New Class of Single-Ion-Conducting Solid Polymer Electrolytes Derived from Polyphenols

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Solid polymer electrolytes (SPEs) continue to be the subject of intense research due to their potential applications in rechargeable lithium batteries, specific ion sensors, electrochromic displays, and other electrochemical devices.[1−9] However, the optimization of key parameters such as ionic conductivity, mechanical strength, and electrochemical stability is necessary for SPEs to be suitable for practical lithium batteries. In recent decades, a large number of studies have focused on incorporating biionic lithium salts, such as lithium bis(trifluoromethanesulfonyl)imide and lithium trifluoromethanesulfonate, into a variety of polymer hosts.[1,9] However, relatively few studies have been performed on SPEs derived from single-ion-conducting electrolytes, probably due to low conductivities and complicated syntheses.[10,11] To our knowledge, no reports have appeared where single-ion conductors are blended with high molecular weight poly(ethylene oxide) (PEO) to improve conductivity, although similar studies have been performed with Nafion (single-ion conductor) to improve protonic conductivity.[12]

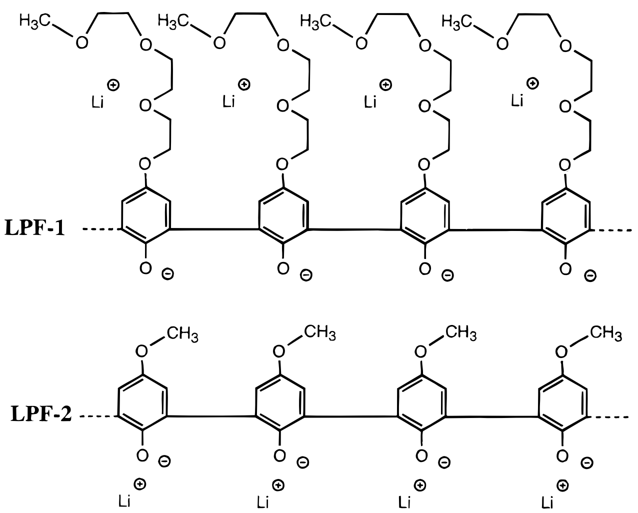

Figure 1. Structures of lithium polyphenolates.

Single-ion conductors have advantages over typical biion-based SPEs. During discharge in biion salt-based SPEs, mobile anions and cations migrate toward the oppositely charged electrodes, thereby polarizing the electrolyte and increasing its resistivity. Recharging the cell then requires more energy, time, and a greater electrochemical potential. This “cell polarization” problem is unique to biionic salt-based SPEs.[13] This problem can be solved by using single-ion based conductors in which the anions are immobilized. In this communication, we report preliminary studies utilizing lithium polyphenolates as a new class of lithium ion source, which, when blended with high molecular weight PEO, give a new type of SPEs that exhibit high ionic conductivities.

The structures of the two lithium polyphenolates, **LPF-1** and **LPF-2**, are shown in Figure 1. The former contains pendant oligoether groups (OEG), whereas the latter has pendant methoxy groups. The difference in lengths of pendant groups was selected to observe differences in conducting behavior of the two polymers in a PEO host. The monomer for **LPF-1** was synthesized in a single step,[14] while the monomer for **LPF-2** is commercially available.

As shown in Scheme 1, the new phenol monomer **1** was prepared by reaction between hydroquinone and a previously reported OEG-tosylate, OEG-OTs.[15] The best reaction conditions were established after a thorough

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(1) (a) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH: New York, 1991. (b) *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: New York, 1993. (c) Alamgir, M.; Abraham, K. M. In *Lithium Batteries: New Materials, Developments and Perspectives*; Pistoia, G., Ed.; Elsevier: Amsterdam, 1994; Vol. 5. (d) *Handbook of Batteries*, 2nd ed.; Linden, D., Ed.; McGraw-Hill: New York, 1995.

(2) Armand, M. *Solid State Ionics* **1994**, *69*, 309.

