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Lithium Ion Conduction in Silatrane Matrices

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Alkoxysilatranes, pentavalent neutral organosilicon compounds, and lithium salts formed amorphous complexes which show ionic conductivity above 10^{-5} S cm^{-1} at room temperature and good thermal stability above 300 °C.

Silatranes, whose general chemical structure is shown in Chart 1, are known as atrane compounds with an intramolecularly pentacoordinated neutral silicon center. Although the structures, chemical behavior,[1,2] and biological activities[3] of silatranes have been studied, much less attention has been paid to them in the field of materials science.[4] Among noncharged hypervalent silicon systems, silatranes possess considerable chemical stability (e.g., low hydrolytic sensitivity) and facile producibility (one-step reaction in many cases) that may allow various applications. Here, we chose alkoxysilatrane as a candidate for ion-conductive matrix because of its low volatility and the large dipole moment (e.g., 5.80 D for ethoxysilatrane),[2] which is enough to dissociate inorganic salts.

Ion-conductive materials with high ionic conductivity and low volatility are the key to developing batteries that can be applied not only to small size mobile electronics but also to large size electronics such as automobiles. Oligo- or poly(ethylene oxide) (PEO)-based solvent-free systems have been investigated over several decades.[5,6] Ionic liquids have been developed as well, because of their negligible volatility and high ionic conductivity.[7] As unique, non-PEO and nonionic liquid systems, we employed haloborane–imidazole and borane–imidazole complexes, since the hypervalent boranes have dipole moments from nitrogen to boron, which readily dissociate salts.[8] Borane–imidazole complexes actually show ionic conductivity of 2×10^{-4} S cm^{-1} (50 °C) when blended with lithium salts. Based on this knowledge, we have developed stable systems by using silatranes.

Ethoxysilatrane and butoxysilatrane[9] were dissolved in anhydrous acetonitrile or THF and then homogeneously mixed with lithium salts; lithium triflate (LiOTf), lithium bis(trifluoromethylsulfonyl)amide (LiTFSA), and lithium hexafluorophosphate ($LiPF_6$). The complexes of the silatranes and salts were obtained by removing the solvents under vacuum (1 Torr) at room temperature for two days. Complete removal of these solvents was confirmed by the ^{1}H NMR spectra. The water content was determined to be <0.1% by Karl-Fischer titration.

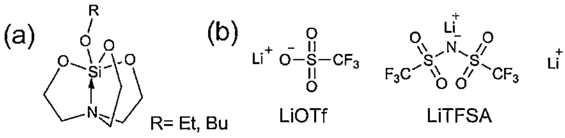

Chart 1. Chemical structures of silatranes (a) and lithium salts (b) that were used in this study.

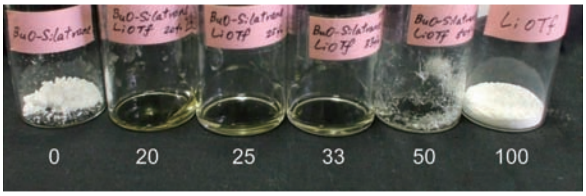

Figure 1. A picture of butoxysilatrane/lithium salt complexes. The numbers in the picture denote the lithium salt concentration (mol %) in the complex.

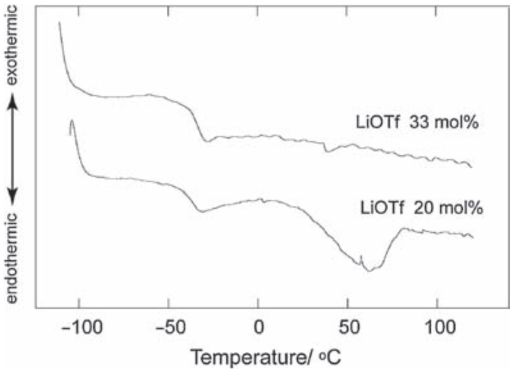

Figure 2. DSC traces of butoxysilatrane/lithium triflate complexes. Salt concentrations are 20 and 33 mol %, respectively.

