

Preparation and Properties of Inorganic-organic Hybrid Li⁺ Ion Conductor by Sol-gel Process

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Inorganic-organic hybrid Li⁺ ion conductors were prepared by the sol-gel process. Tetramethyl orthosilicate (TMOS), polyethylene glycol 200 (PEG₂₀₀) and lithium bis (trifluoro-methylsulfonyl) imide were used as raw materials and H₂O was used as a solvent. Hybrid Li⁺ ion conductor prepared by the sol-gel process showed very high ion conductivities of $\log\sigma_{RT}(\text{S/cm})=-3.73$, $\log\sigma_{60}(\text{S/cm})=-3.00$ at room temperature and 60°C, respectively. Decomposition voltage was 3.1 V.

Key words: Ion Conductor, Hybrid gel, Sol-gel process, Lithium ion, Electrolyte

I. Introduction

The lithium electrolyte is expected to be applied for the high power supply, because lithium is high energy density material. Recently, an electrolyte of lithium-organic solution is used for many applications of battery.¹⁾ However, there are some problems in the battery using organic solution including lithium ion. For example, the liquid electrolyte leaks out when the battery is broken, and the performance deteriorates by evaporation of the electrolytic solution and generation of the dendrite.²⁾ These problems can be solved by using a solid state electrolyte. However, ionic conductivity of the solid state ionic conductor (e.g., glass, ceramics) is lower than that of the liquid state one. The ionic conductivity of polymer has been a topic of major interest. Polymers with ionic conductivity in the range from 10⁻³ to 10⁻⁴ Scm⁻¹ at ambient temperatures have been synthesized. Solid state ionic conductors are expected to be used for several applications, such as mobile phones, artificial internal organs and etc. However, strength of polymers are lower than that of glasses or ceramics. Inorganic-organic hybrid electrolyte is an ideal material for the preparation of solid state battery. To combine high conductivity of organic material and hardness of inorganic material and lithium ions, application of electrolytes spread out.

It is difficult to prepare inorganic - organic hybrid solid state electrolyte in the common method (e.g. conventional sintering processes, melting process), because organic component decomposes and burns at high temperature. A sol-gel process can be used to prepare ceramics and glasses at

lower temperatures than conventional sintering processes, and is well known as a useful method for the preparation of low density open structure material. In general, the sol-gel process has used metal alkoxides or metal salts as raw materials. Alcohol has been used as an organic solvent. Metal alkoxides are mixed with organic solvents, water and a catalyst. A sol solution is transformed to a wet gel by hydrolysis and condensation. Glasses or ceramics are obtained from a wet gel by heat treatment at low temperatures. Therefore, in the sol-gel process, metal alkoxides can be easily bound with many organics.

In this study, we prepared an inorganic-organic hybrid Li⁺ conductor by sol-gel process using tetramethyl orthosilicate (TMOS), polyethylene glycol 200 (PEG₂₀₀) and lithium bis (trifluoro-methylsulfonyl) imide (LiTFSI) as raw materials. It is well known that LiTFSI has high dissociation and stability in the electrical chemistry¹. Inorganic-organic hybrid Li⁺ ion conductors were prepared by the sol-gel process and their electrical properties were investigated.

II. Experimental Procedure

Fig. 1 shows preparation procedure of inorganic-organic hybrid Li⁺ ion conductor. Tetramethyl orthosilicate (TMOS), polyethylene glycol 200 (PEG₂₀₀) and lithium bis (trifluoro-methylsulfonyl) amide (LiTFSI) were used as raw materials. Fig. 2 shows the structure of LiTFSI. H₂O was used as solvent. An inorganic-organic matrix was prepared with TMOS : PEG₂₀₀ : H₂O=1 : 1 : 4 (molar ratio). The inorganic-organic Li⁺ ion conductors were prepared by addition of lithium salt to the matrix; [Li]/[O]=0.02, 0.025, 0.03, 0.05, 0.1,

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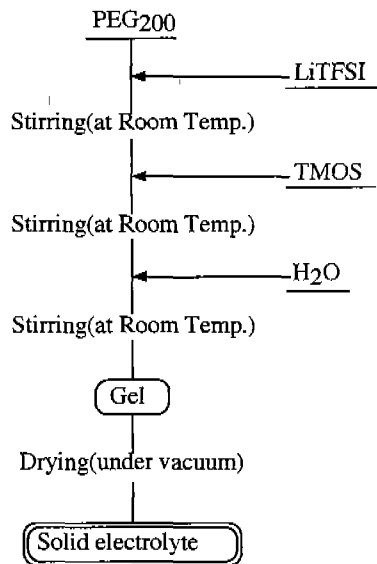


Fig. 1. Preparation procedure of inorganic-organic hybrid Li^+ ion conductor.

