

Thioaluminate Polymer Complexes as Single-Ionic Solid Electrolytes

Ken Onishi, Michiko Matsumoto, and Kiyotaka Shigehara*

Graduate School of Bio-Applications and Systems Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan

Received November 3, 1997

To improve the conductivity of recently reported single-ionic lithium orthoaluminate complex polymer electrolytes, the structure of the complex unit was changed from $[\text{Al}(\text{OR})_4]^-$ to $[\text{Al}(\text{SR})_4]^-$, carrying a larger anion radius. The ionic conductivity of such thioaluminate polymer complexes was about $10^{-5} \text{ S cm}^{-1}$ at room temperature, which was about 10^2 times higher than that of previously reported aluminate complexes. The single-ionic nature of thioaluminate polymer complexes was confirmed by transport number.

Introduction

Solid polymer electrolytes composed of [alkali metal salt/polymer] hybrids, the so-called bi-ionic conductors, have been extensively studied^{1,2} and their ac ionic conductivities of more than $10^{-5} \text{ S cm}^{-1}$ were reported. When such bi-ionic conductors are used in a rechargeable battery, two ionic species, e.g., lithium ion and its counteranion, migrate between two electrodes during the charging and discharging processes. As the transport number (t) of anions is far larger than that of Li^+ ,³ the migration of anions toward the anode causes serious polarization, resulting in a rapid decay of dc conductivity or the time-dependent increase of cell impedance.

To minimize the polarization, the present authors fixed anionic sites to polymer chains^{3–5} to diminish the transversal diffusion of anionic species through the electrolyte films. The first model carrying lithium carboxylate⁴ or sulfonate⁵ as well as oligo(oxyethylene) side chains gave the single-ionic nature but very low conductivity of $10^{-8} \text{ S cm}^{-1}$ due to large ion-dissociation energy. According to the free volume theory, the ionic conductivity σ is represented by eq 1⁷ where σ_0 is the

$$\sigma = \sigma_0 \exp[-\gamma V_f / v \{f_g + \Delta\alpha(T - T_g)\} + \{E_j + (W/2\epsilon)\} / kT] \quad (1)$$

preexponential term; γ , the correction factor for overlapping of free-volume; V_f , the smallest free volume for ion hopping; f_g , the free-volume fraction at T_g ; $\Delta\alpha$, the difference of heat expansion coefficients below and above T_g ; E_j , the energy barrier for ion hopping; W , the ion dissociation energy; and ϵ , the relative permittivity. For

the improvement of ionic conductivity, T_g , W , and E_j should be decreased and ϵ must be high. Since there is no suitable supporting units other than oxyethylene or related structures that exhibit relatively low T_g (ca. -90 to -120 °C), the molecular design is extremely limited and it will no more be possible to enhance the probability of free volume formation. If it is so, we must change the direction, i.e., to decrease W or E_j , or increase ϵ .

To decrease the dissociation energy, the aluminate polymer complexes with large anionic repeating units in the main chain were synthesized, and single-ionic conductivity of about 10^{-6} – $10^{-7} \text{ S cm}^{-1}$ was observed.⁷ In the present study, polyelectrolytes with much larger anionic repeating units of the $[\text{Al}(\text{SR})_4]^-$ type were synthesized and their single-ionic conduction is discussed.

Experimental Section

Materials. Lithium aluminum hydride (LAH) of 0.5 M solution in dimethoxyethane (DME) was used as received. Di-(2-mercaptoethyl)sulfide (DS), furfuryl mercaptan (FM), 2-propanethiol, di(2-mercaptoethyl)ether (DE), and ethanedithiol (ES) were dried over molecular sieves. Oligo(ethylene glycol) monomethyl ether [OGM; $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, $n = 1-3$, and $n_{\text{av}} = 7.2$ ($M_{w,\text{av}} = 350$), 12.1 (550), Polysciences, Inc.] was dried under vacuum at 60–80 °C for a half day, where $M_{w,\text{av}}$ represents the number-average molecular weight. Oligo(ethylene glycol) [OEG; $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$, $m = 1-3$, and $m_{\text{av}} = 4.1$ ($M_{w,\text{av}} = 200$), 6.4 (300), 8.7 (400), 13.2 (600), 22.3 (1000), 34.6 (1540), Wako Pure Chemicals] was dried under vacuum at 20–40 °C for a half day. Furfuryl alcohol (FA) was dried under reduced pressure at 60 °C for a half day. Predisilled DME was dried by refluxing over benzophenone–sodium complex for a half day, redistilled under argon atmosphere, and immediately used.

