A New Proton-Conductive Electrolyte of CsH_2PO_4/SiP_2O_7 Composite for Use in Intermediate Temperature Fuel Cells

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Introduction

Intermediate temperature fuel cells operate at 200-300°C have many attractive advantages, such as, better durability to CO poisoning of Pt electrode, the increase in the rate of electrochemical reactions at the electrode and the increase in the energy conversion efficiency, etc. Cesium dihydrogen phosphate, CsH_2PO_4, is one of the proton conductors known in intermediate temperature range [1]. Temperature dependence of the proton conductivity shows a drastic increase in conductivity at around 230°C because of the phase transition from monoclinic (low temperature phase) to cubic (high temperature phase) under the humid atmosphere [1, 2]. However, CsH_2PO_4 dehydrates and occurs to form $Cs_2H_2P_2O_7$ above 230°C under dry atmosphere, resulting in a decrease in proton conductivity. Consequently, it is necessary to operate the fuel cell under humidified condition.

Recently, the composite electrolyte of CsH_2PO_4/SiO_2 was reported and showed higher conductivity than that of CsH_2PO_4 at low temperature phase [1]. However, the phase transition occurred at around 230°C. In this study, we focused on SiP_2O_7 as a matrix, and synthesized a new proton-conductive electrolyte of CsH_2PO_4/SiP_2O_7 composite. The structural and electrochemical properties of the composite at intermediate temperature have been investigated.

Experimental

Cesium dihydrogen phosphate was synthesized from a mixture of Cs_2CO_3 and H_3PO_4 in molar ratio of 1:1. SiP_2O_7 was prepared from P_2O_5 and SiO_2 as starting materials [3]. X-ray diffraction pattern of the obtained SiP_2O_7 was identical to Form III type reported in literature [3, 4]. Preparation of CsH_2PO_4/SiP_2O_7 composite was as follows: the obtained CsH_2PO_4 was mixed with SiP_2O_7 in the molar ratio of 2:1 and 1:2, and then pressed in to pellets (diameter 10 mm, thickness 1-3 mm). The pellets were calcined at 220°C for 1 h. X-ray diffraction patterns of CsH_2PO_4/SiP_2O_7 composite were obtained with a scanning speed of 2° min^{-1}. Proton conductivity was measured by AC impedance spectroscopy. The applied frequency was in the range of 0.1 Hz to 1 MHz with a voltage amplitude of 30 mV. Pellets were sputtered with gold as electrode. The measurement was conducted at 150-270°C under 30%H_2O/Ar atmosphere. In advance, the sample was kept for 30 min at each temperature to be in steady state.

Result and discussion

Figure 1 shows the X-ray diffraction patterns of CsH_2PO_4/SiP_2O_7 composites (5:1 and 1:2), together with those of CsH_2PO_4 and SiP_2O_7 for comparison. In the XRD patterns of the CsH_2PO_4/SiP_2O_7 composite, broad patterns were obtained. As shown in Figure 1(a), the peak intensity at $2\theta = 23.6^o$ observed for monoclinic CsH_2PO_4 reduced and other peaks disappeared. Furthermore, the main peaks assigned to SiP_2O_7 also disappeared. With an increase in the molar ratio of matrix, SiP_2O_7 were observed as shown in Figure 1(b). These results indicate that CsH_2PO_4 including in composite electrolytes should be in amorphous state and would react with SiP_2O_7 at the interface.

Temperature dependence of the conductivity for CsH_2PO_4/SiP_2O_7 (2:1) composite, CsH_2PO_4 and CsH_2PO_4/SiO_2 composite under 30%H_2O/Ar atmosphere are shown in Figure 2. Pure CsH_2PO_4 and CsH_2PO_4/SiO_2 composite showed a drastic increase in conductivity at around 230°C because of the phase transition. On the other hand, the CsH_2PO_4/SiP_2O_7 composite showed no conductivity-jump and temperature dependency, and exhibited high proton conductivity in the temperature range of 150-270°C. The proton conductivity was evaluated to be about 10 mS cm^{-1} at around 250°C. These results indicate that the amorphous state of the composite electrolyte should be responsible for the high conductivity and the suppression of the phase transition. It was suggested that CsH_2PO_4/SiP_2O_7 composites are promising materials for intermediate temperature fuel cells.

Acknowledgement

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References

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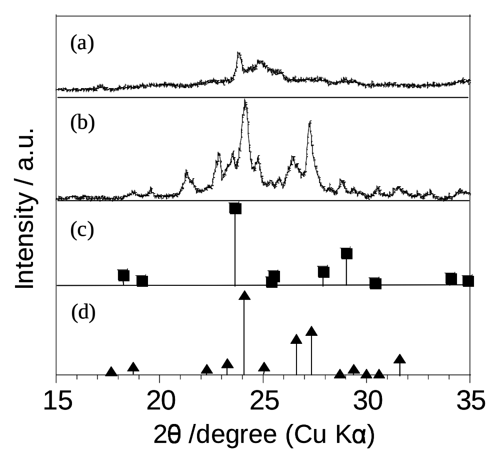

Fig. 1 XRD patterns of CsH_2PO_4-SiP_2O_7.
(a) CsH_2PO_4-SiP_2O_7 (5:1), (b) CsH_2PO_4-SiP_2O_7 (1:2), (c) CsH_2PO_4, (d) SiP_2O_7.

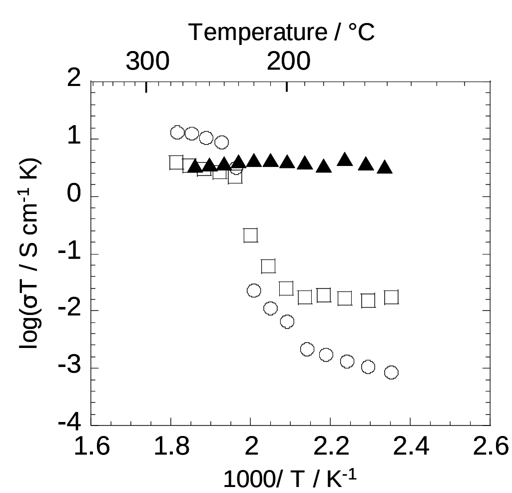

Fig. 2 Temperature dependence of the conductivity in 30%H_2O/Ar. ○: CsH_2PO_4; □: CsH_2PO_4:SiO_2 = 2:1; ▲: CsH_2PO_4:SiP_2O_7 = 2:1.