(3) Abraham, K. M.; Alamgir, M. *Solid State Ionics* **1994**, *70/71*, 203.

(4) Gores, H. J.; Barthel, J. M. G. *Pure Appl. Chem.* **1995**, *67*, 919.

(5) Appetecchi, G. B.; Dautzenberg, G.; Scrosati, B. *J. Electrochem. Soc.* **1996**, *143*, 6.

(6) Chen-Yang, Y. W.; Hwang, J. J.; Chang, F. H. *Macromolecules* **1997**, *30*, 3825.

(7) Abraham, K. M.; Jiang, Z.; Carroll, B. *Chem. Mater.* **1997**, *9*, 1978.

(8) Wu, P.; Holm, S. R.; Duong, A. T.; Dunn, B.; Kaner, R. B. *Chem. Mater.* **1997**, *9*, 1004.

(9) (a) Armand, M.; Gorecki, W.; Andreani, R. In *Second International Symposium on Polymer Electrolytes*; Scrosati, B., Ed.; Elsevier Applied Science: London, 1990; p 91. (b) Raghavan, S. R.; Riley, M. W.; Fedkiw, P. S.; Khan, S. A. *Chem. Mater.* **1998**, *10*, 244 and references therein.

(10) (a) Fujinami, T.; Tokimune, A.; Mehta, M. A.; Shriver, D. F.; Rawsky, G. C. *Chem. Mater.* **1997**, *9*, 2236. (b) Rawsky, G. C.; Fujinami, T.; Shriver, D. F. *Chem. Mater.* **1994**, *6*, 2208. (c) Fujinami, T.; Kazuhiro, S.; Mori, K.; Mehta, M. A. *Chem. Lett.* **1998**, 619.

(11) (a) Benrabah, D.; Sylla, S.; Sanchez, J. Y.; Armand, M. *J. Power Sources* **1995**, *54*, 456. (b) Benrabah, D.; Sylla, S.; Alloin, F.; Sanchez, J. Y.; Armand, M. *Electrochim. Acta* **1995**, *54*, 456.

(12) Lee, W.; Shibasaki, A.; Saito, K.; Sugita, K.; Okuyama, K.; Sugo, T. *J. Electrochem. Soc.* **1996**, *143*, 2795 and references therein.

(13) (a) Doyle, M.; Fuller, T. F.; Newman, J. *Electrochim. Acta* **1994**, *39*, 2073. (b) Mehta, M. A.; Fujinami, T. *Chem. Lett.* **1997**, 915 and references therein. (c) Okamoto, Y.; Zu, Z. S.; McLin, M. G.; Fontanella, J. J.; Pak, Y. S.; Greenbaum, S. G. *Solid State Ionics* **1993**, *60*, 131. (c) Tada, Y.; Sato, M.; Takeno, M.; Nakacho, Y.; Shigehara, K. *Chem. Mater.* **1994**, *6*, 27.

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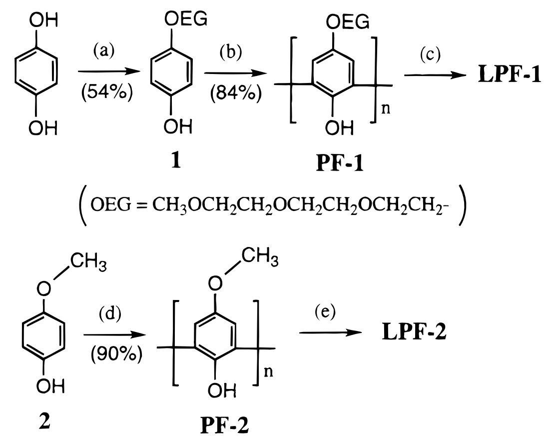
Scheme 1[a]



[a] Conditions: (a) OEG-OTs/KOH/DMSO/room temperature; (b) HRP/H_2O_2, aqueous dioxane/5 °C/room temperature; (c) LiOH; (d) HRP/H_2O_2, aqueous dioxane/5 °C/room temperature; (e) LiOH.

study of various parameters, such as concentration, temperature, time, workup, and purification procedure.[14] The choice of higher solute concentration and ambient temperature favor the formation of monosubstituted product. The preparation of **1** was also performed using OEG-Br[16] in place of OEG-OTs. The yield was about the same. However, the tosylate is easier to prepare in larger quantities from the corresponding alcohol.

