

Synthesis of Aluminate Polymer Complexes as Single-Ionic Solid Electrolytes

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Main-chain anionic polymers with lithium cations, which have oligo(oxyethylene)aluminate chain backbones attached with two side chains of *endo*-methoxy[oligo(oxyethylene)], were prepared, and their ionic conductivities are reported. The ac conductivity of aluminate polymer complex was about 10^{-6} – 10^{-7} S cm⁻¹ at room temperature. As the constant current was observed for [Li/aluminate polymer complex/Li] cells under dc electric field, the single-ionic conduction was confirmed.

Introduction

Solid polymer electrolytes exhibit distinct advantages upon application to extra-thin lithium rechargeable batteries due to much simpler cell constitution, easier processing, and packaging. Particularly, lithium rechargeable batteries that can supply over 3 V from a single unit cell are important for driving large-scale integrations (LSI) or related devices such as liquid-crystal displays (LCD) and electrochromic displays.

Solid polymer electrolytes of [alkali metal salt/polymer] hybrids have been extensively studied¹ and ionic conductivities more than 10⁻⁵ S cm⁻¹ were reported. When used in a rechargeable battery, two ionic species, i.e., lithium ions and their counteranions, migrate between two electrodes during the charging and discharging processes. In such “bi-ionic” conductors, the migration of anions toward the cathode causes polarization, resulting in a serious decay of dc conductivity or the time-dependent increase of cell impedance. On the other hand, the migration of lithium ions via fixed anionic sites is the major event in a “single-ionic” conductor with minimized polarization. To realize the single-ionic nature, side-chain anionic polymers carrying lithium ions as counterparts have been studied as a plausible model.² Lithium carboxylate³ or sulfonate⁴ side-chain structures were most frequently investigated, although the large ion dissociation energy as well as high T_g of these systems decreased the ionic conductivity to ca. 10⁻⁸ S cm⁻¹. Further study is necessary in order to decrease the dissociation energy by utilizing anchored large anionic groups.

A lithium tetra(alkoxy)aluminate unit is a good candidate because the low molecular weight analogues

are known and stable up to 300 °C.⁵ The first studies on those polymer structures by Shriver et al.⁶ on sodium poly(alkoxyaluminate)s established a conductivity of 6.1×10^{-7} S cm⁻¹ at 50 °C and opened the investigation of sodium poly[tetra(alkoxy)aluminate]s. In the present paper are reported the synthesis and ionic conductivity of prescribed aluminate polymer complexes which have two side chains of *endo*-methoxy[oligo(oxyethylene)] and oligo(oxyethylene) main chain.

Experimental Section

Materials. Special grade anhydrous lithium perchlorate for electrolyte use (Kishida Chemicals), and lithium aluminum hydride of 1.0 M solution in tetrahydrofuran (Aldrich) were used as received. 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, Wako Pure Chemicals, and $n_{\text{av}} = 7.2$ ($\text{MW}_{\text{av}} = 350$), 12.1(550), 16.3(750), Polysciences Inc.] were dried under vacuum at 60–80 °C for a half day, where MW_{av} represents the number average molecular weight. Oligo(ethylene glycol) [OEG; $\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_m\text{H}$, $m = 1$ –4, Kishida Chemicals, and $m_{\text{av}} = 4.1$ ($\text{MW}_{\text{av}} = 200$), 6.4(300), 8.7(400), 13.2(600), Wako Pure Chemicals] were dried under vacuum at 20–40 °C for a half day. Predistilled THF and dioxane were dried by refluxing over benzophenone–sodium complex for a half day, redistilled under argon atmosphere, and immediately used.

All experiments hereafter were conducted under dry argon atmosphere in a vacuum-type drybox at room temperature which was mostly 22 ± 3 °C.

