

Comprehensive Study of Solvents for Wet Process Applied to Sulfide-based All Solid State Battery

Pu QIAN, Ph.D.¹Hiroshi SAKAI¹Atsushi OGAWA¹Hiroto MAEYAMA¹Terumi FURUTA¹

ABSTRACT

In the process of creating a wet process for a sulfide-based all solid state battery, it was necessary to search for suitable solvents. A systematic examination was therefore made of solid electrolytes and the reactivity of solvents. A halogen-doped argyrodite solid electrolyte that shows high lithium-ionic conductivity did not react with a hydrocarbon compound containing no polar group. With ethers, esters, ketones, and nitriles, however, the oxygen atoms and nitrogen atoms in their respective polar groups interact strongly with the solid electrolyte and were expected to form complexes with the lithium ions in the electrolyte. However, solvents having an alkyl chain length with a carbon number of four were not found to form complexes and the ionic conductivity of the solid electrolyte had not been markedly diminished. This is thought to occur because the increase in length of alkyl chains decreases the surface area accessible to coordinating oxygen atoms in the solvent molecules, thereby inhibiting the approach of the solvent to the surface of the solid electrolyte. Setting the carbon number of four or greater for the alkyl group chain length as a solvent search index yielded a direction to pursue for practical application of a wet process.

1. Introduction

The lithium-ion battery is an electrical energy storage device that achieves a balance between high energy density and power density, and so its applications are expanding not only in mobile electronic devices but in electric vehicles⁽¹⁾ as well. At the same time, the research continues for energy storage devices that combine still higher energy density with higher power density and great safety⁽²⁾. One candidate for such a device that is receiving attention is the all solid state battery. Sulfide solid electrolyte, in particular, has lithium ion transport number of unity⁽³⁾ and furthermore has at least the same degree of ionic conductivity as the electrolytes in the conventional lithium-ion batteries⁽³⁾⁻⁽⁶⁾. For that reason, research aimed at its practical application, together with oxide solid electrolyte, as a candidate material for a next-generation all solid state battery is underway⁽⁷⁾.

The methods for fabrication of all solid state batteries can be categorized as dry processes and wet processes. Dry processes have been applied for use at the laboratory level in small-scale testing that does not use solvent, directly pressing powder to fabricate all solid state batteries^{(4), (5)}.

For industrial production, on the other hand, wet processes are adopted in manufacturing conventional lithium-ion batteries. These include the preparation of slurry using the large-scale mixers, and the processes of roll-to-roll coating, drying, and pressing. Therefore, there are hopes that wet processes can also be applied in manufacturing all solid state batteries because this approach is expected to raise productivity and reduce costs⁽⁸⁾⁻⁽¹¹⁾. Issues remain with the use of wet processes, however, due to the reaction of sulfide solid electrolyte with highly polar solvents⁽⁸⁾⁻⁽¹⁷⁾. The solvents used in wet processes have the function both of dissolving the polymer binder and of dispersing the component materials, so it may also be anticipated that polar solvents will be used^{(9), (10)}. For that reason, polar solvents that do not react with sulfide solid electrolytes or that have low reactivity are being sought^{(8), (17)}.

The reaction of polar solvent with solid electrolyte can be understood as a kind of solid-liquid interface reaction. This type of reaction proceeds by going through the steps by which the solvent molecules approach the surface of the solid electrolyte, a reaction between the solvent molecules and solid electrolyte occurs, and the reaction product is

¹ Innovative Research Excellence

E-mail: boku_sen@jp.honda

dissolved into the solvent, and so on^{(18), (19)}. It is known that polar groups react with lithium ions in the solid electrolyte, and it is to be expected that if the approach to the surface of the solid electrolyte is inhibited, then the reaction can be inhibited. In this case, non-polar alkyl groups contained in the solvent molecules can be expected to repulse the solid electrolyte surface that has polarity⁽²⁰⁾ and so, as steric hindrance, inhibit the approach of solvent molecules.

Research into the interaction of solvents and solid electrolytes that has been reported to date includes reports that take the solvent donor number⁽⁸⁾ or the solubility parameter⁽¹⁰⁾ as an indicator of polarity. No reports have yet been found, however, that clarify the mechanism of the reaction between solvent polar groups and sulfide solid electrolyte, or that refer to factors that inhibit such reaction.

This paper, therefore, reports on its purpose to search for solvents that do not react with sulfide solid electrolytes or that have low reactivity with them, on its clarification of the mechanism of the reaction of polar groups in the solvent molecules with solid electrolytes, and on its demonstration by experiment and by the methods of computational science that alkyl groups function as a steric hindrance.

2. Experiment

2.1. Materials

For the solid electrolyte, a halogen-doped argyrodite compound expressed by the chemical formula $\text{Li}_{7-3y}\text{PS}_{6-y}\text{X}_y$ ($\text{X} = \text{Cl}$ or Br , $0 < y < 2$) was used⁽⁶⁾. In order to clarify the mechanism of the reaction between the solid electrolyte and polar groups in the solvent molecules, and to clarify steric hindrance by an alkyl chain, the 14 compounds in the five categories shown in Fig. 1 were used as solvents in immersion tests. Category I was ethers, and compounds (1) through (4) in Fig. 1 were used in order to examine the effect of the number of oxygens and the bulkiness of alkyl side-chains. Category II was esters, including those with two or four carbons on the carboxylic acid side, and those with two to four carbons in the alkyl chain on the alcohol side, which were used to examine steric hindrance by side-chains. These were compounds (5) through (9) in Fig. 1. Category III was ketones, which were used to examine the differences between those in chain form and those in ring form. These were compounds (10) through (12) in Fig. 1. Category IV was nitriles, which was compound (13) in Fig. 1. This was used to examine the interaction between nitrile groups and solid electrolyte. Category V was aromatic hydrocarbons. This was examined as a low-polarity solvent. The compounds used as solvents were off-the-shelf reagents subjected first to dehydration by molecular sieve and then to distillation. The residual moisture content was under 30 ppm for all the solvents. The commercially available xylenes [compound (14) in Fig. 1] were mixtures of isomers and included o-, m-, and p-xylene, and these are entered as xylenes. The text from this point on will refer to the solvents by their numbers in Fig. 1.

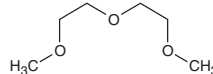
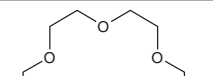
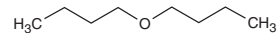
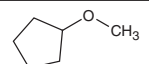
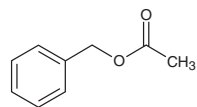
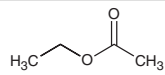
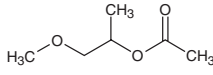
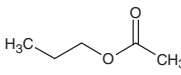
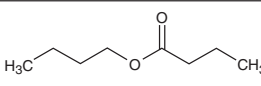
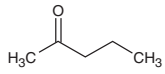
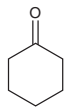
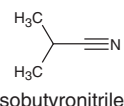
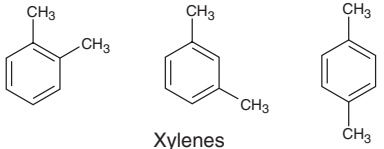
No.	Solvents	Chain length of side groups		
(1)	 Diethylene glycol dimethyl ether	C1	C1	I
(2)	 Diethylene glycol diethyl ether	C2	C2	
(3)	 Dibutyl ether	C4	C4	
(4)	 Cyclopentyl methyl ether	C5	C1	
(5)	 Benzyl acetate	-	C2	II
(6)	 Ethyl acetate	C2	C2	
(7)	 Propylene glycol monomethyl ether acetate (PGMEA)	C1	C2	
(8)	 n-Propyl acetate	C3	C2	
(9)	 n-Butyl n-butoate	C4	C4	
(10)	 2-Pentanone	C1	C3	III
(11)	 Cyclohexanone	-	-	
(12)	 Cyclopentanone	-	-	
(13)	 Isobutyronitrile	C4	0	IV
(14)	 Xylenes			V

Fig. 1 Solvents used for immersion tests

2.2. Evaluation of Solvent and Solid Electrolyte Reactivity

The reactivity of solvent and solid electrolyte was evaluated by means of solvent immersion testing, which was conducted as follows. Solid electrolyte 2 g and solvent 4 g were mixed and left standing for 12 hours in a glass container in a glove box that was constantly purged with argon gas. The mixture was then transferred to a glass tube oven and the solvent was removed under vacuum. All procedures were carried out without exposure to the atmosphere.

