

Short communication

Mechanochemical synthesis of hybrid electrolytes from the Li_2S – P_2S_5 glasses and polyethers

Akitoshi Hayashi*, Takashi Harayama, Fuminori Mizuno, Masahiro Tatsumisago

Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Sakai, Osaka 599-8531, Japan

Received 8 August 2005; received in revised form 5 June 2006; accepted 9 June 2006

Available online 27 July 2006

Abstract

Novel hybrid solid electrolytes were prepared by mechanochemistry using the Li^+ conductive Li_2S – P_2S_5 glasses and –OH terminated oligomers. The P–O–C bonds were observed in FT-IR spectra for the obtained electrolytes, suggesting that the molecular level hybrid materials were synthesized. The addition of small amounts of oligomers into the glass successfully enhanced the conductivity of hybrid electrolytes by lowering glass transition temperature. The hybrid electrolyte with 2 mol% of 1,4-butanediol exhibited the ambient temperature conductivity of $9.7 \times 10^{-5} \text{ S cm}^{-1}$, which is 1.5 times as large as the conductivity of the pristine glass. The hybrid with a polyether showed lower conductivity than the hybrid with 1,4-butanediol. Incorporating oligomer blocks into glass network is a new approach to enhance the conductivity of glass-based solid electrolytes.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Solid electrolyte; Hybrid; Lithium ion; Sulfide glass; Conductivity

1. Introduction

The development of lithium ion conducting solid electrolytes is desired for the materialization of all-solid-state rechargeable lithium batteries with safety and reliability. Inorganic sulfide glasses in the systems Li_2S – P_2S_5 and Li_2S – SiS_2 have a great feature as a solid electrolyte of Li^+ conductivity of $10^{-4} \text{ S cm}^{-1}$ at room temperature [1–3].

Composite electrolytes were prepared from intimate mixtures of sulfide glasses and organic polymers to endow solid electrolytes with acceptable mechanical flexibility, which leads to form a close interfacial contact between electrolyte and electrode in an all-solid-state battery, including a sheet-like flexible battery. Polyethylene oxide-based polymers, styrene–butadiene rubbers, and silicone polymers were used as a binder for the Li^+ conducting glassy electrolytes [4–6]. The drawback of these glass–polymer composite electrolytes is to decrease the conductivity of electrolytes with an addition of insulative polymers.

Recently, we have synthesized molecular level hybrid electrolytes, in which blocks of the sulfide superionic glass structure

are incorporated as an integral part of the polymer structure [7]. In this study, hybrid electrolytes are defined as the electrolytes where chemical bonds are formed between inorganic and organic moieties. The hybrid electrolytes could, in principle, have both a rubbery compliance and high conductivity by moving glass transition temperature (T_g) below ambient temperature. The base hybrid materials were prepared from the mixture of P_2S_5 and –OH terminated oligoethers of variable length, and then Li_2S was reacted with the base hybrids to endow the electrolytes with Li^+ conductivity. Although the T_g of the obtained electrolytes was lowered below ambient, the electrolytes exhibited very low conductivity of $10^{-6} \text{ S cm}^{-1}$, which is two orders of magnitude lower than the Li_2S – P_2S_5 sulfide glasses. One of the reasons of this poor conductivity is a low Li^+ concentration in the electrolytes; the Li_2S content in the hybrid electrolytes was only below 4 mol%.

An alternative strategy for synthesizing hybrid electrolytes with high Li^+ conductivity is to directly use the Li_2S – P_2S_5 sulfide glasses with high Li_2S content as a starting material. The sulfide glasses were prepared by mechanochemical reaction [8,9] and the obtained fine powder has an advantage of high reactivity with organic oligoethers. Mechanochemical process is basically room temperature process and it is available for mixing and reacting organic moieties. Lowering T_g of the

* Corresponding author. Tel.: +81 72 2549334; fax: +81 72 2549910.
E-mail address: hayashi@chem.osakafu-u.ac.jp (A. Hayashi).

glassy electrolytes by incorporating oligoether blocks would improve ambient temperature conductivity of the obtained hybrid electrolytes in parallel with maintaining the decoupled conduction mechanism [10,11] of sulfide superionic glasses.