All experiments including solvent purification, syntheses, cell construction, and measurements hereafter were conducted under dry argon atmosphere (residual oxygen and water less than 10^{-3} and 0.1 ppm, respectively) in a vacuum-type drybox at room temperature that was mostly 22 ± 3 °C unless otherwise stated.

Preparation of Lithium Tetra(isopropylthio)aluminate. To the DME solution of 1 mol of LAH was added

(7) Onishi, K.; Matsumoto, M.; Nakacho, Y.; Shigehara, K. *Chem. Mater.* **1996**, *8*, 469.

* To whom correspondence should be addressed.

(1) Wright, P. V. *Br. Polym. J.* **1975**, *7*, 319.

(2) MacCallum, J. R.; Vincent, C. A. *Polymer electrolyte reviews* **1**, 2; Elsevier Applied Science: London, 1987, 1989.

(3) Tada, Y.; Sato, M.; Takeno, N.; Nakacho, Y.; Shigehara, K. *Chem. Mater.* **1994**, *6*, 27.

(4) Tsuchida, E.; Shigehara, K. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 361.

(5) Kobayashi, N.; Uchiyama, M.; Shigehara, K.; Tsuchida, E. *J. Phys. Chem.* **1985**, *89*, 987.

(6) Miyamoto, T.; Shibayama, K. *J. Appl. Phys.* **1973**, *44*, 5372.

Table 1. Nomenclature and Structure of Polymer Complexes, Where FM and FA Denote Furfuryl Mercaptan and Furfuryl Alcohol, Respectively

nomenclature of polymer complex	starting material		typical structure of repeating unit
	side chain	main chain	
(FM)₂dithioaluminate			
FM-ES	FM	HSCH ₂ CH ₂ SH	
FM-DS	FM	(HSCH ₂ CH ₂) ₂ S	
FM-DE	FM	(HSCH ₂ CH ₂) ₂ O	
(FM)₂dioxoaluminate			
FM-OEG2	FM	HO(CH ₂ CH ₂ O) ₂ H	
FM-OEG3	FM	HO(CH ₂ CH ₂ O) ₃ H	
FM-OEG4	FM	HO(CH ₂ CH ₂ O) _{4,1} H	
FM-OEG6	FM	HO(CH ₂ CH ₂ O) _{6,4} H	
FM-OEG9	FM	HO(CH ₂ CH ₂ O) _{8,7} H	
FM-OEG13	FM	HO(CH ₂ CH ₂ O) _{13,2} H	
FM-OEG22	FM	HO(CH ₂ CH ₂ O) _{22,3} H	
FM-OEG35	FM	HO(CH ₂ CH ₂ O) _{34,6} H	
(RO)₂dithioaluminate			
OGM2-DE	CH ₃ O(CH ₂ CH ₂ O) ₂ OH	(HSCH ₂ CH ₂) ₂ O	
OGM3-DE	CH ₃ O(CH ₂ CH ₂ O) ₃ OH	(HSCH ₂ CH ₂) ₂ O	
OGM7-DE	CH ₃ O(CH ₂ CH ₂ O) _{7,2} OH	(HSCH ₂ CH ₂) ₂ O	
OGM12-DE	CH ₃ O(CH ₂ CH ₂ O) _{12,1} OH	(HSCH ₂ CH ₂) ₂ O	
FA-ES	FA	HSCH ₂ CH ₂ SH	
FA-DS	FA	(HSCH ₂ CH ₂) ₂ S	
FA-DE	FA	(HSCH ₂ CH ₂) ₂ O	
(FA)₂dioxoaluminate			
FA-OEG1	FA	HOCH ₂ CH ₂ OH	
FA-OEG2	FA	HO(CH ₂ CH ₂ O) ₂ H	
FA-OEG3	FA	HO(CH ₂ CH ₂ O) ₃ H	
FA-OEG4	FA	HO(CH ₂ CH ₂ O) _{4,1} H	
FA-OEG6	FA	HO(CH ₂ CH ₂ O) _{6,4} H	
FA-OEG9	FA	HO(CH ₂ CH ₂ O) _{8,7} H	
network tetrathioaluminate[mixing ratio]			
NW-1	FM[2]	(HSCH ₂ CH ₂) ₂ O[1]	
NW-2	FM[3]	(HSCH ₂ CH ₂) ₂ O[2.5]	
NW-3	FM[2]	HSCH ₂ CH ₂ SH[1]	
NW-4	FM[3]	HSCH ₂ CH ₂ SH[2.5]	
NW-5	FM[2]	HSCH ₂ CH ₂ SH[3]	

dropwise the DME solution of 4 mol of 2-propanethiol. The mixture was allowed to react at room temperature for 24 h

and then heated at 60 °C for 6 h. During that period, the amount of evolving hydrogen gas was monitored volumetri-

cally. The solvent was removed by evaporation, and the remaining solid was dried in vacuo for 1 day and then redissolved in C_6D_6 . The resulting solution was studied by NMR spectroscopy.

