

Novel lithium salts exhibiting high lithium ion transference numbers in polymer electrolytes

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Abstract

A variety of lithium aluminates containing two oligoether groups and two electron-withdrawing groups, CF_3CO_2 , CF_3SO_3 , $(\text{CF}_3\text{SO}_2)_2\text{N}$ or $\text{C}_6\text{F}_5\text{O}$, on aluminum atom were prepared. Viscous liquid salts were obtained by incorporation of oligoether substituents containing an average of 7.2 and 11.8 ethylene oxide repeating units. Ionic conductivity of the liquid salt was enhanced by incorporation of electron withdrawing groups on the aluminate center and was dependent on the chain length of oligoether groups. Temperature dependence of ionic conductivity was well fitted to Vogel–Tammann–Fulcher equation, indicating that ion motion was coupled to segmental motion of oligoether chains. Polymer electrolytes were prepared by mixing of the salt and poly(ethylene oxide) and exhibited a high ionic conductivity, a high lithium transference number, a wide potential window, and a good thermal stability.

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1. Introduction

Polymer electrolytes have been attracting much attention for application in solvent free lithium rechargeable batteries. Branched polyethers have been developed in order to obtain high ionic conductivity ($10^{-4} \text{ S cm}^{-1}$ order) but their lithium ion transference numbers (T_+) were usually low. Although single ion conducting polymers tend to exhibit low ionic conductivity due to strong ion pairing between the mobile lithium ions and the anions fixed onto the polymer backbone, they have some advantages in lithium secondary batteries as compared with dual-ion conducting polymers in which concentration gradients increase in a dc field [1].

We have reported that single ion conducting siloxyaluminate polymers [2] exhibited good ionic conductivity. A series of ate complex polymers [3–5] have been prepared by incorporation of bi-functional electron withdrawing groups onto ate complex centers. Recently, polysiloxanes containing trifluoromethylsulfonamide anions and oligoether side chains [6], and polyether containing oxalate capped orthoborates [7] were reported as good single ion conducting polyelectrolytes. Their molecular structures were well designed to weaken ion pairing.

We have reported a simple method for enhancement of lithium ion transference numbers in polyether-salt

complexes by introducing boroxine rings [8–10] or borosiloxane structure [11] as anion trapping groups.

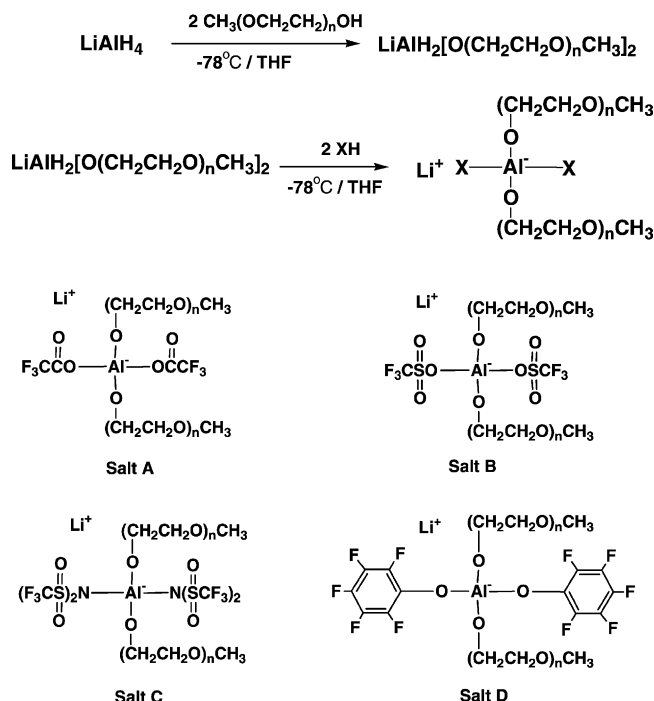
In this paper, we present a new series of lithium aluminates which exhibit good ionic conductivity and high lithium ion transference numbers in polyether-salt systems.

