

Sulfonated polyimide membranes grafted with sulfoalkylated side chains for proton exchange membrane fuel cell (PEMFC) applications

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Abstract

Grafted sulfonated polyimide (SPI) membranes for use as proton-conducting polymer electrolytes for fuel cells were obtained using a fabrication method comprised of thermal-solution imidization and subsequent incorporation of sulfoalkylated grafting agents with different alkyl chain lengths. The additional sulfonic acid ($-\text{SO}_3\text{H}$) groups in the sulfoalkylated side chains of the grafted SPI membranes significantly contributed to enhancing ion exchange capacity (IEC) and proton conductivity, leading to excellent electrochemical single-cell performance. Simultaneously, the alkyl groups in the side chain functioned as an internal plasticizer, resulting in an approximate sevenfold improvement in ductility of the grafted SPI as compared to pristine SPI. Interestingly, grafted SPI with long side chains exhibited lower IEC than that with short side chains. However, a relatively high number of water molecules per $-\text{SO}_3\text{H}$ group and a large amount of bound water caused the SPI membrane grafted with long side chains to have high proton conductivity. Also, the low acidity of the SPI grafted with long side chains leads to improved membrane durability to chemical attacks, such as hydrolysis and radical-induced decomposition. Initially, the electrochemical performance of the grafted SPI membranes was superior to that of Nafion 117, whereas after a long duration for 1100 h in hot water, the single-cell performance of the grafted SPI membranes diminished below that of Nafion 117, indicating a strong dependency of electrochemical performance with membrane stability.

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1. Introduction

Sulfonated polymers have been used in various technical applications such as electrodialysis [1], sensors [2], and pervaporation [3]. Their application has been extended to the field of fuel cells as a potential polymer electrolyte, which is one of key elements affecting the electrochemical performance of the fuel cell system. Up to now, perfluorinated sulfonated acid (PFSA) membranes (e.g. Nafion[®], Aciplex[®], and Flemion[®]) have been considered the predominant choice for proton-conducting polymeric electrolytes due to high proton conductivities in the fully hydrated state and excellent membrane stability to chemical degradation. However, the PFSA membranes are still expensive ($\sim \$800\text{ m}^{-2}$ in 2004 [4]), which may hinder the commercialization of fuel cells. Meanwhile, hydrocarbon-based polymer membranes containing sulfonic acid ($-\text{SO}_3\text{H}$) groups may be

alternative electrolytes because the membranes exhibit relatively low production costs, as well as excellent proton conductivities. Nevertheless, these hydrocarbon membranes have not surpassed PFSA membranes, which have stable C–F bonds, in membrane durability yet.

Membrane stability has been believed to be an important factor limiting long-term performance of fuel cell [5,6]. There have been many approaches, particularly in hydrocarbon membranes, for improving membrane durability and maintaining other membrane properties including proton conductivity and fuel permeability [7–14]. The representative approaches include chemical or physical cross-linking of the polymer matrix that comprises the membranes [10–14] and fabrication of organic–inorganic nanocomposite membranes [13–15]. Cross-linking contributes to the improvement of the membrane resistance to chemicals, such as water and hydrogen peroxide (H_2O_2) [10–14], even in sulfonated polyimide (SPI) systems with weak hydrolytic stability [16]. On the other hand, most of the sulfonated polymers show reduced proton conductivity and low processability after cross-linking. In the case of

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organic–inorganic nanocomposite membranes, inorganic particles, such as nano-sized fumed silica, can retard the membrane degradation derived from hydrolysis via the reduction of free volume elements where absorbed water molecules might remain within the membranes [13,14]. Inorganic particles are also effective for increasing tolerance to a radical attack [15]. In spite of enhanced membrane durability, sulfonated polymers with intrinsically weak chemical structures are still vulnerable to chemical attack. Therefore, it is useful to investigate the relationship between membrane durability and the chemical structure of the polymer materials for the development of a desirable fuel cell membrane with improved chemical resistance. Here, chemical attack by hydrolysis and radical-induced decomposition were investigated.

In the present study, a polyimide was selected as the polymer backbone because its relatively low hydrolytic stability can help us to easily observe changes in membrane properties due to chemical attack within a short time. SO_3H -terminated grafting agents with different alkyl chain lengths $(-\text{CH}_2)_n-\text{SO}_3\text{H}$, $n=2, 3$ and 4 were added to the polymer matrix. The relationship between chemical structure and membrane properties was systematically studied to find an optimal length of sulfoalkylated side chain in the grafted SPIs. Furthermore, the electrochemical single-cell performance of the present system is compared with those of other polyimide systems with different chemical structures and membrane properties using the same PEMFC operation conditions. The strong dependence of the electrochemical performance on the membrane properties, in particular the membrane durability, was investigated as a function of duration of chemical attack.

