Synthesis, Characterization, and Ion Transport Properties of Lithium Ionic Liquids

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INTRODUCTION

Ionic liquids (room temperature molten salts) have many interesting properties as electrolytes, such as negligible vapor pressure and non-flammability. Cations of the ionic liquids, ever reported, are mainly quarternized ammoniums. The ionic liquids having only lithium ion as the cationic species, may have a possibility to develop advanced lithium batteries. In order to lower a melting point of a lithium salt, a decrease in coulombic interaction between the lithium-ion and an anion is required. A lithium salt of an aluminate anion, lithium tetra(hexafluoroisopropyl)aluminate ($LiAl(HFIP)_4$)[1], has a high formula weight (>700), and its anionic charge is delocalized due to the coordination of four electron-withdrawing groups with the central Al-atom. This anionic structure may decrease the coulombic interaction.

$LiAl(HFIP)_4$ has a lower melting point of *ca.*120□C, compared with conventional lithium salts, however the melting point is still higher than room temperature. In addition, the ionic conductivity of the melt at 130□C is about 10^{-5} Scm^{-1}, in spite of the high self-diffusion coefficients of lithium ion and anion of the order of 10^{-6} $cm^2 s^{-1}$.[2] These results suggest that the melt has quite low degree of dissociation and that strong Lewis acidic nature of the lithium ion favors ion pairing, trapped by the electron-rich F and O atoms. On the other hand, the salt is highly soluble in common aprotic solvents, especially in low molecular weight ethers, and exhibit a high ionic conductivity.

Based on these results, this paper deals with preparation and characterization of novel lithium ionic liquids, not only in the bulk but also in aprotic solvents and in a polyether.

EXPERIMENTAL

We propose a new concept for designing a novel anionic structure of lithium salt (see the structure in Scheme 1).[3] The introduction of electron-donating ether ligands in the anionic structure allows the interaction of the Lewis basic site with lithium ion, namely, self-dissociation of the salts. The novel lithium salts were synthesized by a reaction of $LiBH_4$ with stoichiometric amounts of oligo(ethylene glycol) monomethyl ether and fluorinated alcohol in THF at -78□C.[4]

RESULTS AND DISCUSSION

All of the novel lithium salts were colorless and clear liquids at room temperature. In the DSC measurements, only a glass transition temperature (T_g) could be seen without any other heat capacity changes, attributable to the crystallization and melting. The T_gs and physical properties of the liquid lithium salts are shown in Table 1. The ionic conductivity of the liquid lithium salts was approximately 10^{-4}-10^{-5} Scm^{-1} at 30□C. Self-diffusion coefficients of the lithium ion and the anion, determined by PGSE-NMR measurement, are in the order of 10^{-8} $cm^2 s^{-1}$ at the same temperature.

The □$_{imp.}$/□$_{diff.}$, the apparent degree of ionic dissociation[5], is relatively high, which indicates that the large number of ionic carrier contributes to the ionic conduction in the lithium salts. Namely, the lithium salts have relatively high ionic activities and self-dissociation abilities, which suggest that the novel liquid lithium salts are really "*lithium ionic liquids*".

The lithium ionic liquids are incorporated in aprotic solvents and in a polyether. The electrolyte properties are also characterized by means of basic physicochemical, electrochemical, and NMR measurements, and the results will be presented.

Scheme 1 Synthesis of lithium ionic liquids

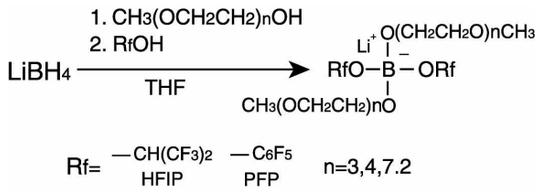

Table 1 Physical properties of ionic liquids

Ionic liquid	ρ (gcm^{-3})	η (mPas)	T_g (℃)	σ ($10^{-5}Scm^{-1}$)	diffuion coeff. D_{anion} ($10^{-8}cm^2s^{-1}$)	diffuion coeff. D_{lithim} ($10^{-8}cm^2s^{-1}$)	$\Lambda_{imp.}/\Lambda_{diff.}$
HFIP-3	1.34	590	-44	1.3	0.87	0.92	0.10
HFIP-4	1.31	490	-54	4.6	1.8	1.3	0.24
HFIP-7.2	1.26	310	-56	3.9	1.1	1.3	0.37
PFP-3	1.42	>1200	-28	0.68	——	——	——
PFP-4	1.33	510	-43	2.4	1.0	0.69	0.23
PFP-7.2	1.27	480	-51	2.7	0.85	0.75	0.39

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