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A New Proton-conductive Electrolyte of NH_4PO_3/TiP_2O_7 Composite for Use in Intermediate Temperature Fuel Cells

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Introduction

Intermediate temperature fuel cells at 250-600°C, in particular around 300°C, have many advantages: 1) Metal and resin are available for the fabrication of cells, 2) energy conversion efficiency becomes higher than that of polymer electrolyte fuel cells (PEFCs), 3) CO poisoning of the electrode is considerably suppressed, etc. Recently, $NH_4PO_3/(NH_4)_2SiP_4O_{13}$ was reported to exhibit 20 mS cm^{-1} and 100 mS cm^{-1} at 300°C under dry and wet atmospheres, respectively [1]. In the composite, NH_4PO_3 is responsible for high ionic conductivity in a supporting matrix of $(NH_4)_2SiP_4O_{13}$ [2]. High ionic conductivity is originated in the partial decomposition of NH_4PO_3 to HPO_3 at around 250°C. Accordingly, a supporting matrix has to be stable and should contribute to ion conduction.

In our previous paper [3], we focused on a supporting matrix and reported a new electrolyte of $(NH_4)_2TiP_4O_{13}$-based material and showed partial decomposition of $(NH_4)_2TiP_4O_{13}$ to TiP_2O_7 should be responsible for high proton conductivity. In this study, we prepared x NH_4PO_3/TiP_2O_7 (x = 0.2-1.0) and studied the proton-transport properties at 150-300°C.

Experimental

Ammonium polyphosphate (NH_4PO_3, APP form I) was synthesized from H_3PO_4, P_2O_5 and urea as starting materials. TiP_2O_7 was prepared from P_2O_5 and SiO_2. Composite electrolytes were prepared from the mixture of obtained TiP_2O_7 and NH_4PO_3 in the various molar ratios as x NH_4PO_3/TiP_2O_7 (x = 0.2–1.0). The obtained mixtures were milled and pressed into pellets. Then, samples were sintered for 10 h at 400°C under an NH_3 gas atmosphere. Proton conductivity was measured by ac impedance spectroscopy under a dry and wet Ar humidified at 20°C atmospheres in the temperature range of 150-300°C.

Results and discussion

X-ray diffraction patterns of x NH_4PO_3/TiP_2O_7 (x = 0.2-1.0) were identical to TiP_2O_7, irrespective of the amount of NH_4PO_3. This results indicate that NH_4PO_3 including in composite electrolytes should be in amorphous state. Arrhenius plots of proton conductivities for x NH_4PO_3/TiP_2O_7 (x = 0.2-1.0) under dry and wet argon atmospheres during the first cooling (temperatures decreasing from 300°C to 150°C) and the second heating (temperatures increasing from 150°C to 300°C) are shown in Figs. 1 and 2, respectively. In advance, each electrolyte was annealed at 300°C for 15-20 h in order to be in the steady state. As shown in Fig. 1, proton conductivity was improved by increasing the molar ratio of NH_4PO_3 at each temperature. This result indicates that NH_4PO_3 is responsible for the high proton conductivity and that TiP_2O_7 serves as a supporting matrix. The conductivities of each sample showed nonlinear behavior against the reciprocal temperatures, but the temperature dependence was almost reversible. The maximum proton conductivity was observed for x = 1.0 and was evaluated to be 24.2 mS cm^{-1} at 250°C. On the other hand, the proton conductivity under the humidified condition increased compared with that under the dry condition, as shown in Fig. 2. Clear temperature dependency of proton conductivity was not observed, and the behavior was almost reversible; proton conductivity showed almost the same value at each temperature. The maximum proton conductivity was observed for x =1.0 and was evaluated to be 66.0 mS cm^{-1} at 200°C. These results indicate that the increase of proton conductivity under a humidified condition should originate from the water absorbed into the electrolyte and hydrolyzed polyphosphates. The conduction mechanism is under investigation.

Acknowledgement

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References

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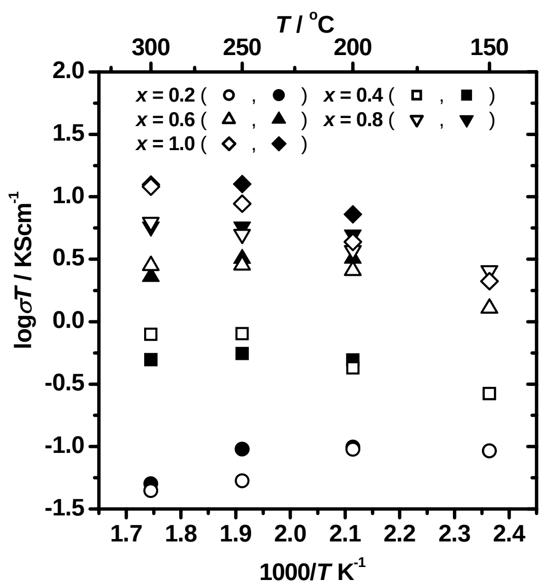

Fig. 1 Arrhenius plots of proton conductivities for x NH_4PO_3/TiP_2O_7 under dry Ar atmosphere, open symbols for first cooling and closed symbols for second heating.

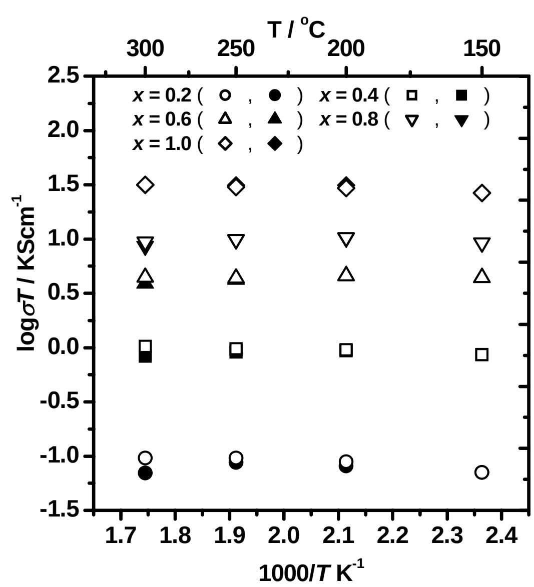

Fig. 2 Arrhenius plots of proton conductivities for x NH_4PO_3/TiP_2O_7 under wet Ar atmosphere humidified at 20°C, open symbols for first cooling and closed symbols for second heating.