2. Experimental

2.1. Materials

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA), 3,5-diaminobenzoic acid (DBA) and 4,4'-diaminodiphenyl ether (ODA) were purchased from Tokyo Kasei Co. (Tokyo, Japan) and used as received. ODA was converted into 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (SODA) via a direct sulfonation as reported in the literature [10–14,17]. Benzoic acid, used as a catalyst, and triethylamine (TEA), used as a liberator of protonated amino groups, were purchased from Aldrich Chemical Co. (WI, USA) and used as received. Isethionic acid sodium salt (ES, $\text{HO}-(\text{CH}_2)_n-\text{SO}_3\text{Na}$, $n=2$, Tokyo Kasei Co., Tokyo, Japan), 3-hydroxy-1-propanesulfonic acid sodium salt (PS, $n=3$, Aldrich, WI, USA), and 4-hydroxy-1-butanedisulfonic acid delta sultone (BS, $n=4$, Tokyo Kasei Co., Tokyo, Japan) were used as thermally activated grafting agents to introduce sulfoalkylated moieties in the polymer matrix. For sulfonated polyimide (SPI) fabrication, *m*-cresol (Aldrich Chemical Co., WI, USA) was used as a solvent.

2.2. Fabrication of SPIs with sulfoalkylated moieties

Pristine SPI, the polymer matrix, was fabricated via a solution-thermal imidization method using 0.58 g (1.6 mmol)

of SODA, 0.37 g (2.4 mmol) of DBA, and 1.07 g (4.0 mmol) of NTDA [10–14]. Pristine SPI was used as a reference sample. Then, ES as a grafting agent was added to a 15 wt.% pristine SPI solution at 80 °C in an amount equivalent with the number of moles of carboxylic acid ($-\text{COOH}$) in DBA. The solution mixture was stirred at 110 °C for 2 h and 160 °C for 8 h to obtain a sulfoalkylated SPI (SPI-*g*-ES). After cooling down to 110 °C, additional *m*-cresol was added to dilute the resulting SPI-*g*-ES (grafting yield (%) = 72%) solution. In the next step, the solution was poured into cold acetone to remove unreacted residual monomers or contaminants. The precipitates were filtered off, washed repeatedly with cold acetone and then dried in a vacuum oven at 110 °C for at least 2 days. Other grafted SPIs, such as SPI-*g*-PS (grafting yield (%) = 78%) and SPI-*g*-BS (grafting yield (%) = 82%), were also fabricated via the same procedure using PS and BS, which have different $(-\text{CH}_2)_n$ -chain lengths.

Wavelength assignments for Fourier transform infrared spectra (FT-IR) of SPI-*g*-BS (KBr): 1680, 1710 cm^{-1} ($\text{C}=\text{O}$), 1470 cm^{-1} ($-\text{O}-\text{CH}_2-$), 1395 cm^{-1} ($\text{C}-\text{N}-\text{C}$), 1252 cm^{-1} ($\text{S}=\text{O}$), 1083 cm^{-1} (SO_3^-), 918 cm^{-1} ($\text{S}-\text{OH}$), 744 cm^{-1} ($\text{O}=\text{C}-\text{N}$), 735 cm^{-1} ($-\text{CH}_2-$).

For comparison, cross-linked SPI (XSPI) membranes were fabricated by adding 1,5-pentanediol (Diol) [10] and *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES) [11] as cross-linkers to the same matrix, as illustrated in Fig. 1.

2.3. Membrane formation and acidification

All SPI membranes were fabricated in TEA-salted ($-\text{SO}_3^-$ -TEA) form using a solution-casting and solvent-evaporation method involving a thermal protocol of 2 h at 80 °C and 10 h at 180 °C. The TEA-salted membranes were soaked in methanol for 6 h to remove any residual solvents and immersed in deionized water for 8 h at room temperature to peel them off from glass plate. Then, the membranes were converted into protonated form ($-\text{SO}_3\text{H}$) by treatment with acid. The membranes were placed in 1 M HCl solution at 30 °C for 8 h and then washed several times in deionized water. All SPI membranes were subsequently kept in a vacuum oven at 160 °C to prevent additional hydrolytic decomposition. In this report, the nominal thickness of the SPI membranes was controlled to $30 \pm 2 \mu\text{m}$ to minimize the thickness effect on proton conductivity and single-cell performance.

2.4. Polymer and membrane characterization

Structural analysis of each SPI membrane was determined by ^1H nuclear magnetic resonance (NMR) spectra; spectra were obtained using a Varian Model NMR 1000 (CA, USA). The ion exchange capacity (IEC, mequiv. g^{-1}), which indicates $-\text{SO}_3\text{H}$ content per unit polymer weight, was measured using a conventional titration method (ASTM 2187) with phenolphthalein indicator. The viscosity (*m*-cresol, dL g^{-1}) measurement of each grafted SPI in TEA-salt form was carried out in the concentration range of 1.0–0.2 g dL^{-1} at 30 °C using an Ostwald viscometer. Water uptake (%) was measured after soaking SPI membranes in water at 30 °C for 1 day. For the measurement, all mem-

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