2. Experimental

LiAlH_4 (1.0 M solution in tetrahydrofuran (THF), Aldrich), trifluoroacetic acid (Aldrich), trifluorosulfonic acid (Aldrich), bis(trifluorosulfon)amide (Aldrich), and pentafluorophenol (Kanto Chemical) were used as supplied. All polyethylene glycol monomethyl ethers (ethylene oxide (EO) repeat unit = 1, 2, 3, 7.2, 11.8, Tokyo Kasei) were dried by nitrogen bubbling and stored before use over molecular sieves. The solvents acetonitrile and tetrahydrofuran (THF) were dried rigorously before use. Poly(ethylene oxide) (PEO, Aldrich, M_w : 5×10^6) was dried at 50°C for 24 h under vacuum.

LiAlH_4 (1 M solution in THF) 6.40 ml (6.40 mmol) was dissolved in 10 ml of dry THF and cooled to -78°C . Polyethylene glycol monomethyl ether (M_w : 350) [PEGMME-(350)] 4.49 g (12.8 mmol) diluted with 10 ml of dry THF was added dropwise to LiAlH_4 solution at -78°C . The reaction mixture was slowly warmed to room temperature and was stirred for 4 h. The reaction mixture was slowly added dropwise to trifluoroacetic acid 1.46 g (12.8 mmol)

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Scheme 1. Synthesis of lithium aluminates containing oligoether groups and electron withdrawing groups.

solution in 10 ml of dry THF at -78°C . The mixture was slowly warmed to room temperature and was stirred for 9 h. After the solvent was removed by heating under reduced pressure (24 h at 70°C), a clear viscous liquid Salt A ($n = 7.2$) was obtained. Other lithium aluminates were synthesized by similar reactions as illustrated in Scheme 1.

PEO 0.0509 g was dissolved in 15 ml of dry acetonitrile. Salt A ($n = 7.2$) 0.305 g solution in 5 ml of dry acetonitrile, was added to the solution. The mixture was stirred for 12 h at room temperature. After the solvent was removed by heating under reduced pressure (24 h at 70°C), polymer electrolyte, Salt A ($n = 7.2$)/PEO (EO/Li = 20/1), was obtained.

In the same way, other lithium aluminate/PEO electrolytes were prepared. Polymer electrolyte films for electrical measurement were obtained by hot pressing between PTFE disks using a PTFE spacer (0.4 mm) to control film thickness.

Ionic conductivities of samples were determined by ac impedance measurement in the frequency 1 MHz to 10 mHz using a Solartron 1260 frequency response analyzer and 1287 electrochemical interface. Samples were sandwiched between stainless steel electrodes under an inert argon atmosphere. Lithium ion transference numbers (T_+) were determined for samples sandwiched between non-blocking lithium electrodes using the combined ac impedance/dc polarization method of Evans modified by Abraham [12,13]. Electrochemical stability was determined by cyclic voltammetry using a Pt working electrode and Pt pseudo reference electrode.

Glass transition temperatures of polymer electrolytes were determined by differential scanning calorimetry

Table 1
Glass transition temperature (T_g) of lithium aluminates

Salt	T_g ($^\circ\text{C}$)		
	$n = 3$	$n = 7.2$	$n = 11.8$
Salt A	-15.5	-63.3	-51.8
Salt B	-	-41.6	-51.3
Salt C	-	-48.8	-53.0
Salt D	-	-50.9	-59.6

(DSC) using a Perkin-Elmer Pyris 1 differential scanning calorimeter. Heat-cool-reheat cycles were performed at a rate of $10^\circ\text{C}/\text{min}$.

3. Results and discussion

Lithium aluminate salts containing oligoether side chain length containing 7.2 EO units or 11.8 EO units were viscous liquids. Salt B ($n = 3$), Salt C ($n = 3$) and Salt D ($n = 3$) with short oligoether chains were waxy solids. Salt A ($n = 3$) was sticky waxy semi solid. T_g value of the salt was observed to be dependent on the length of oligoether chains (Table 1).

Ionic conductivity of Salts A, B and C are shown in Figs. 1–3. Optimum conductivity at room temperature was obtained by using a chain length containing an average of 7.2 EO repeating units for Salt A, longer ether chain length ($n = 11.8$) for Salts B and C. Since the salts containing these oligoether chain lengths also exhibited the lowest T_g .

