

## New Inorganic-Organic Hybrid $\text{Li}^+$ Ion Conducting Polymer Electrolytes

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A new series of inorganic-organic hybrid polymer electrolytes containing the aluminate structure were prepared. Incorporation of stronger Lewis acid sites into the polymer in the region of the aluminate bond was effective for enhancing ionic conductivity. The materials were shown to be single  $\text{Li}^+$  ion conductors.

Polymer electrolytes have been attracting attention because of their potential for use in lithium rechargeable batteries.<sup>1-3</sup> Since it has been reported<sup>4</sup> that improved battery performance is observed for systems containing electrolytes with a  $\text{Li}^+$  transference number close to unity, many groups have focussed on the development of single  $\text{Li}^+$  conductors.<sup>5-7</sup> Here we report the synthesis of a new series of inorganic-organic hybrid polymer electrolytes containing the aluminate anion immobilized onto the polymer backbone. Concepts of molecular design were carefully considered before preparation of these polymers and we therefore describe the relationship between polymer structure and  $\text{Li}^+$  ion conductivity.

Polymers containing the aluminate structure were prepared as illustrated in Figure 1. Hydrosilation of triethyleneglycol

allylmethylether, prepared by the Williams synthesis, gave a product with a linear ether chain attached to the silicon atom (step A). The structure of the intermediate silanol was confirmed by <sup>1</sup>H-NMR and IR spectroscopy. Solutions of  $\text{LiAlH}_4$  in tetrahydofuran (THF) were slowly added to 2 mole equivalents of the required alcohol at -78 °C. After stirring for 1 hour at room temperature, diphenyl silanediol or phenyl boronic acid was added dropwise at -78 °C. Stoichiometric amounts of hydrogen were evolved in both steps. The reaction mixture was stirred at 70 °C for 12 hours and soft polymers containing  $\text{SiPh}_2$  or  $\text{BPh}_3$  groups bonded to the aluminate ion were obtained after removal of the solvent for 12 hours under reduced pressure. Since many of the reagents, intermediates and all of the synthesized polymers were extremely hydrolyzable, all manipulations were carried out on a dry nitrogen / vacuum line or in an argon filled dry box. Ionic conductivities, ( $\sigma$ ), of samples sandwiched between blocking stainless steel electrodes were determined by the ac impedance method.  $\text{Li}^+$  transference numbers, ( $T_+$ ), were determined for samples sandwiched between lithium electrodes by a modified form of the Evans method<sup>8</sup> as described by Abraham.<sup>9</sup>

The room temperature ionic conductivities of the polymers

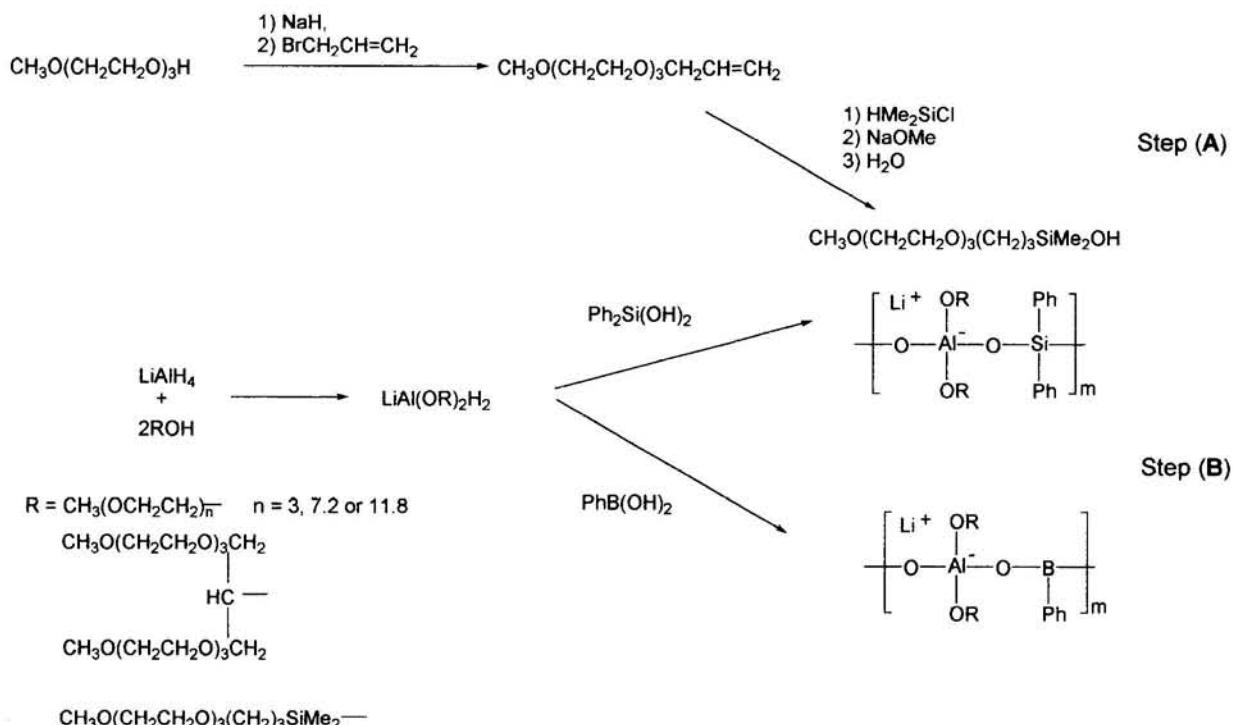


Figure 1. Synthesis of aluminate polymers.

