



Short communication

Enhanced ionic conductivity of intrinsic solid polymer electrolytes using multi-armed oligo(ethylene oxide) plasticizers

Joung-In Lee, Dong Wook Kim, Changjin Lee, Yongku Kang*

Advanced Materials Division, Korea Research Institute of Chemical Technology, P.O. Box 107 Yuseong, 305-600 Daejeon, Republic of Korea

ARTICLE INFO

Article history:

Received 20 October 2009

Received in revised form

24 December 2009

Accepted 16 February 2010

Available online 20 February 2010

Keywords:

Solid polymer electrolytes

Multi-armed plasticizers

Ionic conductivity

Lithium ion batteries

ABSTRACT

In this work, we report on star-shaped plasticizers with the various chain lengths of multi-armed oligo(ethylene oxide) in order to prevent the plasticizers from crystallizing and eventually to enhance the ionic conductivity at low temperature. The multi-armed plasticizers are compared with the linear ones in terms of the ionic conductivity of the polymer electrolytes using them. The ionic conductivity of the polymer electrolytes using the linear plasticizer abruptly decreases below 0 °C, while the temperature dependence of the ionic conductivity of the polymer electrolytes based on the multi-armed plasticizers shows a typical Vogel–Tamman–Fülcher (VTF) relationship in the temperature range from –30 to 100 °C. Such enhanced ionic conductivity at low temperature is because the multi-armed plasticizers are not crystallizing due to the branches or the multi-arms structure. The multi-armed plasticizers are found to be electrochemically stable up to 5.2 V by cyclic voltammetry analysis, which means that they are electrochemically stable enough for the application in the lithium ion batteries.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Since the first report on ionic conductivities of poly(ethylene oxide) (PEO) containing alkali metal salts by Wright et al. [1], there have been a lot of research works to improve the ionic conductivity of the solid polymer electrolytes [2–7]. The solid polymer electrolytes have several advantages over liquid electrolytes or gel-type polymer electrolytes such as better stability especially in high temperature, high specific energy and power, and high flexibility in the cell design. Hence they are considered a promising electrolyte for high energy-density secondary lithium batteries. However, the low ionic conductivity is a main limitation for the solid polymer electrolytes to be commercialized for the batteries.

Low conductivity at the ambient temperature is caused by crystallinity of the PEO-based solid polymer electrolytes. Different approaches have been studied to prevent crystallization of the PEO derivatives. For example, comb-branched polymers [8,9] and chemically cross-linked PEO networks [10–17] have been evaluated for solid polymer electrolytes. In a recent paper, we reported on a cross-linked solid polymer electrolytes with increased ionic conductivity by using the oligo(ethylene oxide) as plasticizer [18]. In the study, we have achieved high ionic conductivity of up to $7.8 \times 10^{-4} \text{ S cm}^{-1}$ at 30 °C by introducing a low molecular weight poly(ethylene oxide)dimethyl ether (PEGDME) as a plas-

ticizer. However, the conductivity decreased drastically at low temperature because the linear plasticizer (PEGDME) was freezing around –10 °C.

In this work, to prevent the plasticizers from freezing and eventually to enhance the ionic conductivity at low temperature, we have introduced star-shaped plasticizers which had the various chain length of multi-armed oligo(ethylene oxide) as shown in Scheme 1a. We compared the resulting cross-linked solid polymer electrolytes based on the multi-armed plasticizers with those containing the linear plasticizers (Scheme 1b) in terms of ionic conductivity and electrochemical stability.