Preparation of (FM)₂dithioaluminate Polymer Complexes. Di(furfurylthio)dithioaluminate polymer complexes were prepared by dropwise addition of a DME solution containing 1 mol of dithiol {DS, DE, or ES} and 2 mol of FM into the DME solution containing 1 mol of LAH at room temperature. The mixture was stirred for 24 h, the solvent was removed in vacuo, and then the product was heated to 70 °C under vacuum for 4 h in order to complete the reaction and the solvent evaporation.

Preparation of (RO)₂dithioaluminate Polymer Complexes. Di(alkoxy)dithioaluminate polymer complexes were prepared by dropwise addition of a DME solution containing 1 mol of DE and 2 mol of OGM into the DME solution containing 1 mol of LAH at room temperature. Then the mixture was treated as described above.

Preparation of (FM)₂dioxoaluminate Polymer Complexes. Di(furfurylthio)dioxoaluminate polymer complexes were prepared by dropwise addition of a DME solution containing 1 mol of OEG and 2 mol of FM into the DME solution containing 1 mol of LAH at room temperature. Then the mixture was treated as described above.

Preparation of (FA)₂dioxoaluminate Polymer Complexes. The procedure is similar to that reported previously⁷ except for the use of 2 mol of FA.

Network Tetrathioaluminate Polymer Complexes. The network tetrathioaluminate polymer complexes were obtained similarly as (FM)₂dithioaluminate polymer complexes by changing the mixing ratio as listed in Table 1.

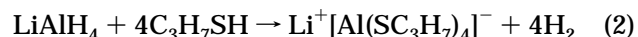
Test Experiments for H₂-Volumetry. The polymer complexes were prepared as described above but without removing the solvent. The mixture was allowed to react at room temperature and then at reflux for prescribed periods during which the amount of evolving H₂ was monitored volumetrically.

Cell Preparation and Measurements. Electrolytes were fabricated into thin films, typically 10 mm dia × 0.1 mm thick, sandwiched between stainless steel or metallic lithium electrodes, and employed for ac or both ac/dc conductivity measurements, respectively. The frequency-dependent impedance was measured by a Solartron 1250 frequency response analyzer/1286 potentiostat (10⁻² Hz to 65 kHz) or HP4194A impedance/gain-phase analyzer (100 Hz to 40 MHz). The time dependence of dc current was measured at room temperature under an applied voltage of 10.0 mV with lithium electrodes using a Hokuto Denko HA501G potentiogalvanostat. As it was noticed from the comparison of ac and dc conductivity that the interfacial impedances between the metallic lithium electrodes and the present polymer complex electrolytes were relatively small (ca. <5% of total impedance), the dc conductivities were calculated without eliminating the interfacial impedance. A portion of polymer complex electrolyte was sealed in a vacuum-tight aluminum container, and differential scanning calorimetry (DSC) was carried out by a Mac Science DSC 3200 apparatus at a heating rate of 20 °C/min.

Results and Discussion

In the present study, a series of polymer complexes with orthoaluminate ionic units shown in Table 1 were examined, and their abbreviated names are given in the order of side-chain followed by main-chain linking atom adjacent to the aluminum atom, such as in (FM)₂dioxoaluminate, where FM(furfurylthio) indicates the side-chain units and dioxo(-O-O-) the main-chain units.

Complex Structure. The reaction between 1 mol of LAH and 4 mol of 2-propanethiol (eq 2) was confirmed to evolve exactly 4 mol of H₂ by volumetric analysis. FT-IR spectroscopy revealed complete disappearance of



Al-H (stretching, 1772 & 1642 cm⁻¹)⁸ and S-H (stretching, 2600 cm⁻¹), while the distinctive absorption peak of Al-S at 500 cm⁻¹ was seen. Also, no Al-H activity was found by titration with methanol after the completion of thioaluminate complex formation. The 500 MHz ¹H NMR spectroscopy of lithium tetra(isopropylthio)aluminate in C_6D_6 showed that the complex was a tetragonal structure, in which each RS⁻ group is tetraequivalent and positioned at the corner of a tetragon; δ (d, methyl) 1.56 ppm, (heptet, methyne) 3.72 ppm. Probably because of the bigger atomic radius of sulfur, this structure is not identical to that of corresponding Li[Al(OR)₄] in which the bond length of Al-OR(axial) is larger than that of other three Al-OR(equatorial).⁹

