Effect Of Structure On The Thermal Stability And Ionic Conductivity Of Zwitterionic Liquids

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Ionic liquids are consisted of only ions. Electrolyte solution for lots of energy devices is one of application of ionic liquids expecting stability and high ionic conductivity. However, ionic liquids are composed of only ions, these ions do not play important roles in these devices. Generally, we need addition of salts into ionic liquids to generate carrier ions. In that case, not only carrier ions but also consisting ions of ionic liquids migrate along with potential gradient. It is necessary to design new ionic liquids to allow target ion to migrate.

We have proposed zwitteionic liquid (ZIL) as ionic liquid where cation and anion were tethered covalently[1]. Although many of them are solid at room temperature, they turned liquid by adding of LiTFSI at room temperature. There is an ionic liquid like interaction between carion site of ZIL and TFSI anion. These liquid have high ionic conductivity: 10^{-4} Scm^{-1}. They also showed high thermal stability and the decomposition temperature about 400^{o}C. Furthermore, lithium transferrence number is larger than 0.5. Selective migration of target ion is expected in zwitterions.

However, design of ZIL is necessary to improve ion conductive character. In this report, thermal properties of various zwitterions were compared. Especially difference of anion species and spacer structure was focused. Moreover, ionic conductivity and thermal stability of ZIL containing equimolar amount of LiTFSI were studied.

Thermal properties were studied using zwitterions having N-ethylimidazolio unit as cation site and carboxylate as anion site tethered with defferent length of spacers. Carboxylate type zwitterions seen in **Fig.1** are prepared by previously reported method[2]. As shown in **Fig.2**, in case of number of CH_2 unit was 1, melting point (Tm) of simple zwitterions was about 250^{o}C, and decomposition temperature (Td) was near Tm. By increasing number of CH_2 unit, Tm was lowered as seen in **Fig.2**. Whereas little change was seen in Td, liquid state was stabilized in wider temperature range. When equimolar amount of LiTFSI was added to zwitterions, they become liquid except for zwitterion having only one of CH_2 unit as spacer chain. After addition of LiTFSI, Td was dramatically improved as seen in **Fig.2** (triangular dots), and the effect was larger when longer spacer was used.

Table 1 shows difference between sulfonate and carboxylate zwitterions having N-ethylimidazolio cation and **n**=4 spacer length. There is a little difference in Tm. Sulfonate type zwitterion has good thermal stability and high transferrence number of lithium cation. On the other hand, carboxylate type zwitterion has good ionic conductivity and slow crystallization. No re-crystallization peak was observed during DSC measurement under slow cooling. As shown above, some structure data were obtained and used to prepare better ion conductive matrix.

References

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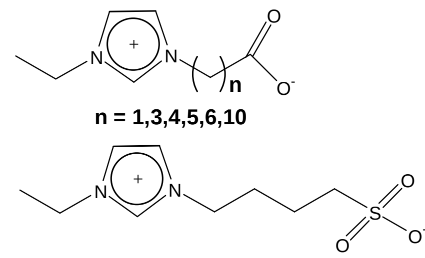

Fig.1 Structure of zwitterions having carboxylate and sulfonate anion site

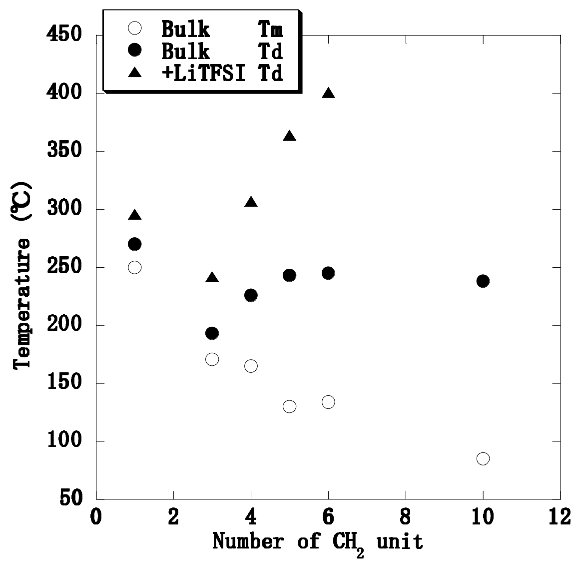

Fig. 2 Comparison of thermal properties with difference of alkyl spacer length of zwitterions having carboxylate anion

Table 1 Comparison of thermal properties and ionic conductivity for ZILs with different anion spieces

	$-SO_3^-$	$-CO_2^-$
Tm(bulk, ^{o}C)	160	167
Td(bulk, ^{o}C)	326	226
Td(+LiTFSI, ^{o}C)	364	307
crystallization	fast	very slow
□$_i$(+LiTFSI, at 50^{o}C,Scm^{-1})	$6.1x10^{-5}$	$1.8x10^{-5}$
t_{Li+}	>0.5	0.1