The temperature dependence of ionic conductivity for the Salts A, B and C are represented by Vogel–Tammann–Fulcher (VTF) equation rather than linear Arrhenius plots:

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

where A and B are constants. T_0 is the Vogel scaling temperature. During the fitting process, an initial value of

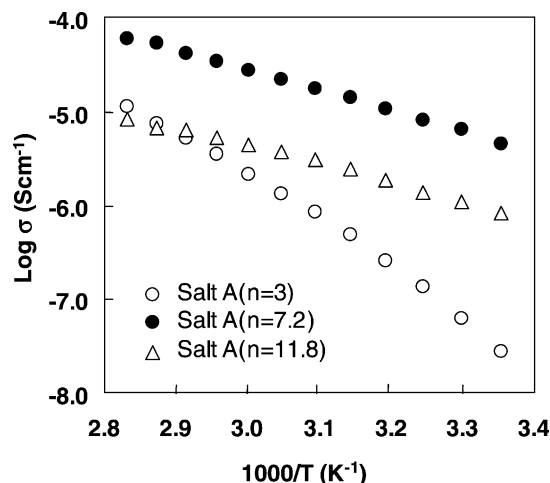


Fig. 1. Temperature dependence of ionic conductivity for Salt A.

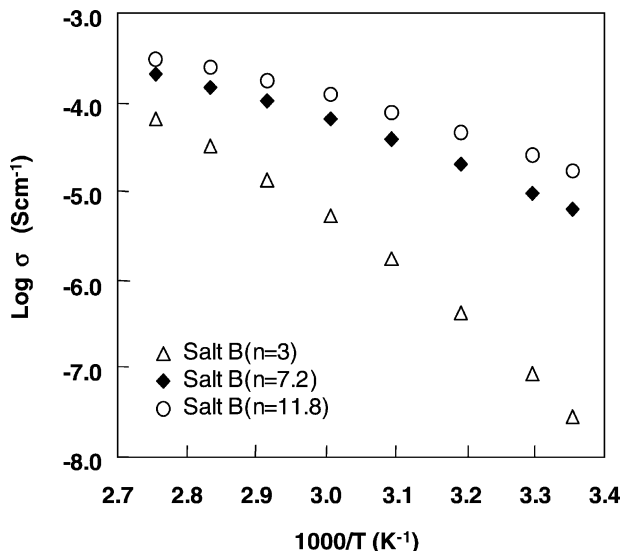


Fig. 2. Temperature dependence of ionic conductivity for Salt B.

T_0 was taken as $T_0 = T_g - 50$. Experimental data of Salt A ($n = 7.2$), Salt B ($n = 11.8$) and Salt C ($n = 11.8$) were well fitted to VTF equation with correlation coefficients better than 0.999, indicating that ion motion in the salt was dependent on segmental motion of the oligoether chains.

Incorporation of electron withdrawing groups onto aluminate anion center is ascribed to promote dissociation of the salt. Ionic conductivity of acetoxy group (CH_3COO) substituted aluminate salt was significantly lower than the value for trifluoroacetoxy substituted aluminate. The order of ionic conductivity is Salt C > Salt B > Salt A as a result of dissociation degree of the salt which is ascribed to electron withdrawing ability of substituents X on aluminate center ($\text{CF}_3\text{COO} < \text{CF}_3\text{SO}_3 < (\text{CF}_3\text{SO}_2)_2\text{N}$). Salt C ($n = 11.8$) exhibited $10^{-4} \text{ S cm}^{-1}$ order of ionic conductivity at 40°C .