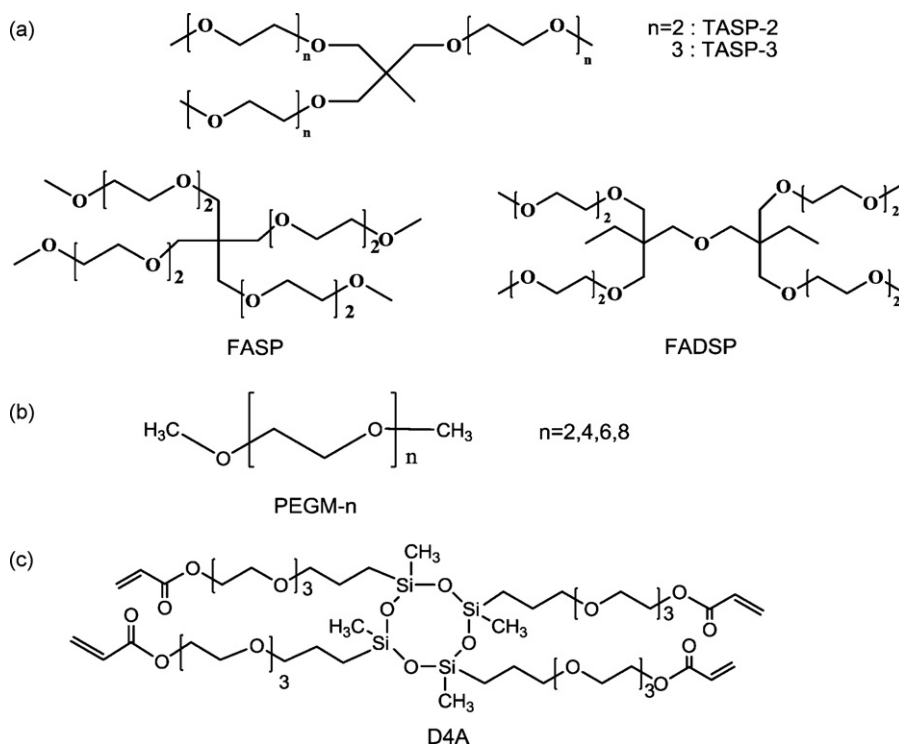
2. Experimental

2.1. Materials

Poly(ethylene glycol)dimethyl ether (PEGDME, average $M_w = 500$), LiCF_3SO_3 and benzoyl peroxide (BPO), 2,4,6,8-tetramethyl cyclotetrasiloxane, tris-(hydroxymethyl) ethane, di(trimethylol propane), and pentaerythritol tetrabromide were obtained from Aldrich Chem. Co. and used as received.

The star-shaped siloxane acrylate cross-linker (D4A, Scheme 1c) was synthesized according to the previous paper [18]. The linear plasticizers (PEGM- n , $n = 2, 4, 6, 8$, Scheme 1b) were prepared by the synthetic methods similar to the previously reported literatures [19]. The multi-armed plasticizers (TASP-2, TASP-3, FASP, and FADSP) were synthesized as described in Scheme 2 and the detailed procedure is as follows.

* Corresponding author. Tel.: +82 42 860 7207; fax: +82 42 860 7200.
E-mail address: ykang@kriict.re.kr (Y. Kang).



Scheme 1. Chemical structures of (a) the multi-armed plasticizers, (b) the linear plasticizers, and (c) the cross-linker synthesized in this work.

