kJ mol^{-1} (0.074 eV). The

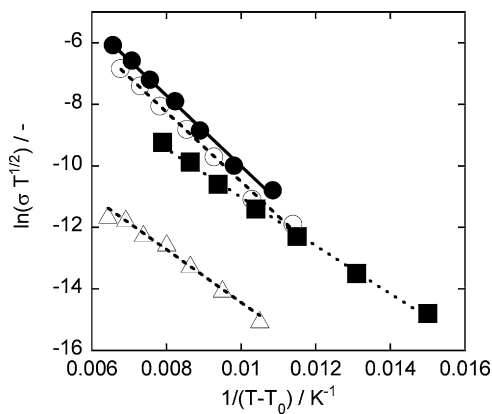


Fig. 4. VTF-plots of the cross-linked poly(oxetane)-based electrolyte films. Closed circle, (DPOX)1(DDOE)1(LiTFSl)2; open circle, (DPOX)1(DDOE)1(LiTFSl)1; closed square, (DPOX)1(DDOE)1(LiBF₄)1; and open triangle, (DPOX)1(DDOE)1 matrix.

A value of the film is $0.003 \text{ S cm}^{-1} \text{ K}^{1/2}$. The value is three orders of magnitudes smaller than that of the electrolyte films with LiTFSl salt. This indicates that the number of the charge carries in the lithium-ion free film is very low and the ions from the photo-initiator did not affect the conducting behavior of the DPOX and DDOE-based electrolyte films. The A value of the films with LiTFSl is larger than that with LiBF₄. This suggests that dissolution ability of LiTFSl is larger than LiBF₄. Higher glass transition temperature of the electrolyte film with LiBF₄ affects their lower conducting behaviors. The estimated activation energy of the DPOX-based electrolyte films is from 6.52 kJ mol^{-1} (0.068 eV) to 9.51 kJ mol^{-1} (0.099 eV). These values are similar to other systems' values; the PEO-based electrolytes with PC or EC as a plasticizer (0.058–0.082 eV) [27], PEG-LiClO₄ system with alumina nano-particles (0.09–0.12 eV) [28], PEO-LiCF₃SO₃ systems (0.090–0.125 eV) [29]. The conduction mechanism of the cross-linked DPOX- and DDOE-based electrolyte films is similar to those of the other electrolyte systems. Dissolution support groups in the cross-linked DPOX- and DDOE-based electrolyte systems are the oligo-ethylene oxide chains in the DDOE monomer, dimethyl phosphate group in the DPOX, and trimethylene oxide chain prepared from ring-opening polymerization of oxetane rings in DPOX and DDOE. The trimethylene oxide chains and oligo-ethylene oxide chains support the migration of ions in the matrix prepared from DPOX and DDOE.

3.3. Polarization behavior of lithium electrode in the electrolyte films with dimethyl phosphate ester group

Fig. 5 shows the polarization curves of a lithium electrode in the (DPOX)1(DDOE)1(LiTFSl)_n, ($n = 1$ or 2) electrolyte films at 328 K. The polarization behaviors indicated that deposition and stripping of lithium on the lithium electrode occurred in the poly(oxetane)-based electrolyte films [21,22]. However, the polarization curves of lithium electrode in the DPOX-based electrolyte film gave asymmetrical forms, which is fairly different from those observed in liquid electrolytes [30]. The cathodic limiting current of lithium in (DPOX)1(DDOE)1(LiTFSl)2 electrolyte was

Table 2
VTF parameters of (DPOX)1(DDOE)1(X)_n electrolyte films.^a

X	n	A (S cm ⁻¹ K ^{1/2})	B (kJ mol ⁻¹)	B (eV)
-	-	0.003	7.14	0.074
LiBF ₄	1	0.042	6.52	0.068
LiTFSl	1	2.21	9.39	0.097
LiTFSl	2	4.24	9.51	0.099

^a $T_0 = T_g - 50$.

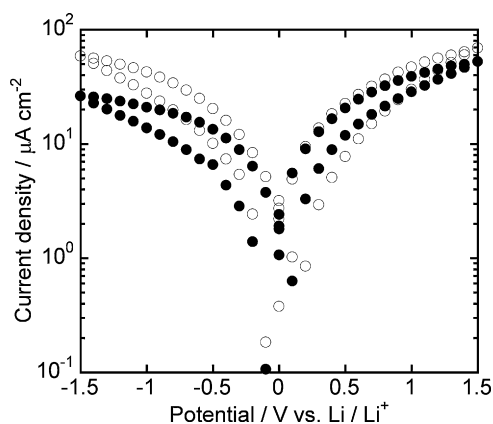


Fig. 5. Polarization curves of lithium electrode in the solid polymer electrolyte. Closed circle, (DPOX)1(DDOE)1(LiTFSI)2; open circle, (DPOX)1(DDOE)1(LiTFSI)1.

much lower than that for anodic polarization and for cathodic polarization in (DPOX)1(DDOE)1(LiTFSI)1 electrolyte film. The reason is not clear. Decrease in concentration of lithium ions at the lithium/(DPOX)1(DDOE)1(LiTFSI)2 interface under the highly cathodic polarized condition may be induced this phenomenon. Trapping of lithium ions by the phosphate groups in the side chains may affect mobility of lithium ions in the (DPOX)-based matrix.

