

CHEMISTRY OF MATERIALS

VOLUME 16, NUMBER 15

JULY 27, 2004

© Copyright 2004 by the American Chemical Society

Communications

Hydrolytically Stable Polyimide Ionomer for Fuel Cell Applications

Naoki Asano, Kenji Miyatake, and Masahiro Watanabe*

Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8510, Japan

Received March 17, 2004

Revised Manuscript Received June 17, 2004

Fuel cells are efficient devices that produce electric power via chemical reaction of fuels and oxygen and therefore have been attracting more and more attention as a clean electric source.^{1–3} Polymer electrolyte fuel cells (PEFCs) using a proton-conductive ionomer as an electrolyte membrane have been extensively studied for application to electric vehicles, residential power sources, and portable devices.^{4–6} One of the challenges in the current PEFC research is to develop novel proton-conductive ionomer membranes useable at higher temperature than 120 °C for improving the total performance of PEFCs.^{7–13} Perfluorosulfonic acid ionomers (such as Nafion) as the state-of-the-art material are not

suitable for high-temperature use since the conductive and mechanical properties are deteriorated above the glass transition temperature (ca. 110 °C). High gas crossover, high cost, and environmental inadaptability are also serious drawbacks of the fluorinated materials.

Sulfonated polyimide ionomers have recently been developed by several groups for the above purpose.^{14–16} We have found that the sulfonated polyimide copolymers incorporated with bulky fluorenyl groups show the highest ever proton conductivity (1.67 S cm⁻¹) for a polymer electrolyte at 120 °C and 100% RH.¹⁷ There is, however, a major catastrophic obstacle that prevents the aromatic polyimide ionomers from being utilized as an electrolyte membrane for PEFCs, that is, the hydrolytic instability. The aromatic imide linkage is susceptible to the nucleophilic attack by water molecules, resulting in the degradation of the polymer main chain through reverse polymerization. Our idea is to lower the hydrolytic susceptibility by increasing the electron density of imide nitrogen atoms. The semiempirical MO calculations (PM3) using model compounds (**1**, **2**) revealed that an imide nitrogen atom attached to an aliphatic group possesses much higher electron density than that attached to a phenyl group (Chart 1). In this communication, we report synthesis and electrolyte properties of novel sulfonated polyimide ionomers containing aliphatic groups both in the main chain and in the side chains.

* To whom correspondence should be addressed. E-mail: m-watanabe@yamanashi.ac.jp.

(1) Appleby, A. J.; Foulkes, F. R. *Fuel Cell Handbook*; Van Nostrand Reinhold: New York, 1989.

(2) Carratte, L.; Friedlich, K. A.; Stimming, U. *Fuel Cells* **2001**, *1*, 5.

(3) Steele, B. C. H.; Heinzel, A. *Nature* **2001**, *414*, 345.

(4) Lemmons, R. J. *J. Power Sources* **1990**, *29*, 251.

(5) Strasser, K. *J. Power Sources* **1992**, *37*, 209.

(6) Kordesch, K.; Simander, G. *Fuel Cells and Their Applications*; Wiley-VCH: Weinheim, 1996.

(7) Savadogo, O. *J. New Mater. Electrochem. Syst.* **1998**, *1*, 47.

(8) Rikukawa, M.; Sanui, K. *Prog. Polym. Sci.* **2000**, *25*, 1463.

(9) Wang, F.; Hickner, M.; Ji, Q.; Harrison, W.; Mechem, J.; Zawodzinski, T. A.; McGrath, J. E. *Macromol. Symp.* **2001**, *175*, 387.

(10) Wei, J. W.; Stone, C.; Steck, A. E. U.S. Patent 5422411, 1995.

(11) Wainright, J. S.; Wang, J.-T.; Weng, D.; Savinell, R. F.; Litt, M. H. *J. Electrochem. Soc.* **1995**, *142*, L121.

(12) Wycisk, R.; Pintauro, P. N. *J. Membr. Sci.* **1996**, *119*, 155.

(13) Jones, D. J.; Roziere, J. *J. Membr. Sci.* **2001**, *185*, 41.

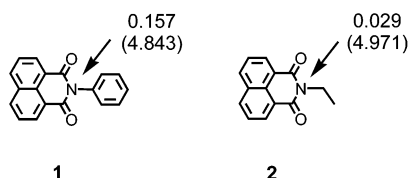
(14) Vallejo, E.; Pourcelly, G.; Gavach, C.; Mercier, R.; Pineri, M. *J. Membr. Sci.* **1999**, *160*, 127.