2.1.1. Synthesis of 1,3-bis-[2-(2-methoxyethoxy)ethoxy]-2-[2-(2-methoxyethoxy)ethoxymethyl]-2-methyl propane (TASP-2)

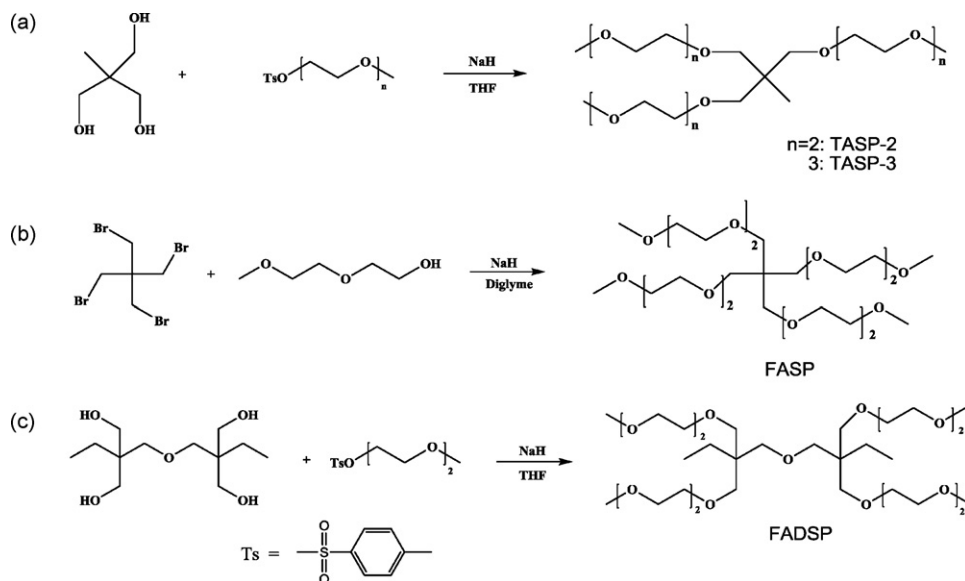
Sodium hydride (3.59 g, 0.14 mol) and tris(hydroxymethyl) ethane (3.0 g, 0.024 mol) were dissolved in anhydrous tetrahydrofuran (80 ml) under nitrogen flow. Diethylene glycol monotosylate (27.36 g, 0.09 mol) was added dropwise and the resulting solution was heated to reflux for 16 h. After the reaction was completed, precipitates were filtered out. The residue was neutralized by adding 2 wt% hydrochloric acid solution and then extracted three times with dichloromethane. The organic layer was dried over anhydrous magnesium sulfate and was concentrated by evaporating the solvent, resulting in 7.2 g of TASP-2 (67%). $^1\text{H NMR}$ (300 MHz, CDCl_3 ,

ppm): δ 0.93 (s, 3H), 3.31 (s, 6H), 3.38 (s, 9H), 3.52–3.6 (m, 24H).

TASP-3 was also prepared by the similar way with TASP-2 using triethylene glycol monotosylate with 66% of yield. $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 0.93 (s, 3H), 3.31 (s, 6H), 3.38 (s, 9H), 3.52–3.72 (m, 36H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ 74.19, 72.27, 71.35, 71.01, 70.95, 70.85, 70.75, 59.33, 41.32, 17.64.

2.1.2. Synthesis of 1,3-bis(2-(2-methoxyethoxy)ethoxy)-2,2-bis((2-(2-methoxyethoxy)ethoxy)methyl) propane (FASP)

Sodium hydride (2.78 g, 0.116 mol) and diethylene glycol monomethyl ether (12.39 g, 0.103 mol) were dissolved in diglyme (60 ml) under nitrogen flow. Pentaerythritol tetrabromide (5.0 g,



Scheme 2. Synthetic routes of the multi-armed plasticizers. (a) TASP, (b) FASP, and (c) FADSP.

0.012 mol) was added dropwise into the solution and heated to reflux overnight. After the reaction was completed and precipitates were filtered out, the solution was neutralized by adding 2 wt% hydrochloric acid solution. The mixture was extracted three times with dichloromethane and then the organic layer was dried over anhydrous magnesium sulfate. The resulting solution was concentrated by evaporating the solvent, producing 0.7 g of FASP (10%). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 3.38 (s, 12H), 3.43 (s, 8H), 3.51–3.57 (m, 16H), 3.59–3.65 (m, 16H). ^{13}C NMR (75 MHz, CDCl_3 , ppm): δ 72.36, 71.39, 70.85, 70.41, 59.37, 45.82.

