Proton Conductivity of $(NH_4)_2SO_4/TiO_2$ Composite for Intermediate Temperature Fuel Cells

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Introduction

Fuel cells convert chemical energy directly to electrical energy cleanly and efficiently. Although various kinds of fuel cells have been studied, there still exist lots of material issues to be solved for commercialization. Intermediate temperature fuel cells at 200-600ºC are promising technology to resolve these problems, i.e., metal and resin are applicable in fabrication and CO poisoning of Pt electrode is much suppressed, etc [1, 2]. Some acidic salts are known as good proton conductors at intermediate temperature, in particular at around 200ºC. However, the mechanical and chemical stability are weak. Recently, the composite electrolytes of acidic salts/inorganic materials were reported to improve the conductivity, mechanical and chemical stability, effectively [3, 4]. In this study, we synthesized a new proton-conductive electrolyte of $(NH_4)_2SO_4/TiO_2$ composite and studied the proton conductivity as an electrolyte for intermediate temperature fuel cells.

Experimental

The composite electrolytes of $(NH_4)_2SO_4/TiO_2$ were synthesized as follows: the mixture of $(NH_4)_2SO_4$ aq. and TiO_2 sol was heated and dried at 100ºC. The obtained powder pressed into pellet, and then calcined at 200ºC for 1 h in air. Proton conductivity was measured by AC impedance spectroscopy in the temperature range of 100-250ºC under various humidified atmospheres. Gold was deposited on the pellets as electrode by sputtering technique. The applied frequency was in the range of 0.1 Hz to 1 MHz with voltage amplitude of 50 mV.

Results and discussion

Time dependences of the conductivities for $(NH_4)_2SO_4/TiO_2$ composites at 250ºC under dry Ar and 30% H_2O/Ar are shown in Fig. 1. For each sample, the conductivity increased with annealing time up to 5 h, and then decreased gradually. The increase of conductivity could be originated from the decomposition of $(NH_4)_2SO_4$, resulting in the increase in the number of ionic carriers:

$$(NH_4)_2SO_4 \rightarrow (NH_4)HSO_4 + NH_3 \tag{1}$$

On the other hand, the gradual decrease was caused by the decrease of carriers:

$$(NH_4)HSO_4 \rightarrow NH_3 + SO_3 + H_2O \tag{2}$$

For each sample, the conductivities under a wet atmosphere were higher than that under a dry atmosphere. This result suggests that the proton conduction would be promoted by water. The proton conductivity was improved by increasing the molar ratio of $(NH_4)_2SO_4$ at each condition. This result indicates that $(NH_4)_2SO_4$ is responsible for the high proton conductivity. However, the composite of $(NH_4)_2SO_4/TiO_2$ (9/1) was unstable and melted after 5 h under a wet atmosphere. On the other hand, $(NH_4)_2SO_4/TiO_2$ (8/2) was stable. These results indicate that TiO_2 as a matrix prohibits the proton conduction, but increases the mechanical strength.

Arrhenius plots of the conductivities for $(NH_4)_2SO_4/TiO_2$ (9/1) composite under various humidified atmospheres during several heating-cooling cycles are shown in Fig. 2. Prior to the measurements, the composite was annealed at 250ºC for 10 h in order to be in steady state. When the humidity was changed, the sample was annealed in the same condition. The slops of the conductivities became gradual with the increase of temperature and the temperature dependences of the conductivities were almost reversible under each atmosphere. These results indicate that the interface of $(NH_4)_2SO_4/TiO_2$ would influence the proton conduction mechanism at high temperatures. The conductivity increased with humidity and the highest value was evaluated to be 35 mS cm^{-1} under 7.3% H_2O/Ar at 250ºC. This result suggests that the increase of proton conductivity under a humidified condition would be originated in the water absorbed into the electrolyte.

Acknowledgement

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References

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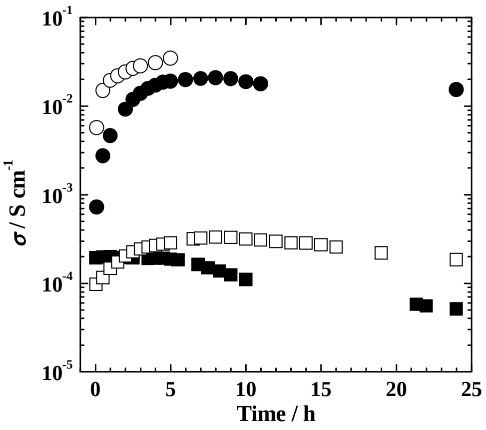

Fig. 1 Time dependences of the conductivities for $(NH_4)_2SO_4/TiO_2$ composites at 250ºC under dry Ar (filled symbols) and 30% H_2O/Ar (open symbols). ●, ○: $(NH_4)_2SO_4/TiO_2$ (9/1); ■, □: $(NH_4)_2SO_4/TiO_2$ (8/2).

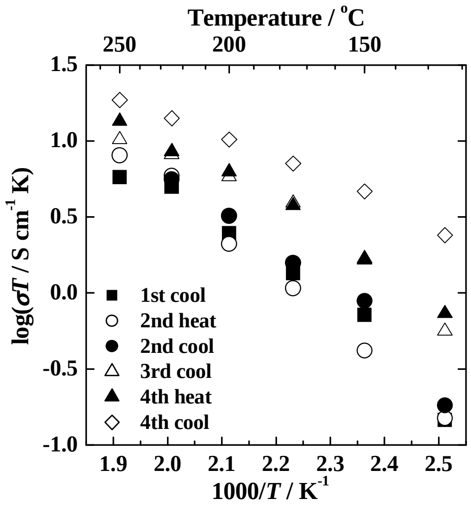

Fig. 2 Arrhenius plots of the conductivities for $(NH_4)_2SO_4/TiO_2$ (9/1) composite. ■, ○, ●: Under dry Ar; △, ▲: under 4.2% H_2O/Ar; ◇: under 7.3% H_2O/Ar.