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Plastic crystalline lithium salt with solid-state ionic conductivity and high lithium transport number†

Makoto Moriya,^{ab} Daiki Kato,^a Wataru Sakamoto^a and Toshinobu Yogo^{*a}

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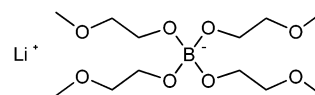
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Plastic crystallinity of lithium salt, $[\text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$ (**1**), and its solid-state ionic conductivity are disclosed. The addition of small amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to borate **1** led to the drastic increase of the ionic conductivity and lithium transport number of the electrolyte.

Plastic crystal (PC) is a solid in the mesophase between a liquid and a crystal. It shows some disorder in molecular orientation or conformation within the crystalline lattice. Recently, the mixture of lithium salt with PC has attracted considerable attention owing to its potential application as a solid electrolyte.^{1–5} Because electrolytes in current lithium ion batteries (LIBs) consist of flammable organic liquids that can cause a serious accident when the electrolyte solution leaks and then combusts, novel solid lithium electrolytes are required.^{6–9}

Previous work on the synthesis of solid PC-based electrolytes mainly focused on the addition of lithium salt to plastic crystalline materials such as tetraalkylammonium, or heterocyclic cations.^{2–5} These electrolytes show high ionic conductivities. However, the lithium transport numbers (t_{Li^+}) of these materials are low since these PCs consist of transportable ionic species. Nevertheless, when a neutral plastic crystalline matrix, such as succinonitrile, is used, the conduction of the counter anion of lithium salt leads to a decrease in t_{Li^+} . Low t_{Li^+} values cause a large internal resistance of battery as a result of the gradient of the ionic concentration of the electrolyte. For this reason, a novel strategy to increase t_{Li^+} of the PC-based electrolyte is necessary for the development of next-generation batteries.

To increase the t_{Li^+} value of the PC-based electrolyte, we developed a plastic crystalline lithium salt. In general, the size of the counter anions in the lithium salt is larger than that of the lithium ions. Therefore, anion conduction is inhibited in the plastic crystalline lithium salt, yielding a large t_{Li^+} value. Based on this idea, we investigated the molecular design of a counter anion using borate that is based on the structure of

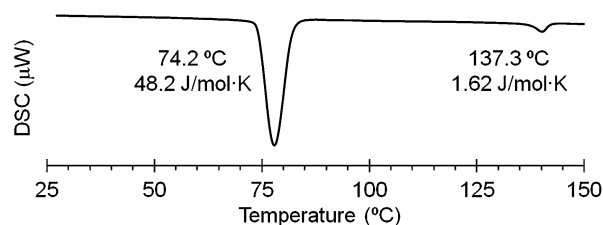
Fig. 1 Molecular structure of lithium borate **1**.

pentaerythritol, which shows plastic crystallinity under thermal conditions.^{10,11} Herein, we show the plastic crystallinity of lithium salt, $[\text{LiB}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_4]$ (**1**), with solid-state ionic conductivity and high lithium transport number (t_{Li^+}) (Fig. 1).

Sochor *et al.* reported that the reaction of 2-methoxyethyl ester of boric acid with lithium hydride resulted in the formation of a mixture of **1** and LiBH_4 .^{12,13} It is the first report about borate **1**, although the isolation of **1** has never been investigated. In this study, we prepared **1** *via* a one-pot ligand exchange reaction using $[\text{LiB}(\text{OCH}_3)_4]$ ¹⁴ as a starting material. The solution of $[\text{LiB}(\text{OCH}_3)_4]$ in 2-methoxymethanol was refluxed under a nitrogen atmosphere for 24 h followed by the removal of the solvent under reduced pressure. Crystallization from hot acetonitrile gave **1** as a white powder in a 71% yield. The XRD pattern of **1** measured at room temperature showed strong diffractions, indicating that this compound is a crystalline solid at ambient temperatures (Fig. S1, ESI†).

The formation of **1** was confirmed by the NMR spectra (Fig. S2, S3 and S4, ESI†). The ¹H NMR spectrum of **1** measured in CDCl_3 gave three signals at 3.52 and 3.44 ppm, assignable to methylene protons, and at 3.31 ppm, attributable to the methyl group, in an intensity ratio of 2 : 2 : 3 (Fig. S2, ESI†). In the ¹¹B NMR, the signal of **1** appeared at 2.64 ppm (Fig. S4, ESI†).

Fig. 2 depicts the differential scanning calorimetry (DSC) curve of **1** measured from 25 to 150 °C under a nitrogen flow. Borate **1** afforded two endothermic peaks at 74.2 and 137.3 °C. The first peak is attributed to the phase transition from crystal

Fig. 2 DSC curve of **1**.

^a Division of Nanomaterial Science, EcoTopia Science Institute, Nagoya University, 464-8603, Furo-cho, Chikusa-ku, Nagoya, Japan. E-mail: yogo@esi.nagoya-u.ac.jp; Fax: +81 52 789 2121; Tel: +81 52 789 2750

^b PRESTO, Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012 Japan

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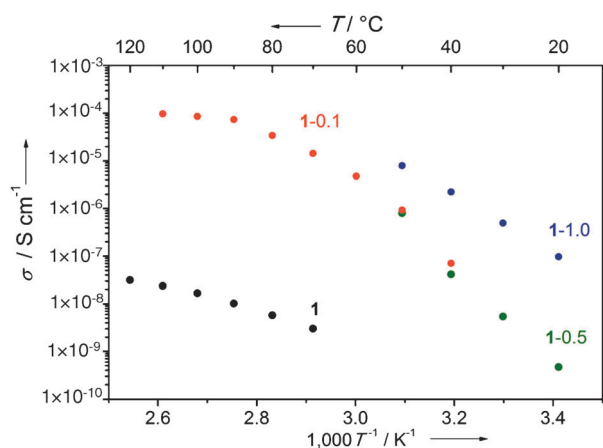