2.1.3. Synthesis of 1,3-bis(2-(2-methoxyethoxy)ethoxy)-2,2-bis(2-(2-methoxyethoxy)ethoxy)methyl propane (FADSP)

Sodium hydride (2.3 g, 0.096 mol) and di(trimethylol propane) (3.0 g, 0.012 mol) were dissolved in anhydrous tetrahydrofuran (60 ml) under nitrogen flow. Diethylene glycol monotosylate (16.41 g, 0.060 mol) was added dropwise into the solution and heated to reflux overnight. After the reaction was completed and precipitates were filtered out, the solution was neutralized by adding 2 wt% hydrochloric acid solution. The mixture was extracted three times with dichloromethane and then the organic layer was dried over anhydrous magnesium sulfate. The resulting solution was concentrated by evaporating the solvent, producing 6.24 g of FADSP (80%). ^1H NMR (300 MHz, CDCl_3 , ppm): δ 0.8–0.85 (t, 6H), 1.37 (d, 4H), 3.2 (s, 4H), 3.3 (s, 8H), 3.38 (s, 12H), 3.5–3.66 (m, 32H).

2.2. Preparation of the solid polymer electrolytes

The solid polymer electrolytes were prepared by cross-linking the homogeneous precursor solution which was composed of cross-linker (D4A, 30 wt%), plasticizers (70 wt%), lithium salt (LiCF_3SO_3), and initiator (BPO). The concentration of lithium salt was adjusted such that the $[\text{EO}]/[\text{Li}]$ molar ratio of the polymer electrolyte was 15. The precursor solution was injected in gap (100 μm) between the substrates, such as ITO glass, lithium and nickel. All samples were prepared in a glove box under argon atmosphere, and they were thermally cross-linked in a oven at 100 °C for 20 min.

2.3. Instrumentation

The melting point (T_m) and the glass transition temperature (T_g) of the materials were determined by using a differential scanning calorimeter (DSC) (TA Instruments, model universal V2.5H) under the nitrogen flow. The conductivity measurement was carried out by coating the polymer electrolytes onto the pre-patterned ITO cell [20]. The ac impedance of the conductivity cell was measured by an impedance analyzer (Zahner Elektrik model IM6). 10 mV ac amplitude was applied with a frequency sweep from 1 Hz to 1 MHz. The temperature of the sample was controlled by a programmable oven. The electrochemical stability window of the solid polymer electrolyte was measured by cyclic voltammetry (EG&G model 270 potentiostat) at 30 °C. A nickel plate (Aldrich, 0.125 mm thick, >99.9%) was used for a working electrode and a lithium metal foil (FMC Co.) for a counter and reference electrode. These test cells were assembled by sandwiching the solid polymer electrolyte between the two electrodes.

3. Results and discussion

The cross-linked solid polymer electrolytes were prepared by in situ radical initiated cross-linking reaction of a homogeneous precursor solution of siloxane cross-linker (D4A, 30 wt%), plasticizers (70 wt%), lithium salt (LiCF_3SO_3), and thermal radical initiator (BPO). Self-supporting films could be obtained by addition of the

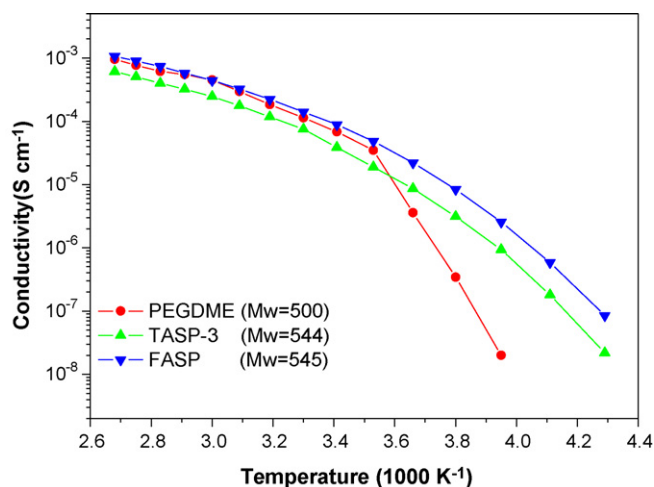


Fig. 1. Comparison of the ionic conductivities between the solid polymer electrolytes based on the linear plasticizer and the multi-armed ones with a similar molecular weight.

plasticizers up to 70 wt% into the polymer electrolytes. Ionic conductivities of the cross-linked polymer electrolytes were compared between the linear plasticizer (PEGDME) and multi-armed ones (TASP-3, FASP) with a similar molecular weight as shown in Fig. 1. The linear plasticizer achieved a little high or similar ionic conductivity when compared with the multi-armed ones at and above the room temperature. However, the ionic conductivity of the polymer electrolytes based on PEGDME suddenly decreased below 0 °C, while the temperature dependence of the ionic conductivity of the polymer electrolytes using multi-armed plasticizers showed a typical Vogel–Tamman–Fülcher (VTF) relationship.

