Proton conductivity of $(NH_4)_xK_{x\text{-}1}PO_3$ electrolyte

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Ammonium polyphosphate, NH_4PO_3, is known to have a high proton conductivity at about 300°C, especially in humidified gases (about 100 mS cm^{-1} at 300°C), and is a promising electrolyte material for use in intermediate temperature fuel cells. Though as-prepared NH_4PO_3 does not show appreciable proton conductivity, thermal decomposition of NH_4PO_3 to HPO_3 increases the proton conductivity at temperatures higher than 200°C. However, the NH_4PO_3-HPO_3 mixture does not have enough thermal stability at 300°C; hence, it is used as a composite with matrix materials such as $(NH_4)_2SiP_4O_{13}$ and $(NH_4)_2TiP_4O_{13}$ to increase the thermal stability [1, 2, 3].

In the present study, the NH_4^+ ion in NH_4PO_3 was partly substituted with a nonvolatile alkaline cation, K^+, which has approximately the same ionic radius as that of NH_4^+, to increase the thermal stability. The $(NH_4)_xK_{1\text{-}x}PO_3$ electrolytes were prepared, and their proton conductivity and thermal stability were measured**.** Furthermore, $(NH_4)_xK_{1\text{-}x}PO_3$ samples with low NH_4^+ contents ($x \leq 0.1$) were prepared to investigate the mechanism of proton conduction.

The $(NH_4)_xK_{1\text{-}x}PO_3$ electrolytes were characterized by ion chromatography (IC) X-ray diffraction (XRD), thermogravimetry (TG), and scanning electron microscopy (SEM). The contents of K^+ and NH_4^+ were determined by ion chromatography, and were 20-44% of expected x values for $(NH_4)_xK_{1\text{-}x}PO_3$. Figure 1 shows the XRD patterns of the $(NH_4)_xK_{1\text{-}x}PO_3$ electrolytes. The peaks at *ca.* 26° gradually shift to lower angles with an increase in the content of NH_4^+ and this tendency indicates the formation of solid solutions $(NH_4)_xK_{1\text{-}x}PO_3$, in which the NH_4^+ ion occupied part of the K^+ sites in monoclinic KPO_3.

$(NH_4)_{0.20}K_{0.80}PO_3$ electrolyte exhibited a high stability at 300°C and showed a high proton conductivity of 4.57×10^{-3} S cm^{-1} in dry Ar. Even at 400°C, the electrolyte was stable, and its conductivity reached 8.04×10^{-3} S cm^{-1}.

The proton conductivity of $(NH_4)_{0.05}K_{0.95}PO_3$ electrolyte initially increased at 300°C in dry Ar as shown in Figure 2. But after reaching the maximum (1.14×10^{-3} S cm^{-1}), it decreased gradually with an elapse of time. The results of thermogravimetry showed a 2.8% loss of the mass after being kept at 300ºC for 100 h, which suggested that NH_3 (and other unknown components) were volatilized during heating. Figure 3 shows the SEM images of $(NH_4)_{0.05}K_{0.95}PO_3$ electrolyte (a) after heat-treated at 400°C for 12 hours in NH_3 atmosphere, (b) after hold at 300°C for 24 hours in dry Ar, and (c) after hold at 300°C over 100 hours in dry Ar. It was revealed that the electrolyte separated into two phases; crystalline KPO_3 and an amorphous phase (HPO_3) when heated at 300°C. The former acted as a matrix, and the latter worked as a proton conductor. On the other hand, the amorphous phase almost disappeared after heating at 300°C for more than 100 h. This was due to vaporization of the amorphous phase, which results in the gradual decrease in proton conductivity.

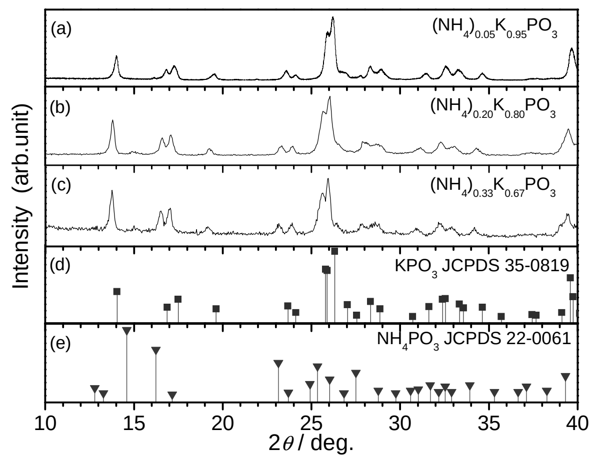

Figure 1 XRD patterns of (a) $(NH_4)_{0.05}K_{0.95}PO_3$, (b) $(NH_4)_{0.20}K_{0.80}PO_3$, (C) $(NH_4)_{0.33}K_{0.67}PO_3$, (d) KPO_3 (JCPDS 35-0819), and (e) NH_4PO_3 (JCPDS 22-0061).

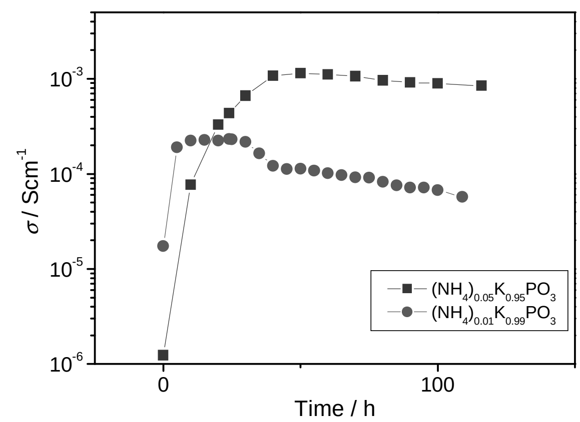

Figure 2 Time dependence of proton conductivity for $(NH_4)_xK_{x\text{-}1}PO_3$ electrolyte at 300°C in dry Ar (50 ml min^{-1}).

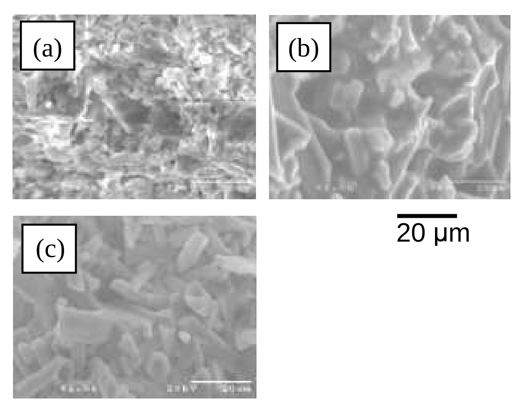

Figure 3 SEM images of $(NH_4)_{0.05}K_{0.95}PO_3$ electrolyte (a) after heat-treated at 400°C for 12 hours in NH_3 atmosphere, (b) after hold at 300°C for 24 hours in dry Ar, and (c) after hold at 300°C over 100 hours in dry Ar.

References

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