**Table 1.** Ionic conductivities of aluminate polymers

$[\text{Li}^+\text{OAl}^+(\text{OR})_2\text{OMPh}_{(1\text{ or }2)}]_m$ at 25 °C				
R	No.	M = Si /Scm <sup>-1</sup>	No.	M = B /Scm <sup>-1</sup>
CH <sub>3</sub> (EO) <sub>3</sub>	(1)	1.7 x 10 <sup>-9</sup>	(5)	2.8x10 <sup>-8</sup>
CH <sub>3</sub> (EO) <sub>7.2</sub>	(2)	3.4 x 10 <sup>-8</sup>	(6)	3.5x10 <sup>-6</sup>
CH <sub>3</sub> (EO) <sub>11.8</sub>	(3)	<10 <sup>-9</sup>	(7)	5.3x10 <sup>-7</sup>
[CH <sub>3</sub> (EO) <sub>3</sub> OCH <sub>2</sub> ] <sub>2</sub> CH	-	-	(8)	1.5x10 <sup>-6</sup>
CH <sub>3</sub> (EO) <sub>3</sub> O(CH <sub>2</sub> ) <sub>3</sub> Si(CH <sub>3</sub> ) <sub>2</sub>	(4)	7.5 x 10 <sup>-9</sup>	(9)	1.4x10 <sup>-7</sup>
EO = OCH <sub>2</sub> CH <sub>2</sub>				

prepared are shown in Table 1. For each system studied, it was clear that incorporation of the stronger Lewis acid BPh next to the Al-O bond resulted in greater ionic conductivities compared to systems containing SiPh<sub>2</sub>. Incorporation of a strong Lewis acid gives rise to a greater reduction of electron density on the aluminate ion as a result of more effective (pπ-pπ) delocalization. This will reduce ion pairing which is one of the major factors responsible for the low ionic conductivities often observed in polyelectrolytes where the anion is immobilized on the polymer backbone. In addition the increased steric hindrance of two phenyl groups in the case of SiPh<sub>2</sub> will hinder the motion of the oligoether side chains which are responsible for providing the organic ion conducting pathway through the system. In a similar manner to that described above, comparison of polymers (1) and (4) and (5) and (9) showed that the incorporation of a silicon atom between the aluminate ion and the ether side chain was effective for producing a 4 to 5 fold conductivity enhancement. This was also ascribed to more effective charge delocalization via silicon - oxygen dπ-pπ bonding.

Upon increasing the length of the oligoether side chain from n = 3 to n = 7.2, an enhancement in ionic conductivity was observed. A further increase in the chain length however resulted in a reduction in conductivity. By increasing the chain length the proportion of the organic conducting region in the system is increased, increasing the mobility of the Li<sup>+</sup> ions through the system and accounting for the conductivity enhancement between n = 3 and n = 7. Concomitantly, however, there is a net reduction in the Li<sup>+</sup> ion concentration in the system and for long ether chains, an increase in chain entanglement. This would account for the reduction in conductivity between n = 7.3 and n = 11.8.

Since Watanabe has recently reported<sup>10</sup> that more highly branched polyether systems give rise to greater ionic

conductivities and lower activation energies for conduction, polymer (8) containing a branched oligoether side chain was prepared. Comparison of polymers (6) and (8) which contained a similar number of ether oxygen atoms however showed that in this case a very slight reduction in room temperature conductivity was observed when the branched ether chain was used. The transference number determined at room temperature (25 °C) for polymer (8) was found to be equal to unity showing that this material was effectively a single Li<sup>+</sup> ion conductor. This is to be expected for a system such as this where the anions are immobilized on the polymer backbone and as such should more correctly be termed a polyelectrolyte. In addition, the interfacial impedance was not observed to increase over the timescale of the transference number measurement indicating the stability of the polymer with respect to lithium metal.

In conclusion, using new concepts of molecular design, we have prepared a series of polymer electrolytes containing the aluminate structure. Incorporation of strong Lewis acids in the region of the Al-O bond and oligoether side chains of moderate length is effective for obtaining enhanced ionic conductivity. A Li<sup>+</sup> transference number of unity was obtained illustrating the single ion conducting nature of these materials.

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#### References

- 1 D. Fauteux, A. Massucco, M. McLin, M. Van Buren, and J. Shi, *Electrochim. Acta*, **40**, 2185 (1995).
- 2 K.M. Abraham and Z. Jiang, *J. Electrochem. Soc.*, **143**, 1 (1996).
- 3 Y. Aihara, M. Kodama, K. Nakahara, H. Okise, and K. Murata, *J. Power Sources*, **65**, 143 (1997).
- 4 M. Doyle, T.F. Fuller, and J. Newman, *Electrochim. Acta*, **39**, 2073 (1994).
- 5 L.C. Hardy and D.F. Shriver, *J. Am. Chem. Soc.*, **107**, 3823 (1995).
- 6 D. Benrabah, S. Sylla, F. Alloin, J-Y Sanchez, and M. Armand, *Electrochim. Acta*, **40**, 2259 (1995).
- 7 T. Fujinami, A. Tokimune, M.A. Mehta, D.F. Shriver, and G.C. Rawsky, *Chem. Mater.*, **9**, 2236 (1997).
- 8 J. Evans, C.A. Vincent, and P.G. Bruce, *Polymer*, **28**, 2234 (1987).
- 9 K.M. Abraham, Z. Jiang, and B. Carroll, *Chem. Mater.*, **9**, 1978 (1997).
- 10 M. Watanabe, Presented at the 23<sup>rd</sup> Symposium on Solid State Ionics in Japan, Nagoya, 1997, Abstr., 2C16.