Corresponding polymer complexes listed in Table 1 also generated the stoichiometric amount of H₂. The changes in FT-IR spectra were the same as described above. As the reaction of LAH with diols or dithiols might proceed statistically, every polymer complex turned insoluble after the final evaporation of the reaction solvent during the film formation, possibly due to cross-linking. The result of DSC measurement up to 150 °C for the polymer complexes of FM-ES or FM-DE showed no evidence of melting or phase transitions, indicating amorphous structures. Under this temperature range in the dry argon atmosphere, the polymer complexes did not show any weight loss, color change, and decrease of ionic conductivity. Prolonged contact with freshly cleaved metallic lithium surface did not influence the ionic conductivity.

Ionic Conductivity of Polymer Complexes. The ac conductivities of (FM)₂dithioaluminate polymer complexes are summarized in Table 2. Their physical properties were mostly affected by the kind of the main-chain dithiol, to give a yellow tacky solid (DE), a colorless hard solid (DS), and a yellow soft solid (ES). The best ac conductivity of 1.1 × 10⁻⁵ S cm⁻¹ was obtained when ES was used as the main-chain unit, namely in the case of FM-ES system. This value is about 10² times higher than the ac ionic conductivity of the -{Li⁺[Al(OGM)₂(OEG)]⁻}_p- type tetralkoxyaluminate polymer complexes reported earlier.⁷ To distinguish the reason for the high ionic conductivity of the FM-ES system, a series of analogous polymer complexes were examined.

As the furfuryl side-chain units and four sulfur atoms coordinating the Al atoms are the distinct structural characteristics of the present (FM)₂dithioaluminate polymer complexes, initially our investigation was focused on whether (1) a larger anion radius of [Al(SR)₄]⁻ is essential or (2) a furfuryl side-chain group is specific to high ionic conduction.

Table 3 summarizes the ac conductivity of (FM)₂dioxoaluminate polymers that carry two furfurylthio side-chain units and the -(OCH₂CH₂)_nO- main chain. The ionic conductivity decreased when the S atoms of the main chain were replaced by the O atoms. Dialkoxydithioaluminate composed of -(OCH₂CH₂)_m-OCH₃ or furfuryloxy side chains and -S-S- main

(8) Fusek, J.; Hanousek, F.; Haruda, F. *Chem. Commun.* **1976**, 41, 187.

(9) Hilal, M.; Kader, A. *Chem. Ber.* **1970**, 103, 1225.

Table 2. ac Conductivity of (FM)₂Dithioaluminate Polymer Complex

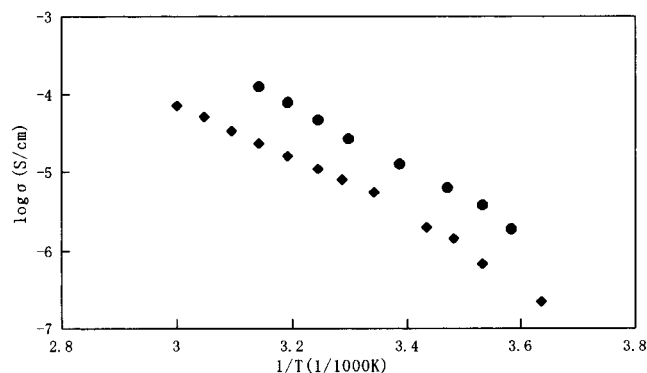
complex	$\sigma(10^7 \text{ S cm}^{-1})$	appearance
FM-ES	110	yellow soft solid
FM-DS	36	colorless hard solid
FM-DE	51	yellow tacky solid

Table 3. ac Conductivity (FM)₂Dioxyaluminate Polymer Complex

complex	$\sigma(10^7 \text{ S cm}^{-1})$	appearance
FM-OEG2	0.03	rigid solid
FM-OEG3	0.05	solid
FM-OEG4	0.08	hard solid
FM-OEG6	0.28	hard solid
FM-OEG9	5.4	solid
FM-OEG13	11	solid
FM-OEG22	24	waxy solid
FM-OEG35	37	waxy solid