The abrupt decrease in the ionic conductivity could be explained by the thermodynamic nature of the linear plasticizer PEGDME. Fig. 2 shows T_m and T_g of the linear plasticizer as well as the multi-armed ones measured by DSC analysis. Three plasticizers with a similar molecular weight exhibited a similar T_g at about -70 °C. The linear plasticizer showed a large endothermic peak around 0 °C, indicating that the plasticizer became crystalline below the temperature. Such crystallization below 0 °C should be the reason why the polymer electrolytes containing the linear plasticizer exhibited a very poor ionic conductivity at low temperature. It has been commonly known that the crystalline domain hinders or blocks the lithium ion transport in the solid polymer electrolytes [21]. In

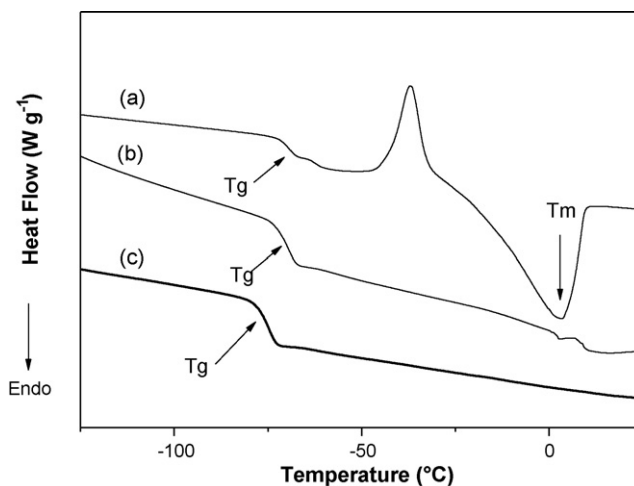


Fig. 2. DSC thermograms of solid polymer electrolytes plasticized with (a) PEGDME, (b) TASP-3, and (c) FASP. The arrows are pointing T_g or T_m .

