FUEL CELL PERFORMANCE USING PROTON CONDUCTING POLYMERS BASED ON HYDROCARBON POLYMERS (II)

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Operation of polymer electrolyte fuel cells at high temperatures (> 100 ºC) without further humidify can minimize CO poisoning of Pt catalyst, improve the energy efficiency, and reduce the size of fuel cell systems. Acid doped polymer electrolytes such as PBI/H_3PO_4 complexes show high proton conductivity even at high temperatures above 100 ºC under anhydrous conditions.[1]

In this study, poly(benzimidazole-imide) (PIBI) (Scheme 1) was synthesized as a basic hydrocarbon polymer, which has more rigid structure compared with PBI. Fabrication of PIBI/H_3PO_4 complexes were attempted, and the proton conductivity and fuel cell performances without humidify for the PIBI/H_3PO_4 membrane were also investigated.

Experimental

PIBI was synthesized by one-step polymerization of naphthalene-1,4,5,8-tetracarboxylic dianhydride and 2,2'-bis(*m*-aminophenyl)-5,5'-bibenzimidazole in *N,N'*-dimethylacetamide at 180 ºC.[2] The inherent viscosity (η_{inh}) of PIBI was measured with a sulfuric acid solution at a concentration of 0.2 g/dL at 30 ºC. PIBI/H_3PO_4 complexes were prepared by immersing PIBI cast films in H_3PO_4/methanol solutions with various concentrations. Proton conductivity of the PIBI/H_3PO_4 films was evaluated by the complex impedance method under anhydrous conditions at the temperature range of 40 to 160 ºC. The fuel cell performance of the PIBI/H_3PO_4 film was determined at the cell temperatures above 120 ºC by using dry hydrogen and dry air gases as the fuel and oxidant, respectively.

Result and discussion

The synthesis of PIBI was confirmed by FT-IR measurements, and the η_{inh} of PIBI was observed to be 0.85 dL/g. The formation of PIBI/H_3PO_4 was also confirmed by FT-IR measurements. The NH_2^+ stretching band was observed in the range from 2000 to 3600 cm^{-1} due to the interactions between H_3PO_4 and imidazole groups. Two characteristic absorption bands of HPO_4^{2-} and $H_2PO_4^-$ for PIBI/H_3PO_4 appeared at 950 and 1100 cm^{-1}, respectively. The doping level of H_3PO_4 increased with the concentration of H_3PO_4, and the maximum absorption as much as 358 wt. % was obtained.

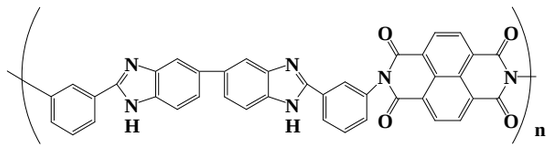
Thermal stability of PIBI/H_3PO_4 membranes was investigated by TG-DTA. The thermal decomposition temperature was about 150 ºC irrespective of H_3PO_4 doping level. It was considered that this decomposition is due to the loss of water caused by the dehydration of H_3PO_4 molecules. The TG-DTA analyses indicated that PIBI/H_3PO_4 membranes were thermally stable for fuel cell applications.

Figure 1 shows the Arrhenius plots of conductivity for PIBI/H_3PO_4 membranes with various H_3PO_4 contents under anhydrous conditions. The conductivity of PIBI/H_3PO_4 membranes increased with H_3PO_4 doping level and temperature, and reached 6.8×10^{-2} S/cm at 358 wt. % of doping level and at 160 ºC. The proton conduction of the PIBI/H_3PO_4 is assumed to occur according to the Grotthus mechanism, which involves an exchange of protons between H_3PO_4 and HPO_4^{2-} or $H_2PO_4^-$.[3]

Figure 2 shows cell potential vs. current density for a 13 cm^2 hydrogen/air PEFC based on a PIBI/H_3PO_4 (H_3PO_4: 358 wt. %) membrane as a function of cell temperature at 2 ata of supply gas pressure without humidify. The performance of the PIBI/H_3PO_4 membrane raised with increasing cell temperature, and the open circuit voltage and limiting current density were 0.90 V and 1250 mA/cm^2 at 160 ºC, respectively.

Reference

[1] M. Rikukawa and K. Sanui, *Prog. Polym. Sci.*, **25**, 1463 (2000).
[2] J. Preston and W. B. Black, *J. Polym. Sci., A-1*, **5**, 2429 (1967).
[3] M. Kawahara, J. Morita, M. Rikukawa, K. Sanui, N. Ogata, *Electrochim. Acta*, **45,** 1395 (2000).



Scheme 1 Structure of PIBI.

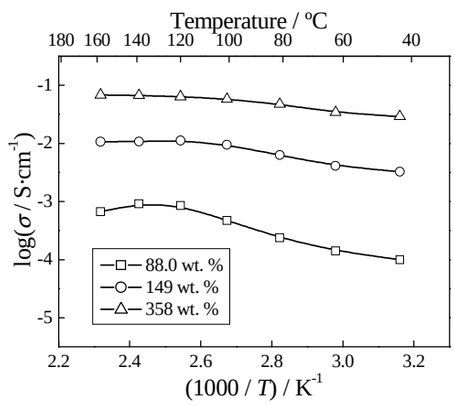


Figure 1 Arrhenius plots of conductivity for PIBI/H_3PO_4 membranes with various H_3PO_4 contents.

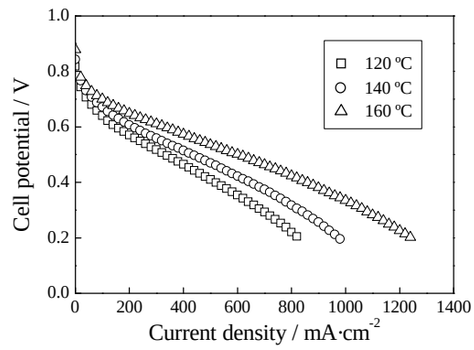


Figure 2 Cell potential vs. current density for a H_2/air PEFC based on a PIBI/H_3PO_4 (358 wt. %) membrane as a function of cell temperature at 2 ata of supply gas pressure without humidify.