Salt D exhibited good conductivity similar to Salt A (Fig. 4). In the Salt D, pentafluorophenoxy groups act as

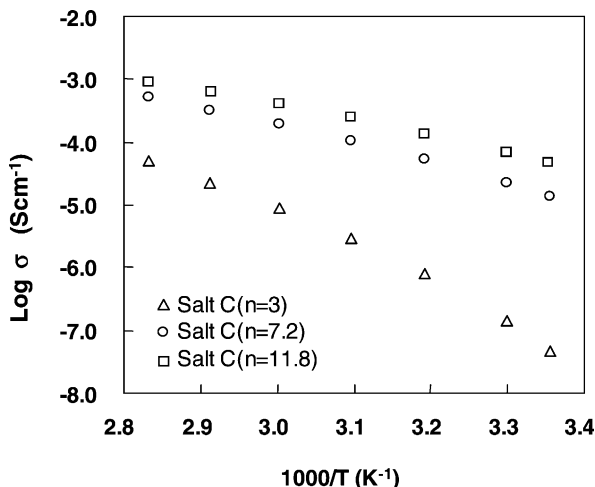


Fig. 3. Temperature dependence of ionic conductivity for Salt C.

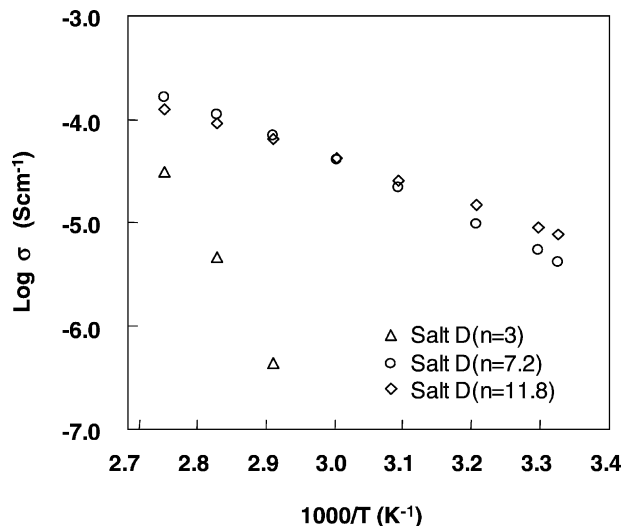


Fig. 4. Temperature dependence of ionic conductivity for Salt D.

not only electron withdrawing groups but also sterically hindered groups for the cation contact with the anion. It has been reported that bulky groups around anions were effective to enhance ionic conductivity of polyelectrolytes [14].

Polymer electrolytes were prepared by incorporation of PEO to the lithium aluminates. All resulting polymer films were soft. Crystallinity (χ) of Salt A (EO/Li = 20/1) was evaluated by enthalpy of fusion (ΔH) of PEO phase in DSC measurement (Table 2). Crystallinity reduced with increasing oligoether chain length in Salt A. The temperature dependence of ionic conductivity for Salt A/PEO electrolytes is shown in Fig. 5. Optimum conductivity was obtained by using a chain length containing 7.2 EO units and it was consistent with lowest degree of crystallinity of the polymer electrolytes. Optimum conductivity for the polymer electrolyte was obtained by using 20/1 of EO/Li ratio. The ionic conductivity of Salt A ($n = 7.2$)/PEO at room temperature was higher than that for $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}/\text{PEO}$ (EO/Li = 20/1) in which ionic conductivity was reduced at lower temperature than 50°C due to crystallization of PEO. This result suggests that Salt A plasticizes PEO effectively.

The ionic conductivities of Salt B ($n = 7.2$)/PEO (EO/Li = 20/1) and Salt C ($n = 7.2$)/PEO (EO/Li = 20/1) were higher than Salt A ($n = 7.2$)/PEO (EO/Li = 20/1) as shown in Fig. 6. Salt C ($n = 7.2$)/PEO (EO/Li = 20/1) electrolyte exhibited $10^{-4} \text{ S cm}^{-1}$ order of ionic conductivity at 40°C . Salt D ($n = 7.2$)/PEO (EO/Li = 20/1) exhibited lower

Table 2
Crystallinity (χ) of Salt A/PEO systems PEO/Li = 20/1

Sample	T_m ($^\circ\text{C}$)	$\Delta H/W$ (J/g)	χ
Salt A ($n = 7.2$)/PEO	50.8	20.4	0.09
Salt A ($n = 3$)/PEO	55.9	53.98	0.25
Salt A ($n = 2$)/PEO	57.3	61.12	0.29
Salt A ($n = 1$)/PEO	59.1	66.19	0.31

