Proton Conducting Membrane Prepared from Organic-Inorganic Hybrid Precursor for Intermediate Temperature Fuel Cells

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Abstract

Proton conducting membranes were prepared by using epoxy-resin-silica hybrid polymer as flexible matrix and Cs-doped phosphotungstic acid PWA (Cs-PWA) as proton conducting networks. Cs-PWA was well dispersed and the membranes exhibited good flexibility. Thermogravimetric analysis indicated that the membranes were stable at temperatures up to about 230°C. Proton conductivity of the membrane with a weight ratio of Cs-PWA/E201=1.6 were about 8.1×10^{-4} Scm^{-1} at 160°C and 80% relative humidity. Their conductivity was improved by increasing volume fraction of Cs-PWA, which was successful after Cs-PWA was ground to nano-sized particles.

Introduction

In many researches on Polymer electrolyte membrane fuel cells (PEMFCs), protonic conducting membranes that work at above 100°C have been strongly required in order to solve the inactivation of Pt catalyst by CO, to reduce the amount of Pt, and to improve the quality of exhaust gas as heat sources. Protonic conducting membranes consisting of organic-inorganic composites are attractive because of their flexibility of organic matrix and high protonic conductivity at elevated temperatures of inorganic materials. In this study, we employed an organic-inorganic compound "Compoceran E201®" consisting of epoxy monomer and siloxane (E201, Arakawa Chemical Industries, LTD.) as matrix. With E201, better dispersion of inorganic materials in the matrix is expected because siloxane part exhibits affinity to inorganic materials. We report the preparation and proton conductivity of membranes synthesized by dispersing Cs doped phosphotungstic acid (Cs-PWA) as inorganic proton conductors in E201.

Experimental

Cs-PWA was synthesized by mecahnochemical reaction of Cs_2SO_4 and PWA by using a ball-mill.[1)] Cs-PWA was dispersed and well stirred in E201 dissolved in acetone.

After 2-ethyl-4-methylimidazol was added as a hardener of epoxy parts of E201, the solution was spread on PTFE dish and heated at 60°C for 4 hours to form a membrane. The membrane thus obtained is denoted as Cs-PWA:E201(x) where x is the wait ratio of Cs-PWA to E201. The dispersion of Cs-PWA was observed by using FE-SEM. Thermalgravimetry analysis (TGA) was conducted to study the thermal stability of and the composition the membranes. The proton conductivity of the membranes were investigated by measuring a.c. impedance in the frequency range from 10^6 to 0.1 Hz at 80-160°C with a relative humidity of 20 to 80%.

Results and Discussions

Membranes Cs-PWA:E201(x) exhibited good homogeneity, smoothness and flexibility up to x = 1.6. FE-SEM observation revealed Cs-PWA particles were well dispersed in the matrix. TGA confirmed the thermal stability up to 230°C. Table 1 shows the weight and volume fraction of Cs-PWA in the membranes that were estimated from the results of TGA and density. Figure 1 shows temperature dependence of proton conductivity of Cs-PWA:E201(x). The proton conductivity was independent of Cs-PWA composition for $x \leq 0.5$, while was enhanced by about one order of magnitude for x = 1.6. As listed in table 1, at x = 1.6, the volume fraction of Cs-PWA in the membrane was 27% and close to the threshold of percolation network. This means the partial network of Cs-PWA was formed for x = 1.6. In order to obtain higher proton conductivity, higher incorporation of Cs-PWA is required, which was successfully achieved by increasing the amount of Cs-PWA that were nano-sized by ball milling to improve the dispersion in the matrix. The results on the membrane consisting of the nano-sized Cs-PWA will be reported in the poster.

Table 1. Weight fraction and volume fraction of Cs-PWA in Cs-PWA:E201(x).

x	Weight fraction (wt%)	Volume fraction (vol%)
0.1	6.5	1.6
0.3	28.2	8.6
0.5	37.1	12
1.6	61.1	27

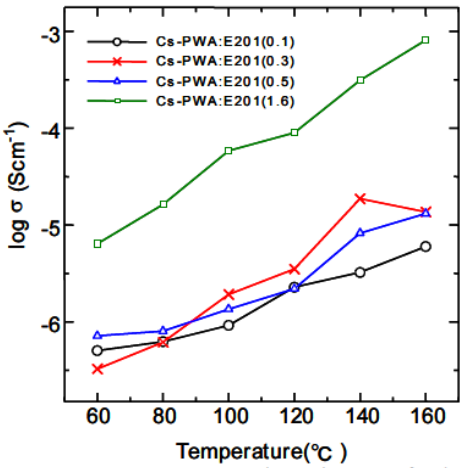

Fig. 1. Temperature dependence of the conductivity for Cs-PWA:E201(x) under R.H. of 80 %.

References

1. A. Matsuda, et al, *Solid State Ionics*, **178**, 723-727 (2007).