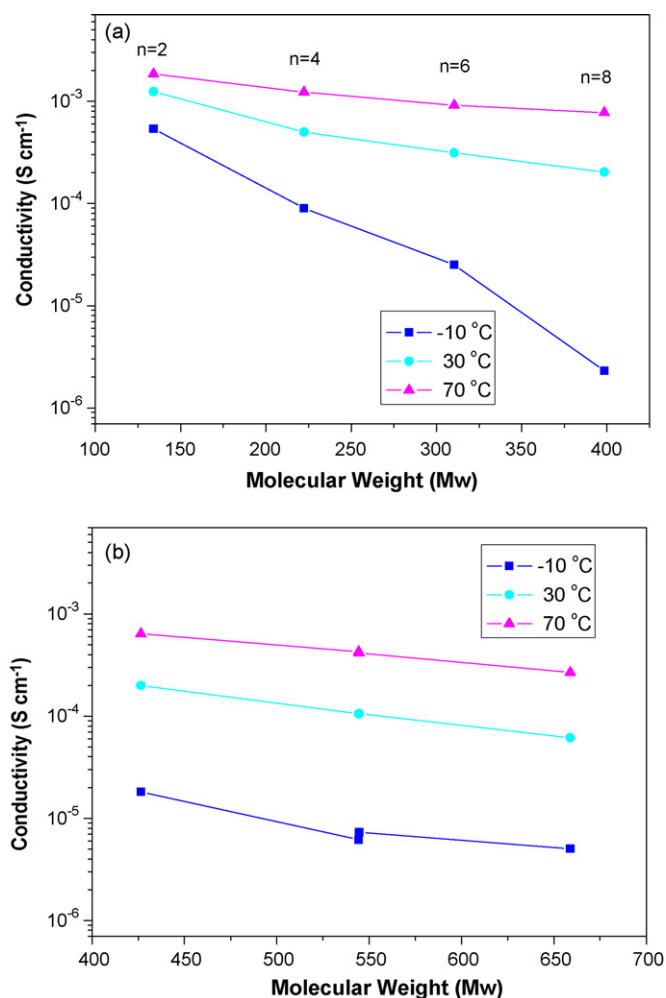


Fig. 3. Effect of the molecular weight of the plasticizers on the ionic conductivity of the solid polymer electrolytes. (a) The linear plasticizers, PEGM- n ($n = 2, 4, 6, 8$) and (b) the multi-armed plasticizers (TASP-2 (Mw = 427), TASP-3 (Mw = 544), FASP (Mw = 545), FADSP (Mw = 659)).

contrast, the multi-armed plasticizers possessed no freezing point because the multi-arms or branches prevented the plasticizers from crystallizing.

Another advantage of the multi-armed plasticizers over the linear ones could be observed in Fig. 3, which shows the effect of the molecular weight of the plasticizers on the ionic conductivity. We have synthesized several linear plasticizers with a different molecular weight in the range of 100–400. For long-term stability, the high molecular weight plasticizers are preferred in the polymer electrolytes although they lead to a lower ionic conductivity. Fig. 3(a) shows clearly such tendency that the ionic conductivity of the polymer electrolytes is greatly decreasing especially at low temperature ($-10\text{ }^{\circ}\text{C}$) with increase of the molecular weight of the linear plasticizers. However, it is surprising that in case of the multi-armed plasticizers the ionic conductivity of the polymer electrolytes did not decrease too much with the increase of the molecular weight as shown in Fig. 3(b).

Such different effect of the plasticizers' molecular weight on the ionic conductivity could be explained by the T_g variation with the molecular weight. The glass transition temperature is greatly affecting the lithium ion transport. The lower the T_g goes, the higher the ionic conductivity becomes. The linear plasticizers exhibited a higher T_g as their molecular weight became larger as shown in Fig. 4(a). This explains why the ionic conductivity of the polymer electrolytes was decreasing greatly especially at low temperature