In order to evaluate the performance of the solid electrolytes before and after solvent immersion testing, their degrees of ionic conductivity were measured. Pellets of compressed solid electrolyte were fabricated in zirconia tubes of 10 mm inner diameter and their ionic conductivity was measured by the electrochemical impedance spectroscopy (EIS). The voltage amplitude was set to 10 mV and the frequency was swept from 1 MHz to 0.1 Hz during EIS measurement. The figure obtained by dividing the conductivity value of the solid electrolyte after solvent immersion testing by the value before immersion was taken as the conductivity retention rate.

2.3. Infrared Absorption Spectra

The degradation reaction in the solid electrolyte caused by solvent molecules is thought to occur due to coordination of polar groups in the solvent molecules to the solid electrolyte, which is followed by dissolution of the coordinated intermediate into the solvent⁽¹⁵⁾⁻⁽¹⁷⁾. In order to verify the course of this reaction, solid electrolyte was immersed in each of the solvents and then the infrared absorption spectra (IR spectra) of the electrolytes were measured before and after vacuum drying. If the polar groups were coordinated to the lithium ions in the solid electrolyte, then a shift in the infrared absorption bands could be expected^{(21), (22)}. In addition, the dissolution of the coordinated intermediate into the solvent can be expected to destroy the skeleton structure of the solid electrolyte, and the absorption bands of the solid electrolyte could also be expected to change. Measurements were made using a TENSOR 37 infrared absorption spectrophotometer made by Bruker Corporation, and they were carried out using a Platinum ATR, diamond attenuated total reflection (ATR) attachment. An original airtight sample chamber was used for sample setting and measurement without exposure to the atmosphere.

2.4. Gas Chromatography Mass Spectrometry

In order to evaluate the solvent degradation reaction, the solvents were subjected to gas chromatography mass spectrometry (GCMS). The GCMS-QP2010 Ultra manufactured by Shimadzu Corporation was used for measurement. For the column, the Restek Rtx-5MS glass capillary column with a length of 30 m, inner diameter of 0.25 mm, and membrane thickness of 0.25 μm . Helium gas

Table 1 Calculation conditions of DMol³

Basis function	dnp
Pseudopotential	None (All electron)
Functional	GGA-blyp
Orbital cutoff length	3.7 Å
SCF tolerance	1×10^{-6}

was used for the carrier gas. Compounds were identified using the NIST08 library with the GCMS solution analysis software (version 2.70) that was supplied with the device. The peaks from impurities that became mixed in during the course of testing were removed from the analysis results.

2.5. Estimation of Coordinating Oxygen Atom Reactivity by Computational Science

In order to clarify the influence of steric hindrance by alkyl chains that inhibit the approach by solvent molecules to the solid electrolyte surface, the surface area accessible to coordinating oxygen atoms in the solvent molecules was estimated from the structure of a molecular model. The molecular model structure was decided using DMol³⁽²³⁾⁻⁽²⁵⁾, which is a first-principles electronic structure calculating program in Materials Studio 2020. The main calculation conditions are shown in Table 1. The surface area of coordinating oxygen atoms determined to be accessible relative to the decided molecular structure was estimated by the conceptual approach of the Connolly surface⁽²⁵⁾ (Fig. 2), which uses a sphere as a probe of the atoms represented as spheres in the molecular model. The probe sphere is placed in contact with an atom and rolled across it, and the track made by the probe is taken as the surface area. This estimate was calculated using an original program developed here and coded in the Python language. In order to examine the influence of the steric hindrance, the esters (6), (8), and (9) in category II and the ketone (10) in category III, all in Fig. 1, were selected for calculation.

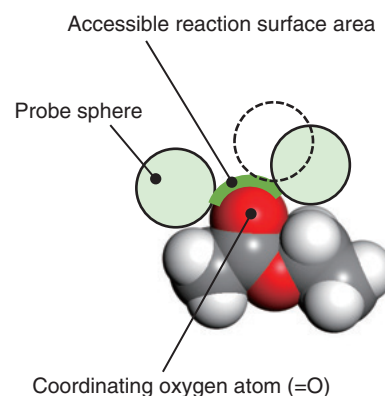


Fig. 2 Accessible reaction surface area based on Connolly surface

3. Results

3.1. Results of Solvent Immersion Testing

Figure 3 shows the results for measurement of the ionic conductivity of solid electrolyte after immersion. The retention of ionic conductivity by solid electrolyte after immersion relative to its ionic conductivity before immersion is shown as a bar graph. The electrolytes that had been immersed in the ether in category I, dibutyl ether [solvent (3) in Fig. 1], the ester in category II, n-butyl n-butoate [solvent (9) in Fig. 1], the isobutyronitrile in category IV [solvent (13) in Fig. 1], and the low polar solvent xylene in category V [solvent (14) in Fig. 1] showed retention of 98% or higher. In addition, the electrolytes that had been immersed in the category I ether cyclopentyl methyl ether [solvent (4) in Fig. 1] and the category II ester n-propyl acetate [solvent (8) in Fig. 1] showed retention of 87% and 79%, respectively. In contrast with these, the electrolytes that had been immersed in the category I ether diethylene glycol dimethyl ether [solvent (1) in Fig. 1], the category III ketones cyclohexanone [solvent (11) in Fig. 1] and cyclopentanone [solvent (12) in Fig. 1] showed almost no signs of ionic conductivity. When the solvents other than these were used, the ionic conductivity retained ranged between 17% and 47%.

The solid electrolyte used for this research was a light beige-colored powder. Figure 4 shows a photograph of the solid electrolyte immersed in a number of solvents. When immersed for 12 hours in ethyl acetate [solvent (6) in Fig. 1], the solvent took on a yellow color while the powder turned brown [(6) in Fig. 4]. After immersion for 12 hours in solvent (9) and solvent (13), those solvents turned a light yellow and light blue, respectively, but the color of the solid electrolyte remained largely unchanged [(9) and (13) in Fig. 4]. After immersion of the solid electrolyte in solvent (11), the solvent took on a yellow color and the powder became a viscous paste [(11) in Fig. 4]. Although

there is no photograph showing this, the other solvents in which immersion resulted in a lower retention of ionic conductivity tended to exhibit changes in color, increases in viscosity, and other such changes.