In the present study, inorganic–organic hybrid electrolytes combining Li^+ conducting glasses and $(\text{CH}_2\text{--CH}_2\text{--O})_n$ segments were prepared by the mechanochemical method; the starting materials were the $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ (mol%) sulfide glass and --OH terminated oligoethers with several molecular weights. Local structure of the obtained materials was analyzed by Fourier-transform infrared (FT-IR) spectroscopy. Thermal and electrical properties of the hybrid materials were examined. The effects of varying chain lengths of the oligoethers and proportions relative to the sulfide glass on conductivity and T_g of the hybrids were investigated.

2. Experimental

Lithium ion conducting sulfide glasses in the system $\text{Li}_2\text{S}\text{--P}_2\text{S}_5$ were prepared by the mechanochemical method [8,9]. Reagent-grade Li_2S (Furuuchi Chem., 99.9%) and P_2S_5 (Aldrich, 99%) crystalline powders were used as starting materials. The mechanochemical treatment was carried out for batches (1 g) of the mixed materials at the composition $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ (mol%) in an alumina pot (volume of 45 mL) with 10 alumina balls (10 mm in diameter) using a high-energy planetary ball mill apparatus (Fritsch Pulverisette 7). Fine glassy powder was obtained after mechanical milling for 20 h at the constant rotation speed of 370 rpm. Hybrid materials were prepared by mechanochemical reaction between the obtained sulfide glass and several kinds of oligomers. Reagent-grade diethylene glycol (DEG), poly(ethylene glycol)s (PEG) with molecular weights of 400 and 1000, polyethylene glycol dimethyl ether (PEGDME) with molecular weights of 500, and 1,4-butanediol were all purchased from Aldrich and used as received. One of those oligomers was added to the glassy powders, and then mechanochemical treatment was carried out. The milling condition was the almost same as the one used for glass preparation except for the milling periods for 5 h using alumina balls with 5 mm in diameter. All the processes were conducted at room temperature in a dry Ar-filled glove box.

FT-IR spectra of the obtained materials were collected using a FT-IR spectrometer (Perkin-Elmer, Spectrum GX). The samples were mixed with anhydrous liquid paraffin and the obtained slurry was sandwiched between two KRS-5 plates in a dry box. The FT-IR measurements were carried out in dry N_2 atmosphere. Differential thermal analysis (DTA) was carried out using a thermal analyzer (Rigaku, Thermo-plus 8110) for the obtained powder samples sealed in an Al pan in a dry Ar filled glove box. Electrical conductivities were measured for the pelletized samples obtained by the cold press (3700 kg cm^{-2}) of the powder samples; the diameter and thickness of the pellets were 10 mm and about 1 mm, respectively. AC impedance measurements were carried out in dry Ar atmosphere using a Solartron 1260 impedance analyzer in a frequency range of 100 Hz to 15 MHz.

