



Effect of end-group cross-linking on transport properties of sulfonated poly(phenylene sulfide nitrile)s for proton exchange membranes



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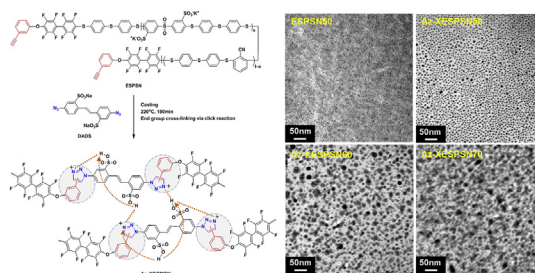
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HIGHLIGHTS

- The end-group cross-linked membranes were prepared by click reaction.
- The membranes showed excellent proton conductivity and single cell performances.
- The cross-linked membrane exhibited much improved long-term durability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 September 2015

Received in revised form

12 January 2016

Accepted 13 January 2016

Available online 1 February 2016

Keywords:

Proton exchange membrane

Cross-linking

Click reaction

Fuel cells

ABSTRACT

A series of end-group cross-linked membranes (Az-XESPSN) were prepared by click reaction to investigate the effects of cross-linking on the morphology and proton transport properties of proton exchange membranes. The morphological transformations resulting from thermal annealing and cross-linking were observed by means of atomic force microscopy (AFM) and transmission electron microscopy (TEM). Compared to the non-cross-linked ESPSN membranes, the Az-XESPSN membranes exhibited lower water uptake and improved mechanical and chemical stabilities. In addition, the Az-XESPSN membranes exhibited higher proton conductivities ($0.018\text{--}0.028\text{ S cm}^{-1}$) compared to those of the ESPSN membranes ($0.0044\text{--}0.0053\text{ S cm}^{-1}$) and Nafion 212 (0.0061 S cm^{-1}), particularly in conditions of elevated temperature ($120\text{ }^{\circ}\text{C}$) and low relative humidity (35%). Such enhancements can be attributed to a synergistic effect of well-defined hydrophilic ionic clusters and triazole groups that function as proton carriers under anhydrous conditions. Furthermore, the Az-XESPSN membranes exhibited significantly enhanced single cell performance and long-term stability compared to those of ESPSN membranes.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been widely studied as alternative energy sources for automobiles, portable devices, and stationary power generation due to their high energy conversion efficiency, high energy density, and

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environmental friendliness [1]. As a key component of PEMFCs, the proton exchange membrane (PEM) is required to separate the hydrogen fuel from the oxidant and provide an ionic pathway for proton transport [2,3]. The most widely used electrolytes for PEM fuel cells are perfluorosulfonic acid (PFSA) polymers such as Nafion, due to their excellent mechanical and chemical stabilities and their high proton conductivity in the hydrated state. However, PFSA membranes typically show several drawbacks, including a limitation of maximum operating temperature below the boiling point of water (<100 °C), high fuel permeability, and high cost which prevent their applicability to PEMFCs [4–6]. PEM fuel cells that can be operated at high temperature under anhydrous conditions are highly desirable to attain better catalyst CO tolerance, higher electrode kinetic activity, and simpler water management and cooling systems [7–9]. Therefore, considerable research has been carried out to develop PEMs that can operate in high temperature and low humidity conditions, such as modified PFSA membranes [10], aromatic hydrocarbon polymers [11], inorganic–organic composite membranes [12,13], and base-doped acidic polymer membranes [14,15]. At elevated temperatures, the additives (*i.e.*, inorganic compounds, bases, etc.) used in such composite membranes act as proton carriers, replacing the role of water. Though these composite membranes exhibit high proton conductivity at high temperature conditions, they suffer from inherent drawbacks such as leakage of composite materials and high production cost [16].

To improve the proton conductivity in low humidity conditions, it would be preferable for the membrane morphology to display a distinct separation between hydrophilic and hydrophobic nanophases with high interconnectivity between hydrophilic domains [17–19]. Typically, a high degree of sulfonation (DS) leads to the development of a well-defined microstructure of interconnected hydrophilic domains and a high charge carrier concentration, resulting in high proton conductivity [2]. However, high DS usually leads to excessive water swelling which eventually causes failure of a membrane electrolyte assembly (MEA). Cross-linking is one of the promising approaches to achieve desired properties relevant to fuel cell performance and PEM durability, including high proton conductivity, water uptake, and mechanical and chemical stabilities [20]. However, most of the cross-linking methods involve the removal of sulfonic acid groups, which decreases the proton conductivity [21,22]. On the other hand, the end-group cross-linking method not only improves thermal and dimensional stabilities but also provides reasonable proton conductivity without decreasing the ion exchange capacity (IEC) [23].