Preparation of Lithium Tetra(alkoxy)aluminate. Lithium tetra(alkoxy)aluminates were prepared by dropwise addition of a THF or dioxane solution containing 4 mol of OGM into a THF solution containing 1 mol of lithium aluminum hydride (LAH) at 0 °C. The mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo, and then the product was heated to 80 °C under vacuum for 4 h in order to complete the reaction and solvent evaporation. As a reference experiment, the original 1.0 M solution of lithium aluminum hydride was diluted with the same volume of THF as that used in the reaction described above and maintained for the same period at the same temperature as described above. With the passage of dry argon carrier gas, the resulting solution was titrated with *tert*-butyl alcohol. From the amount of evolved hydrogen gas determined by gas chromatography, it was calculated that more than 99% of LAH is active.

Preparation of Aluminate Complex Dimers. To a solution containing 2 mol of LAH, the THF or dioxane solution

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(1) (a) Wright, P. V. *Br. Polym. J.* **1975**, 7, 319. (b) *Polymer electrolyte reviews*; MacCallum, J. R., Vincent, C. A., Eds.; Elsevier Applied Science: London, 1987, 1989; Vols. 1 and 2.

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

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

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

(5) Brown, H.; McFarlin, R. *J. Am. Chem. Soc.* **1958**, 80, 5372.

(6) Doan, K.; Ratner, M.; Shriver, D. *Chem. Mater.* **1991**, 3, 418.

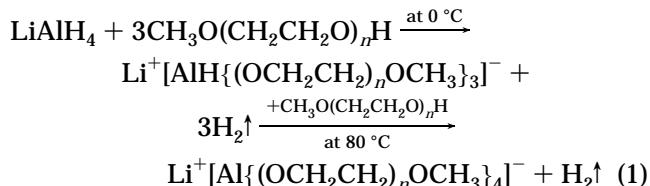
containing 1 mol of OEG and 6 mol of OGM was added at 0 °C under argon atmosphere. The mixture was then treated similarly as described above.

Preparation of Aluminate Polymer Complexes. The mixed solution of 1 mol of OEG and 2 mol of OGM in THF or dioxane was added dropwise into a solution containing 1 mol of LAH at 0 °C, allowed to react, and then treated as described above. Before the final stage of evaporation, lithium perchlorate was doped if necessary.

Sample Preparation and Measurements. Electrolytes were fabricated into thin films typically in a size of 10 mm diameter × 0.1 mm, sandwiched between stainless steel or metallic lithium electrodes and used for ac or both ac and dc conductivity measurements, respectively. The frequency-dependent impedance of the samples was measured by a Solartron 1250 frequency response analyzer/1286 potentiostat (10⁻² Hz to 65 k Hz). The time dependence of dc conductivity of the samples was measured at room temperature under an applied voltage of 1.0–5.0 V with lithium electrodes using a Hokuto Denko HB104 function generator/HA501 potentiogalvanostat. As it was noticed from the ac conductivity measurements for the same samples prior to the dc experiments that the interfacial impedances between the metallic lithium electrodes and the present aluminate complex electrolytes were relatively small (ca. <5% of total impedance), the dc conductivities were calculated without eliminating the interfacial impedances.

Results and Discussion

The reaction between lithium aluminum hydride (LAH) and 4 equiv of alcohols had been known to yield H₂ and stable lithium tetra(alkoxy)aluminate complexes since 1947.⁷ In the case of the reaction between *tert*-butyl alcohol with LAH for instance, lithium tri-*tert*-butoxyaluminum hydride is formed as intermediate at ambient temperatures. This is further converted to lithium tetra-*tert*-butoxyaluminate, a complex that is very stable up to 300 °C but extremely sensitive to moisture. As shown in eq 1 the analogous reaction with



OGMs yielded lithium tri(OGM)aluminum hydride as intermediate at low temperatures and then converted to lithium tetra(OGM)aluminate complexes upon further reaction at elevated temperatures. Unfortunately such aluminate complexes were even more sensitive to trace amounts of water. Although every effort has been made, no analysis or characterization other than by IR spectroscopy has succeeded. In the FT-IR spectra, complete disappearance of ν(O–H) at 3420 cm⁻¹, ν(Al–H) at 1779 and 1642 cm⁻¹⁸ was confirmed, while the distinct absorption peak of ν(Al–O) at 700 cm⁻¹ was seen. Also, no Al–H activity was found by titration after the completion of tetra(OGM)aluminate formation.