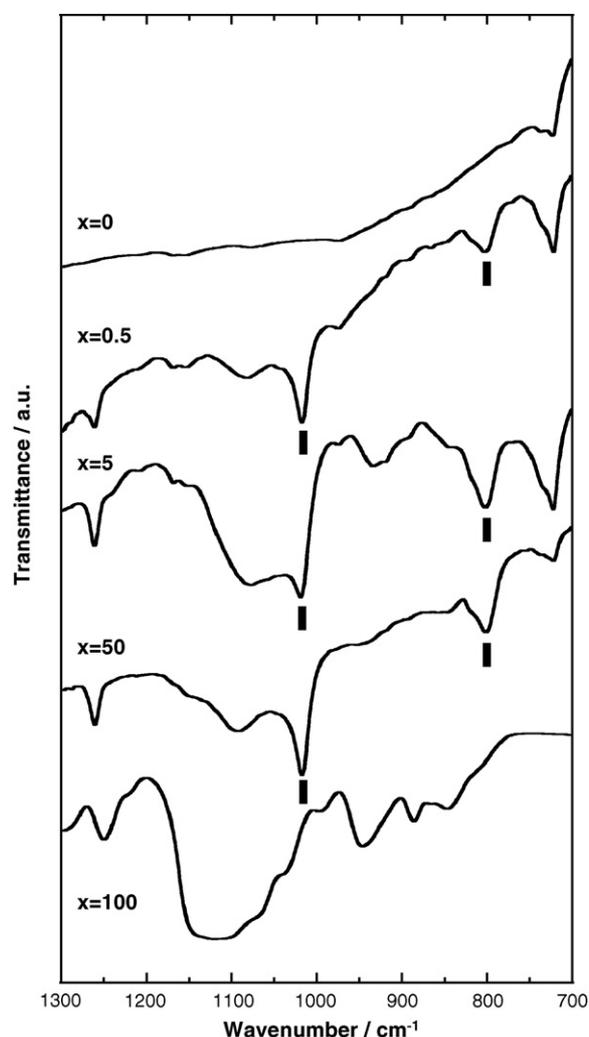


Fig. 1. FT-IR spectra of the $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5\text{ glass})\cdot x\text{PEG400}$ (mol%) materials obtained by a mechanochemical technique. The spectra of the pristine sulfide glass ($x=0$) and PEG400 ($x=100$) are also shown in this figure.

3. Results and discussion

The mixtures of the $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ (mol%) glass and PEG400 with the compositions $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5\text{ glass})\cdot x\text{PEG400}$ (mol%) were reacted by mechanochemistry. Solid fine powders with a few micrometer in diameter were obtained in the compositions 20 mol% PEG400 or less, while viscous liquids were obtained in the compositions of 30 mol% PEG400 or more. The pelletized sample with 20 mol% PEG400 can be distorted by tweezers, suggesting that the addition of PEG400 provides flexibility to the glassy electrolytes.

Fig. 1 shows FT-IR spectra of the $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5\text{ glass})\cdot x\text{PEG400}$ (mol%) materials obtained by the mechanochemical method. FT-IR spectra of the milled materials ($x=0.5, 5,$ and 50) show obvious new bands at 800 and 1020 cm^{-1} , which are not present in the starting materials such as the glass ($x=0$) and PEG400 ($x=100$). These bands are attributable to P--O--C bonds [12], and we confirmed that these IR bands were also observed for reagent-grade chemicals with P--O--C bonds such as triethyl phosphate and trimethyl

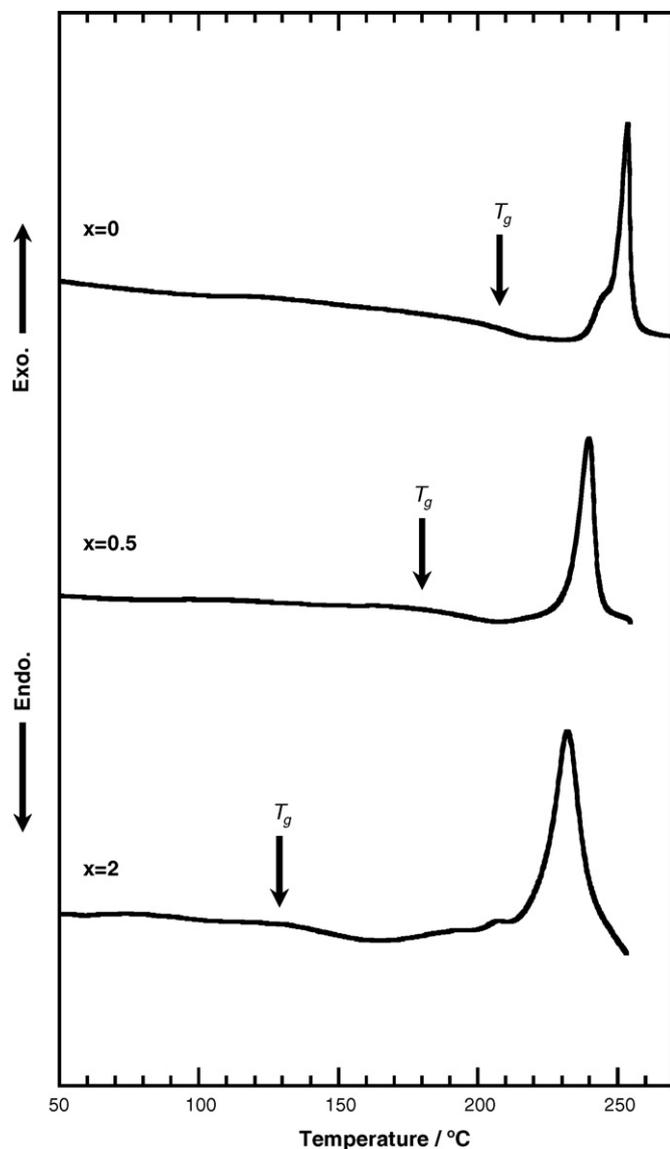


Fig. 2. DTA curves of the $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5 \text{ glass})\cdot x\text{PEG400}$ (mol%) hybrid materials prepared by a mechanochemical technique.