The polyphenols, **PF-1** and **PF-2**, were synthesized by enzymatic polymerization of the corresponding phenol monomers (Scheme 1).[17] The polymerization reactions were performed by using an enzyme, horseradish peroxidase-II (HRP), in the presence of hydrogen peroxide.[18] The polymerization of **1** was performed in both aqueous ethanol and dioxane at different solvent proportions. Aqueous dioxane (about 1:1) was found most suitable for these phenol monomers. Polyphenol **PF-2** was prepared by following the optimized conditions for **PF-1**. The lithiated polyphenolates, **LPF-1** and **LPF-2**, were obtained by reaction with lithium hydroxide in aqueous dioxane.[19] Neither lithium salt displayed the O−H stretching bands observed in the infrared spectra of the corresponding polyphenols.

Analytical characterization of monomer **1** and the polyphenols were in complete agreement with the proposed structures. The molecular weights of the polyphenols, **PF-1** and **PF-2**, were determined by both gel permeation chromatography (GPC) and laser light scattering techniques.[20] For **PF-1**, the former method afforded a relative M_w (polystyrene as standard) near 3700 (with a polydispersity index of 1.6) while the latter method provided an absolute M_w value near 10 000. These values compare well with the highest known molecular weights for polyphenols prepared by the enzymatic polymerization of other phenolic systems.[17d] The relative M_w of **PF-2** was measured at 950, with a polydispersity index of 1.8. The thermal stability of **LPF-1** was found to be satisfactory, with complete stability at 200 °C and 10% weight loss not occurring until 340 °C in a nitrogen atmosphere (Figure 2).

To improve the mechanical strength of **LPF-1** and to study its viability as an immobilized lithium ion source, three PEO-based electrolyte films containing the ratio of the number of repeat units of PEO per repeat unit of **LPF-1** (n = 10, 20, and 30) were prepared. The films were produced by casting an acetonitrile solution of high molecular weight (4×10^6) PEO and **LPF-1** on polished Teflon plates. The solvent was allowed to evaporate slowly in a glovebox (moisture content < 1 ppm). The process takes about 7 days to obtain void-free samples. The films were further dried at 60 °C under high vacuum overnight. The physical appearance of **LPF-1** films was transparent as opposed to a opaque for **LPF-2** films.

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(14) **Synthesis of Monomer 1.** In a 500-mL single-neck round-bottomed flask fitted with a mechanical stirrer, were placed hydroquinone (30.88 g, 279.71 mmol), OEG-OTs[13] (88.96 g, 279.75 mmol), KOH (46.97 g, 837.11 mmol) and 200 mL of DMSO. The mixture was stirred overnight at room temperature (water bath), and then transferred to a separatory funnel using 50 mL of water. The solution was extracted 3× with diethyl ether (100, 50, and 50 mL) to remove both unreacted tosylate and disubstituted byproduct. The solution was then acidified with 50 mL of concentrated HCl and extracted 3× with chloroform (100, 50, and 50 mL); the combined organic layers were washed twice with 100 mL of water, dried over $MgSO_4$, and concentrated in vacuo. The product, which contained traces of sludge, was further purified by filtering through a column (alumina) with ethyl acetate: methanol (95:5) as eluent. Yield: 38.5 g (54%, straw colored liquid). FT-IR (neat): 3333, 2877, 1663, 1511, 1453, 1354, 1234, 1103, 945, 830, 756 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.72−6.83 (m, 4H), 4.02 (t, 2H), 3.81 (t, 2H), 3.73−3.66 (m, 6H), 3.58 (t, 2H), 3.38 (s, 3H), 2.65 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 151.8, 150.4, 115.7, 115.3, 71.5, 70.2, 70.1, 69.5, 67.6, 58.6, 39.9 ppm. Anal. Calcd for $C_{13}H_{20}O_5$: C, 60.94; H, 7.81. Found: C, 60.83; H, 7.90.

