

Proton conductivity and properties of sulfonated polyarylenethioether sulfones as proton exchange membranes in fuel cells

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Abstract

A series of high molecular weight proton exchange membrane (PEM) materials, based on sulfonated polyarylenethioether sulfone (SPTES) copolymers, has been developed utilizing an all aromatic polymer backbone with bulky organic endcaps, along with a high sulfonic acid content that enhances water retention and high temperature application. The SPTES copolymers containing up to two sulfonic acid units per polymer repeat unit are expected to maximize the membrane water uptake as well as the proton conductivity. The evaluation of these PEMs resulted in a wide variation of proton conductivities in the range of 100–215 mS/cm at 65 °C and 85% relative humidity; the measured proton conductivities were found to be temperature and humidity dependent. This new class of SPTES copolymer materials for PEMs has been demonstrated to be superior to the state-of-the-art Nafion membranes with respect to proton conductivity as well as high temperature PEM use. Crown Copyright © 2006 Published by Elsevier B.V. All rights reserved.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are energy converters and are attractive for a variety of power needs at low operating temperatures (60–100 °C) due to their energy efficiency and environmental compatibility [1,2]. In PEMFCs, the polymer membrane is one of the most critical components. The PEMFCs function electrochemically by the oxidation of hydrogen (fuel) at the anode and reduction of oxygen at the cathode. At the heart of the fuel cell is the membrane electrode assembly (MEA), which consists of a proton exchange membrane, catalyst layer, and gas diffusion layers (GDL). The principal function of the membrane is to permit the transport of protons generated at the anode, while prohibiting direct contact with the fuel and the oxidant. Thus, the performance of the organic PEM used as electrolytes and separators, are crucial to the functioning of these types of fuel cells [3].

At present, Nafion-H, which is based on a perfluorinated ionomer, is the only commercially available, state-of-the-art membrane successfully used in PEMFC [4]. Although it has good chemical and physical properties for use in fuel cell applications, it has severe performance limitations at temperatures higher than 80 °C and at low humidity. These conditions lead to a dramatic loss of proton conductivity due to membrane dehydration [5]. In addition, the cost of Nafion is extremely high due to the complex and extensive chemistry required for synthesis. Hydrocarbon polymers containing polar groups that retain high amounts of water over a wide temperature range are particularly attractive and relatively much cheaper to synthesize than perfluorinated polymers.

There are two strategies to prepare sulfonated hydrocarbon polymers. The first one is post-sulfonation of prepared polymers by different sulfonation agents such as concentrated sulfuric acid, fuming sulfuric acid, chlorosulfonic acid, trimethylsilyl chlorosulfonate, and sulfur trioxide–triethyl phosphate complex. The other method is direct polymerization of designed sulfonated monomers [6]. In the post-sulfonation reactions, aromatic electrophilic substitution by the sulfonic acid groups is usually restricted to the activated position ortho to the aromatic

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ether bond, which might deteriorate the chemical stability of the polymer because of the cleavage of the ether linkage. In addition, the sulfonic acid groups are relatively easy to eliminate from the activated aromatic ring via desulfonation. Moreover, the degree of sulfonation is difficult to control, and too high a sulfonation degree often results in the solubility of functionalized polymers in water. Finally, post-sulfonation might also cause the partial degradation and cross-linking of the polymers especially when strong sulfonation agents such as chlorosulfonic acid are employed. In direct polymerization, monomers with the sulfonic acid groups attached to the deactivated aromatic rings are used to prepare sulfonated polymers. It is expected that the attachment of the sulfonic acid groups to the deactivated ring positions might provide chemical stability and enhance the acidity of the resulting polymer structure, resulting in more facile proton transport [7]. Much effort has been expended in the development of new proton conducting polymers by direct polymerization. The sulfonic acid groups were attached onto highly stable aromatic polymers, such as poly(ether ether ketone) [8], polyethersulfone [9,10], polyimide [11], and poly(phenylene sulfide) [12]. These polymers generally exhibit good thermal and chemical stabilities and high proton conductivities. However, fuel cells made from these membranes generally fail in a relatively short time, presumably by a combination of hydrolytic and oxidative degradation.

