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Electrolyte properties of 1-alkyl-2,3,5-trimethylpyrazolium cation-based room-temperature ionic liquids for lithium secondary batteries

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ABSTRACT

The physicochemical and electrochemical properties of three 1-alkyl-2,3,5-trimethylpyrazolium cation-based room-temperature ionic liquids with various alkyl chain lengths were investigated. The temperature dependences of density, viscosity, and ionic conductivity were obtained by precise measurements. Electrolyte properties of these room-temperature ionic liquids were also examined from the viewpoint of their uses in lithium secondary batteries ([$LiCoO_2$ positive electrode|electrolyte|lithium metal negative electrode]). It was found that the alkyl chain length affects the charge–discharge performances of cells.

1. Introduction

Room-temperature ionic liquids (room-temperature molten salts, RTILs) are liquid salts consisting of only cations (positive ions) and anions (negative ions) and have desirable and interesting properties, for example, low flammability and low volatility (negligible vapor pressure), high ionic conductivity, and thermal and electrochemical stability [1]. RTILs have unlimited possibilities through synthetic chemistry by varying the combination of cations and anions and they also have various promising physicochemical properties and can be used in task-specific applications. For example, RTILs have been attracting attentions as safe lithium secondary battery electrolytes for use in high-performance, large-scale energy storage devices, such as electric power load-leveling systems for customer usages and natural power storage systems (PV, wind power) [2–4]. However, the relatively high viscosities of common RTILs (e.g., imidazolium and quaternary ammonium cation systems), which are attributed to the strong interactions (e.g., coulombic forces) and intramolecular (e.g., rotational) energies, are serious issues. In this study, we studied three different 1-alkyl-2,3,5-trimethylpyrazolium cation-based RTILs (alkyl: ethyl, propyl, and butyl), which retain relatively low viscosity with increasing cationic molecular weight. The physicochemical (density, viscosity, ionic conductivity) and electrochemical (battery performances) properties were investigated.

2. Experimental

2.1. Samples

RTILs based on 1-alkyl-2,3,5-trimethylpyrazolium bis (trifluoromethanesulfonyl) amide (purchased from Kanto Kagaku, synthesized by Japan Carlit) were used as the RTIL samples, and the chemical structures are shown in Fig. 1. The samples contained an ethyl (ETMP-TFSA, M_w: 419.36), propyl (PTMP-TFSA, M_w: 431.37) or butyl (BTMP-TFSA, M_w: 447.42) groups. The RTIL samples were dried in a vacuum chamber at 323 K for more than 48 h and stored in a dry argon-filled glove box ([O_2] < 0.4 ppm, [H_2O] < 0.1 ppm, Miwa Mfg. Co., Ltd.) before various measurements were performed.

2.2. Measurements of physical properties of RTILs

Density (ρ) and viscosity (η) measurements were performed using a thermoregulated Stabinger-type density/viscosity meter

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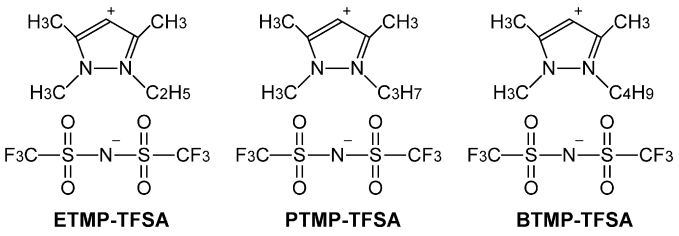

Fig. 1. Chemical structures of 1-alkyl-2,3,5-trimethylpyrazolium cation-based room-temperature ionic liquids (ETMP-TFSA, PTMP-TFSA, and BTMP-TFSA).

(SVM3000G2, Anton Paar). The temperature was controlled in the range of 80–10 °C while cooling. Ionic conductivity (σ) was 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, frequency region: 200 kHz–50 mHz, impressed voltage: 10 mV) at temperatures between 80 and −40 °C while cooling.

2.3. Preparation and evaluation of lithium secondary batteries using RTILs

Lithium secondary battery characteristics were investigated using [$LiCoO_2$ positive electrode|RTIL electrolyte|lithium metal negative electrode] cells. The positive electrode sheet was composed of $LiCoO_2$ (85 wt.%) as the active material, acetylene black (9 wt.%, Denka) as an electrically conductive additive, and PVDF (6 wt.%, Kureha Chemical) as a binder polymer. These constitutive materials were thoroughly agitated together in a homogenizer with *N*-methylpyrrolidone (NMP). The obtained positive electrode paste was uniformly applied onto an aluminum current collector using an automatic applicator. After drying the applied paste, the positive electrode sheet was compressed using a roll-press machine to increase packing density and to improve electrical conductivity (electrode thickness after roll-pressing: 15 μm, electrode loading: 3 mg cm^{-2}). The positive electrode sheet, separator, RTIL–Li-TFSA binary electrolyte (Li-TFSA concentration: 0.32 mol kg^{-1}), and lithium metal negative electrode were encapsulated into 2032-type coin cells. To ensure complete penetration of the electrolyte into the high-density pressed positive electrode sheet, the prepared battery was aged at 60 °C for more than 18 h. Then, charge–discharge tests were performed on the cells at 3.0–4.2 V with a current density of 0.05 mA cm^{-2} (constant current charge–constant current discharge). AC impedance measurements were performed at every cycle in the charged state (frequency region: 200 kHz–50 mHz, impressed voltage: 10 mV, Princeton Applied Research VMP2/Z). The cycle number dependences of the impedance spectra, which were obtained using the fitting program ZSimpWin will be discussed below. All measurements were performed at 30 °C.

