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Highly proton conductive polyimide electrolytes containing fluorenyl groups†

Kenji Miyatake, Hua Zhou, Hiroyuki Uchida and Masahiro Watanabe*
Clean Energy Research Center, University of Yamanashi, 4 Takeda, Kofu 400-8510, Japan.
E-mail: mwatanab@ab11.yamanashi.ac.jp

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Novel sulfonated polyimides containing fluorenyl groups show good thermal and oxidative stability as well as a high proton conductivity of 1.67 S cm^{-1} at 120 °C and 100% RH.

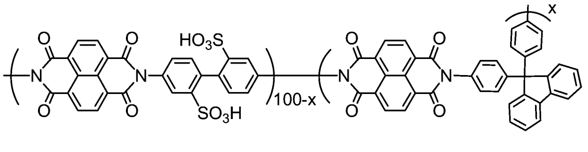
Fuel cells are attractive alternatives to combustion engines as electrical power sources because of their high efficiencies and low pollution levels.[1] Polymer electrolyte fuel cells (PEFCs) operating under moderate temperature (60–80 °C) are currently being developed as the most promising candidates for mobile and portable applications. It is desirable, however, to operate cells at rather higher temperature (> 120 °C) in order to improve the cell performance. One of the most important issues for the commercialization of high temperature PEFCs concerns polymer electrolyte membranes, for which several specific and demanding properties are required; high proton conductivity (at least 0.01 S cm^{-1}), low gas (H_2, O_2 or methanol) permeability, stability to heat, oxidation and hydrolysis.[2] The perfluorosulfonic acid polymer known as Nafion® manufactured by Du Pout is a bench mark material and has been most widely used for this application. Since protons migrate as hydronium ions, it is crucial to retain water molecules within hydrophilic domains of membranes. At elevated temperatures above 100 °C, perfluorosulfonic acid polymer suffers from lowered conductivity due to the loss of water. Lack of interaction (or cross-linking) among polymer chains gives rise to insufficient mechanical strength. There has been extensive research work to develop alternative proton conductive polymer electrolyte membranes.[3–8]

Functionalization of stable aromatic polymers with acidic groups is one of the available options. Sulfonated poly(ether ether ketone)s (PEEK)s[3] and phosphoric acid doped polybenzimidazole (PBI),[4] for example, have been reported. Since the sulfonated aromatic diamine 4,4′-diamino-2,2′-biphenyldisulfonic acid (DAPS) is readily commercially available there have been investigations on the synthesis of sulfonated polyimides by the polycondensation of DAPS with aryltetracarboxylic dianhydride.[9–11] Litt *et al*. recently synthesized a series of sulfonated polyimide copolymers having bulky hydrophobic components.[9,10] As one of the comonomers, 5 mol% of 4,4′-(9-fluorenylidene) dianiline (FDA) was used to produce nanopore-containing polyimides. The polymer membrane showed high proton conductivity on the order of 10^{-1} S cm^{-1} at 80 °C and 100% relative humidity, however, the oxidation stability was not high enough. Further, it was deliquescent when exposed to water vapor at 100 °C.

Assuming that the introduction of more FDA should improve the stability and create larger interchain domains in which water molecules are confined, we have synthesized sulfonated polyimides containing fluorenyl groups with composition of up to 60 mol% (SPIH-*x*, where *x* refers to the mole fraction of fluorenyl group, Fig. 1). This communication describes our preliminary results on these sulfonated polyimide copolymers, which show very high proton conductivity (1.67 S cm^{-1}) at 120 °C and 100% RH with good thermal and oxidative stability.

The copolymerization of DAPS, FDA and 1,4,5,8-naphthalenetetracarboxylic dianhydride (TCND) was carried out in *m*-cresol at 175 °C for 15 h in the presence of triethylamine and benzoic acid as catalysts, followed by *in-situ* imidization at 195 °C for 5 h. The reaction should be performed under a pure nitrogen atmosphere in order to avoid oxidation of the amines and other unfavorable side reactions. The resulting dark red viscous solution was cast onto a plane glass plate and dried to give a polymer salt (SPIS) which was washed several times with ethanol containing 1.0 M HNO_3. A flexible and self-standing film with a thickness of *ca.* 50 μm was obtained after drying in vacuum. The films have a brown color typical for aromatic polyimides and are soluble in polar organic solvents such as DMAC, NMP and DMSO. The chemical structure of the acidified polymers (SPIH) was analyzed by ^{1}H NMR spectroscopy to confirm the copolymer composition as expected from the feed monomer ratios. The IR spectra also support the structure in which no residual impurities (solvents, benzoic acid and triethylamine derived salts) were observed. The complete cyclization (or imidization) was supported by the absence of absorption peaks assigned to NH groups in these spectra. The ion exchange capacity (IEC) of the polymers was confirmed by back titration using 0.005 M sodium hydroxide solution and 0.005 M hydrochloric acid: for example, SPIH-30 has a measured IEC of 2.40 meq. g^{-1} (the calculated IEC is 2.42 meq. g^{-1}).