3.2. Infrared Absorption Spectra of Solid Electrolyte Before Drying

In order to compare the effect from polar groups and the effect of steric hindrance from alkyl chains, the results for a total of five solvents, consisting of two solvents each from category I and II and one from category III, were compared. Figure 5 shows a comparison of spectra for the solvent and solid electrolyte before and after immersion, arranged from top to bottom. For solvent (1) and solvent (6), which produced large decreases in ionic conductivity of the solid electrolyte after immersion testing, comparison with results before immersion showed major changes [Fig. 5(a) and (c)]. In the case of solvent (1) [Fig. 5(a)], almost all the solvent absorption peaks were split apart, suggesting that the solvent molecules were coordinated to the solid electrolyte⁽²²⁾. An absorption shift resulting from the P-S bond of the solid electrolyte at 560 cm^{-1} was also observed⁽²⁶⁾, suggesting that a change in the solid electrolyte skeleton had occurred. In the case of solvent (6) [Fig. 5(c)], the peak attributable to the P-S bond of the solid electrolyte at 560 cm^{-1} had become broader (marked with a ○ symbol), and of the peaks attributable to the solvent, the peak (1736 cm^{-1}) attributable to the C=O bond of the ethyl acetate became a shoulder peak (1707 cm^{-1} , marked by ▼). This suggests that a portion of the solvent has coordinated to solid electrolyte components⁽²¹⁾. When using the category III solvent (12) [Fig. 5(e)], the series of peaks resulting from H_2O (marked with a ▼ symbol) were stronger than the solvent and solid electrolyte absorption peaks. It can be estimated from this that the solvent and solid electrolyte were degrading and that H_2O was being generated.

In contrast with these, when solvent (3) [Fig. 5(b)] and solvent (9) [Fig. 5(d)] were used as the solvent, no changes in spectra were observed that would have been due to coordination of solvent molecules to solid electrolyte or

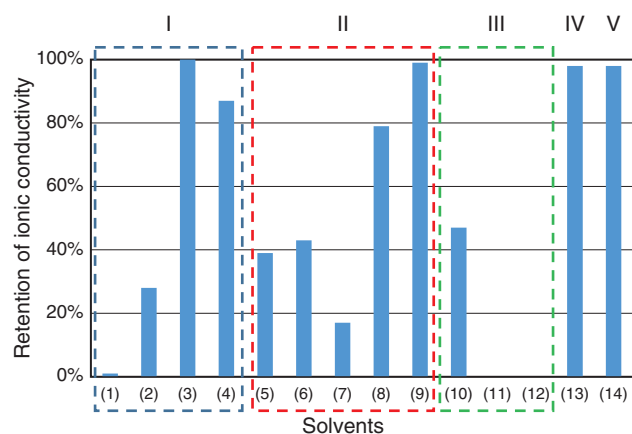


Fig. 3 Retention of ionic conductivity of solid electrolyte after immersion tests

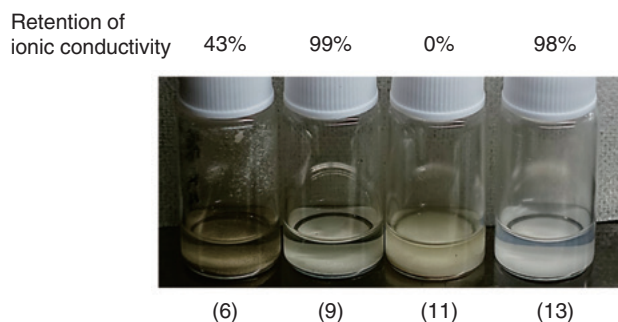


Fig. 4 Photographs of solid electrolyte immersed in solvents (6), (9), (11), and (13)

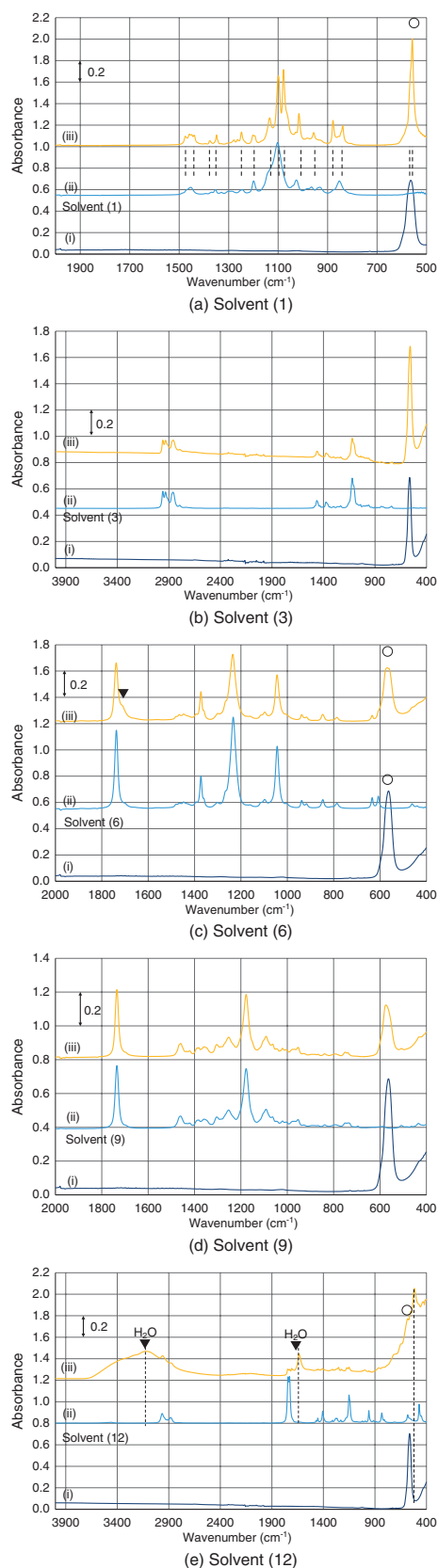


Fig. 5 Infrared absorption spectra of argyrodite solid electrolyte (i), solvents (ii), and wet electrolytes after immersion tests (iii)

collapse of molecular skeleton of solid electrolyte. Although the graphs of this are not shown here, no changes in spectra were observed, either, when solvent (13) and solvent (14) were used.

3.3. Infrared Absorption Spectra of Solid Electrolyte in Dried State

Figure 6 shows the infrared absorption spectra of solid electrolytes before immersion in their respective solvents and following vacuum drying after immersion, or in other words, after the volatile components and nonvolatile components have separated. Absorption attributable to P-S bonds in molecules of the solid electrolyte ($\text{Li}_{7-y}\text{PS}_{6-y}\text{X}_y$, $0 < y < 2$) have their main peak (marked with a ∇ symbol) at 560 cm^{-1} ⁽²⁶⁾. The absorption of Li-S and Li-X bonds, however, appears at 250 cm^{-1} in the far infrared region, and so is omitted here. A small peak at 1033 cm^{-1} (marked with a $\bullet$ symbol) attributable to the P-O bond was also observed⁽²⁷⁾.