Table 4. ac Conductivity of (RO)₂Dithioaluminate Polymer Complex

complex	$\sigma(10^7 \text{ S cm}^{-1})$	appearance
OGM2-DE	0.001	rigid solid
OGM3-DE	0.82	tacky solid
OGM7-DE	4.6	tacky solid
OGM12-DE	1.9	tacky solid
FA-ES	below 10^{-10}	rigid solid
FA-DS	below 10^{-10}	rigid solid
FA-DE	below 10^{-10}	rigid solid

**Figure 1.** Temperature dependence of ac conductivity: ●, FM-ES; ◆, FM-DE.

chains gave similarly low conductivity (Table 4). Comparing the data given in Tables 3 and 4, the existence of proximal furfuryl groups is likely to enhance the ion dissociation, but the satisfactory ionic conductivity was observed only when a longer and softer main chain created enough free volume for ion hopping. However, the polymer complex composed of two furfuryloxy side chains and all oligo(oxyethylene) main chain gave much lower ionic conductivity than the previously reported oxyethylene-based aluminate polymer complexes.

Thus, in summary, the coordination of four sulfur atoms to give a bigger anion radius is essential to achieve the high ionic conductivity. It is interesting to compare (FM)₂dithioaluminate with {CH₃(SCH₂CH₂)_{*m*}S}₂-dithioaluminate which may have more flexibility to create free volume for ion hopping. Unfortunately, *endo*-methylthio[oligo(ethylene sulfide)] is not commercially available; thus, we could not examine the effect of flexibility in the present study.

Figure 1 shows the temperature dependence of ac ionic conductivities of polymer complexes FM-ES and FM-DE. The plots of $\log \sigma$ and $1/T$ show a curved trend,

Table 5. ac Conductivity of (FA)₂Dioxyaluminate Polymer Complexes

complex	$\sigma(10^7 \text{ S cm}^{-1})$
FA-OEG1	0.01
FA-OEG2	0.03
FA-OEG3	0.56
FA-OEG4	0.11
FA-OEG6	2.0
FA-OEG9	5.8

Table 6. ac Conductivity of Network Tetrathioaluminate Polymer Complexes

complex	$\sigma(10^7 \text{ S cm}^{-1})$	appearance
NW-1	51	yellow tacky solid
NW-2	7.7	yellow solid
NW-3	110	yellow soft solid
NW-4	56	yellow rigid solid
NW-5	110	colorless hard solid

which indicates that the ionic conduction obeys the Vogel–Tamman–Fulcher (VTF) and Williams–Landel–Ferry (WLF) mechanism, derived by the free volume model. As already pointed out from the results of DSC measurement, no phase transition or melting point was distinguished from Figure 1.

These polymer complexes were prepared from stoichiometric mixtures, for instance, of 2 mol of monofunctional thiol, 1 mol of dithiol, and 1 mol of LAH. The statistical reaction might provide a partially cross-linked structure, and therefore, each complex turned insoluble after the film formation process at elevated temperatures. Since such insoluble complex films are easy to handle, the intentional cross-linking was attempted by changing the mixing ratio of monofunctional thiols and dithiols but without perturbing the stoichiometry vs LAH. As listed in Table 6, the polymer complex became tougher and easier to handle without depressing the ionic conductivity.

Transfer Number. With neglecting the ion–ion electrostatic interaction, Vincent et al.^{10,11} have shown that the initial and steady-state currents are given, respectively, by eqs 3 and 4 under the low electric field where the ohmic conduction is confirmed.

$$I^0 = \Delta V / (R_1^0 + R_2) = \Delta V / (R_1^0 + k/\sigma) \quad (3)$$

$$I^S = \Delta V / (R_1^S + k/t_+ \sigma) \quad (4)$$

ΔV is the potential applied across the cell; k , the cell constant; t_+ , the cation-transfer number; σ , the (dc) conductivity of electrolyte; R_2 , the electrolyte resistance; R_1^0 and R_1^S , the initial and steady-state resistance; and I^0 and I^S , the initial and steady-state current.

From eqs 3 and 4, we can derive $\sigma = I^0 k / (\Delta V - I^0 R_1^0)$, and therefore eq 5 is obtained.

$$t_+ = I^S (\Delta V - I^0 R_1^0) / I^0 (\Delta V - I^S R_1^S) \quad (5)$$

Figure 2 shows the time dependence of dc current measured by using metallic lithium electrodes under 10.0 mV potential. From the initial and steady-state ac impedance recorded before the dc potential was applied and right after the prolonged dc measurement,

(10) Bruce, P. G.; Vincent, C. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1987**, 225, 1.