The DTA analyses showed that the SPIHs do not have glass transition temperature due to their whole aromatic rigid structure. In TGA curves for the SPIHs, two-step weight loss is observed. The first weight loss from 20 to 170 °C is ascribed to the loss of absorbed water and the second above 280 °C represents the decomposition of the polymer, presumably *via* the loss of sulfonic acid groups. The decomposition temperature is almost as high as that of Nafion.[12] Because of their hydrophilic nature, the SPIHs absorb water when soaked in water or left under humidified conditions. The water uptake of the samples was evaluated by measuring the weight change between dried and humidified (at 85 °C and 93% relative humidity for 2 h) membranes (Fig. 2). As expected, SPIH-0 showed the highest water uptake (103 wt%) due to its highest sulfonic acid content (equivalent weight per sulfonic acid (EW) for this polymer is 288). The water uptake decreases to 51 wt% for SPIH-10 and to 20 wt% for SPIH-20 with increasing the amount of fluorenyl groups. It is noticeable that the water uptake increases to 57 wt% for SPIH-30 in spite of the enhanced hydrophobicity. We assume that the bulky fluorenyl groups force each polymer chain apart to produce large interchain separations, in which water molecules could be confined. The



SPIH-x (x = 0 - 60)

Fig. 1 Chemical structure of sulfonated polyimides SPIH-0 to -60.

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† Eleupplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b210296j/

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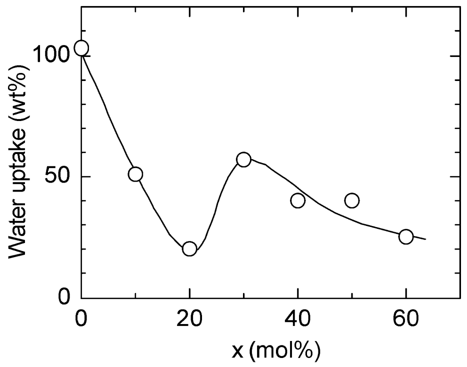

Fig. 2 Water uptake of SPIH-0 to -60 at 85 °C and 93% RH.

water uptake gradually decreases again to 25 wt% for SPIH-60.

In order to evaluate the oxidation stability of the SPIHs, film samples were treated with Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. Although SPIHs-0 and -05 are not stable and dissolved into solution soon after soaking, the stability is improved with an increase of the amount of fluorenyl moieties. More than 2 h was required before the polymers SPIH-30 to -60 started to dissolve (or decompose) and SPIH-60 withstands the solution for almost 5 h. This oxidation stability is very high for a polymer electrolyte material based on a nonfluorinated hydrocarbon skeleton. It has been reported that polyether[13] and polyimide[14] electrolytes dissolved into Fenton's reagent within several hours under milder conditions (at 25 °C).

Proton conductivity measurements were performed by means of complex impedance analyses using four probes with the frequency between 10 Hz and 200 kHz. The film sample was placed in a closed cell to keep the relative humidity at 100%. All the polyimides show conductivities > 0.01 S cm^{-1} at 20 °C, as shown in Fig. 3. The conductivity increases with an increase of temperature. At 100 °C, SPIH-30 shows a high conductivity of 1.27 S cm^{-1}, which is much higher than that of Nafion (0.17 S cm^{-1}) under the same conditions. The conductivities of SPIH-30 to -60 do not decrease even above 100 °C, indicating a good capability of holding water. This behavior is not common for proton conduction in hydrated polymer electrolytes. The proton conducting behavior is consistent with the water uptake results in Fig. 2, supporting the assumption of water molecules in a space produced by the fluorenyl groups. This water would not evaporate easily so that the conductivity keeps increasing above 100 °C for all of SPIH-x samples with $x > 30$ although the relative conductivity decreases with increasing x due to the increase of the EW value. A conductivity as high as 1.67 S cm^{-1} was obtained for SPIH-30 at 120 °C. To the best of our knowledge, this is the highest proton conductivity reported for polymer electrolyte membranes. The conductivity shows an Arrhenius-type temperature dependence. The activation energy estimated from the slope in Fig. 3 is *ca.* 21 kJ mol^{-1} for the SPIHs. This value is comparable to that of Nafion,[15] indicating that both share the similar conduction mechanism involving hydronium ions.

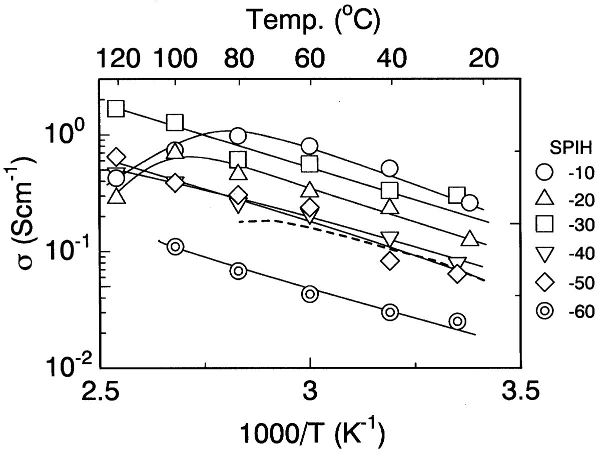

Fig. 3 Temperature dependence of the proton conductivity of SPIH-10 to -60 and that of Nafion® 112 (dotted line) at 100% RH.

In conclusion, a series of new sulfonated polyimide copolymers containing fluorenyl groups was synthesized as a potential electrolyte for high temperature PEFCs. The copolymers revealed hydrophilicity (with unique water uptake behavior depending on the amount of fluorenyl groups) and oxidation stability. The bulky fluorenyl groups when incorporated at a level of 30–60 mol% into the polymer are believed to cause confinement of water molecules, resulting in high proton conductivity (up to 1.67 S cm^{-1} at 120 °C and 100% RH).

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