After immersion of the solid electrolyte in solvent (1), as shown in Fig. 6, the electrolyte's infrared absorption spectra main peak at 560 cm^{-1} has split into the two peaks

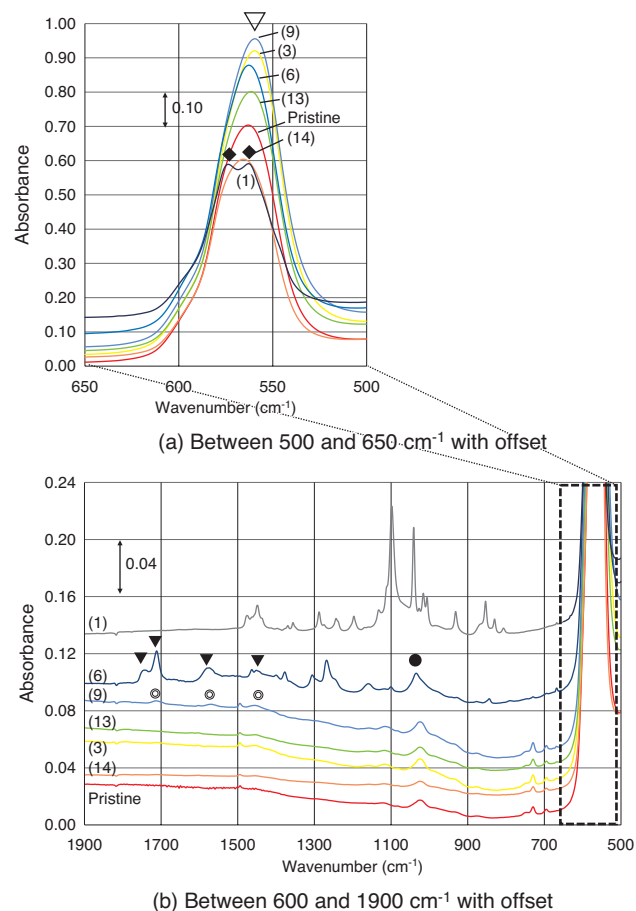


Fig. 6 Infrared absorption spectra of argyrodite solid electrolyte before and after immersion tests in solvents (1), (3), (6), (9), (13), and (14)

at 563 cm^{-1} and 574 cm^{-1} in Fig. 6(a) (marked with a $\blacklozenge$ symbol), suggesting that the argyrodite skeleton has degraded. A number of new peaks also appeared in the range from 800 to 1500 cm^{-1} , suggesting the existence of degradation products. With solvent (3), which belongs to the same category I, practically no change in the infrared absorption spectra was observed even after immersion and drying [(3) in Fig. 6], so it appears that the solid electrolyte did not experience any degradation due to the solvent. The ionic conductivity of the solid electrolyte did not decrease, either, after immersion in this solvent. With the solvents other than these, conspicuous change was not found after immersion in solvent (13) [(13) in Fig. 6] and solvent (14) [(14) in Fig. 6], and the solid electrolyte retained ionic conductivity of 98% or higher even after immersion in these solvents.

Next, a comparison was made of the solid electrolyte spectra after immersion in solvent (6) and solvent (9), which are two esters in category II. Of the ester molecules, solvent (6) has a carbon number of two both on the alcohol side and on the carboxylic acid side [(6) in Fig. 6], and no change was seen in the main peak of the spectrum at 560 cm^{-1} . New peaks did appear, however, at 1743 , 1711 , 1574 , and 1451 cm^{-1} (marked with a $\blacktriangledown$ symbol) and the absorption strength had increased at 1033 cm^{-1} (marked with a $\bullet$ symbol). The absorption at 1743 cm^{-1} can be attributed to ester bonds in residual solvent, and the absorption at 1711 cm^{-1} can be attributed to solvent molecule coordination to solid electrolyte⁽²¹⁾. The remaining absorption at 1574 cm^{-1} can be attributed to lithium acetate, which is a hydrolysis product of the ester. The broad shoulder peak at 1451 cm^{-1} and the absorption at 1033 cm^{-1} (marked with a $\bullet$ symbol) can be attributed to P=O or P-O-Li ⁽²⁷⁾. There were also a number of unattributed peaks in the range from 1100 to 1400 cm^{-1} , and these can be inferred to be from degradation products. It can be implied from these results that immersion of solid electrolyte in solvent (6) caused a portion of ester molecule to coordinate to the solid electrolyte so that a portion of the solid electrolyte degraded, but that the main skeleton was maintained.

Solvent (9) has a carbon number of four both on the alcohol side and on the carboxylic acid side, and it was noted above that ionic conductivity of 99% was maintained after immersion of the solid electrolyte. Its infrared absorption spectra did not show change in the main peak at 560 cm^{-1} [(9) in Fig. 6(a)]. New absorption was seen at 1707 , 1562 , and 1438 cm^{-1} [(9) in Fig. 6(b); marked with a $\odot$ symbol], and these can be attributed to solvent molecules coordinated to sulfide solid electrolytes and to the hydrolysis product *n*-butyric acid lithium salt, respectively. The strength of these absorption peaks is low by comparison with the case of solvent (6), however, indicating that there were only small amounts of the coordinated solvent and the hydrolysis product. No absorption was observed at 1748 cm^{-1} , which indicates that no residual free solvent was to be found.

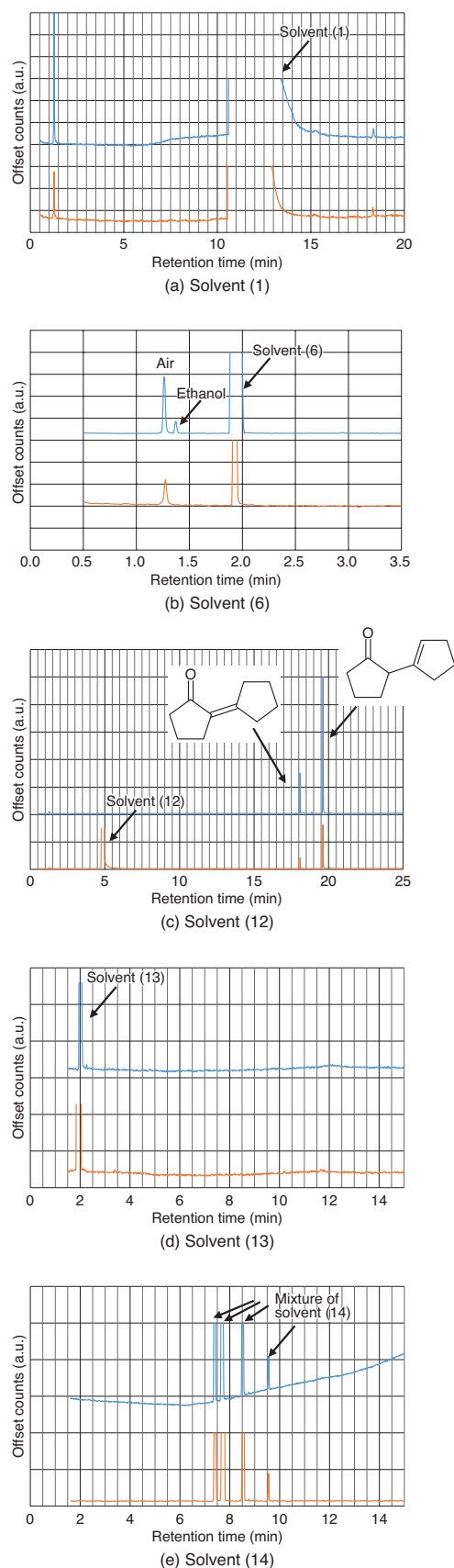


Fig. 7 GCMS chromatograms of solvents before (lower) and after (upper) immersion tests

3.4. Mass Spectrometry of Solvent After Immersion

Following immersion, the volatile components, including solvent, and the nonvolatile components, including solid electrolyte, were separated by vacuum drying in order to ascertain the solvent degradation products resulting from immersion testing. GCMS was then used to conduct qualitative analysis of the volatile components. Figure 7 shows the GCMS analysis results for the volatile components.

