

Novel Sulfonated Polyimide Membranes for Fuel Cell Application

Fengxia Zai¹, Xiaoxia Guo¹, Jianhua Fang^{*1}, and Ken-ichi Okamoto²

¹School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, P.R. China.

²Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University, 2-16-1 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

Fax: 86-21-54741297

E-mail: jhfang@sjtu.edu.cn

INTRODUCTION Six-membered ring sulfonated polyimides (SPIs) have been identified as one of the most promising membrane materials for fuel cell application. The structure of sulfonated diamine moieties greatly influences the performance of SPIs. In this presentation, we report on the synthesis of a series of novel SPIs (Figure 1) from 4,4'-bis(4-aminophenoxy)benzophenone-3,3'-disulfonic acid (BAPBPDS) and 4,4'-bis(4-aminophenylthio)benzophenone-3,3'-disulfonic acid (BAPTBPDS) and their proton conductivity, water uptake and water stability are also described.

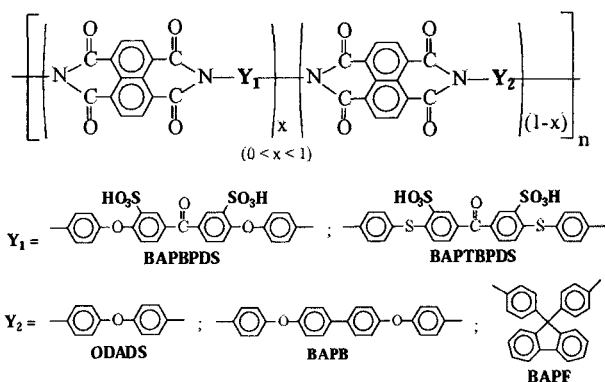


Figure 1 Chemical structure of various novel sulfonated polyimides.

EXPERIMENTAL BAPBPDS and BAPTBPDS were synthesized by reacting 4,4'-dichlorobenzophenone-3,3'-disulfonic acid disodium salt with p-aminophenol or p-aminothiophenol in 1-methyl-pyrrolidinone (NMP) in the presence of K_2CO_3 at 175 °C for 24 h. A series of SPIs were synthesized by one-step polymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), sulfonated diamines (BAPBPDS and BAPTBPDS) and common nonsulfonated diamines in *m*-cresol in the presence of triethylamine (Et_3N) and benzoic acid at 80 °C for 4 h and 180 °C for 16 h.

RESULTS AND DISCUSSION Two kinds of new sulfonated diamine monomers, BAPBPDS and BAPTBPDS, were successfully synthesized by two-step reactions with high yields, and the structures were characterized. A series of SPIs were prepared by conventional one-step polymerization method from NTDA, BAPBPDS and BAPTBPDS and common non-sulfonated diamines (4,4'-diaminodiphenyl ether (ODA), 9,9-bis(4-aminophenyl)fluorene (BAPF), 4,4-bis(4-aminophenoxy)biphenyl (BAPB)). The ion exchange capacities (IECs) of these SPIs were controlled to be about 2.0 meq/g by regulating the molar ratio between the sulfonated diamines and the non-sulfonated ones. The resulting SPIs showed good solubility in dimethylsulfoxide (DMSO) and NMP. The sulfonic acid groups of the SPIs started to decompose above 250 °C indicating high thermal stability of these SPIs. The proton conductivities of the SPI membranes strongly depend on the relative humidity, whereas the structural effect is less significant. At low relative humidities (< 50%), the SPI membranes displayed rather low proton conductivities (< 0.01 S/cm). The proton conductivities increased rapidly with an increase in relative humidity. In water (60 °C) all the membranes showed proton conductivities over 0.1 S/cm which is comparable to that of Nafion 117. The water stability of the SPI membranes is strongly dependent on the chemical structure of SPIs and the test temperature. BAPTBPDS-based SPI membranes showed much better water stability than BAPBPDS-based ones. NTDA-BAPTBPDS/ODA(2/1), for example, did not lose mechanical strength after being soaked in deionized water at 80 °C for more than 1000 h, whereas NTDA-BAPBPDS/ODA(2/1) was broken (when lightly bent) after being soaked in deionized water at the same temperature for 390 h. This is attributed to the higher basicity of BAPTBPDS moiety resulting from the larger electronic-donating effect of thio bond than that of ether bond. At 100 °C, the water stability of all the SPI membranes deteriorated drastically and cross-linked treatment is in progress in order to improve the membrane stability.