phosphite. It was revealed that the IR bands at about 3500 cm^{-1} , which are due to $-\text{OH}$ groups in PEG400, completely vanished in the milled samples. Therefore, the formation of $\text{P}-\text{O}-\text{C}$ bonds suggests that hybrid materials are formed by the reaction between inorganic and organic moieties: the $\text{P}-\text{S}-\text{P}$ network in inorganic $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$ sulfide glass and the $-\text{OH}$ group in organic PEG400.

Fig. 2 shows DTA curves of the $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5 \text{ glass})\cdot x\text{PEG400}$ (mol%) hybrid materials. An endothermic change due to glass transition and a sharp exothermic peak due to crystallization are observed in all the samples. The glass transition temperatures (T_g) tend to lower with increasing the PEG400 content; the hybrid material with 2 mol% PEG400 shows T_g of 130°C , which is lower by 80°C than the pristine sulfide glass.

Fig. 3 shows the temperature dependence of electrical conductivity for the $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5 \text{ glass})\cdot x\text{PEG400}$ (mol%) hybrid materials. Our targeted electrolytes are in solid

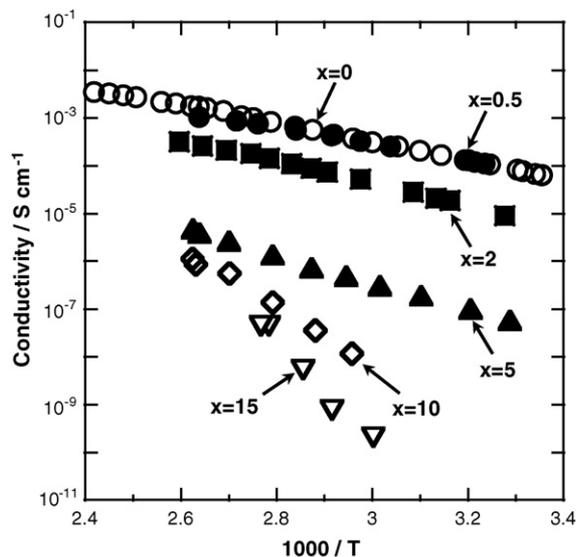


Fig. 3. Temperature dependence of electrical conductivities for the $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5 \text{ glass})\cdot x\text{PEG400}$ (mol%) hybrid solid electrolytes.

state and hence we focused on the compositions 20 mol% PEG400 or less. The conductivities for all the samples obey the Arrhenius equation of the narrow temperature region from 25 to 100°C . The pure glass shows the conductivity of $6.3 \times 10^{-5}\text{ S cm}^{-1}$ at room temperature and the activation energy of 36 kJ mol^{-1} for conduction [9]. The conductivity is drastically decreased, and the activation energy for conduction is increased with an addition of 10 mol% PEG400 or more. The decrease in conductivity and the increase in activation energy of the hybrid materials are probably due to the fact that the addition of insulative PEG400 to the glass decreases lithium ion concentration and leads to disrupt continuous conducting paths for Li^+ in the hybrid materials. In spite of decreasing Li^+ concentration, the addition of 0.5 mol% PEG400 keeps almost the same conductivity of $6.8 \times 10^{-5}\text{ S cm}^{-1}$ and activation energy of 35 kJ mol^{-1} as the pristine glass. The decrease in T_g were observed at this composition as shown in Fig. 2. Lowering T_g of the sulfide glass by combined with small amounts of oligoethers is a potential way to improve conductive behaviors of glass-based solid electrolytes.

