Water Content of Hydrophobic Ammonium Imide-Type Room Temperature Ionic Liquid

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Ionic liquids consisting of aliphatic quaternary ammonium cation and imide-type anion have a wide electrochemical window larger than 5 V. We have been investigating the electrodeposition of metals, *e.g.* Cu, Zn, Ni, and Mg, from one of the ionic liquids, trimethyl-*n*-hexylammonium bis((trifluoromethyl)sulfonyl)amide (TMHA-Tf_2N).[1,2] These ionic liquids are considered to be hydrophobic, since the anions have -CF_3 group(s). It was found, however, that a certain amount of water remained in the ionic liquid even after dehydration *in vacuo* and that the residual water affected the electrodeposits from the ionic liquid. In the present study, we examined the temperature dependence of the content of the residual water and concomitant change in some physical properties of the ionic liquid TMHA-Tf_2N.

The ionic liquid TMHA-Tf_2N was synthesized in an ambient atmosphere by the reaction of trimethyl-*n*-hexylammonium bromide with lithium bis((trifluoromethyl)-sulfonyl)amide as

$$n\text{-}C_6H_{13}(CH_3)_3NBr + LiN(SO_2CF_3)_2 = n\text{-}C_6H_{13}(CH_3)_3N^+N^-(SO_2CF_3)_2 + LiBr \quad (1)$$

The resulting TMHA-Tf_2N was dried *in vacuo* at 120 ˚C for 2 hours with a liquid nitrogen trap and then allowed to stand in contact with the atmosphere. The temperature of the ionic liquid was controlled to be constant between 30 to 150 ˚C. The amount of water was measured by the Karl-Fischer method. Viscosity and electric conductivity were measured by a vibration-type viscometer and a conventional conductivity measuring cell.

At the beginning, the ionic liquid absorbed water from the atmosphere and the water content was increased with the elapse of time. After that, the water content reached a constant value. This saturated water content was decreased with the rising the temperature of the ionic liquid. Figure 1 shows the relationship between the saturated content of water and temperature of the ionic liquid. The water content at 30 ˚C was about 800 ppm, which corresponds to 5.9×10^{-3} mol dm^{-3} in molarity or 1.9×10^{-2} in mole fraction. In contrast, the water content was decreased to below 200 ppm when the temperature was raised to about 150 ˚C, indicating that the residual water in the ionic liquid can be removed only by heating without reducing the pressure.

Figure 2 shows changes in the water content of the ionic liquid and of the water vapor pressure of the atmosphere. It was clear that the water content depended on the water vapor pressure. The viscosity (η) of the ionic liquid was decreased with the rising temperature, the conductivity (Λ) was simultaneously increased. Although η decreased and Λ also increased with the increasing water content, the influence of the water content on these parameters was found to be much smaller than that of the temperature.

In Figure 3, all the Λ and η pairs measured at various temperatures with various water contents were plotted together. The relationship between log Λ and log η gives a straight line with the gradient of –1, indicating that the Walden's rule (2) is applicable to ionic liquids contain a measure of water, unless the water content exceeds the saturated value at each temperature.

$$\Lambda\eta = K \quad (K\text{: constant}) \quad (2)$$

Table I summarizes the saturated water content together with Λ and η of the ionic liquid at two temperatures: 49 and 99 ˚C. The data were taken first at 49 ˚C (left column), then at 99 ˚C (middle) and again at 49 ˚C (right). After the heating and cooling cycle, the properties of the ionic liquid did not change, demonstrating that when water and the ionic liquid are mixed with each other, an irreversible chemical reaction does not occur.

1. K. Murase and Y. Awakura, *Trans. Mater. Res. Soc. Jpn.*, **29**, 55 (2004).
2. K. Murase *et al.*, *J. Appl. Electrochem.*, **31**, 1089 (2001).

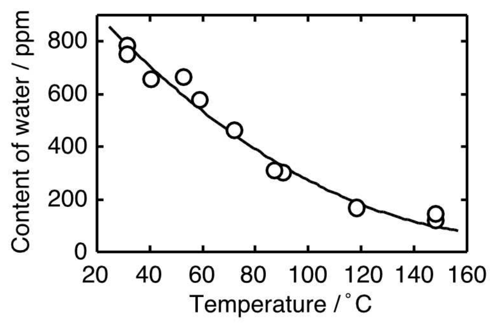

Fig.1 Saturated content of H_2O in TMHA-Tf_2N

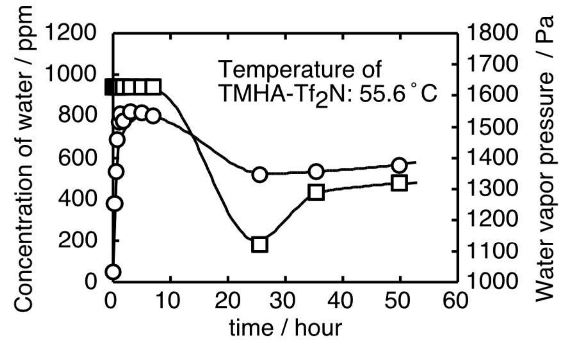

Fig. 2 Changes of the vapor pressure of water in the atmosphere and of the water content in TMHA-Tf_2N

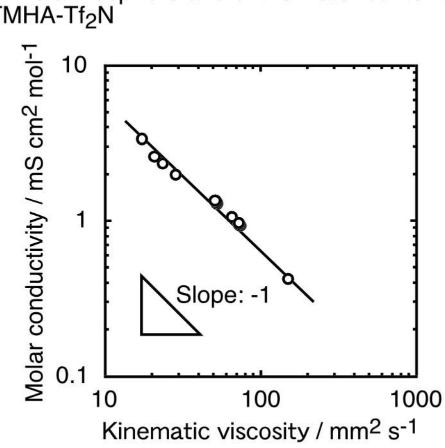

Fig.3 Relationship between the viscosity and conductivity of TMHA-Tf_2N with or without containing water

Table I Properties of TMHA-Tf_2N saturated with water before and after heating to 99 ˚C

	49 ˚C	99 ˚C	49 ˚C
Saturated content of H_2O / ppm	457	151	446
Λ / S cm^2 mol^{-1}	2.07	4.50	2.10
η / mm^2 s^{-1}	62.3	13.2	62.4