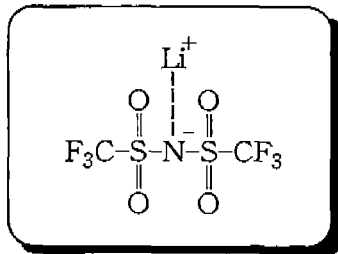


Fig. 2. Structure of bis(trifluoro-methylsulfonyl)imide.

respectively. In order to investigate an influence of TMOS on the ionic conductivity of samples, samples without TMOS were prepared. The samples without TMOS were prepared with molar ratios of $[\text{Li}]/[\text{O}]=0.02, 0.025, 0.03, 0.05, 0.1$, respectively. To obtain a gel, these raw materials were mixed with H_2O for 24 h at room temperature, and the gel was dried at 80°C under vacuum. Thermogravimetric and differential thermal analysis (TG-DTA) of the $[\text{Li}]/[\text{O}]=0.05$ sample were performed at a heating rate of $5^\circ\text{C}/\text{min}$ using a Rigaku model MJ800KT2. Electrical properties (AC) of the samples were measured using Hewlett Packard impedance/gain-phase analyzer HP4194A system, in the range from 100 Hz to 15 MHz. Electrical properties (DC) of the samples were measured using ADVANTEST R6145 DC VOLTAGE CURRENT SOURCE and ADVANTEST TR684 DIGITAL MULTIMETER with GP-IB controlled by NEC PC-9801RX computer.

Ion transport numbers were calculated by following equation.

$$\rho = 1 - I_f/I_\infty \quad (\text{Eq. 1})$$

Where, $I_0[\text{A}]$ is initial electric current ($t=0[\text{sec.}]$) and $I_\infty[\text{A}]$ is final electric current ($t=\infty$).

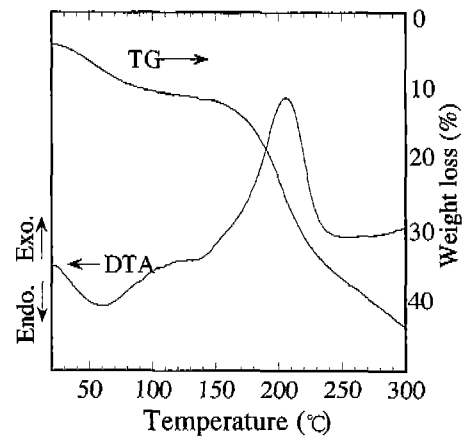


Fig. 3. TG-DTA curves of hybrid gel (polyethylene glycol: Tetra methyl orthosilicate=1:1 molar ratio).

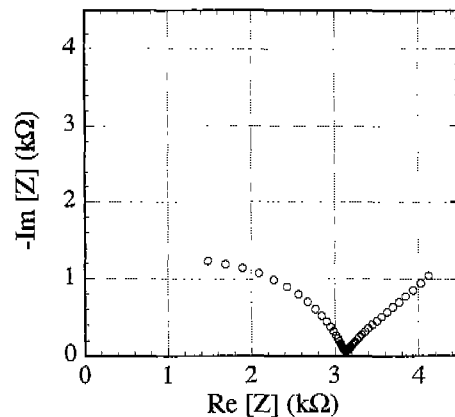


Fig. 4. Cole-cole plot of the $[\text{Li}]/[\text{O}]=0.05$ sample.