3. Results and discussion

3.1. Bulk properties of RTILs

Fig. 2 shows the temperature dependences of density (ρ) for ETMP-TFSA, PTMP-TFSA, and BTMP-TFSA. The densities of the pyrazolium cation-based RTILs decreased in the order ETMP-TFSA > PTMP-TFSA > BTMP-TFSA in the measured temperature range. For example, the densities at 30 °C ($\rho_{30\,°C}$) were 1.454 (ETMP-TFSA), 1.421 (PTMP-TFSA), and 1.388 g cm^{-3} (BTMP-TFSA). The densities decreased with the alkyl chain length, similarly to in the widely reported 1,3-alkyl imidazolium cation-based systems [5]. Generally, in a narrow range of temperatures, ρ (g cm^{-3}) can be

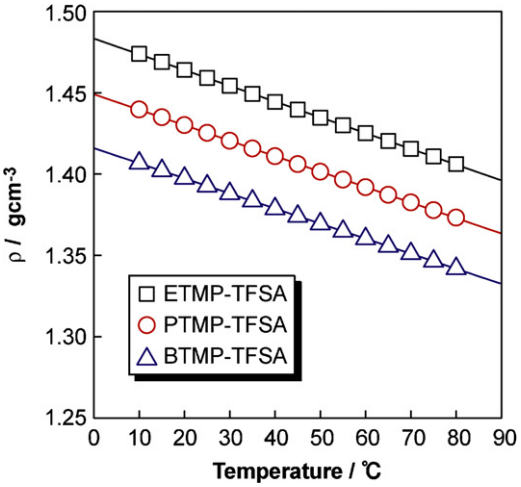

Fig. 2. Temperature dependences of density (ρ) for 1-alkyl-2,3,5-trimethylpyrazolium cation-based room-temperature ionic liquids upon cooling (80–10 °C).

Table 1
Density equation ($\rho = b - aT$) parameters and molar concentration at 30 °C (M_{30}) for ETMP-TFSA, PTMP-TFSA, and BTMP-TFSA.

Ionic liquids	a ($\times 10^{-4}$ g cm^{-3} K^{-1})	b (g cm^{-3})	M_{30} ($\times 10^{-3}$ mol cm^{-3})
ETMP-TFSA	9.691	1.483	3.468
PTMP-TFSA	9.514	1.449	3.293
BTMP-TFSA	9.269	1.415	3.102

expressed as follows:

$$\rho = b - aT, \quad (1)$$

where a, b, and T are the coefficient of volume expansion (g cm^{-3} K^{-1}), the density at 0 K (g cm^{-3}), and temperature (K), respectively. In the present system a strong linear relationship ($r > 0.9999$) with temperature was obtained for all RTILs. The best-fit parameters of Eq. (1) are summarized in Table 1. The molar concentration (at 30 °C; M_{30}/mol cm^{-3}) and the degree of expansion of pyrazolium cation-based RTILs also decreased with the alkyl chain length of the RTILs as well as ρ.

Fig. 3 shows the temperature dependences of viscosity (η) for ETMP-TFSA, PTMP-TFSA, and BTMP-TFSA. The values of η for ETMP-TFSA, PTMP-TFSA, and BTMP-TFSA at 30 °C were 68, 62,

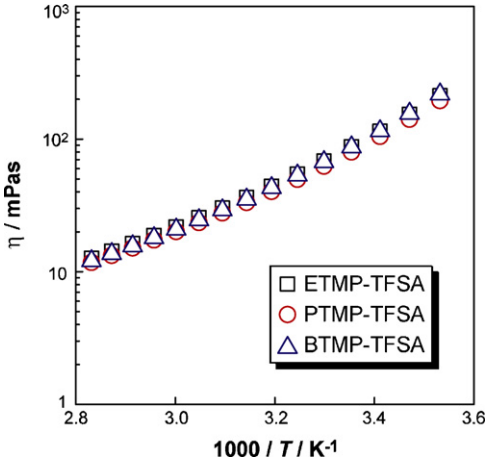

Fig. 3. Temperature dependences of viscosity (η) for 1-alkyl-2,3,5-trimethylpyrazolium cation-based room-temperature ionic liquids upon cooling (80–10 °C).