(15) Lauter, U.; Meyer, W. H.; Wegner, G. *Macromolecules* **1997**, *30*, 2092.

(16) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1995**, *117*, 4437.

(17) (a) Akkara, J. A.; Senecal, K.; Kaplan, D. L. *J. Polym. Sci.: Part A.; Polym. Chem. Ed.* **1991**, 29, 1561. (b) Akkara, J.; Bruno, F.; Mandal, B. K.; Tripathy, S. K.; Kaplan, D. L. U.S. Patent 5,143,828, 1992. (c) Ayyagari, M. S.; Marx, K. A.; Tripathy, S. K.; Akkara, J. A.; Kaplan, D. L. *Macromolecules* **1995**, *28*, 5192. (d) Premachandran, R. S.; Banerjee, S.; Wu, X. K.; John, V. T.; McPherson, G. L.; Akkara, J. A.; Ayyagari, M.; Kaplan, D. L. *Macromolecules* **1996**, *29*, 6452. (e) Ayyagari, M.; Akkara, J. A. *Polym. Mater. Sci. Eng.* **1997**, *76*, 610. (f) Alva, K. S.; Sarma, R.; Marx, K. A.; Kumar, J.; Tripathy, S. K.; Akkara, J. A.; Kaplan, D. L. *Proc. SPIE-Int. Soc. Opt. Eng.* **1997**, 3040, 210.

(18) **Synthesis of PF-1**. In a 250-mL single-neck round-bottomed flask fitted with a mechanical stirrer, 8.31 g (34.46 mmol) of monomer **1**, dissolved in 25 mL of dioxane, was added to an ice cold (5 °C) solution of 24 mg of HRP-II in 55 mL of HEPES buffer. To the mixture was added 5 mL of 30% hydrogen peroxide solution in five portions (1 mL, 10-min interval). With stirring, the solution was allowed to come to room temperature and then stirred overnight. Dioxane was removed under reduced pressure on a rotovap, and the highly viscous polymer was separated from the aqueous phase. The aqueous phase was decanted off, and the contents of the flask were washed with water (3×) and isopentane (2×), and the residue dried at 50 °C under high vacuum to give 7.1 g (86%) of **1** as a deep red waxy solid. FT-IR (neat): 3318, 2876, 1674, 1510, 1454, 1387, 1353, 1285, 1234, 1108, 1067, 948, 830, 756 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.82 (s, 1H), 6.75 (s, 1H), 4.05 (m, 2H), 3.79 (m, 2H), 3.75−3.57 (m, 6H), 3.53 (t, 2H), 3.36 (s, 3H), 2.40 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 152.7, 151.8, 150.7, 115.7, 115.3, 71.6, 70.2, 69.5, 67.8, 58.7 ppm. Anal. Calcd for $C_{13}H_{18}O_5$: C, 61.42; H, 7.07. Found: C, 61.27; H, 6.85. Synthesis of **PF-2**. The **PF-2** was prepared from *p*-methoxyphenol by following the aforementioned procedure, to give a light brown solid in 90% yield.

(19) **Lithiation of Polyphenols.** Lithiation of polyphenols (**PF-1** or **PF-2**) was performed by dissolving the polymer (4 g) in 20 mL of dioxane, followed by addition of a solution of LiOH (1 equiv with respect to the repeat unit) in 10 mL of water. The solution was stirred for 30 min and evaporated to dryness on a rotovap. Final drying was performed at high vacuum at 60 °C. The lithiated polymer salts (**LPF-1** and **LPF-2**) were obtained as dry dark red powders. The salts were hygroscopic and stored in a glovebox. FT-IR of **LPF-1** (KBr): 2878, 1673, 1510, 1456, 1388, 1353, 1284, 1232, 1109, 1067, 946, 831, 755 cm^{-1}.

