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Effect of SiO_2 additive in catalyst layer and electrolyte on the performance for mesothermal fuel cell using room temperature molten salts

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Introduction

For the widespread of polymer electrolyte fuel cells (PEFCs), the improvements of the performance are needed, and there are a lot of issues such as CO poisoning of anode electrocatalyst, complexity of water management system and slow oxygen reduction kinetics. Mesothermal operation without humidification of PEFCs is an effective challenge to solve these issues.

We have focused on room temperature molten salts (RTMSs) for a novel proton conductive electrolyte. Among them, diethylmethylammonium trifluoromethansulfonate ([dema][TfO]) has high ionic conductivity with great activities for fuel cell electrode reactions and good thermal stability.[1] To apply RTMSs for PEFC improvements of ionic conductivity and mechanical properties are needed. We already found that solid acid additive such as SiO_2 to the RTMs applied membrane improves ionic conductivity and compression strength.[3 4] However, the effect of SiO_2 additive on the performance of the PEFCs is not yet clarified.

In this study, we determined effect of SiO_2 additive on the performance of the PEFCs using [dema][TfO] /sulfonated polyimide (SPI) electrolytes to evaluate RTMS/SPI/solid acid system for PEFCs.

Experimental

Composite membranes were prepared using a solution casting method. Appropriate amounts of the [dema][TfO], the SPI and *m*-cresol were mixed and stirred overnight at 60°C, and then SiO_2 (specific surface area: 175-225 m^2 g^{-1}, Aldrich) added to them at room temperature and stirred overnight. Evaporation of *m*-cresol at 60°C gave a composite membrane.

Catalyst inks were prepared by mixing Pt/C, (46.5 wt. %-Pt, Tanaka Kikinzoku Kogyo Co. Ltd.), carbon black (Denka Black Denki Kagaku Kogyo Kabushiki Kaisha) treated with mixed acid (H_2SO_4:HNO_3 3:1), PTFE (60 wt. % dispersion, Dupont Mitsui Fluorochemicals Co.Ltd.), and mixture of pure water and 2-propanol in the weight ratio of 10:3. The catalyst layer was coated on gas diffusion layer (310 μm, Toray) by doctor blade method, and hot pressed under 3 MPa at 120 °C, and then sintered in N_2 atmosphere at 350 °C.

Membrane electrode assemblies (MEAs) were placed in a single-cell holder. Polarization characteristic of the MEAs were evaluated at 120°C with H_2 and O_2 fed without humidification. Ionic resistances of the MEAs were determined AC impedance method during the polarization measurements.

Results and discussion

The polarization curves of the MEAs with and without 15 wt. % of SiO_2 fed dry H_2/O_2 of different flow rates at 120°C are shown in Figure 1. Open and close symbols represent flow rates of H_2/O_2 = 4/2 and, 12/6 ml min^{-1}, respectively. Square and circle symbols represent Zero, and 15 wt. % of SiO_2 addition, respectively. The SiO_2 added membrane showed higher cell voltage than the SiO_2 free membrane in whole current density region. For the SiO_2 free membrane, cell voltage significantly decreased due to gas flow rate increase. Generally, since the amount of water in a cell balances on production and evaporation rate, at an operating condition, the amount of absorbed water amount is fixed by affinity of water. The SiO_2 additive stabilized the cell performance against gas flow rate increase. This clearly indicates that the presence of SiO_2 increases affinity of water and inhibits dry up.

To evaluate of the current change due to gas flow rate change, Figure 2 shows the relationship between the ratio of current change due to gas flow rate change, which is $\Delta i/i$ (= | $(i_{H2/O2=4/2} - i_{H2/O2=12/6})/i_{H2/O2=4/2}$|×100[%]) at 0.2, 0.4 and 0.6V as a function of the amount of SiO_2 addition. The $\Delta i/i$ almost linearly decreased with increase of the SiO_2, and was almost the same for 0.2, 0.4 and 0.6V. Particularly, 15 wt. % SiO_2 added membrane was the best in performance and ionic conductivity of the high flow rate, and stability in performance due to gas flow rate change. Ionic conductivity increased with the amount of SiO_2 and slightly decreased with increase with gas flow rate for the SiO_2 added membrane. However, ionic conductivity change is not large enough to explain the cell voltage change. Therefore, SiO_2 addition would improve the stability of three phase boundaries, and inhibit the fluctuations of reaction polarization, too.

Reference

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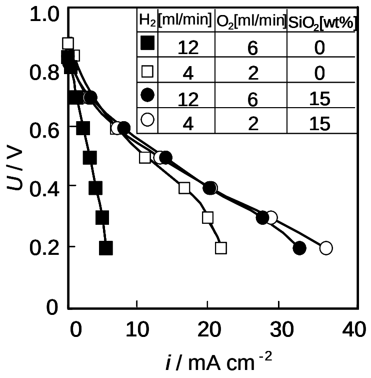

Fig. 1 Performances of small size single cells with [dema][TfO] / SPI membrane with and without SiO_2 addition fed dry H_2/O_2 of 12/6 and 4/2 ml min^{-1} at 120°C.

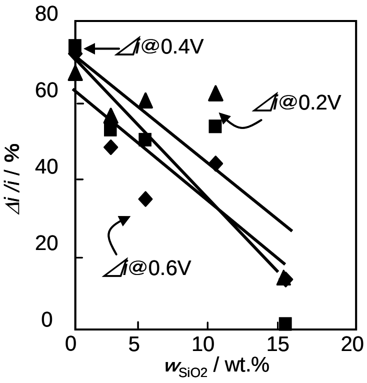

Fig. 2 The ratio of the current change due to the flow rate change between 12/6 and 4/2 ml min^{-1} of H_2/O_2 at 120°C as a function of the amount of SiO_2 addition.