The hybrid electrolytes were synthesized by using several kinds of oligomers. The volume ratio of the electrolytes was fixed to $\text{glass/oligomer}=97/3$, which corresponds to the composition of 0.5 mol% PEG400 exhibiting the highest conductivity in the glass-PEG400 system. The volume ratio of glass/oligomer was calculated from the weight ratio and the densities of the glass (1.9 g cm^{-3}) and the oligomers ($1.0\text{--}1.2\text{ g cm}^{-3}$). Fig. 4 shows the temperature dependence of conductivities of the electrolytes prepared from the sulfide glass and one of oligomers such as DEG, PEG400, PEG1000, PEGDME and 1,4-butanediol. Table 1 lists conductivity at 25°C (σ_{25}) and activation energy for conduction (E_a), which are determined from Fig. 4, of the hybrid electrolytes. T_g determined by DTA measurements is also listed in Table 1.

The obtained materials with DEG, PEG400, PEG1000, and 1,4-butanediol showed characteristic bands due to $\text{P}-\text{O}-\text{C}$ bonds

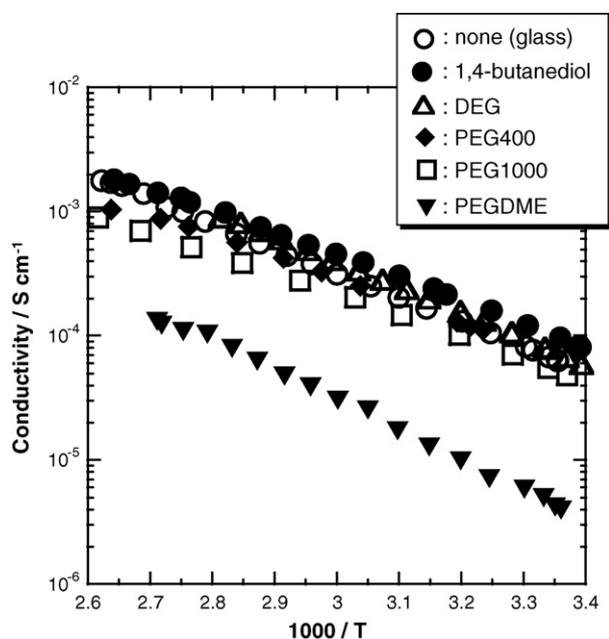


Fig. 4. Temperature dependence of electrical conductivities of the hybrid electrolytes prepared from the $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ (mol%) sulfide glass and one of oligomers such as DEG, PEG400, PEG1000, and 1,4-butanediol. The hybrid compositions are listed in Table 1. The conductivity data of the composite electrolyte, which is the intimate mixture of the sulfide glass and PEGDME, is also shown for comparison.

in FT-IR spectra, suggesting that the hybrid electrolytes were formed. On the other hand, the composite electrolyte with the intimate mixture of the sulfide glass and PEGDME was obtained because no bands due to P–O–C bonds were observed by the FT-IR measurements. The T_g of the hybrid materials decreased with an addition of oligomers as shown in Table 1, while the T_g of the composite with PEGDME was the same as the one of the pristine glass. The composite electrolyte with PEGDME shows considerably lower conductivity ($4.2 \times 10^{-6} \text{ S cm}^{-1}$) and higher activation energy for conduction (46 kJ mol^{-1}) than the hybrid materials with the other oligomers. Because of the insulative nature of oligomers, the formation of chemical bonds between the glass and the oligomer is indispensable to exhibit high conductivity of solid electrolytes.

In the cases of using oligoethers with different molecular weight, the hybrids added with DEG and PEG400 show almost the same conductivities as the pristine glass, while the addition

Table 1
Glass transition temperature (T_g), conductivity at 25°C (σ_{25}), and activation energy for conduction (E_a) for the hybrid electrolytes in the system $(100-x)(0.7\text{Li}_2\text{S}\cdot 0.3\text{P}_2\text{S}_5 \text{ glass})\cdot x$ oligomer (mol%)

Oligomer	x (mol%)	T_g ($^\circ\text{C}$)	σ_{25} (S cm^{-1})	E_a (kJ mol^{-1})
None	–	210	6.3×10^{-5}	36
DEG	2	183	7.0×10^{-5}	38
PEG400	0.5	181	6.8×10^{-5}	35
PEG1000	0.2	–	5.1×10^{-5}	34
PEGDME ^a	0.4	210	4.2×10^{-6}	46
1,4-Butanediol	2	180	9.7×10^{-5}	34

^a The obtained sample with PEGDME is not a hybrid material. See the text in detail.

of PEG1000 leads to decrease the conductivity of the hybrids; an increase in molecular weight of PEG from 400 to 1000 decreases the conductivity. High viscosity of PEG1000 probably affects the decline of conductivity for the hybrid electrolytes.

