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 zwitterionic 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 cation site of ZIL and TFSI anion. These liquid have high ionic conductivity: \(10^{-3}\) S cm\(^{-1}\). They also showed high thermal stability and the decomposition temperature about 400°C. Furthermore, lithium transference 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-ethylimidazolium unit as cation site and carbamate as anion site tethered with different 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°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-ethylimidazolium cation and n=4 spacer length. There is a little difference in Tm. Sulfonate type zwitterion has good thermal stability and high transference number of lithium cation. On the other hand, carboxylate type zwitterion has good ionic conductivity and slow crystallization. No recrystallization 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