Recently, the azide–alkyne click reaction (Huisgen 1,3-dipolar cycloaddition) has been researched for use in various applications; it has the advantages of high efficiency, fast reaction rate, and mild reaction conditions. This simple and efficient methodology can be utilized for cross-linking and functionalization in polymer structures by controlling the curing temperature, stoichiometry, and composition [24,25].

In our previous study, end-group cross-linked sulfonated poly(phenylene sulfide nitrile) (XESPSN) membranes showed enhanced mechanical and chemical stabilities and well-ordered hydrophilic and hydrophobic nanophase separation due to the unusual morphological transformation induced by thermal cross-linking at 250 °C, a temperature at which both thermal annealing and cross-linking effects occurred [26]. The observed membrane morphology played a critical role in the XESPSN membranes; they exhibited higher proton conductivities and enhanced single cell performance compared with those of pristine membranes, particularly at elevated temperature and low relative humidity condition [27].

In the present study, we prepared novel end-group cross-linked

membranes (Az-XESPSN) using cross-linker containing azide groups and the end-group cross-linkable polymer ESPSN, *via* the thermally induced click reaction. Az-XESPSN membranes contain basic triazole groups (*N*-heterocycles) that act as proton carriers under low humidity conditions by the Grotthuss proton conduction mechanism [28]. The triazole groups could facilitate proton transfer more easily than other *N*-heterocycles due to the multiple nitrogen atoms in the structure. Moreover, proton transfer pathways can form continuous networks with anhydrous proton carrier pathways [29]. Compared with the previous studies, we have developed a facile method to enhance the proton conductivity of membranes especially at elevated temperature and low RH conditions by forming anhydrous proton transfer pathways and low energy barrier pathways with sulfonic acid–triazole acid–base pairs. The effects of cross-linking on the proton conductivity and membrane morphology derived from the thermally activated transformation were investigated in the present work. The Az-XESPSN membranes showed improved chemical and dimensional stabilities and improved electrochemical performance compared with those of the ESPSN membranes. Furthermore, the single cell performance and durability of the Az-XESPSN membranes at elevated temperature were investigated in the present work (Scheme 1).

2. Experimental

2.1. Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS), 4,4'-thiobisbenzene thiol (TBBT), 3-ethynylphenol, *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), toluene, and 4,4'-diazido-2,2'-stilbenedisulfonic acid disodium salt tetrahydrate (DADS) were purchased from Sigma-Aldrich Co. (WI, USA). 2,6-dichlorobenzonitrile (DCBN), decafluorobiphenyl (DFBP), and potassium carbonate (K_2CO_3) were purchased from TCI Co. (Tokyo, Japan). DCDPS was converted to 3,3'-disulfonate-4,4'-dichlorodiphenyl sulfone (SDCDPS) by using fuming sulfuric acid (20% SO_3 , Sigma-Aldrich).

2.2. Synthesis of ESPSN

End-group cross-linkable sulfonated poly(phenylene sulfone nitrile) (ESPSN) random copolymers were synthesized by a nucleophilic aromatic substitution reaction (Scheme S1). One example of the preparation of ESPSN polymer follows: TBBT (1.2520 g, 5 mmol), SDCDPS (1.5147 g, 3.5 mmol), DCBN (0.2838 g, 1.6 mmol), K_2CO_3 (1.0365 g, 7.5 mmol), DMAc (20 ml), and toluene (10 ml) were added into a 250 ml four-neck flask equipped with a mechanical stirrer and a nitrogen inlet. The reaction mixture was heated at 140 °C for 6 h to activate the monomer and to dehydrate the system. After removing the water and toluene, the solution mixture was heated to 165 °C and held at this temperature for 24 h. A solution of DFBP (0.4198 g, 0.3 mmol) in DMAc (10 ml) was added and stirred at 120 °C for 12 h. Then, a solution of 3-ethynylphenol (0.1380 g, 0.3 mmol), DMAc (10 ml), and toluene (5 ml) was added to the reaction mixture and the reaction was held at 120 °C for 6 h. After polymerization, the reaction mixture was cooled and precipitated in a 7:3 isopropanol/water mixture. The precipitated polymer was filtered and then dried at 120 °C under vacuum for 1 d. Yield: 93%. 1H NMR (DMSO- d_6): δ 8.21 (s, 2H), 7.71 (s, 2H) 7.61–7.52 (m, 16H) 7.48 (d, 1H) 7.24 (d, 2H) 6.88 (d, 2H) 4.23 (s, 1H). FT-IR (film, cm^{-1}): 2230 ($-C\equiv N$ stretching) 1320 ($-SO_2-$ stretching) 1235, 1056, 1010 ($-SO_3Na$ symmetric and asymmetric stretching).

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