Proton conduction of RTMS – acid system

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1. Introduction

The electrolyte of present polymer electrolyte fuel cells (PEFCs) that is presently used is perfluorosulfonic acid (PFSA) membrane. The proton conduction is hopping like mechanism through swollen water. For this reason, present PEFCs are difficult to operate over 100 °C under atmospheric pressure, which lead water loss. Room temperature molten salts (RTMSs) have thermal stability, nearly zero vapor pressure, chemical and electrochemical stabilities, and high ionic conductivity. The PFSA membrane impregnated with RTMS has shown good ion conductivity at over 100 °C [1], but the proton conduction was not clear. The adsorption and desorption of proton on Pt were observed during cyclic voltammogram in EMITFSI (1-ethyl- 3-methyl-imidazolium bis (trifluoromethylsulfonyl) imide) - sulfuric acid system [2].

In this study, to evaluate the applicability of the RTMSs - acid system for PEFC, the thermal stability and the proton conduction of RTMS - acid (liquid and membrane) systems have been evaluated using thermogravimetry, electrochemical methods and DC 4 probe method.

2. Experimental

The thermal stability and the proton conduction have been investigated for RTMSs - HTf (CH_3SO_3H) liquid and RTMSs - PFSA membranes. EMITFSI and EMITf (1-ethyl-3-methyl- imidazolium trifluoromethane-sulfate) were used as RTMSs and Nafion was used as PFSA. A membrane was prepared from RTMS and 5% Nafion solution (Aldrich).

The thermal stability was determined by a thermogravimetry under air. The proton conductivity was measured by DC 4 probe method under hydrogen atmosphere. The temperature range was 30 - 150 °C. The electrodes were Pt and the expected electrode reactions during DC loading electrolysis were

$$\tfrac{1}{2} H_2 \rightarrow H^+ + e^- \text{ (Anode) and}$$

$$H^+ + e^- \rightarrow \tfrac{1}{2} H_2 \text{ (Cathode)}$$

3. Results and Discussion

The thermal stability of RTMS - Nafion membrane is shown in Fig. 1. Although the water absorbed Nafion lost free water up to 100 °C and restrained water up to 280 °C, the weight of RTMS - Nafion membrane did not change up to 330 °C. Nafion without RTMS was unstable above 280 °C. RTMS - Nafion membrane was stabilized by RTMS. The sulfuric group of Nafion would be changed to salt like form from hydrogen form.

The steady state current at fixed potential increased under hydrogen atmosphere, compared with that under nitrogen atmosphere for all RTMS - acid systems. This phenomenon would indicate the proton conduction through the membrane. Figure 2 shows the proton conductivities of RTMS - acid systems as a function of temperature under dry hydrogen atmosphere with water swollen Nafion membrane. These conductions mostly take place by proton. The conductivities of RTMS - acid systems and Nafion under moisten atmosphere increased with temperature and reversible for temperature change, although that of Nafion under dry hydrogen decreased with the increase of temperature and showed irreversible behavior in the cooling process. The conductivity of RTMS - HTf liquid was about 10^{-1} S cm^{-1} and that of RTMS - Nafion membrane was about 10^{-3} S cm^{-1} at 150°C. These values are high under dry condition. The apparent activation energy, which was the slope of Fig. 2, of Nafion - EMITFSI was higher than that of liquid system. This might be related that the acid group of Nafion was fixed to polymer structure in the membrane. The high proton conductivities of RTMS - acid systems over 100 °C would show the possibility of the application of the proton conductor of PEFCs.

Acknowledgment

This study was supported by Technology Research Grant Program in '01 from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

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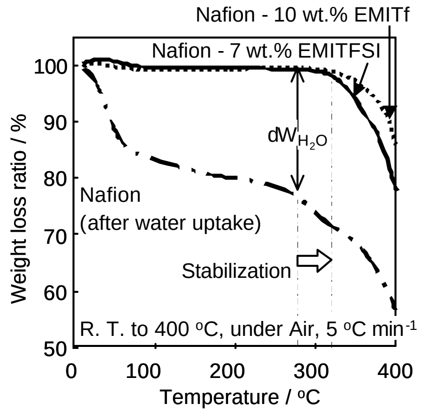

Fig. 1 Thermal stability of RTMS – PFSA membrane.

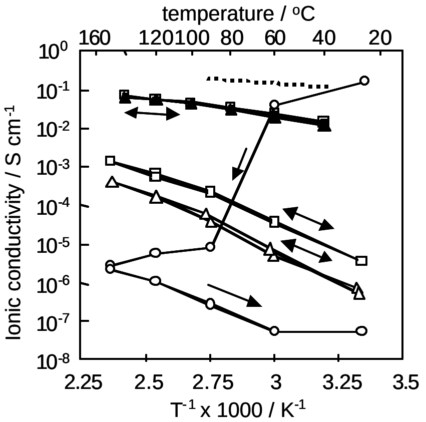

Fig. 2 Proton conductivity of RTMS - acid system as a function of temperature under dry hydrogen.

—○— Nafion 117
—△— Re-cast Nafion - 13 wt.% EMITFSI
—□— Re-cast Nafion - 11 wt.% EMITf
—▲— EMITFSI : HTf = 9 : 1 (mol)
—■— EMITf : HTf = 9:1 (mol)
······ Nafion 117 (under moisten H_2)