As the starting materials and solvents were well-purified to exclude trace water, the contamination of impurities (namely LiOH and unreacted HO-carrying

(7) Finholt, A.; Bond, A.; Schlesinger, H. *J. Am. Chem. Soc.* **1947**, *69*, 1199.

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

Table 1. Ac Conductivity of Lithium Tetraalkoxyaluminate, Li⁺[Al{OCH₂CH₂)_nOCH₃}₄]⁻

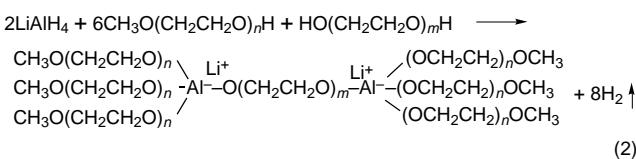
<i>n</i>	σ (S cm ⁻¹)	note
1	4.7×10^{-6}	soft solid
2	2.2×10^{-5}	viscous solid
3	1.1×10^{-5}	viscous solid
7.2	4.1×10^{-7}	tacky solid
12.1	3.7×10^{-7}	waxy solid
16.3	1.9×10^{-8}	waxy solid

Table 2. Ac Conductivity of Aluminate Dimer Complexes, Li₂⁺[{CH₃O(CH₂CH₂O)_n}₃Al–O(CH₂CH₂O)_m–Al{OCH₂CH₂)_nOCH₃}₂]⁻

<i>n</i>	<i>m</i>	σ (S cm ⁻¹)	note
1	1	2.0×10^{-8}	brittle solid
1	3	4.9×10^{-7}	brittle solid
1	4	6.6×10^{-7}	brittle solid
2	1	1.9×10^{-6}	tacky solid
2	3	4.5×10^{-6}	viscous liquid
2	4	3.3×10^{-6}	tacky solid
3	1	1.3×10^{-5}	brittle solid
3	3	3.7×10^{-6}	viscous liquid
3	4	2.3×10^{-6}	tacky solid

OGMs) which may influence the results of conductivity measurements were negligible. Especially, the surface of a freshly cut metallic lithium electrode employed in dc measurements still retained its mirror reflectivity after prolonged contact with the sample.

The ac conductivities of lithium tetra(OGM)aluminate complexes are summarized in Table 1. All electrolytes were colorless and the apparent properties were changed by the length of oxyethylene repeating units, *n*, from soft solid (*n* = 1), viscous liquid (2, 3), tacky solid (7.2), to waxy solid (*n* > ~12). Their ac conductivity was greatly influenced by the fluidity or segmental motion of oxyethylene units and showed the maximum conductivity of 2.2×10^{-5} S cm⁻¹ when the sample was viscous liquid, *n* = 2. Because the rapid translational diffusion is permitted in the fluidal systems, the dc conductivities of most such monomeric complexes sustained at reasonable values, but those results will be discussed elsewhere:



Aluminate dimer complexes were prepared by reacting the mixture of 6 equiv OGMs, 2 –OH equiv of OEGs, and 2 equiv LAH as given in eq 2. Although the desired dimer structure could be the major portion, some “statistical” mixing might cause the formation of either monomeric or oligomeric complexes. The two-step addition, e.g., (1) OGMs at first and then OEGs into LAH or (2) in the inverted way, did not provide much help. The result of (1) was the same as that of prescribed one-shot mixing, and the addition procedure (2) caused partial polymerization, yielding insoluble parts. The ac conductivities of aluminate dimer complexes summarized in Table 2 resembles the tendency similar to the monomer complexes, i.e., the more flexible (fluidal), the higher the conductivity. However, it is noteworthy that the ac conductivity was still sustained at the level of 10^{-5} – 10^{-6} S cm⁻¹ even in solid-phase dimers. These results were encouraging to the possibil-