No volatile solvent degradation products were detected

in the four ethers of category I. Figure 7(a) shows the results for solvent (1) as an example. With the esters in category II, however, alcohol, which is a hydrolysis product, was detected. Figure 7(b) shows the results for solvent (6) as an example. Ethanol was detected, and it can be inferred that hydrolysis occurred during immersion testing. These results agree with the infrared absorption spectra results. With the ketones in category III, aldol condensation products of the various ketones were detected. Figure 7(c) shows the example of solvent (12). Since H₂O is produced

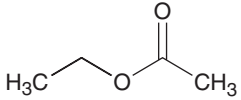
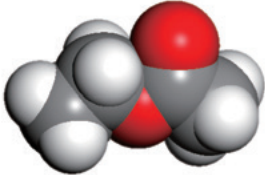
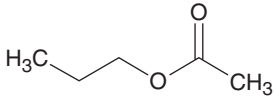
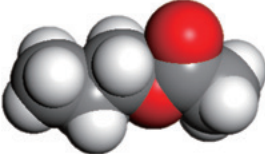
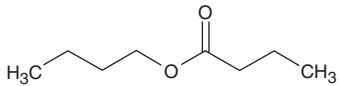
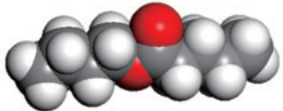
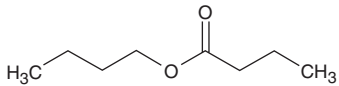
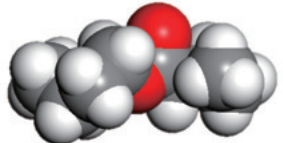
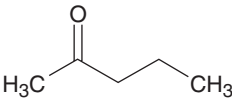
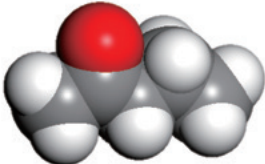
No.	Solvents	Molecular model	Reaction surface area (Å ²)		
			Probe radius 1.82 Å	Probe radius 10 Å	
(6)	 Ethyl acetate $\text{CH}_3\text{-C(=O)O-C}_2\text{H}_5$		10.55	4.94	II
(8)	 n-Propyl acetate $\text{CH}_3\text{-C(=O)O-C}_3\text{H}_7$		10.41	4.94	
(9)	 n-Butyl n-butanoate $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-C(=O)O-C}_4\text{H}_9$		6.47	1.69	
(9')	 n-Butyl n-butanoate $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-C(=O)O-C}_4\text{H}_9$		6.31	1.53	
(10)	 2-Pentanone $\text{CH}_3\text{-C(=O)-CH}_2\text{-CH}_2\text{-CH}_3$		9.43	4.58	III

Fig. 8 Calculation results of molecular structure and accessible reaction surface area

as a by-product of aldol condensation, these results agree with the infrared absorption spectra results [Fig. 7(c)].

With the category IV solvent (13) [Fig. 7(d)] and the category V solvent (14) [Fig. 7(e)], on the other hand, no new reaction products were detected from their volatile components after immersion. This suggested that immersion testing did not result in solvent degradation, or that the degradation products were not volatile.

3.5. Surface Area Accessible to Coordinating Oxygen Atoms

For the category II esters (6), (8), and (9) and the category III ketone (10) that were selected for calculation, the molecular model structure calculated using DMol³ and the surface area accessible to coordinating oxygen atoms calculated from that are shown in Fig. 8. The calculations were made with the respective assumptions for a molecule (probe) that approaches the surface assumed as a sphere the size of a lithium atom with a radius of 1.82 Å and as a sphere with a radius of 10 Å assumed as having the unevenness of the solid electrolyte surface. Regarding solvent (9), the case of a structure that is not linear is assumed, and so a folded structure was calculated and an additional calculation was performed as solvent (9)' in Fig. 8. The alkyl chain with a folded structure of solvent (9)' shows a slight difference in area from the solvent (9) structure, which is not folded. There was no major difference.

The indications were that this surface area accessible to coordinating oxygen atoms decreases as the alkyl chain lengthens. It was also found that when the probe radius is 10 Å, the value for solvent (9), which retained the ionic conductivity of the solid electrolyte after immersion testing, was one-half or less the values for solvents (6), (8), and (10), which saw the ionic conductivity decrease.

4. Discussion of the Mechanism of Reaction between Solid Electrolyte and Solvent

It is known that hydrocarbons, including aliphatics and aromatics, do not react with sulfide solid electrolytes^{(8), (10)}. In the present research, the solid electrolyte retained 98% of its ionic conductivity after immersion in solvent (14), which is an aromatic hydrocarbon. Given results that include the solid electrolyte infrared absorption spectra [(14) in Fig. 6] and the fact that GCMS analysis of the solvent [Fig. 7(e)] did not detect any reaction product, the solid electrolyte and solvent (14) can be considered not to have reacted.

The oxygen atoms contained in ethers, esters, and ketones, and the nitrogen atoms contained in nitriles are known to coordinate to lithium ions because of their respective electron-donating properties^{(21), (22), (28)}. Among those compounds, it is known that those with alkyl chain lengths of about carbon number two coordinate to the lithium ions in the sulfide solid electrolyte and cause the electrolyte components to dissolve or to swell⁽²⁹⁾⁻⁽³¹⁾. Given

that coordination by a portion of the solvents has been observed in the infrared absorption spectra, as noted above, it was determined that coordination by solvents was also occurring under the conditions of the present research. Even among those compounds that contain polar groups, however, there were those that did greatly decrease the ionic conductivity of the solid electrolyte and others that mainly did not decrease it. Specifically, compounds that have an

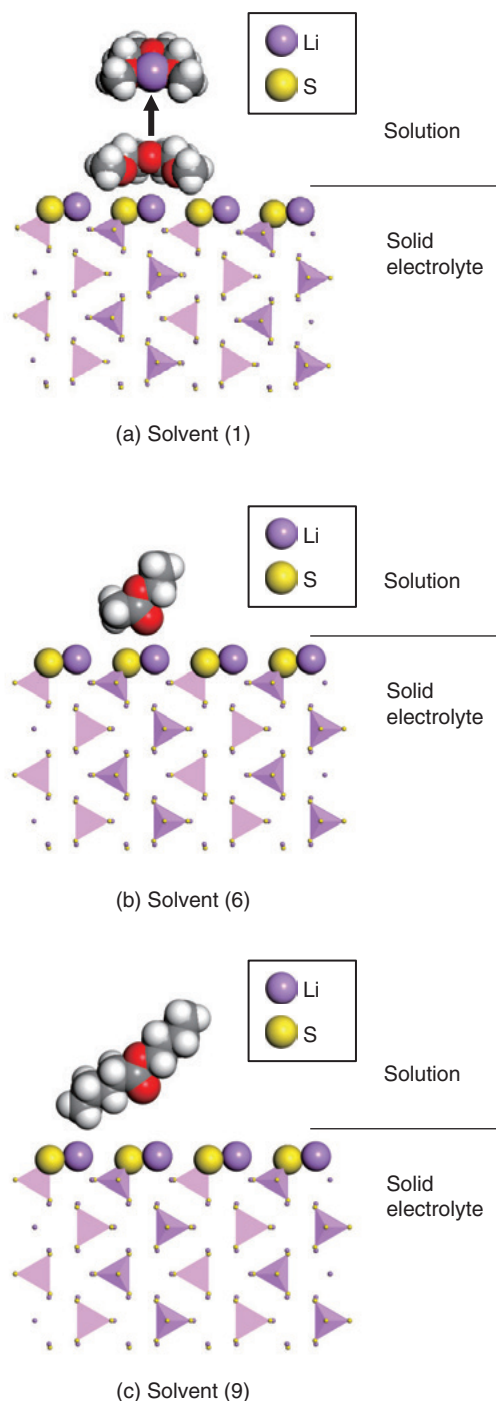


Fig. 9 Schematic chart of interaction between solid electrolyte and solutions

alkyl chain with a carbon number of four on both sides of the functional group generally did not decrease the ionic conductivity of the solid electrolyte, but those having alkyl chains with a carbon number of two did greatly decrease the ionic conductivity. It can be considered from these results that alkyl chains with a carbon number of four, by their steric hindrance, inhibit reaction between solvent molecules and solid electrolyte.