In some preliminary reports, we reported the synthesis of sulfonated polyarylenethioether sulfone homopolymer [13] and highly sulfonated polyarylenethioether sulfone copolymer [14] by direct polymerization employing sulfolane as the polar aprotic solvent. The studies indicated that the polymers have good film-forming capabilities and exhibit hydrophilicity. The hydrated polymer membranes have shown high proton conductivity. These properties imply the potential usefulness of the materials as PEMs in hydrogen fuel cells. More recently, McGrath and co-workers reported [15] the synthesis and characterization of polyarylenethioether sulfone with lower degrees of disulfonation (20–50 mol%) by direct polymerization using 1-methyl-2-pyrrolidinone as solvent. These copolymers were characterized by NMR, FTIR, TGA, etc., and the proton conductivity of the copolymers was measured in water (in the fully hydrated state) at 30 °C to reach values of 160 mS/cm for the copolymer with the highest sulfonic acid content.

In this article, we report the synthesis and characterization of high molecular weight polyarylenethioether sulfone copolymers with a high sulfonic acid content (50–80 mol% disulfonated polymer unit) that enhances water retention and can consequently allow elevated temperature operation, designed to overcome the limitations of Nafion. The objective of this work is to produce thermally and hydrolytically stable sulfonated aromatic copolymers with high proton conductivities, measured under

controlled relative humidity. Adjusting the relative amounts of the sulfonated and the unsulfonated monomers for the preparation of a series of highly sulfonated copolymers led to the tailorability of the thermal, mechanical and electrochemical properties of the PEMs as well as their solvent solubilities and hydration sensitivities. Furthermore, endcapping of these highly sulfonated copolymers takes advantage of the bulky aromatic end group to minimize or even preclude water solubility of these copolymers without adversely affecting their proton conductivity. The end-capped sulfonated copolymers maintained a high conductivity, while exhibiting enhanced water resistance. Operational MEAs fabricated with SPTES copolymers were characterized. The overall fuel cell performance based on SPTES-based PEMs was superior to that of Nafion under the evaluation conditions.

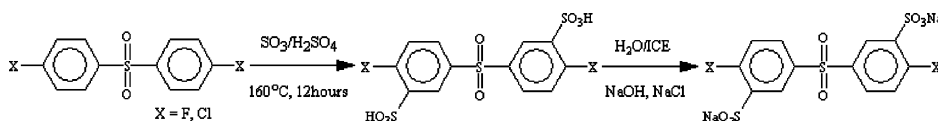
2. Experimental

2.1. Materials

4,4'-Thiobisbenzethiol (98%, GC, TCI America Chemical) was recrystallized from toluene and dried at 80 °C in vacuum oven prior to use. 4-Fluorophenylsulfone (99%) and 4-chlorophenylsulfone (98%) were purchased from Sigma-Aldrich, recrystallized from isopropanol, and dried at 80 °C in a vacuum oven. Potassium carbonate (99%, ACS reagent, Sigma-Aldrich Co.), tetramethylenesulfone (Sulfolane, 99%, Sigma-Aldrich Co.), 4-fluorobiphenyl (97%, Sigma-Aldrich Co.), 4-chlorobiphenyl sulfone (96%, Sigma-Aldrich Co.), sulfuric acid (Fuming, 30% SO₃, Sigma-Aldrich Co.), 2-propanol (Fisher Scientific), 1-methyl-2-pyrrolidinone (NMP, Anhydride, 99%, Sigma-Aldrich Co.), and *N,N*-dimethylacetamide (DMAc, Anhydrous, 99%, Sigma-Aldrich Co.) were used as received. Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

2.2. Sulfonated monomer synthesis

Disodium 3,3'-disulfonate-4,4'-difluorodiphenylsulfone and disodium 3,3'-disulfonate-4,4'-dichlorodiphenylsulfone were prepared using an optimized procedure developed from reported approaches [9]. A typical reaction is represented in Scheme 1, the procedure is as follows: 4-fluorophenylsulfone (25.4 g, 0.1 mol) was dissolved in 50 ml of 30% fuming sulfuric acid in a 100 ml, single-necked flask equipped with a magnetic stirrer and a drying tube. The solution was heated to 160 °C for 12 h to produce a homogeneous solution. Then, it was poured into 300 ml of ice water under stirring. Next, an aqueous solution of 4 M sodium hydroxide was added, which reduced the pH to 6–7. One hundred and twenty grams of sodium chloride were added to salt out the



Scheme 1. Synthesis of disodium sulfonated monomers.

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