The conductive behavior of the hybrid with the oligoether DEG is compared with that of the hybrid with 1,4-butanediol as an alkanediol without ether oxygens. Both two oligomers have the same carbon number of 4. The hybrid with 1,4-butanediol exhibits the conductivity of $9.7 \times 10^{-5} \text{ S cm}^{-1}$, which is higher than that of the pristine glass and the hybrid with DEG. The activation energy of 34 kJ mol^{-1} for the former hybrid is smaller than that of the glass and the hybrid with DEG. The degree of lowering T_g with an addition of 1,4-butanediol is almost the same as that with DEG, and then the difference on conductive behavior of two hybrids is not explained from the viewpoint of T_g . The ether oxygen in DEG would play a role in a weak trap site for Li^+ in the hybrid electrolytes and, therefore, the hybrids with 1,4-butanediol shows superior Li^+ conduction. It is found that the oligomer structure affects the conductive behavior of the hybrid electrolytes.

4. Conclusions

Novel inorganic–organic hybrid electrolytes were synthesized by the mechanochemical method using the Li^+ conductive $70\text{Li}_2\text{S}\cdot 30\text{P}_2\text{S}_5$ glass and oligomers. The formation of P–O–C bonds between the glass and an –OH terminated oligomer is a key to obtain highly conductive hybrid electrolytes. The addition of small amounts of oligomers into the glass enhanced the conductivity of hybrid electrolytes by lowering T_g . The hybrid electrolytes with 2 mol% of 1,4-butanediol exhibited the ambient temperature conductivity of $9.7 \times 10^{-5} \text{ S cm}^{-1}$. The alkanediol without ether oxygens would be a more suitable oligomer to form hybrid electrolytes than an oligoether because ether oxygens work as a weak trap for Li^+ conduction. The effects of the molecular weight of oligoethers (i.e. chain length) on conductivity were also investigated. The conductivity tended to decrease with an increase in molecular weight from PEG400 to PEG1000. Incorporating oligomer blocks into glass network is a new approach to enhance the conductivity of glass-based solid electrolytes.

Acknowledgement

This work was supported by the Grant-in-Aid for Scientific Research on Section for Young Scientists (B) from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

- [1] R. Mercier, J.P. Malugani, B. Fahys, G. Robert, *Solid State Ionics* 5 (1981) 663.
- [2] A. Pradel, M. Ribes, *Solid State Ionics* 18–19 (1986) 351.
- [3] T. Minami, A. Hayashi, M. Tatsumisago, *Solid State Ionics* 136–137 (2000) 1015.
- [4] J. Cho, G. Kim, H. Lim, M. Liu, *J. Electrochem. Soc.* 145 (1998) 1949.

- [5] S. Kohjiya, T. Kitade, Y. Ikeda, A. Hayashi, A. Matsuda, M. Tatsumisago, T. Minami, *Solid State Ionics* 154–155 (2002) 1.
- [6] T. Inada, K. Takada, A. Kajiyama, M. Kouguchi, H. Sasaki, S. Kondo, M. Watanabe, M. Murayama, R. Kanno, *Solid State Ionics* 158 (2003) 275.
- [7] A. Hayashi, L. Wang, C.A. Angell, *Electrochem. Acta* 48 (2003) 2003.
- [8] A. Hayashi, S. Hama, H. Morimoto, M. Tatsumisago, T. Minami, *J. Am. Ceram. Soc.* 84 (2001) 477.
- [9] M. Tatsumisago, S. Hama, A. Hayashi, H. Morimoto, T. Minami, *Solid State Ionics* 154–155 (2002) 635.
- [10] C.A. Angell, *Annu. Rev. Phys. Chem.* 43 (1992) 693.
- [11] C.A. Angell, J. Fan, C. Liu, Q. Lu, E. Sanchez, K. Xu, *Solid State Ionics* 69 (1994) 343.
- [12] D.E.C. Corbridge, in: M. Grayson, E.J. Griffith (Eds.), *Topics in Phosphorus Chemistry*, vol. 6, John Wiley & Sons Inc., New York, 1969, pp. 278–281.