Various methods are used to quantify steric hindrance, and there have been reports about taking the volume derived from the van der Waals radii of the molecules as a standard^{(32), (33)}. For the present research, however, the accessible surface area was used as an index of how readily coordinated atoms can approach the solid electrolyte. This chapter focuses primarily on solvents having an alkyl chain length with a carbon number of two to four, and argues in terms of the relationship between the carbon number of the alkyl chain and the surface area.

4.1. Mechanism of Reaction between Solid Electrolyte and Ethers

The oxygen in ether molecules is known to coordinate to ions of alkali metal, including lithium, because of its electron-donating properties^{(22), (28)}. It has also been reported that ether oxygen coordinates to the lithium ions in Li_2S and causes dissolution of the Li_2S , and also that it forms a complex with Li_3PS_4 ^{(12), (13), (28)}. When ether as a solvent comes in contact with a sulfide solid electrolyte, therefore, it is thought to coordinate to the lithium ions on the surface of the solid electrolyte. Considering the infrared absorption spectra of the solid electrolyte after immersion and the solvent [Fig. 5(a) and (1) in Fig. 6], it is considered that solvent (1), which is a polyether, has separated from the surface in the form of a complex that remains coordinated to solid electrolyte components and so has caused degradation of the solid electrolyte [Fig. 9(a)]. The spectra for solvent (2), which is also categorized as a polyether, are not shown in the graph, but it was found from experimental results to show a tendency similar to solvent (1). The alkyl chains bonded to oxygen atoms in these molecules have lengths with carbon numbers of one and two. The alkyl chains bonded to oxygen atoms in solvent (3), however, have lengths with a carbon number of four, and it became clear from the infrared absorption spectra results [Fig. 5(b) and (3) in Fig. 6] that the ether oxygen is not coordinated to the lithium ions. When the calculation results for surface area accessible to coordinating oxygen atoms are taken into account, it is reasonable to consider that the approach of solvent molecules to the surface of the solid electrolyte is inhibited by the steric hindrance of the alkyl chains, weakening their ability to coordinate to the lithium ions, so that the lithium ions in the sulfide solid electrolyte cannot be dissociated from the solid state. It was for this reason that solvent molecules did not remain on the surface of the solid electrolyte after drying [(3) in Fig. 6]. As a result, it is thought that degradation of the solid electrolyte

did not occur and no decrease in ionic conductivity due to immersion in solvent (3) was observed.

The reaction between solid electrolyte and solvent is a reaction that occurs at the solid-liquid interface, and in order for the reaction to proceed, it is necessary for a new active interface to stay in constant contact with the liquid. In the case of solvents (1) and (2), which are polyethers, there are multiple electron-donating oxygens in the molecules. It is considered that the capability to form complexes is therefore high, so that complexes more readily form and begin to dissolve into the liquid solution [Fig. 9(a)], and new solid state surface is constantly being exposed. On the other hand, there is only one oxygen atom in the molecule, and in the case of solvent (3), which is an ether having alkyl chains with length of carbon number four, the complex is not formed and the components of the solid electrolyte do not readily begin to dissolve into the solvent. It is considered that a reaction did not proceed because of this.

4.2. Mechanism of Reaction between Solid Electrolyte and Nitriles

It has already been reported that acetonitriles having an alkyl chain length with a carbon number of two dissolve the solid electrolyte^{(30), (31)}. This is thought to be because the nitrogen atoms in the nitrile groups form complexes with the lithium ions in the sulfide solid electrolyte and, with themselves as solvent, dissolve the complexes⁽²¹⁾. The solvent (13) used in this research, however, is a compound with the carbon number of four, and although a portion of solvent changed color due to immersion, the volatile component nitrile was not observed among the degradation products [Fig. 7(d)] and the ionic conductivity of the solid electrolyte was not greatly decreased (Fig. 3). The solvent having changed to a bluish color suggested that a portion of Li_2S had dissolved out⁽³⁰⁾, but the fact that the infrared absorption spectra did not show nitrile having coordinated to the lithium ions, and the fact that the ionic conductivity of the solid electrolyte did not decrease, can be explained as being because the extent of Li_2S components dissolving out was small. This can be considered to occur because compounds having alkyl chains with a large steric hindrance interfere with the degradation of the solid electrolyte, as in the case of the ethers.

4.3. Mechanism of Reaction between Solid Electrolyte and Esters

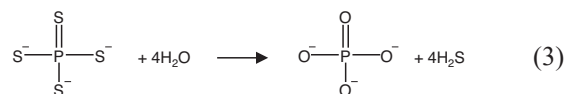
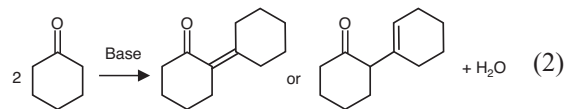
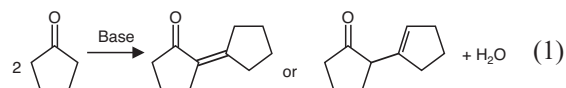
Solvent (6) is an ester having an alkyl chain length with a carbon number of two, and it has already been reported that it forms complexes with Li_2S and Li_3PS_4 ⁽¹⁵⁾⁻⁽¹⁷⁾. It has also been confirmed in the present research that solvent (6) is coordinated to the lithium ions in the solid electrolyte [Fig. 5(c)]. No coordination was found, however, in solvent (9), which has an alkyl chain length with a carbon number of four [Fig. 5(d)]. It is also the case in the present research, as noted in the previous chapter, that immersion of the solid electrolyte in esters results in hydrolysis products of esters.

These are, in other words, the nonvolatile components consisting of carboxylic acid and carboxylic acid lithium salt [(6) and (9) in Fig. 6], and the volatile component consisting of alcohol [Fig. 7(b)]. In light of the fact that carboxylic acid lithium salt was detected in the solid electrolyte after drying, it was inferred that the hydrolysis products of esters also contribute to the degradation of the solid electrolyte. The residual moisture content of solvents used in this research was under 30 ppm, and even this extremely small amount of moisture resulted in hydrolysis taking place. On the other hand, it was also found from the infrared absorption spectra results noted above that the amount of hydrolysis product differed according to the type and length of alkyl chains making up the esters. The strength of the infrared absorption peak attributable to the hydrolysis product of solvent (9) with its longer alkyl chain was weaker than that of solvent (6), which has a shorter alkyl chain, indicating that the amount of that product was smaller [(6) and (9) in Fig. 6(b)]. In addition, the amount of hydrolysis product was larger with solvent (5), which has a benzyl group.