(15) Litt, M.; Zhang, Y.; Savinell, R. F.; Wainright, J. S. *Polym. Prepr.* **1999**, *40*, 480.

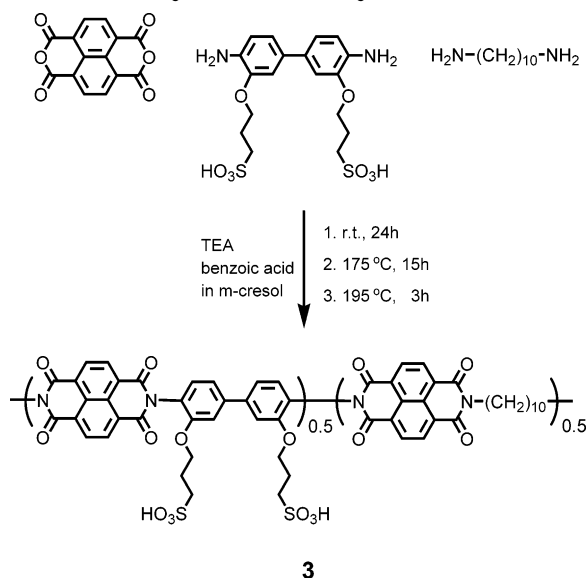
(16) Guo, X.; Fang, J.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* **2002**, *35*, 6707.

(17) Miyatake, K.; Zhou, H.; Uchida, H.; Watanabe, M. *Chem. Commun.* **2003**, 368.

Chart 1. Net Atomic Charge and Atom Electron Density (in Parentheses) of Nitrogen Atom for *N*-Phenyl-1,8-naphthalimide (1) and *N*-Ethyl-1,8-naphthalimide (2) Calculated by the PM3 Method



Scheme 1. Synthesis of Polyimide Ionomer 3



The title polyimide ionomer **3** was synthesized by the polycondensation of 1,4,5,8-naphthalene tetracarboxylic dianhydride, 3,3'-bis(sulfopropoxy)-4,4'-diaminobiphenyl, and decamethylenediamine (Scheme 1). The copolymer composition was set at 50 mol % so that the equivalent weight per sulfonic acid group was to be 549 g/equiv (IEC = 1.82 mequiv/g). The experimental IEC of **3** was 1.84 mequiv/g estimated from the ^1H NMR spectrum. The polymerization proceeded well in *m*-cresol solution to give a high-molecular-weight polyimide ionomer **3**. The detailed procedure for the polymerization and the membrane preparation is given in the Supporting Information, which also includes the ^1H NMR spectrum. The stability of **3** was investigated under both dry and wet conditions. TG analysis under a dry nitrogen atmosphere showed two step weight losses: the first one from room temperature to 180 °C due to the desorption of water molecules and the second one above 250 °C due to the degradation (loss of sulfonic acid groups). The high thermal stability is comparable to that of other sulfonated hydrocarbon polymers or perfluorinated ionomers.⁸ In the DSC analyses, a very small thermal transition was observed at ca. 150 °C, which would be ascribed to the glass transition temperature.

The hydrolytic stability was evaluated by treating the membrane sample at 140 °C and 100% RH as an accelerated testing. In our previous experiments, no polyimide ionomers have endured the testing for 24 h while Nafion 112 is intact.¹⁸ The membrane of **3** showed much better hydrolytic stability without any changes

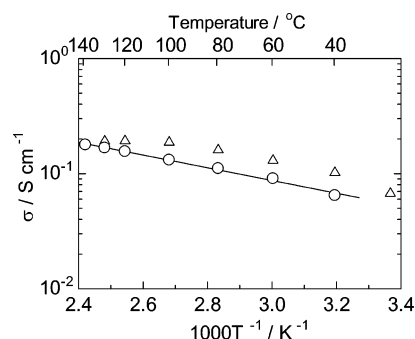


Figure 1. Temperature dependence of the proton conductivity of **3** (○) and Nafion 112 (Δ) at 100% RH.

in appearance, flexibility, and toughness after 1 week. The ^1H NMR analyses revealed that the membrane has the IEC of 1.76 mequiv/g after the testing. The membrane was also subjected to oxidative stability testing in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm FeSO_4) at 80 °C. It took 55 min before the dissolution of the membrane commenced. After 1 h, the membrane still retained its shape and flexibility. This dissolving behavior of **3** is comparable to that of the whole aromatic polyimide ionomers,^{17,19} indicating that the introduction of aliphatic groups did not deteriorate the oxidative stability.