Table 1. Ionic Conductivity of the Hybrid Samples Dependence On Lithium Concentration

Sample	Conductivity [$\mu\text{S}/\text{cm}$]
$[\text{Li}]/[\text{O}]=0.020$	31.4
$[\text{Li}]/[\text{O}]=0.025$	67.0
$[\text{Li}]/[\text{O}]=0.030$	51.7
$[\text{Li}]/[\text{O}]=0.050$	182
$[\text{Li}]/[\text{O}]=0.100$	112

III. Results

Prepared hybrid gel was transparent. The starting solution without TMOS did not gel. Fig. 3 shows TG-DTA curves. An endothermic peak from 20 to 100°C was observed due to evaporation of H_2O and methanol. An endothermic peak from 130 to 230°C was due to decomposition and burn out of unreacted alkoxy groups of TMOS and PEG_{200} . A color of the gel heat treated at 130°C was brown because organics contained in the gel did not burn completely. Fig. 4 shows the Cole-Cole plot of the $[\text{Li}]/[\text{O}]=0.05$ sample. Table 1

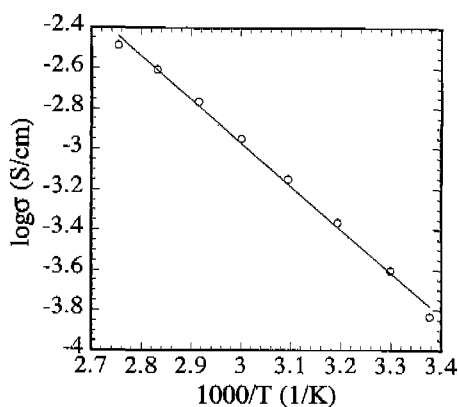


Fig. 5. Temperature dependence of the ionic conductivity of [Li]/[O]=0.05 sample.

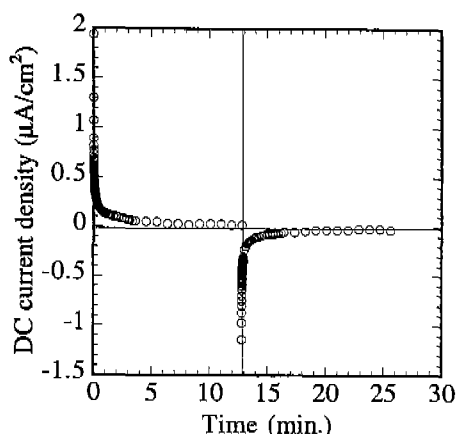


Fig. 6. Time of applying voltage 1.5 V dependent on current density of the [Li]/[O]=0.05 sample.

shows resistance of the samples. These resistances were calculated from the Cole-Cole plots. The conductivity of the hybrid conductor increased with increasing addition of Li salt. The conductivity of the hybrid conductor increased up to [Li]/[O]=0.1.

Fig. 5 shows temperature dependence of the conductivity of [Li]/[O]=0.05 hybrid conductor. An Arrhenius plot of the [Li]/[O]=0.05 sample was not linear. Conductivity of the sample without TMOS ([Li]/[O]=0.05) was $\sigma_{(0.05)liq.} = 3.21 \times 10^{-4}$ at room temperature. Fig. 6 shows the results of DC current measurement of the [Li]/[O]=0.05 sample. Current density decreased rapidly with increasing time of the applied voltage, and became constant current. From the difference between the initial current density and the final one, the ion transport number of the hybrid conductor ([Li]/[O]=0.05) was determined to be about 0.98. Fig. 7 shows the result of I-V measurement. It was possible that 3.1 V in which the gradient changes in I-V measurement was considered as the decomposition voltage.

IV. Discussion

The samples was prepared with TMOS:PEG₂₀₀:H₂O=

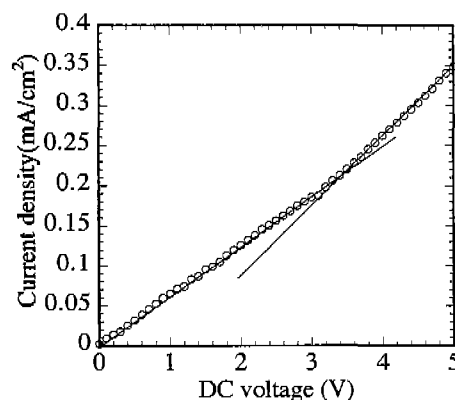


Fig. 7. Dependence of applied voltage on current density of the [Li]/[O]=0.05 sample.

1:1:4 (molar ratio) because in order to leave to small amount of non-hydrolyzed alkoxy group in the gel. The hybrid gel seems to have high flexibility and high ionic conductivity due to small amount of non-hydrolyzed alkoxy group in the gel. We prepared the samples at 80°C under vacuum by rotary pump because the sample decomposes above 100°C. Prepared samples under the above condition were transparent.