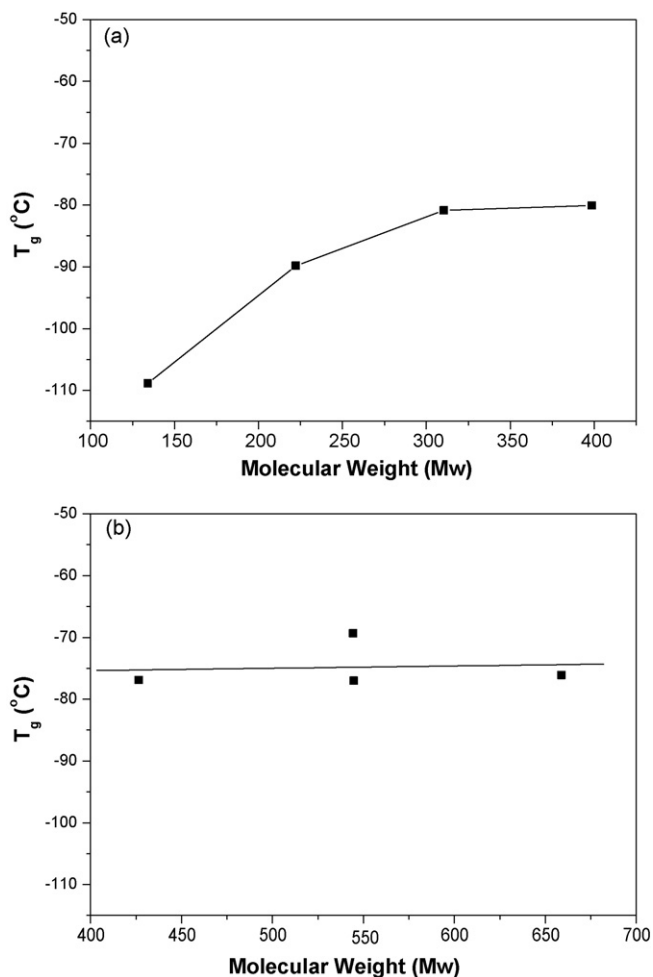


Fig. 4. Effect of the molecular weight of the plasticizers on T_g of the solid polymer electrolytes. (a) The linear plasticizers, PEGM- n ($n = 2, 4, 6, 8$) and (b) the multi-armed plasticizers (TASP-2 (Mw = 427), TASP-3 (Mw = 544), FASP (Mw = 545), FADSP (Mw = 659)).

($-10\text{ }^{\circ}\text{C}$) with increase of the molecular weight of the linear plasticizers. In case of the multi-armed plasticizers as shown in Fig. 4(b), the T_g remains almost same irrespective of the molecular weight. Hence the ionic conductivities of the polymer electrolytes exhibited little change with the increase of the molecular weight of the multi-armed plasticizers.

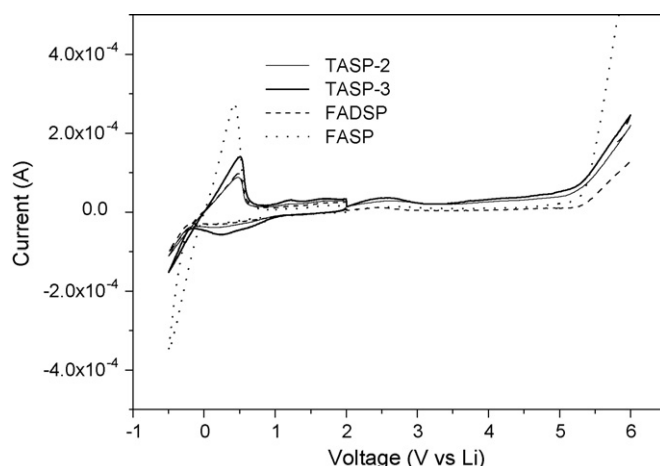


Fig. 5. Cyclic voltammetry plots of the multi-armed plasticizers.

Fig. 5 shows the cyclic voltammograms of the polymer electrolytes using the several multi-armed plasticizers. Oxidative degradation of the polymer electrolyte started around 5.2 V at all the solid polymer electrolytes with the plasticizers, which means that they are electrochemically stable enough for the application in the lithium ion batteries. Even though the molecular weight and the structure were different, all the plasticizers showed not much different electrochemical property of the resulting solid polymer electrolyte. When compared with our previous result [18], it was found that the electrochemical stability seemed almost similar between the linear and multi-armed plasticizers.

4. Conclusions

In this work, we have introduced the multi-armed plasticizers into the solid polymer electrolyte in order to prevent the plasticizers from freezing and eventually to enhance the ionic conductivity at low temperature. The experimental results showed that multi-armed plasticizers allowed for the solid polymer electrolytes to have much better ionic conductivity at low temperature than the linear plasticizers, which became crystalline below 0 °C. The multi-armed plasticizers were electrochemically stable up to 5.2 V. The experimental results indicate that the multi-armed plasticizers are promising additives to enhance the ionic conductivity at low temperature for lithium polymer batteries.

Acknowledgements

This research was supported by the research program (KK-0902-B0) of Korea Research Council for Industrial Science & Technology.

