# Synthesis and Properties of Novel Polyimides Containing Sulfonated Aromatic Side Chains

Zhaoxia HU[1], Yin. YIN[2], Hidetoshi KITA[1], and Ken-ichi OKAMOTO[1]
[1]Faculty of Engineering, [2]Venture Business Laboratory, Yamaguchi University

Polymer electrolyte fuel cells (PEFCs) are the most promising power sources in the future for their high energy-efficiency and environmental friendship. Sulfonated polyimides (SPIs) are considered as one of the most promising materials for their good film-forming ability and proton conduction properties. We have reported SPIs based on 2,2'-bis(3-sulfopropoxy) benzidine, which did not have satisfactory long-term water stability for its alkoxy side group.[1] Here, we report a novel sulfonated diamine bearing sulfonated aromatic side group, 2,2'-(4-sulfophenyl) benzidine (2,2'-BSPhB), the corresponding SPIs based on it and their properties.

The novel sulfonated diamine was synthesized from 2,2'-diphenyl benzidine by direct sulfonation with fuming sulfuric acid at 60 °C for 2 h. The SPIs were synthesized with 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) according to the method previously reported. [2] The chemical structure of the corresponding SPIs is shown in Figure 1. The SPIs were prepared by means of high temperature polymerization in *m*-cresol and the membranes were prepared by *m*-cresol solution casting. Properties such as viscosity, water uptake, size change and proton conductivity were investigated and are summarized in Table 1. The resulting SPIs showed high reduced-viscosity of 3.1-6.6 dL/g. They showed anisotropic membrane swelling behavior in water, that is, much larger swelling in membrane thickness direction than in plane direction. They showed reasonably good water stability and high proton conductivity.

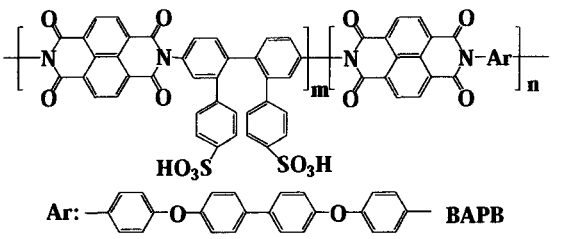


Fig. 1 Chemical structure of novel SPI.

Table 1 Properties of novel SPI membrane.

| code | NTDA-based SPIs | IEC[a] (meq/g) | $\eta_r$[b] (dL/g) | *WU*[c] (wt%) | λ | Size Change[c] $\Delta t_c$ | Size Change[c] $\Delta l_c$ | $\sigma$ (*10$^{-3}$S/cm)[d] 50% | 70%RH | in water |
|---|---|---|---|---|---|---|---|---|---|---|
| M1 | 2,2'-BSPhB | 2.74 | 6.6 | 207 | 41.8 | - | - | - | - | - |
| M2 | 2,2'-BSPhB/BAPB(2/1)-r | 1.95 | 4.4 | 73 | 20.8 | 0.34 | 0.034 | 11 | 39 | 140 |
| M3 | 2,2'-BSPhB/BAPB(3/2)-r | 1.77 | 4.5 | 74 | 23.2 | 0.24 | 0.04 | 8.5 | 36 | 127 |
| M4 | 2,2'-BSPhB/BAPB(3/2)-s | 1.77 | 3.1 | - | - | 0.33 | 0.03 | - | - | - |

[a] calculated values; [b] at 35 °C with 0.5g/dL solution in *m*-cresol; [c] at r.t.; [d] at 60 °C.

## References

1. Y. Yin, O. Yamada, K. Tanaka, K. Okamoto, *Polym. J.*,38, 197-210 (2006).
2. Z. X. Hu, Y. Yin, S. W. Chen, O. Yamada, K. Tanaka, H. Kita, K. Okamoto, *J. Polym. Sci. Part A: Polym. Chem., 44, 2862-2892 (2006)*

Correspondence: e-mail okamotok@yamaguchi-u.ac.jp; TEL +081-836-85-9660; FAX +081-836-85-9601