Proton conductivity of the membrane of **3** (50 μm in thickness) was measured at 100% RH and compared with that of Nafion 112 (Figure 1). It is noted that although the conductivity of **3** was slightly lower than that of Nafion 112 below 100 °C, it was comparable at higher temperature. The highest conductivity of 0.18 S cm^{-1} was obtained for **3** at 140 °C, while the measurement was not possible for Nafion 112 with the same thickness of 50 μm at such high temperature due to the loss of mechanical strength. The proton conductivity of **3** showed Arrhenius-type temperature dependence even above the boiling temperature of water, implying good water-holding capability of the rigid polyimide architecture. The apparent activation energy (E_a) for the proton conduction of **3** was estimated to be 10.3 kJ mol^{-1} from the slope of the linear line in Figure 1. The E_a value is smaller than that of the whole aromatic polyimide ionomer (21 kJ mol^{-1}).¹⁷ It is generally considered that both the migration of hydronium ions (vehicle mechanism) and the structure diffusion (Grotthuss mechanism) are responsible for the proton conduction in hydrated polymer membranes.²⁰ The difference in E_a might result from the different contributions of the two different mechanisms or from the easier molecular motion of **3** than the whole aromatic ionomers. Detailed mechanistic analyses are currently under investigation and will be reported elsewhere. The conductivity measurement was carried out at 120 °C and 100% RH in a longer time scale (Figure 2). The membrane of **3** showed the constant conductivity value of 0.15 S cm^{-1} within acceptable errors for 10 days to confirm the excellent hydrolytic stability.

The humidity dependence of the proton conductivity was also investigated at 80, 100, and 120 °C (Figure 3).

(18) Unpublished data.

(19) Miyatake, K.; Asano, N.; Watanabe, M. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 3901.

(20) Kreuer, K. D. *Chem. Mater.* **1996**, *8*, 610.

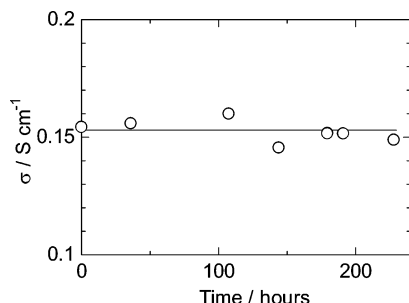


Figure 2. Durability of the proton conductivity of **3** at 120 °C and 100% RH.

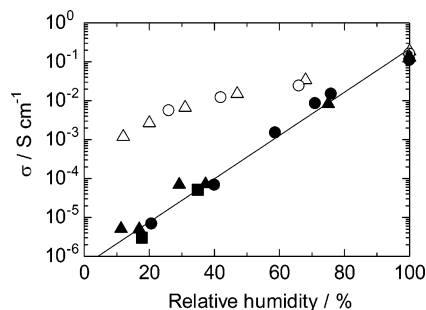


Figure 3. Humidity dependence of the proton conductivity of **3** (solid) and Nafion 112 (open). Circle, triangle, and square symbols represent the data at 80, 100, and 120 °C, respectively.

At higher RH than 70%, **3** showed comparable conductivity to that of Nafion 112. At low RH, however, the conductivity decreased down to the order of $<10^{-4}$ S cm $^{-1}$. This is the common behavior observed for hydrocarbon-based ionomers, probably due to the lack of the formation of properly ordered microphase separation for

the proton conduction compared to the perfluorinated ionomers.²¹ The lower acidity of Ar–SO $_3$ H than that of –CF $_2$ –SO $_3$ H should also be responsible under the low-humidity conditions. The conductivities for both **3** and Nafion 112 are relatively independent of the temperature. It is assumed that the carrier concentration rather than the mobility and/or the diffusibility would be more important for the proton conduction when membranes are not fully hydrated.

In conclusion, we have incorporated aliphatic groups into a sulfonated polyimide ionomer both in the main chain and in the side chains in order to improve the hydrolytic stability. The new polyimide ionomer was very stable to hydrolysis and oxidation. The proton conductivity is comparable to or even better than that of Nafion 112 at high temperature and at high RH conditions. These preliminary results have proved its potential availability as an electrolyte for high-temperature PEFCs.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research (16750160) and the fund for Leading Project from MEXT Japan, and by the Industrial Technology Research Grant Program in 02B70007c from NEDO.

Supporting Information Available: Experimental details of polymerization, membrane preparation, and ^1H NMR spectrum, and proton conductivity measurement of **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

CM049550C

(21) Kreuer, K. D. *J. Membr. Sci.* **2001**, 185, 29.