In light of the above results, it can be said that both the coordination of ester groups to the solid electrolyte and the binding of the hydrolysis product to the solid electrolyte are contributing to the degradation reaction of the solid electrolyte due to esters. When the probe radius is 10 Å, it became clear from the calculation results for surface area accessible to coordinating oxygen atoms with solvents (6) and (9) that the value for solvent (9) with an alkyl chain length with a carbon number of four was smaller than the value for solvent (6) with an alkyl chain length with a carbon number of two [(6) and (9) in Fig. 8]. It can be inferred that the molecules of solvent (6) were able to approach the solid electrolyte [Fig. 9(b)], but those of solvent (9) were inhibited from approaching the solid electrolyte by the alkyl chains [Fig. 9(c)].

4.4. Mechanism of Reaction between Solid Electrolyte and Ketones

As a result of the immersion of solid electrolyte in ketones, the ionic conductivity of the solid electrolyte was greatly reduced [(10), (11), and (12) in Fig. 3]. GCMS analysis of the volatile components detected aldol condensation products of the ketones [Fig. 7(c)]. In the presence of acid catalyst or base catalyst, ketones cause an aldol condensation reaction⁽³⁴⁾. This reaction causes condensation of two ketone molecules and also produces H₂O as a by-product [Eqs. (1) and (2)]. In the case of the present research, the sulfide solid electrolyte is thought to act as a solid-state base catalyst. The sulfide solid electrolyte, however, is known to react with H₂O and undergo degradation [Eq. (3)]. It is considered, therefore, that the degradation reaction with water that is a by-product of aldol condensation also contributes to the decrease in ionic conductivity of the solid electrolyte resulting from immersion in ketones.



In addition to forming complexes with the components of sulfide solid electrolyte, therefore, ketones also produce H₂O through the aldol condensation reaction, and two degradation reactions are thought to occur simultaneously. Compared with the ketone (10) in chain form, immersion in ketones (11) and (12) in ring form caused greater reduction of the ionic conductivity of the solid electrolyte. This can be explained by the fact that self aldol condensation reaction rate is faster with ring form ketones⁽³⁵⁾. In light of the above results, it is to be expected that when using ketones as solvent, it is preferable to use compounds with greater steric hindrance that inhibit the approach to the surface of the solid electrolyte acting as a catalyst because this will inhibit aldol condensation.

When the above results are combined, it can be said that the mechanism of the reaction between solvent and solid electrolyte differs with the differences in functional groups, and that the steric hindrance of the solvent molecules inhibited the reaction. In order to examine the solvents used in a wet process, it is necessary to think comprehensively about the functional groups of the solvents and their steric hindrance. It has become clear from the present research that solvents with greater steric hindrance tend not to react readily with the solid electrolyte.

5. Conclusion

A systematic examination was made of the reactivity of a series of solvents and sulfide solid electrolytes in order to search for solvents to apply in a wet process for an all solid state battery. This yielded clarification of the mechanism of reaction between solvent and solid electrolyte.

- (1) The oxygen atoms and nitrogen atoms in polar groups form complexes with the lithium ions in the solid electrolyte. The dissolution of those complexes in the solvent causes a degradation reaction in the solid electrolyte.
- (2) Simultaneously with these reactions, the residual moisture content of less than 30 ppm in the solvent causes hydrolysis to occur in the esters, and the hydrolysis product reacts with the solid electrolyte.
- (3) With ketones, an aldol condensation reaction occurs that takes the solid electrolyte as a base catalyst. The H₂O that is a by-product of this reaction also undergoes a

reaction that causes degradation of the solid electrolyte.

It became clear that in order to inhibit the series of reactions caused by the mechanisms of these reactions, effective candidate solvents would be hydrocarbons that do not contain polar groups and ethers, esters, and nitriles that have alkyl groups with carbon numbers of four or higher that act as a steric hindrance. Together with recognition that the residual moisture content of the solvent needs to be limited to an extremely small amount, the research yielded directions to pursue toward the practical application of wet processes.

References

- (1) (a) Armand, M., Tarascon, J.-M.: Building better batteries, *Nature*, Vol. 451, p. 652-657, (2008);
(b) Balali, Y., Stegen, S.: Review of energy storage systems for vehicles based on technology, environmental impacts, and costs, *Renewable and Sustainable Energy Reviews*, Vol. 135, Article 110185, (2021)
- (2) <https://www.nedo.go.jp/content/100919683.pdf>
- (3) Kato, Y., Hori, S., Kanno, R.: $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ -Type Superionic Conductors: Synthesis, Structure, and Ionic Transportation, *Advanced energy materials*, Vol. 10, Issue 42, p. 2002153, (2020)
- (4) Kamaya, N., Homma, K., Yamakawa, Y., Hirayama, M., Kanno, R., Yonemura, M., Kamiyama, T., Kato, Y., Hama, S., Kawamoto, K., Mitsui, A.: A lithium superionic conductor, *Nature Materials*, Vol. 10, p. 682-686, (2011)
- (5) Kato, Y., Hori, S., Saito, T., Suzuki, K., Hirayama, M., Mitsui, A., Yonemura, M., Iba, H., Kanno, R.: High-power all-solid-state batteries using sulfide superionic conductors, *Nature Energy*, Vol. 1, p. 1-7, (2016)
- (6) Zhang, Q., Cao, D., Ma, Y., Natan, A., Aurora, P., Zhu, H.: Sulfide-Based Solid-State Electrolytes: Synthesis, Stability, and Potential for All-Solid-State Batteries, *Advanced Materials*, Vol. 31, Issue 44, p. 1901131, (2019)
- (7) Zheng, Y., Yao, Y., Ou, J., Li, M., Luo, D., Dou, H., Li, Z., Amine, K., Yu, A., Chen, Z.: A review of composite solid-state electrolytes for lithium batteries: fundamentals, key materials and advanced structures, *Chemical Society Reviews*, Vol. 49, Issue 23, p. 8790-8839, (2020)
- (8) Yamamoto, M., Terauchi, Y., Sakuda, A., Takahashi, M.: Binder-free sheet-type all-solid-state batteries with enhanced rate capabilities and high energy densities, *Scientific Reports*, Vol. 8, Article number 1212, (2018)
- (9) Riphaut, N., Strobl, P., Stiaszny, B., Zinkevich, T., Yavuz, M., Schnell, J., Indris, S., Gasteiger, H. A., Sedlmaier, S. J.: Slurry-Based Processing of Solid Electrolytes: A Comparative Binder Study, *Journal of The Electrochemical Society*, Vol. 165, No. 16, A3993-A3999, (2018)
- (10) Lee, K., Kim, S., Park, J., Park, S. H., Coskun, A., Jung, D. S., Cho, W., Choi, J. W.: Selection of Binder and Solvent for Solution-Processed All-Solid-State Battery, *Journal of The Electrochemical Society*, Vol. 164, No. 9, A2075-A2081, (2017)
- (11) Chen, K., Shinjo, S., Sakuda, A., Yamamoto, K., Uchiyama, T., Kuratani, K., Takeuchi, T., Orikasa, Y., Hayashi, A., Tatsumisago, M., Kimura, Y., Nakamura, T., Amezawa, K., Uchimoto, Y.: Morphological Effect on Reaction Distribution Influenced by Binder Materials in Composite Electrodes for Sheet-type All-Solid-State Lithium-Ion Batteries with the Sulfide-based Solid Electrolyte, *The Journal of Physical Chemistry C*, Vol. 123, Issue 6, p. 3292-3298, (2019)
- (12) Oh, D. Y., Nam, Y. J., Park, K. H., Jung, S. H., Cho, S.-J., Kim, Y. K., Lee, Y.-G., Lee, S.-Y., Jung, Y. S.: Excellent Compatibility of Solvate Ionic Liquids with Sulfide Solid Electrolytes: Toward Favorable Ionic Contacts in Bulk-Type All-Solid-State Lithium-Ion Batteries, *Advanced Energy Materials*, Vol. 5, Issue 22, p. 1500865, (2015)
- (13) Nam, Y. J., Cho, S.-J., Oh, D. Y., Lim, J.-M., Kim, S. Y., Song, J. H., Lee, Y.-G., Lee, S.-Y., Jung, Y. S.: Bendable and Thin Sulfide Solid Electrolyte Film: A New Electrolyte Opportunity for Free-Standing and Stackable High-Energy All-Solid-State Lithium-Ion Batteries, *Nano Letters*, Vol. 15, Issue 5, p. 3317-3323, (2015)
- (14) Riphaut, N., Stiaszny, B., Beyer, H., Indris, S., Gasteiger, H. A., Sedlmaier, S. J.: Understanding Chemical Stability Issues between Different Solid Electrolytes in All-Solid-State Batteries, *Journal of The Electrochemical Society*, Vol. 166, No. 6, A975-A983, (2019)
- (15) Yubuchi, S., Uematsu, M., Hotehama, C., Sakuda, A., Hayashi, A., Tatsumisago, M.: An argyrodite sulfide-based superionic conductor synthesized by a liquid-phase technique with tetrahydrofuran and ethanol, *J. Mater. Chem. A*, Vol. 7, p. 558-566, (2019)
- (16) Yubuchi, S., Uematsu, M., Deguchi, M., Hayashi, A., Tatsumisago, M.: Lithium-Ion-Conducting Argyrodite-Type $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I) Solid Electrolytes Prepared by a Liquid-Phase Technique Using Ethanol as a Solvent, *ACS Applied Energy materials*, Vol. 1, Issue 8, p. 3622-3629, (2018)
- (17) Phuc, N. H. H., Totani, M., Morikawa, K., Muto, H., Matsuda, A.: Preparation of Li_3PS_4 solid electrolyte using ethyl acetate as synthetic medium, *Solid State Ionics*, Vol. 288, p. 240-243, (2016)
- (18) Barrow, G. M.: Physical chemistry, International student edition, 7th printing, Chapter 21, Surface and heterogeneous catalysis, p. 731-754, (1983)
- (19) Fujimoto, K.: Kinetic Studies on Mineral Dissolution into Aqueous Solution: Reaction at Solid/Water Interface and Mass Transport, *Journal of the Mineralogical Society of Japan*, Vol. 24, No. 3, p. 159-