Table 3. Relationship between Ac Conductivity and *m* of Aluminate Polymer Complex When *n* Is Fixed to 3

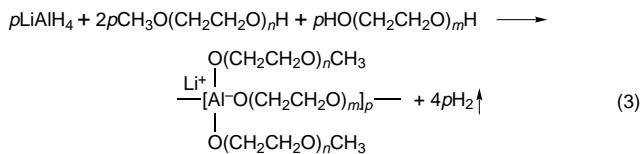
<i>m</i>	σ (S cm $^{-1}$)	note
1	2.3×10^{-8}	tacky solid
2	2.3×10^{-7}	soft solid
3	7.5×10^{-7}	soft solid
4	4.3×10^{-7}	tacky solid
4.1	4.3×10^{-7}	tacky solid
6.4	3.2×10^{-7}	tacky solid
8.7	2.0×10^{-7}	tacky solid
13.2	8.5×10^{-8}	hard solid
6.4 ^a	2.8×10^{-5}	hard solid

^a 5 wt % of LiClO₄ was doped.

Table 4. Relationship between Ac Conductivity and *m* of Aluminate Polymer Complex When *n* Is Fixed to 7.2

<i>m</i>	σ (S cm $^{-1}$)	note
1	1.3×10^{-7}	soft solid
2	1.2×10^{-7}	soft solid
3	5.7×10^{-7}	soft solid
4	1.4×10^{-6}	soft solid
4.1	3.3×10^{-7}	solid
6.4	1.0×10^{-7}	solid
8.7	7.5×10^{-8}	solid
13.2	3.9×10^{-8}	solid

ity of fast ion transport in analogous solid polymeric materials:



Aluminate polymer complexes were prepared as shown in eq 3 by a reaction similar to that to form the dimer complexes, after completion of the reaction and solvent evaporation at 80 °C, the product turned into insoluble solids. As nothing was recovered from the filtrate formed by THF or dioxane which was added to swell the insoluble solids, the products were concluded to be polymer complexes with plausible cross-linking, and there was no occurrence of very low molecular weight complexes. The FT-IR spectra of those aluminate polymer complexes were similar to those obtained for the monomer complexes; i.e., disappearance of $\nu(\text{Al---H})$ (1779, 1642), $\nu(\text{O---H})$ (3420) and appearance of $\nu(\text{Al---O})$ (700 cm $^{-1}$).

The value of *n* was chosen to be more than 3, because upon considering the results of aluminate dimer complexes, it was decided that the existence of flexible side chains with suitable segmental motion might provide the best possibility of the free-volume formation for lithium ion hopping. In Tables 3 and 4 are summarized the results of ac conductivity measurement when *n* was fixed to 3 or 7.2, respectively. The highest conductivities in each series were about 10 $^{-6}$ S cm $^{-1}$, i.e., 7.5×10^{-7} S cm $^{-1}$ (Table 3, *n* = 3, *m* = 3) and 1.4×10^{-6} S cm $^{-1}$ (Table 4, *n* = 7.2, *m* = 4). If these high ionic conductivities persist the dc electric field, such polymer complex electrolytes will be valid for practical use.

To evaluate the nature of single-ionic conduction, the polymer samples were sandwiched between metallic lithium electrode, and the time dependences of dc conductivities were examined. The results for two polymer complexes of (*n* = 3, *m* = 6.4) and (*n* = 3, *m* = 8.7) as well as one reference sample doped with LiClO₄