(20) GPC: Tetrahydrofuran (THF) and *m*-styragel column (Waters, kept at 40 °C) were used as a mobile phase and stationary phase, respectively. DAWN-DSP-F laser light scattering system (Wyatt Technology) was used to obtain absolute molecular weights in THF solutions.

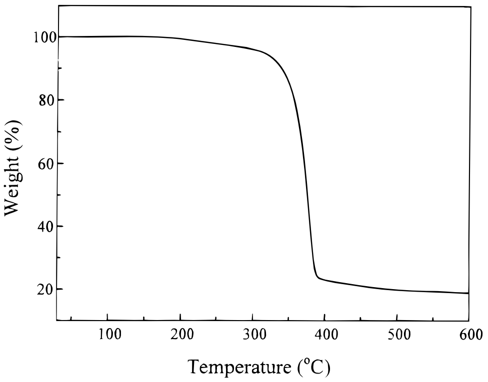

Figure 2. Thermal stability of **LPF-1** under nitrogen atmosphere.

The ionic conductivities of the prepared SPEs were measured using the ac impedance method[7] and the results are shown in Figure 3. The highest conductivities were obtained for the host−salt ratio of 20. The room-temperature ionic conductivity of this film was determined to be 4×10^{-5} S/cm. This value is comparable to the best known single-ion-conducting SPEs reported thus far.[10] We attribute the high conductivities to the incorporation of pendant polyether chains in **LPF-1** which provide a plasticizing effect and enhance PEO long-chain segmental motion. The relationship between conductivity and salt concentration is evident and typical for PEO-based SPEs containing biion conductors such as lithium bis(trifluoromethanesulfonyl) imide.[9,21] The decrease in conductivity at higher loading is an anomaly we are currently investigating. Since **LPF-1** showed the highest conductivities at a host−salt ratio of 20, a similar SPE using **LPF-2** was also prepared. As anticipated, the ionic conductivities of these films showed comparatively lower values, because of the absence of the plasticizing pendant OEG groups on **LPF-2** (Figure 3).

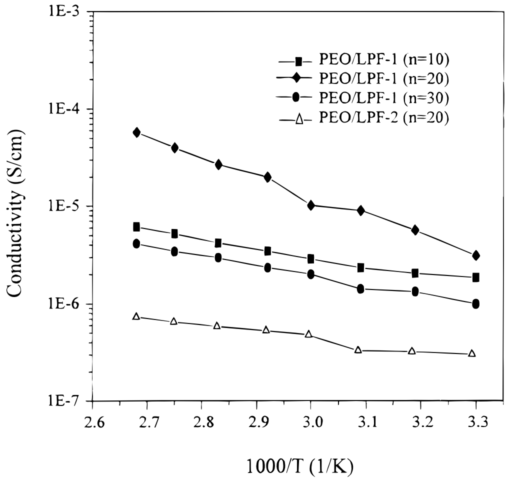

Figure 3. Ionic conductivities of PEO-lithium polyphenolate blends (*n* represents the number of repeat units of PEO per repeat unit of lithium polyphenolate).

In conclusion, we have prepared a new phenol monomer that was enzymatically polymerized to produce a new class of polyphenol-based single-ion-conducting electrolyte in a short, efficient reaction sequence. The lithium polyphenolate, **LPF-1**, containing pendant flexible oligoether groups, showed high ionic conductivities. Further studies will include enhancement of conductivities by use of external plasticizers and by incorporating longer oligoether chains. Electrochemical behavior in prototype cells and measurement of transport properties will also be investigated.

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(21) Linford, R. G. In *Applications of Electroactive Polymers*; Scrosati, B., Ed.; Chapman & Hall: New York, 1993; p 7.