Photographs of the butoxysilatrane/LiOTf complexes with a variety of salt concentration (0, 20, 25, 33, 50, and 100 mol %) are shown in Figure 1. Among those, 0 and 100 mol % are pristine butoxysilatrane and LiOTf, respectively. These pristine materials are crystals, while the complexes with the salt concentration of 25 and 33 mol % were obtained as amorphous materials. The 20 and 50 mol % samples were also obtained as amorphous at first but partially crystallized during storage for several months. The observed melting points of these complexes were considerably lower than those of pristine materials. The differential scanning calorimetry (DSC) traces for butoxysilatrane/LiOTf complexes are shown in Figure 2. Melting point (T_m) and glass-transition temperature (T_g) of a series of butoxysilatrane complexes are summarized in Table 1. Similar behavior was observed for the ethoxysilatrane complexes. The solution ^{1}H, ^{13}C, and ^{29}Si NMR spectra of the obtained complexes were almost the same as those of the pristine butoxysilatrane, showing that the silatrane was not decomposed at the complex-formation stage. We also checked the lithium salt dissociation in tetraethoxysilane (TEOS) for comparison; how-

Table 1. Summary of thermal properties of butoxysilatrane/lithium salt complexes

	Salt concentration /mol %	T_m/°C[a]	T_g/°C[a]
	0 (pristine silatrane)	106	nd[b]
LiOTf	20	62.0	−41.3
	25	nd[b]	−39.5
	33	nd[b]	−36.7
	50	43.8	−27.9
	100 (pristine LiOTf)	>300	—
LiTFSA	20	nd[b]	−46.1
	25	50.6	−47.1
	33	45.7	−38.6
	50	39.6	−49.8
	100 (pristine LiTFSA)	238[c]	—
$LiPF_6$	20	nd[b]	−12.3
	100 (pristine $LiPF_6$)	194[d,e]	—

[a]Determined by DSC. [b]nd: not detected. [c]Ref 10. [d]Decomposition temperature. [e]Ref 11.

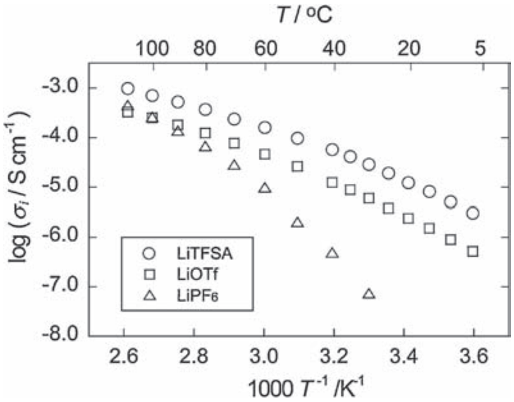

Figure 3. Temperature dependence of the ionic conductivity for butoxysilatrane/lithium salt complexes (cooling scan). The lithium salt concentration is 20 mol % for each case.

ever LiTFSA and LiOTf did not dissolve into TEOS (see the Supporting Infomation[14]). This indicates that the lithium salt dissociation in silatrane is enhanced by the high polarity of the hypervalent structure.

The very high polarity of silatrane should induce a large number of carrier ions. However, strong dipole–ion interaction generally disturbs the ions from migration. In the case of silatrane, the T_g's of the lithium salt complexes were low enough to expect that ionic conductivity takes place. The ionic conductivity of the obtained complexes was measured by complex impedance spectroscopy, and most of the lithium salt complexes showed good values exceeding 10^{-6} S cm^{-1} at ambient temperature and some achieved 10^{-3} S cm^{-1} at 100 °C (Figure 3). These values are as high as those of borane–imidazole systems. Specific values of all systems are summarized in Table 2. The relatively high ionic conductivity of LiTFSA complexes is probably caused by the highly dissociative nature of LiTFSA.[12] In the case of LiOTf complexes, the maximum of the ionic conductivity was found at the salt concentration of 25 mol %. This behavior is similar to conventional organic electrolyte solution or polymer electrolytes; the ionic conductivity reaches maximum because the increasing number of carrier ion and the suppression of ion mobility (increasing T_g or viscosity) are balanced at the salt concentration. LiTFSA complexes, however, showed a simple increase of ionic conductivity up to 50 mol %. This might be caused by the plasticizing effect by LiTFSA,[13] which is observed as the low T_g of this system (Table 1).