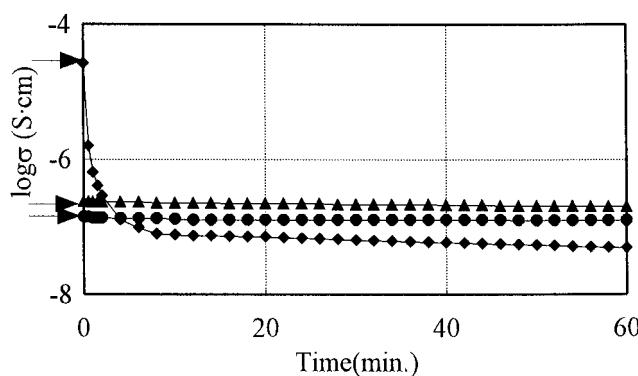


Figure 1. Time-dependence of dc conductivity of aluminate polymer complex *n* = 3, *m* = 6.4 (▲), *n* = 3, *m* = 8.7 (●), *n* = 3, *m* = 6.4, [LiClO₄] = 5wt % (◆).

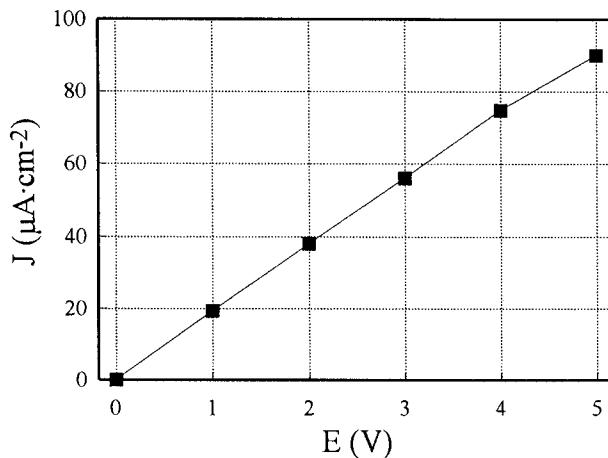


Figure 2. Relationship between the stationary dc current density and the applied dc voltage for the polymer complex of *n* = 3 and *m*_{av} = 13.2, thickness = 100 μm .

(*n* = 3, *m* = 6.4, [LiClO₄] = 5 wt %) are compared in Figure 1. In the present systems, the interfacial impedance is relatively small; therefore, the ac conductivities calculated from the value of bulk impedance (shown by arrows in Figure 1) well coincided with the initial value of dc conductivities. Although the dc conductivities of polymer complexes decreased to some extent at the initial stage due to the change of interfacial charge-transfer impedance, they sustained the high values even after prolonged application of 1 V dc potential. The ac conductivities measured immediately after the dc experiments showed exactly the same values as those obtained in advance. These results reflect good evidences for single-ionic conduction in the present polymer complexes. By contrast, the ionic conductivity of the LiClO₄-doped sample decayed in a short period from 10 $^{-5}$ to less than 10 $^{-8}$ S cm $^{-1}$. It is well-known that the hybrids of LiClO₄ and a polymer carrying oxyethylene repeating units exhibited very high ac conductivity, but bi-ionic nature.⁹ Such bi-ionic nature caused the polarization under dc electric field and the serious decay of dc conductivity might not allow the hybrid type bi-ionic conductors to be utilized in batteries.

In Figure 2 are shown the relationship between the dc current density and the applied dc voltage for the polymer complex of *n* = 3 and *m*_{av} = 13.2. Up to 5 V, the ohmic conduction was clearly seen, while the

relationship for the corresponding LiClO₄-doped systems deviated from the linear line and gave irreproducible results probably due to the electrolytic decomposition of perchlorate anion when applied voltage was larger than 3 V.

Thus, the difference in the results between the polymer complexes carrying anchored anionic groups and the hybrids is very clear in the present study and demonstrates that the single-ionic conduction is valid in solid electrolytes where the translational diffusion of ions are limited. Further studies on the single-ionic nature of aluminate polymer complexes will be reported elsewhere.

Conclusion

New single-ionic aluminate polymer complexes were synthesized. These complexes conduct about 10⁻⁶–10⁻⁷ S cm⁻¹ at room temperature upon prolonged apply of dc. Comparison with the hybrid system demonstrated the validity of single-ionic conduction.

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