4. Conclusion

We prepared the fire-retardant solid polymer electrolytes from the oxetane derivative with dimethyl phosphate ester group (DPOX). The fire retardant and self-extinguishable properties of the DPOX-based electrolyte films are induced from the alkyl phosphate structure as similar fire-retardant mechanism by organic phosphate compounds, which form char layer on the surface of the materials. Conductivity of the DPOX-based electrolyte films is in the range from $5.15 \mu\text{S cm}^{-1}$ to 0.122 mS cm^{-1} at 353 K. Temperature dependence of conductivity is VTF-type one. The estimated activation energy of conduction is in the range from 6.52 kJ mol^{-1} (0.068 eV) to 9.51 kJ mol^{-1} (0.099 eV). Polarization behavior of lithium electrode in the DPOX-based electrolyte shows asymmetrical forms, which is fairly different from those observed in liquid electrolytes. Current hysteresis, especially, at cathodic polarization is also observed.

Acknowledgements

This work was partially financial supported by Grant-in-Aid for Scientific Research (C), KAKENHI (21560883) and Electric Technology Research Foundation of Chugoku.

References

- [1] F. Laoutid, L. Bonnaud, M. Alexandre, J.M. Lopez-Cuesta, P. Dubois, *Materials Science and Engineering R: Reports* 63 (2009) 100–125.
- [2] S.S. Zhang, K. Xu, T.R. Jow, *Journal of Power Sources* 113 (2003) 166–172.
- [3] X.L. Yao, S. Xie, C.H. Chen, Q.S. Wang, J.H. Sun, Y.L. Li, S.X. Lu, *Journal of Power Sources* 144 (2005) 170–175.
- [4] J.K. Feng, X.P. Ai, Y.L. Cao, H.X. Yang, *Journal of Power Sources* 177 (2008) 194–198.
- [5] H.F. Xiang, H.Y. Xu, Z.Z. Wang, C.H. Chen, *Journal of Power Sources* 173 (2007) 562–564.
- [6] Y.E. Hyung, D.R. Vissers, K. Amine, *Journal of Power Sources* 119–121 (2003) 383–387.
- [7] E.G. Shim, T.H. Nam, J.G. Kim, H.S. Kim, S.I. Moon, *Journal of Power Sources* 172 (2007) 919–924.
- [8] D.H. Doughty, E.P. Roth, C.C. Crafts, G. Nagasubramanian, G. Henriksen, K. Amine, *Journal of Power Sources* 146 (2005) 116–120.
- [9] Q. Wang, P. Ping, J. Sun, C. Chen, *Journal of Power Sources* 196 (2011) 5960–5965.
- [10] H. Akashi, K. Sekai, K.I. Tanaka, *Electrochimica Acta* 43 (1998) 1193–1197.
- [11] H. Akashi, K.I. Tanaka, K. Sekai, *Journal of Power Sources* 104 (2002) 241–247.
- [12] H. Akashi, K.I. Tanaka, K. Sekai, *Journal of the Electrochemical Society* 145 (1998) 881–887.
- [13] B.S. Lalia, T. Fujita, N. Yoshimoto, M. Egashira, M. Morita, *Journal of Power Sources* 186 (2009) 211–215.
- [14] M. Morita, Y. Niida, N. Yoshimoto, K. Adachi, *Journal of Power Sources* 146 (2005) 427–430.
- [15] Y. Li, H. Zhan, L. Wu, Z. Li, Y. Zhou, *Solid State Ionics* 177 (2006) 1179–1183.
- [16] J.B. Kerr, G. Liu, L.A. Curtiss, P.C. Redfern, *Electrochimica Acta* 48 (2003) 2305–2309.
- [17] G. Liu, C.L. Reeder, X. Sun, J.B. Kerr, *Solid State Ionics* 175 (2004) 781–783.
- [18] Y. Miwa, H. Tsutsumi, T. Oishi, *Polymer Journal* 33 (2001) 568–574.
- [19] Y. Miwa, H. Tsutsumi, T. Oishi, *Polymer Journal* 33 (2001) 927–933.
- [20] Y. Miwa, H. Tsutsumi, T. Oishi, *Electrochemistry* 70 (2002) 264–269.
- [21] Y. Shintani, H. Tsutsumi, *Journal of Power Sources* 195 (2010) 2863–2869.
- [22] Y. Shintani, H. Tsutsumi, *Electrochemistry* 78 (2010) 387–389.
- [23] J.V. Crivello, *Polymer* 46 (2005) 12109–12117.
- [24] J.V. Crivello, B. Falk, M.R. Zonca, *Journal of Polymer Science Part A: Polymer Chemistry* 42 (2004) 1630–1646.
- [25] P.G. Bruce, F.M. Gray, 6. Polymer electrolytes II: physical principles, in: P.G. Bruce (Ed.), *Solid State Electrochemistry*, Cambridge University Press, 1995, pp. 119–162.
- [26] M.A. Ratner, P. Johansson, D.F. Shriver, *MRS Bulletin* 25 (2000) 31–37.
- [27] Y.-J. Wang, Y. Pan, D. Kim, *Polymer International* 56 (2007) 381–388.
- [28] T.J. Singh, S.V. Bhat, *Journal of Power Sources* 129 (2004) 280–287.
- [29] N.K. Karan, D.K. Pradhan, R. Thomas, B. Natesan, R.S. Katiyar, *Solid State Ionics* 179 (2008) 689–696.
- [30] Y. Matsuda, M. Morita, H. Tsutsumi, *Journal of Power Sources* 44 (1993) 439–443.