Fig. 3 Conductivities of **1** (black), **1-0.1** (red), **1-0.5** (green), and **1-1.0** (blue) as a function of temperature.

to plastic crystal (PC) and the second peak to melting. The small entropy value, $1.6 \text{ J K}^{-1} \text{ mol}^{-1}$, for the second peak for **1** supported the existence of a PC phase in **1** since these values were less than the criterion set by Timmermans:¹⁵ $\Delta S_m < 20 \text{ J K}^{-1} \text{ mol}^{-1}$. To the best of our knowledge, **1** is the first example of a plastic crystalline lithium salt.

To analyze the ionic conductivity of the plastic crystalline lithium salts, the powder of the lithium salt was dried under reduced pressure for at least 48 h, followed by pressing into a disk. The disk was placed between a pair of stainless-steel electrodes in a cell for ac impedance measurements. The ac impedance data showed a well-defined semicircle and a low-frequency spike (Fig. S5, ESI†). These data indicated that the grain boundary resistances of the electrolyte were quite small.

The conductivities of lithium borate **1** were measured over a temperature range from 20 to 120 °C (Fig. 3). The ionic conductivities were calculated from the touchdown point on the Z' -axis in a Nyquist plot of the products, which indicated the resistance of the sample. The conductive behavior clearly correlated to the observations from thermal analysis. With increasing temperature, the ionic conductivity of **1** increased from $1.51 \times 10^{-9} \text{ S cm}^{-1}$ to $3.14 \times 10^{-8} \text{ S cm}^{-1}$ in the plastic crystalline phase.

To improve the conductive property, small amounts of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were added to **1** to give **1-*n*** (n = amount of LiTFSI). Fig. 3 shows ionic conductivities of the obtained electrolytes. This figure clearly indicates that the addition of LiTFSI to **1** led to a dramatic increase in the ionic conductivity. Conductivities of **1** and **1-0.1** measured at 90 °C were 1.02×10^{-8} and $7.41 \times 10^{-5} \text{ S cm}^{-1}$, respectively. Surprisingly, the addition of only 0.1 equivalents of LiTFSI increased the ionic conductivity approximately 7000 times. The electrochemical stability of **1-0.1** is shown in Fig. S6 (ESI†). The measurement revealed a stability window between 1.9 and 3.6 V at 80 °C.

The lithium transport numbers of electrolytes were determined via a DC impedance polarization method using lithium foils as non-blocking electrodes.¹⁶ Borates **1** and **1-0.1** showed similar t_{Li^+} values, which were *ca.* 0.3 at 80 °C (Fig. S7, ESI†). The literature reports a common coordination number of lithium complexes from 4 to 6.¹⁷ Borate **1** provided multiple

coordination sites for the lithium ions since **1** possessed eight oxygen atoms on its glyme chains. Therefore, a part of the borate anion in **1** did not interact with the lithium ion. Conduction of the free anions took place, decreasing the t_{Li^+} of **1**.

Interestingly, **1-0.1** showed an increased t_{Li^+} value of 0.7 at 40 °C (Fig. S8, ESI†). Since the DSC curve of **1-0.1** (Fig. S10, ESI†) was almost identical to that of **1** (Fig. 3), **1-0.1** behaved as a crystal below 74 °C, indicating that the ionic conduction through **1-0.1** occurred both under the crystalline state and the plastic crystalline phase. The conduction mechanism through the crystal and the PC phases of **1-0.1** should have been different. In the crystal lattice of **1-0.1**, defects were probably introduced by the addition of small amounts of LiTFSI. Hence, lithium ion conduction in the crystal phase of **1-0.1** likely occurred *via* a hopping mechanism through the vacant space in the crystal lattice. Previous reports proposed a similar conduction mechanism in regards to the crystalline polymer electrolytes.^{18–22} Since the volume of the lithium ion was small compared with that of the anions in **1-0.1**, the lithium ion conduction proceeded preferentially to give a large t_{Li^+} value. In general, the electrolytes consisted of an ionic matrix and lithium salt possessed a low t_{Li^+} , which was approximately 0.01–0.35.^{23–26} Compared with the reports, **1-0.1** showed very large t_{Li^+} values since this electrolyte was a solid composed of only lithium salts.

The t_{Li^+} of **1-0.5** and **1-1.0** at 40 °C were 0.6 and 0.1, respectively. Because the addition of large amount of LiTFSI to **1** increased the TFSI anion content in the electrolyte, the increased conduction of the TFSI anion reduced the t_{Li^+} value. **1** existed as a crystal at room temperature, and changed to a plastic product above *ca.* 80 °C. The addition of more than 0.5 equivalents of LiTFSI to **1** led to a decrease in the melting point. The melting points of **1-0.5** and **1-1.0** were 51.6 and 54.1 °C, respectively, as shown in Fig. S11 and S12 (ESI†). On the other hand, **1-2.0** was a room-temperature ionic liquid with high viscosity, although it was composed of only two lithium salts without matrix materials.

We demonstrated a new concept in the construction of solid lithium electrolytes based on PCs with large t_{Li^+} . We developed the novel lithium salt **1** using the simple ligand exchange reaction of borate. Borate **1** showed plastic crystallinity and solid-state ionic conductivity. With the addition of small amounts of LiTFSI to **1**, we succeeded not only in drastically increasing ionic conductivity but also in inducing a large t_{Li^+} .

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