References

- [1] (a) D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589;
(b) P.V. Wright, *Br. Polym. J.* 7 (1975) 319.
- [2] M.B. Armand, J.M. Chabagno, M.J. Duclot, *Fast Ion Transport in Solid*, Elsevier, New York, 1979.
- [3] R.C. Agrawal, G.P. Pandey, *J. Phys. D: Appl. Phys.* 41 (2008) 223001.
- [4] (a) Y. Takeda, N. Imanishi, O. Yamamoto, *Electrochemistry* 77 (2009) 784;
(b) T. Niitani, M. Amaike, H. Nakano, K. Dokko, K. Kanamura, *J. Electrochem. Soc.* 156 (2009) A577.
- [5] F. Kaneko, S. Wada, M. Nakayama, M. Wakihara, J. Koki, S. Kuroki, *Adv. Funct. Mater.* 19 (2009) 918.
- [6] T.M.W.J. Bandara, B.-E. Mellander, I. Albinsson, M.A.K.L. Dissanayake, *Solid State Ionics* 80 (2009) 362.
- [7] (a) Y. Kang, Y.-H. Seo, D.W. Kim, C. Lee, *Macromol. Res.* 12 (2004) 431;
(b) D.S. Kim, K.H. Shin, H.B. Park, Y.M. Lee, *Macromol. Res.* 12 (2004) 413.
- [8] X.G. Sun, C.L. Reeder, J.B. Kerr, *Macromolecules* 37 (2004) 2219.
- [9] J.M.G. Cowie, *Polym. Int.* 47 (1998) 20.
- [10] Z. Ying, N. Costantini, M. Mierzwa, T. Pakula, D. Neugebauer, K. Matyjaszewski, *Polymer* 45 (2004) 6333.
- [11] Z. Wen, T. Itoh, T. Uno, M. Kubo, T. Wen, O. Yamamoto, *Solid State Ionics* 175 (2004) 739.
- [12] C.L. Cheng, C.C. Wan, Y.Y. Wang, *J. Power Sources* 134 (2004) 202.
- [13] (a) Y.M. Lee, D.-H. Ko, J.Y. Lee, J.-K. Park, *Electrochim. Acta* 52 (2006) 1582;
(b) J.Y. Lee, D.-H. Ko, Y.M. Lee, W.-H. Seol, J.-K. Park, *J. Power Sources* 174 (2007) 603.
- [14] D.M. Tigelaar, M.A.B. Meador, J.D. Kinder, W.R. Bennett, *Macromolecules* 39 (2006) 120.
- [15] T. Itoh, S. Gotoh, S. Horii, S. Hashimoto, T. Uno, M. Kubo, T. Fujinami, O. Yamamoto, *J. Power Sources* 146 (2005) 371.
- [16] R. Uchiyama, K. Kusagawa, K. Hanai, N. Imanishi, A. Hirano, Y. Takeda, *Solid State Ionics* 180 (2009) 205.
- [17] C.-C. Liao, H.-Y. Wu, D. Saikia, Y.-C. Pan, Y.-K. Chen, G.T.K. Fey, H.-M. Kao, *Macromolecules* 41 (2008) 8956.
- [18] Y. Kang, J. Lee, J.-I. Lee, C. Lee, *J. Power Sources* 165 (2007) 92.
- [19] (a) Y. Matoba, S. Matsui, M. Tabuchi, T. Sakai, *J. Power Sources* 137 (2004) 284;
(b) K. Miura, M. Yanagida, H. Higobashi, T. Endo, *Eur. Patent No.* EP-839487 (1998).;
(c) K. Miura, S. Shoji, T. Sakashita, Y. Matoba, *PCT Int. No.* WO-9807772 (1998).
- [20] (a) Y. Kang, H.J. Kim, E. Kim, B. Oh, J.H. Cho, *J. Power Sources* 92 (2001) 255;
(b) Y. Kang, H.J. Kim, E. Kim, B. Oh, J.H. Cho, *Proc. Electrochem. Soc.* 25–99 (1999) 534.
- [21] (a) H.R. Allcock, S.E. Kuharick, C.S. Reed, M.E. Napierala, *Macromolecules* 29 (1996) 3384;
(b) A. Nishimoto, K. Agehara, N. Furuya, T. Watanabe, M. Watanabe, *Macromolecules* 32 (1999) 1541.