- 168, (1995) (in Japanese)
- (20) Whitesides, G. M., Laibinis, P. E.: Wet chemical approaches to the characterization of organic surfaces: self-assembled monolayers, wetting, and the physical-organic chemistry of the solid-liquid interface, *Langmuir*, Vol. 6, Issue 1, p. 87-96, (1990)
- (21) Barthel, J., Buchner, R., Wismeth, E.: FTIR Spectroscopy of Ion Solvation of LiClO_4 and LiSCN in Acetonitrile, Benzonitrile, and Propylene Carbonate, *Journal of Solution Chemistry*, Vol. 29, No. 10, p. 937-954, (2000)
- (22) Seneviratne, V., Frech, R., Furneaux, J. E., Khan, M.: Characterization of Crystalline and Solution Phases of Diglyme- LiSbF_6 , *The Journal of Physical Chemistry B*, Vol. 108, No. 24, p. 8124-8128, (2004)
- (23) Delley, B.: An all-electron numerical method for solving the local density functional for polyatomic molecules, *The Journal of Chemical Physics*, Vol. 92, Issue 1, p. 508-517, (1990)
- (24) Delley, B.: From molecules to solids with the DMol³ approach, *The Journal of Chemical Physics*, Vol. 113, Issue 18, p. 7756-7764, (2000)
- (25) Connolly, M. L.: Analytical molecular surface calculation, *Journal of Applied Crystallography*, Vol. 16, Issue 5, p. 548-558, (1983)
- (26) Nakayama, J.: The Infra-red Absorption Spectra of Organophosphorus Compounds, *Journal of Synthetic Organic Chemistry, Japan*, Vol. 28, No. 2, p. 132-143, (1970) (in Japanese)
- (27) Arai, Y., Yasue, T.: Introduction to Experimental Solid State Chemistry (XI), 7 Infrared Absorption Spectroscopy (2), *Gypsum & Lime*, No. 188, p. 47-60, (1984) (in Japanese)
- (28) Olsher, U., Izatt, R. M., Bradshaw, J. S., Dalley, N. K.: Coordination Chemistry of Lithium Ion: A Crystal and Molecular Structure Review, *Chemical Reviews*, Vol. 91, Issue 2, p. 137-164, (1991)
- (29) Zhou, L., Park, K.-H., Sun, X., Lalère, F., Adermann, T., Hartmann, P., Nazar, L. F.: Solvent-Engineered Design of Argyrodite $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) Solid Electrolytes with High Ionic Conductivity, *ACS Energy Letters*, Vol. 4, Issue 1, p. 265-270, (2019)
- (30) Wang, Z., Jiang, Y., Wu, J., Jiang, Y., Huang, S., Zhao, B., Chen, Z., Zhang, J.: Reaction mechanism of $\text{Li}_2\text{S-P}_2\text{S}_5$ system in acetonitrile based on wet chemical synthesis of $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte, *Chemical Engineering Journal*, Vol. 393, Article 124706, (2020)
- (31) Wang, Y., Lu, D., Bowden, M., El Khoury, P. Z., Han, K. S., Deng, Z. D., Xiao, J., Zhang, J.-G., Liu, J.: Mechanism of Formation of $\text{Li}_7\text{P}_3\text{S}_{11}$ Solid Electrolytes through Liquid Phase Synthesis, *Chemistry of Materials*, Vol. 30, Issue 3, p. 990-997, (2018)
- (32) Qian, P., Matsuda, M., Miyashita, T.: Chiral molecular recognition in polymer Langmuir-Blodgett films containing axially chiral binaphthyl groups, *Journal of the American Chemical Society*, Vol. 115, Issue 13, p. 5624-5628, (1993)
- (33) Qian, P., Nanjo, H., Yokoyama, T., Suzuki, T. M., Akasaka, K., Ohru, H.: Chiral molecular patterns of self-assembled ion pairs composed of (R, S), (S)-16-methyloctadecanoic acid and 4,4'-bipyridine, *Chemical Communications*, Vol. 20, p. 2021-2022, (2000)
- (34) Mahajan, Y. S., Kamath, R. S., Kumbhar, P. S., Mahajani, S. M.: Self-Condensation of Cyclohexanone over Ion Exchange Resin Catalysts: Kinetics and Selectivity Aspects, *Industrial & Engineering Chemistry Research*, Vol. 47, Issue 1, p. 25-33, (2008)
- (35) Iwata, M., Emoto, S.: Aldol Condensation of Aldehydes with Ketones Promoted by the Copper(II) Ion. Orientation to the Chemical Model for Metalloaldolases, *Bulletin of the Chemical Society of Japan*, Vol. 49, No. 5, p. 1369-1374, (1976)

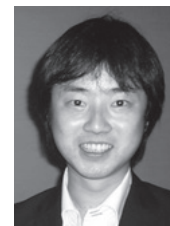
■ Author ■



Pu QIAN



Hiroshi SAKAI



Atsushi OGAWA



Hiroto MAEYAMA



Terumi FURUTA