All samples were amorphous over all temperatures for electrical measurements. Cole-cole plot of the samples wasn't a semicircle. Usually, cole-cole plot of the crystalline ionic conductor is observed as a semicircle; We observed one semicircle due to the interface between conductor and electrode and another semicircle due to mobile Li⁺ in the conductor. The conductivity of the hybrid conductor was calculated from the cole-cole plot. The conductivity of the sample increased when the additional Li salt quantity was increased up to [Li]/[O]=0.05, and in the dosage over it, it decreased. This low conductivity was thought that mobility of Li⁺ was decreased because Li⁺ became excessive. Generally, the temperature dependence of ionic conductivity of the organic polymers are classified in three types of the definition.^{3,4}

- Type 1) An Arrhenius plot of conductivity versus temperature is linear. Gradient of the line and activation energy change frequently at particular temperature. In this measurement range, the crystalline sample doesn't modify.
- Type 2) An Arrhenius plot of conductivity versus temperature is linear up to particular temperature. That plots doesn't agree with linear relationship in the higher temperature range. In this measurement temperature, a crystalline sample changes to amorphous gradually with increasing temperature.
- Type 3) In the electrical measurement temperature range, an Arrhenius plot of conductivity versus temperature is a straight line bend in the top. This relationship is often observed with an amorphous sample.

In our work, the Arrhenius plot of conductivity versus temperature of the sample ([Li]/[O]=0.05) wasn't linear in the measured temperature range. Curve of the Arrhenius

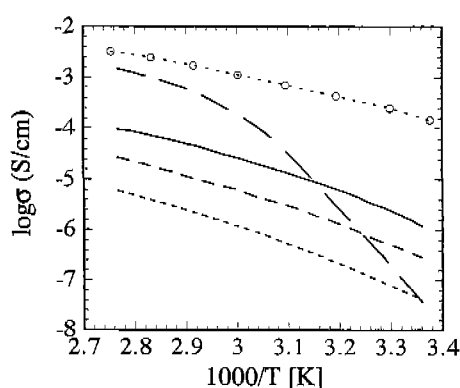


Fig. 8. Temperature dependence of ionic conductivity. (a) (b) ----, (c) —, (d) - · - · - ·, (e): (a) polyethylene glycol (preparation sample), (b) poly (ethylene oxide), (c) poly (propylene oxide), (d) poly [bis (methoxyethoxyethoxy) phosphazene] and (e) poly [bis (ethoxyethoxybutyl) silane].

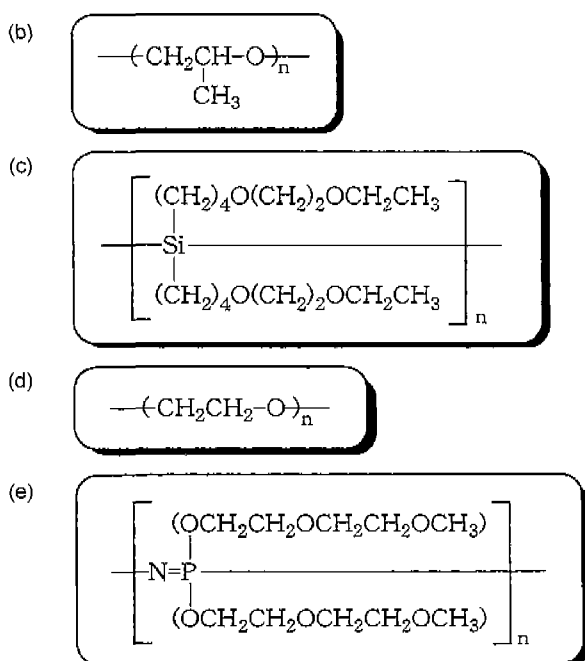


Fig. 9. Structure of polymers. (b) poly(ethylene oxide), (c) poly(propylene oxide), (d) poly[bis(methoxyethoxyethoxy) phosphazene] and (e) poly[bis(ethoxyethoxybutyl)silane].

plot for the sample shows the shape that is a convex for the top. In the other words, the Arrhenius plot is sorted in type 3.^{3,4)}