Table 2. Summary of ionic conductivity of butoxysilatrane/lithium salt complexes[a]

	Salt concentration /mol %	Conductivity σ_i/S cm^{-1}		
		25 °C	60 °C	100 °C
	0	nd[b]	nd[b]	nd[b]
LiOTf	20	3.9×10^{-6}	0.05×10^{-3}	0.25×10^{-3}
	25	9.6×10^{-6}	0.16×10^{-3}	0.90×10^{-3}
	33	10.5×10^{-6}	0.10×10^{-3}	0.52×10^{-3}
	50	0.7×10^{-6}	0.02×10^{-3}	0.23×10^{-3}
LiTFSA	20	8.5×10^{-6}	0.11×10^{-3}	0.89×10^{-3}
	25	1.0×10^{-6}	0.16×10^{-3}	0.95×10^{-3}
	33	5.1×10^{-6}	0.19×10^{-3}	1.11×10^{-3}
	50	17.1×10^{-6}	0.32×10^{-3}	1.58×10^{-3}
$LiPF_6$	20	nd[b]	0.01×10^{-3}	0.26×10^{-3}

[a]Values of cooling scan from 100 to 0 °C. [b]nd: not detected.

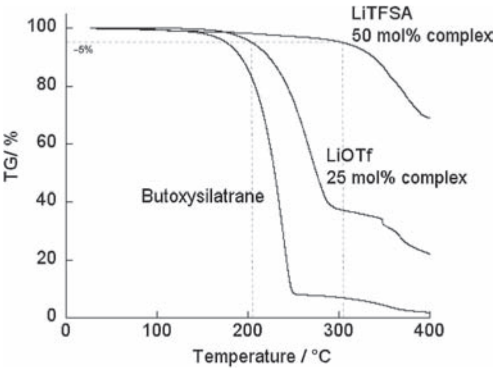

Figure 4. Thermogravimetric traces of butoxysilatrane/lithium salt complexes and pristine butoxysilatrane. Data was corrected under a N_2 gas atmosphere at a heating rate of 10 °C min^{-1}.

Thermal stability of the butoxysilatrane/lithium salt complexes was estimated by thermogravimetric analysis (TGA) in a nitrogen gas atmosphere. Figure 4 depicts the TGA trace of pristine silatrane and lithium salt complexes that have the optimum salt concentrations for the ionic conductivity. The Li salt complex showed the decomposition onset at higher temperature than that of pristine butoxysilatrane. The temperature of 5% weight loss ($T_d(-5)$) was 205 °C for the LiOTf complex. The LiTFSA complex showed significantly improved thermal stability, with $T_d(-5) = 305$ °C. However, the reason for this improvement of thermal stability is not yet clear.

In summary, we found that alkoxysilatranes readily form amorphous complexes with lithium salts. The ionic conductivity of the complex was good as a solvent-free system, 10^{-5} S cm^{-1}

at ambient temperature. LiTFSA complexes showed high thermal stability over 300 °C along with high ionic conductivity achieving $10^{-3}\,\mathrm{S\,cm^{-1}}$ (100 °C), suggesting that silatranes can be a lithium-ion-conductive matrix for high temperature use. This is the first report describing the potential of atrane compounds as ion-conductive matrices. Atranes usually show high thermal and chemical stability and are readily accessible. Studies to improve the conductivity by tuning the silatrane structure as well as by changing the center element of the atranes are now in progress.

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.