SYNTHESIS OF ANHYDROUS PROTON CONDUCTING POLYMERS CONSISTING OF BASIC POLY(ETHERSULFONE)

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The operation of polymer electrolyte fuel cells (PEFCs) at high temperature (100-200 ºC) has been considered to provide many advantages such as improved carbon monoxide tolerance of the platinum electrode. Anhydrous proton conducting polymers such as phosphoric acid doped poly(benzimidazole) (PBI) are attractive candidates for high temperature PEFCs because of their excellent thermal stability and high proton conductivity at high temperatures.[1-2] However, the mechanical properties of highly phosphoric acid doped PBI membranes were insufficient for the fuel cell applications at elevated temperatures. In this study, an amine functionalized poly(ethersulfone)s (APES) were synthesized and blended with PBI in order to improve the mechanical and electrochemical properties.

Experimental

APES was synthesized from 4,4'-difluoro-2,2'-diaminodiphenylsulfone and bisphenol S.[3] APES was characterized by elemental analysis, ^{1}H-NMR, and FT-IR spectroscopy. *N,N'*-dimethylacetamide solution of PBI-APES (PBI:APES = 71:29(w/w)) was cast onto a glass plate and dried at 80 ºC for 24 h in order to obtain a free-standing film. PBI-APES/H_3PO_4 complexes were prepared by immersing PBI-APES films into phosphoric acid/methanol mixed solutions with various concentrations for 72 h. Proton conductivity of phosphoric acid doped polymers was evaluated by the complex impedance method with a vector impedance meter (Hewlett-Packard 4192A). The fuel cell performance was measured by using dry hydrogen and dry air gases as the fuel and oxidant, respectively.

Result and discussion

The weight-average molecular weight of APES was 10,800, as determined by gel permeation chromatography. FT-IR measurements confirmed the presence of amine groups in APES.

The thermal stability of PBI-APES/H_3PO_4 complexes was investigated by using TG-DTA. The TG curve of the complexes exhibited a weight loss about 160 ºC due to dehydration of phosphoric acid. The TG-DTA analyses clearly indicated that PBI-APES/H_3PO_4 complexes are thermally stable for high temperature fuel cell applications.

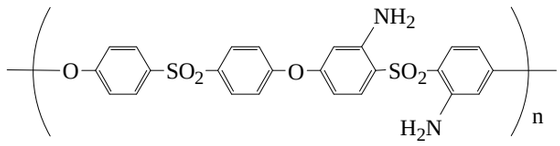
The mechanical properties for PBI-APES/H_3PO_4 complexes were measured at 25 ºC in air. The tensile strength of PBI-APES/H_3PO_4 complexes was higher than that of typical PBI/H_3PO_4 complexes irrespective of H_3PO_4 contents. PBI-APES/H_3PO_4 complex doped with 149 wt.% phosphoric acid showed tensile strength of about 25 MPa.

Temperature dependence of conductivity for an anhydrous PBI-APES/H_3PO_4 complex doped with 149 wt.% phosphoric acid is shown Figure 1. The conductivity of the PBI-APES/H_3PO_4 complex increased with temperature and was about 4 times higher than that of the PBI/H_3PO_4 complex doped with 179 wt.% phosphoric acid.

Figure 2 shows cell potential and power density vs. current density for a 13 cm^2 hydrogen/air PEFC based on an PBI-APES/H_3PO_4 complex (121 wt.%) at 2 ata of supply gas pressure and at 160-180 ºC of cell temperature without humidify. The performance of PBI-APES /H_3PO_4 complex raised with increasing the cell temperature, and the open circuit voltage and maximum power density were 0.94 V and 295 mW/cm^2, respectively.

Reference

[1] M. Kawahara, J. Morita, M. Rikukawa, K. Sanui, and N. Ogata, *Electrocim. Acta*, **45**, 1395 (2000).
[2] J. -T. Wang, R. F. Savinell, J. Wainright, M. Litt, and H. Yu, *Electrocim. Acta*, **41**, 193 (1996)
[3] F. A. Bottino, A. Mamo, A. Recca, J. Brady, A. C. Street, and P. T. McGrail, *Polymer*, **34**, 2901 (1993)



Scheme Structure of APES.

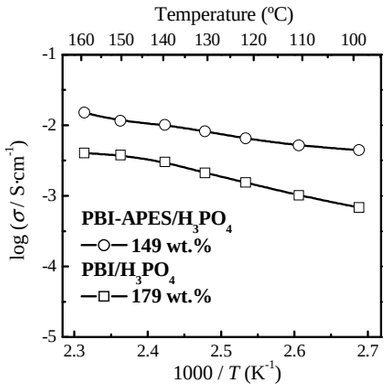


Figure 1 Arrhenius plots of conductivity for anhydrous PBI-APES/H_3PO_4 and PBI/H_3PO_4 complexes.

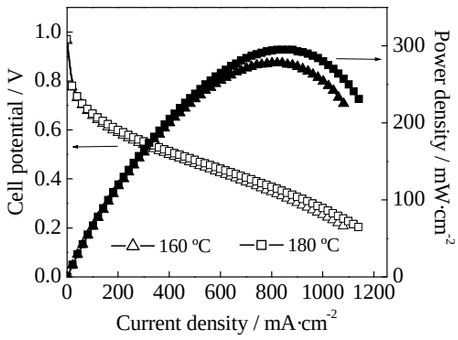


Figure 2 Cell potential and power density vs. current density for a H_2/air PEFC based on a PBI-APES/H_3PO_4 complex (121 wt.%) at 2 ata of gas pressure and at 160-180 ºC of cell temperature without humidify.