Fig. 8 and 9 show the temperature dependence of ionic conductivity and structures of polymers, respectively. (a) prepared sample for $[\text{Li}]/[\text{O}]=0.05$, (b) poly(ethylene oxide) (PEO)- LiClO_4 ; $[\text{Li}]/[\text{O}]=0.083$,⁵⁾ (c) poly(propylene oxide) (PPO)- LiCF_3SO_3 ; $[\text{Li}]/[\text{O}]=0.111$,⁶⁾ (d) poly[bis(methoxyethoxyethoxy) phosphazene](PMEEP)- LiCF_3SO_3 ; $[\text{Li}]/[\text{O}]=0.25$,⁷⁾ (e) poly[bis(ethoxyethoxybutyl)silane]- LiCF_3SO_3 ; $[\text{Li}]/[\text{O}]=0.25$.⁸⁾ Conductivity of the prepared sample was higher than that of the others in the measurement temperatures. The conductivity of the samples (a), (b) and (c) were higher than that of the (d)

and (e). (b) and (c) containing polyether polymer. Lyons *et al.*⁷⁾ reported that polymer electrolytes having ether bonds, i.e. $[(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}(\text{CH}_2)_4)_2\text{Si}]_n$, were the poorest ionic conductors because it crystallized by addition of lithium triflate. The ionic conductivity decreased with increasing glass transition temperature for crystallization. A polyethylene glycol in the sample has a great effect on ionic conductivity. These reasons are given in the following.

1) PEG₂₀₀ is amorphous in the measured temperature range.

2) PEG₂₀₀ is mobile molecule because it has short side chains.

3) The structure of PEG₂₀₀ in the sample has regularity because the bridge are formed between

PEG₂₀₀ and siloxane polymer.

4) A glass transition temperature of the sample is not increased by addition of lithium salts.

Lithium ions as a carrier were solvated by a polar group (polyether). If lithium ions move with segmentation of polar group, high conductivity is obtained. In this time, the segmentation of a long side chain is lower than that of a short side chain. Therefore, a conductivity is changed with species of additional lithium salt. The conductivity of the sample using LiClO_4 decreased rapidly above 60°C. This phenomenon is explained that a structure of sample is changed from amorphous to crystalline by dissociation of lithium salts. The sample (b) shows type 1) behavior. Since $(\text{CF}_3\text{SO}_3)_2^-$ form LiTFSI and CF_3SO_3^- form LiCF_3SO_3 have electrically been stabilized, the matrix does not be transformed from the amorphous to the crystal by addition of LiTFSI and LiCF_3SO_3 . Therefore, the prepared sample, (b) and (c) show type 3) conduction. An activation energy of prepared conductor calculated from Fig. 8 was $E_a=9.50$ (kcal/mol). The activation energy of the prepared conductor was almost equal to that of (c), (d) and (e) conductor. However, it is not clear why the activation energies were almost equal to one another. A decomposition voltage of the sample was 3.1 V. Electromotive force of a commercialized manganese battery is 1.5 V. The prepared hybrid ionic conductor in this report is expected to apply for a solid state battery. The sample without TMOS did not form solid gel. However, the conductivity of the sample (liquid state) without TMOS [$\sigma_{0.05\text{liq.}}=3.21 \times 10^{-4}$ ($\log \sigma_{0.05\text{liq.}}=-3.49$)] was about two times of that with TMOS.

V. Conclusion

Inorganic-organic hybrid Li^+ ion conductors could be prepared from sol-gel process using tetramethyl orthosilicate, polyethylene glycol 200 and lithium bis(trifluoro-methylsulfonfyl)amide. The ionic conductivity of the conductors prepared at 80°C changed with additional quantity of lithium salt. Hybrid conductor ($[\text{Li}]/[\text{O}]=0.05$) showed very high ionic conductivity $\sigma_{RT}(\text{S/cm})=1.82 \times 10^{-4}$, $\sigma_{60}(\text{S/cm})=1.0 \times 10^{-3}$ at room temperature and 60°C, respectively. An Arrhenius plot of conductivity versus temperature wasn't linear in the

range measured. Curve of the Arrhenius plot for the sample shows the shape that is a convex for the top. The ion transport number of the hybrid conductor ([Li]/[O]=0.05) was about 0.98. Because decomposition voltage of the sample was 3.1 V, the hybrid ionic conductor is expected to apply for highly electromotive force battery.

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