# Phase transition and conductive acceleration of phosphonium-cation-based room-temperature ionic liquid†

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**An unusual ionic conduction phenomenon related to the phase transition of a novel phosphonium-cation-based room-temperature ionic liquid (RTIL) is reported; we found that in the phase change upon cooling, a clear increase in ionic conductivity was seen as the temperature was lowered, which differs from widely known conventional RTILs; clearly, our finding of abnormality of the correlation between temperature change and ionic conduction is the first observation in the electrolyte field.**

Room-temperature ionic liquids (RTILs)[1] are melted salts composed of only cations and anions without any solvent, and have many desirable properties required for electrolyte materials for use in energy conversion and storage devices, such as lithium secondary batteries,[2] electric double-layer capacitors,[3] fuel cells,[4] dye-sensitised solar cells,[5] field-effect transistors,[6] electrochemical actuators[7] and so on, owing to their low flammability, low volatility,[8] high ionic conductivity, and high thermal stability. Various physical properties of RTILs (*i.e.* melting point, density, viscosity, and degree of dissociation) are governed by molecular weight, molecular geometrical symmetry, cation–anion interactions, ionicity, and other properties. Owing to these considerations, recently, many RTILs composed of cations of various chemical structures (*i.e.* imidazolium, ammonium, phosphonium, sulfonium, *etc.*), which are so-called 'designer solvents', have been reported by synthetic chemists. In particular, phosphonium-cation-based RTILs were reported as electrochemically stable RTILs owing to their wide charge distribution.[9] In addition, it is interesting that some RTILs exhibit liquid crystal[10] or plastic crystal[11–13] phases owing to their specific molecular architecture (*i.e.* framework, main element, substituent group) and the unique change in the ionic conduction mechanism of their phase transitions.[14] Here, we report unusual ionic conduction related with the phase transition of a novel phosphonium-cation-based RTIL. Discussions will be made on the relationships between many phase transition points and 'unique' ionic conduction changes precisely.

Triethyl(methoxymethyl)phosphonium bis(trifluoromethylsulfonyl)amide (TEMMP-TFSA; Nippon Chemical Industrial Co., Ltd., most stable cation structure: Fig. 1) and its LiTFSA binary electrolyte (LiTFSA concentration: 0.32 mol kg$^{-1}$) were prepared for measurements. Ionic conductivities ($\sigma$) were measured on SUS/electrolyte/SUS hermetically-closed cells and determined by the complex impedance method, using an AC impedance analyzer (Princeton Applied Research, PARSTAT-2263, 200 kHz-50 mHz; impressed voltage: 10 mV) at temperatures between 80 and $-30$ °C with cooling and heating processes. The samples were thermally equilibrated at each temperature for at least 90 min prior to the measurements. Reproducibilities of $\sigma$ measurement data were very good. Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments EXSTAR6000 DSC at temperatures between 100 and $-100$ °C with cooling and heating rates of 2.0 °C min$^{-1}$. Viscosities were measured between 80 and 10 °C with a cooling process.

Fig. 2 shows the Arrhenius plots of $\sigma$ calculated from the impedance spectra of neat TEMMP-TFSA and the LiTFSA binary electrolyte. On cooling, the temperature dependence of $\sigma$ of neat TEMMP-TFSA can be classified into three clear temperature regions. We assume that the three types of ionic conduction behavior are associated with the phase changes [in this study, phases (I)–(III)]. Usually for most conventional ionic conductors (*e.g.* non-aqueous electrolytes, polymer electrolytes, inorganic electrolytes, RTILs and plastic crystals), more than two types of clear conduction change with temperature changes were not reported. The temperature changes

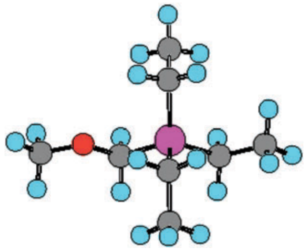

**Fig. 1** Most stable structure of TEMMP cation calculated from relative energies of rotamers at the MP2/6-311G**//HF/6-311G** level (pink: phosphorus; red: oxygen; grey: carbon; light blue: hydrogen).

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† Electronic supplementary information (ESI) available: Structure, Arrhenius plots of $\sigma$ and $\eta$, DSC thermograms, calculated relative energies of rotamers and $^1$H NMR spectra for the TEMMP-TFSA or TEMEP-TFSA RTILs. See DOI: 10.1039/b809309a

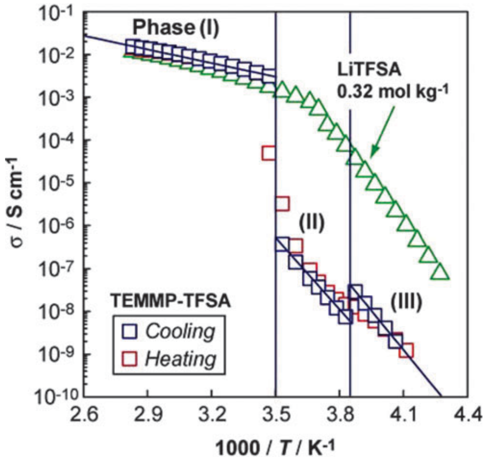

**Fig. 2** Arrhenius plots of ionic conductivity ($\sigma$) for TEMMP-TFSA (blue: cooling; red: heating) and LiTFSA binary electrolyte (LiTFSA concentration: 0.32 mol $kg^{-1}$).