(11) Evans, J.; Vincent, C. A.; Bruce, P. G. *Polymer* **1987**, 28, 2324.

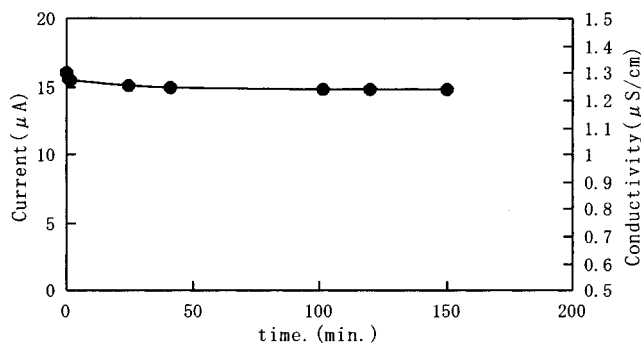


Figure 2. Time dependence of dc current of NW-4 under an applied voltage of 10.0 mV and dc conductivity.

respectively, R_1^0 and R_1^S were determined to be 550 and 600 Ω . By using the initial dc current of $I^0 = 16.09 \mu\text{A}$ and steady-state current $I^S = 14.83 \mu\text{A}$ obtained from time-dc current curve, the cation-transfer number was calculated according to eq 5 as $t_+ = 0.96$. Such high cation-transfer number indicates that the diffusion of macromolecular anions from the cathode to the anode is not likely; the present polymer complexes are confirmed to have the nature of a single-ionic conductor.

There are three kinds of batteries in which the transport of lithium ions is essential, i.e., (1) lithium ion intercalation compounds coupled with chalcogenides, such as [graphite(Li^+)/electrolyte/ TiS_2], (2) metallic lithium coupled with chalcogenides such as [Li/electrolyte/ TiS_2], and (3) metallic lithium coupled with doped *p*-type polymer conductor such as, [Li/electrolyte/poly(aniline) $^+X^-$]. The batteries of type 1 and 2 do not need X^- transport, therefore, it is preferable to use single-ionic conductors or electrolytes with the large lithium ion transport number, i.e., $t_+ > t_-$. Type 1 batteries, the so-called lithium ion batteries, are safer than the other two types because the use of hazardous metallic lithium is avoided. The present single-ionic conductors could be used in batteries of the type 1 or 2, and the results will be presented in future papers.

As already discussed above, the addition of lithium salts may change the nature of polyelectrolytes from single-ionic to bi-ionic. When the electrode material of which redox reaction is associated with X^- transfer, e.g.,

as when poly(aniline) $^+X^-$ is used as a cathode, or in other words, when the electrode system of type 3 battery is used with the bi-ionic conductors of $t_+ \cong t_-$, it is possible to obtain reasonably high constant current during the discharging and charging processes. In the type 3 battery, both the egress and ingress of X^- from/to the poly(aniline) electrode are important as well as the transport of lithium ions. When the electrolyte solution is used in such battery, careful choice of lithium salt dissolved in solution is necessary to adjust $t_+ = t_-$. If the common bi-ionic solid electrolytes such as LiX/poly(oxyethylene) [POE] hybrids are employed instead, the practical current density is limited to very low values due to severe polarization attributed to the imbalance of transport numbers, i.e., $t_+ < t_-$. As the lithium salts miscible with POE are relatively few, such as LiClO_4 , LiBF_4 , LiPF_6 , LiCF_3SO_3 , etc., and the majority of ionic conduction is brought about by the anion transport, there is almost no way to improve the imbalance in the case of LiX/POE hybrids. However, in the present single-ionic polymer complex, we can change the balance of transport numbers from $t_+ = 1$ ($t_- = 0$) to $t_+ = t_-$ by controlling the kind and amount of the added lithium salts. Thus, the single-ionic conductors are of considerable significance because of their wide applicability to every Li battery system.

Conclusion

New single-ionic thioaluminate polymer complexes were synthesized. These complexes gave high ionic conductivity of about $10^{-5} \text{ S cm}^{-1}$ at room temperature upon prolonged application of dc potential. This value was about 10^2 times higher than the conductivity obtained previously for the corresponding aluminate polymer complexes. Tougher polymer complex films suitable for battery applications were obtained by cross-linking without decreasing their ionic conductivity.

Acknowledgment. This research is partially supported by the foundation for the scientific research from the Ministry of Education, Science and Culture, Japan (No. 07554062).

CM970717U