Development of new complex hydrides with sodium fast-ionic conductivity

Complex hydride $Na_2(BH_4)(NH_2)$ can be a potential candidate for solid electrolytes for next-generation sodium ion batteries due to the high sodium ionic conductivity and high electrochemical stability. In this study, we have experimentally investigated the effect of chloride substitution in $Na_2(BH_4)(NH_2)$ on the ionic conductivity.

We have reported that the complex hydride $Na_2(BH_4)(NH_2)$ consisting of Na^+, $[BH_4]^-$ and $[NH_2]^-$ exhibits sodium fast-ionic conductivity at room temperature because of the specific antiperovskite-type structure with vacancies in the Na^+ site [1]. We have also found that substitution of halide ions such as Cl^- for $[BH_4]^-$ and $[NH_2]^-$ is effective to enhance lithium ionic conductivities of Li-based complex hydrides in our previous studies [2]. In this study, we have experimentally investigated the effect of chloride substitution in $Na_2(BH_4)(NH_2)$ on the ionic conductivity.

$Na_2(BH_4)(NH_2)$ and NaCl were mechanically milled in the molar ratio of 9 : 1, followed by heat treatment at 180 °C under Ar. Figure 1 compares the powder X-ray diffraction profiles of $Na_2(BH_4)(NH_2)$ and $9Na_2(BH_4)(NH_2)$ + NaCl. The diffraction peaks of the antiperovskite-type structure shifted to higher angle clearly for $9Na_2(BH_4)(NH_2)$ + NaCl. The result suggests that although small amount of unknown phase was also included, the $[BH_4]^-$ complex anions were partially substituted by Cl^- in $9Na_2(BH_4)(NH_2)$ + NaCl, judging from the ionic radii of $[BH_4]^-$ (2.05 Å), $[NH_2]^-$ (1.68 Å) and Cl^- (1.68 Å).

The sodium ionic conductivity of $9Na_2(BH_4)(NH_2)$ + NaCl was measured by ac impedance method in the temperature range from 27 °C to 150 °C, as shown in Figure 2. The ionic conductivity of $Na_2(BH_4)(NH_2)$ was as high as 2×10^{-6} S/cm at 27 °C and it increased with increasing temperature. However, $9Na_2(BH_4)(NH_2)$ + NaCl showed one-tenth lower ionic conductivity than $Na_2(BH_4)(NH_2)$.

We have recently found out a strong correlation between reorientational motion of complex anions and mobility of cations in complex hydrides [3]. The smaller crystal lattice of $9Na_2(BH_4)(NH_2)$ + NaCl due to the partial substitution of Cl^- for $[BH_4]^-$ may make the reorientational motions of $[BH_4]^-$ and/or $[NH_2]^-$ slower, which could result in the lower ionic conductivity by heightening the Na^+ diffusional barrier. We will accomplish the higher ionic conductivity by substitution of larger halide ions such as I^- in the near future.

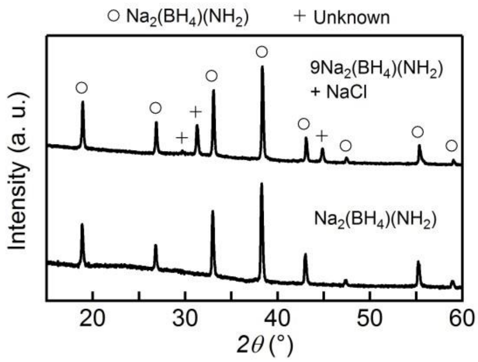

Fig. 1 X-ray diffraction profiles of $Na_2(BH_4)(NH_2)$ and $9Na_2(BH_4)(NH_2)$ + NaCl.

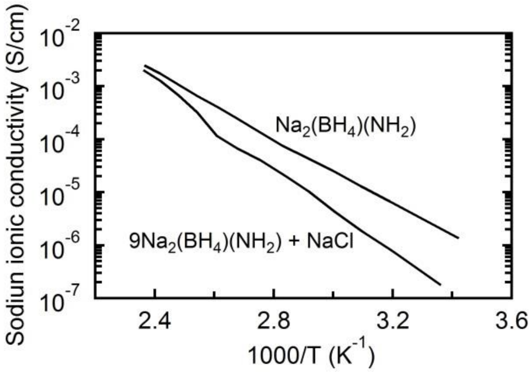

Fig. 2 Temperature dependences of ionic conductivities of $Na_2(BH_4)(NH_2)$ and $9Na_2(BH_4)(NH_2)$ + NaCl.

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