of phase (I) to phase (II), and phase (II) to phase (III) were from 10 to 15 °C and from −12 to −15 °C, respectively. In phase (I), a relatively high $\sigma$ of $5.3 \times 10^{-3}$ S $cm^{-1}$ at 30 °C and a low activation energy ($E_a$) of approximately 21 kJ $mol^{-1}$ were obtained. On the other hand, the aspect was significantly different in phase (II), and $\sigma$ rapidly decreased to by four orders of magnitude ($3.8 \times 10^{-7}$ S $cm^{-1}$ at 10 °C) compared with 15 °C ($3.1 \times 10^{-3}$ S $cm^{-1}$). The apparent $E_a$ was approximately 109 kJ $mol^{-1}$, which is five times greater than that in phase (I). The ionic conductivity $\sigma$ is generally expressed as the product of the carrier number of ions, the valence of the ion species, and the mobility of the ions. In this study, significant relationships between temperature and $\sigma$ were deduced to be related to the mobility of the ions. In other words, a marked viscosity change (transition for the solid-state phase) was observed until 10 °C. In addition, surprisingly, when the temperature decreased in the phase (II) region, an increase in $\sigma$ was found with the change from phase (II) to phase (III) (−12 °C: $7.5 \times 10^{-9}$ S $cm^{-1}$; −15 °C: $2.9 \times 10^{-8}$ S $cm^{-1}$; apparent $E_a$: 118 kJ $mol^{-1}$). To the best of our knowledge, any notable increase in $\sigma$ according to the temperature decrease has not been a reported phenomenon so far. At present, the reorientation of the ionic conduction path for the acceleration of ionic conduction might be expected. The apparent $E_a$ of phase (III) was 118 kJ $mol^{-1}$, which is similar to that in phase (II). The limiting temperature was –30 °C, where $\sigma$ could scarcely be measured. Although the effect of the heating process corresponded well to that of cooling, the change in $\sigma$ according to the phase change from phase (III) to (II) was small compared with that of cooling.

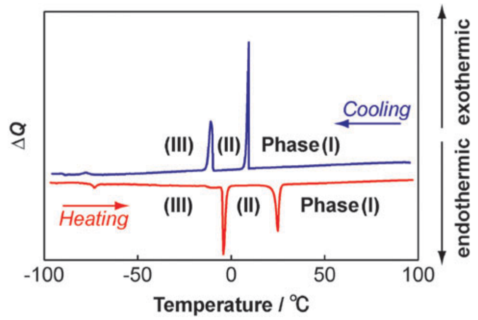

**Fig. 3** DSC thermogram of TEMMP-TFSA (blue: cooling; red: heating).

On the other hand, no such phase changes were confirmed with triethyl(2-ethoxymethyl)phosphonium bis(trifluoromethylsulfonyl)amide (TEMEP-TFSA, see ESI†), which has a similar chemical structure to TEMMP-TFSA, suggesting that the position of the oxygen atom in TEMMP plays an important role in the phase changes. In particular, it is expected that the flexible and short methoxymethyl base connecting the central phosphorus atom should lead to these phenomena, by taking into consideration the results of TEMMP-TFSA. With regard to the LiTFSA binary electrolyte system, a $\sigma$ value of $5.3 \times 10^{-3}$ S $cm^{-1}$ was obtained at 30 °C, which was 62% that of bulk TEMMP-TFSA. Unlike in the case of bulk TEMMP-TFSA, no rapid decrease in $\sigma$ was confirmed, and the temperature dependences of $\sigma$, which were classified at approximately –5 °C into two apparent $E_a$ values, were observed (high-temperature region: 27 kJ $mol^{-1}$, low-temperature region: 126 kJ $mol^{-1}$). Thus, typical plastic crystal behavior, that is, the achievement of a solid-state high lithium ionic conductor, is expected.

To observe detailed phase transition behavior from the thermal aspect, DSC measurements were performed. Fig. 3 shows the DSC thermogram of TEMMP-TFSA. Two distinct heat peaks of transformation were observed in both cooling and heating processes, and these observations agreed with the phase changes confirmed by the ionic conductivity measurement (in the case of cooling, phase (I) to phase (II): 9 °C; phase (II) to phase (III): −10 °C). The phase changes (I)↔(II) showed significant hysteresis compared with (II)↔(III), and were consistent with the result of $\sigma$. Although the phase transition (II)↔(III) was a solid–solid transition (checked by viscosity measurement and visual observation, see the ESI†), the activation of the conduction that causes the increase in $\sigma$ (mainly, an increase in ionic mobility) is expected. Previously, MacFarlane *et al.* reported two or more phase transition heatings of plastic crystals related to RTILs.[11,12] They did not observe any accompanying marked change in $\sigma$ or inversion of $\sigma$ against temperature decreases. All transition enthalpies ($\Delta H$ values) were less than 20 kJ $mol^{-1}$, and flexible plastic crystal-like transitions were expected.[12] Clearly, our finding of abnormality of the correlation between temperature change and ionic conduction is the first observation in the electrolyte field. We will promote the research and development of RTILs, which includes X-ray analysis (crystalline structure and solution conformation), diffusive property measurement, and computer chemistry (*ab initio* calculations and MD simulations) for the determination of the origin of RTILs.

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