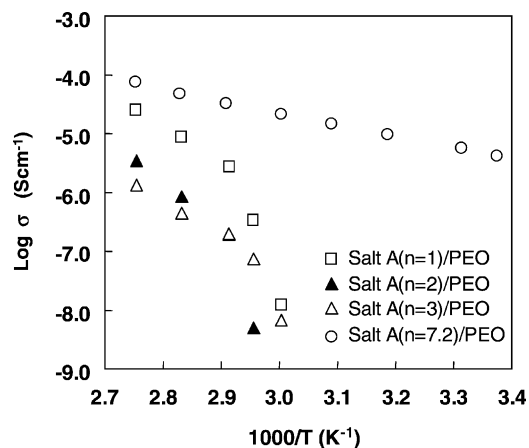


Fig. 5. Temperature dependence of ionic conductivity for Salt A/PEO systems (EO/Li = 20/1).

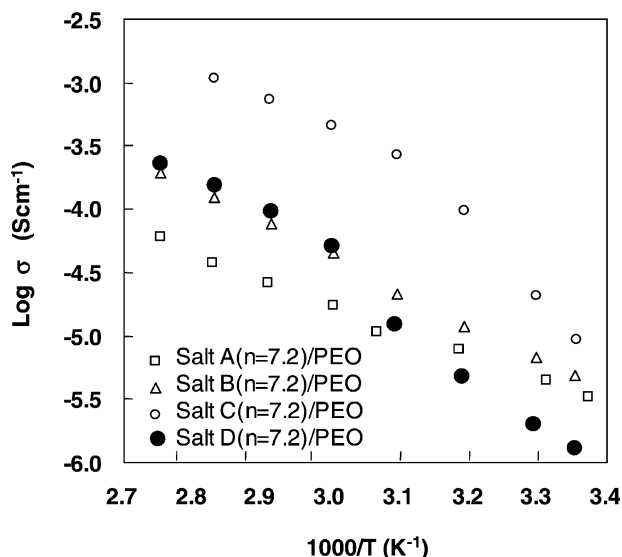


Fig. 6. Temperature dependence of ionic conductivity for Salt/PEO systems (EO/Li = 20/1).

conductivity below 50 °C since Salt A plasticized PEO effectively compared with Salt D. A higher conductivity was observed for Salt D (7.2)/PEO above melting point (56 °C) of PEO in Salt D (7.2)/PEO due to the promoted dissociation of Salt D.

The lithium ion transference numbers T_+ were determined for Salt A/PEO electrolytes. Salt A ($n = 7.2$)/PEO (EO/Li = 20/1) exhibited extremely high lithium ion transference number ($T_+ = 0.78$). The T_+ value for Salt A/PEO was reduced with reduced oligoether chain length. Salt A ($n = 3$)/PEO, Salt A ($n = 2$)/PEO and Salt A ($n = 1$)/PEO exhibited 0.50, 0.46 and 0.44 of T_+ , respectively. These T_+ values are higher than 0.19 of T_+ for the non-oligoether salt system, $\text{LiAl}(\text{OCOCF}_3)_4/\text{PEO}$ (EO/Li = 20/1) or ordinary

lithium salt/PEO systems. We, therefore, conclude that the aluminate anion is immobilized to a high degree by incorporation of oligoether chains which interact with the ether chain of PEO.

Salts A and D exhibited good electrochemical stability in the region of 4.7 and 4.5 V. In addition, DSC measurements indicated that the lithium aluminates were thermally stable (>250 °C).

4. Conclusion

Novel lithium aluminates containing two oligoether groups and two electron-withdrawing groups on aluminate center were prepared. Ionic conductivity is enhanced by incorporation of strongly electron withdrawing groups and moderate chain length of oligoether groups on aluminate center. Lithium transference numbers of the polymer electrolytes composed of lithium aluminates and PEO are quite high compared with an ordinal lithium salt/PEO systems. Although the battery performance using lithium aluminates has not been studied, these salts show great promise for the future.

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