



Surface orientation of hydrophilic groups in sulfonated poly(ether ether ketone) membranes

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ARTICLE INFO

Article history:

Received 4 April 2013

Accepted 24 June 2013

Available online 9 July 2013

Keywords:

Surface molecular reorientation

Wetting

PEM

Sulfonated poly(ether ether ketone)

SPEEK

ABSTRACT

Sulfonated poly(ether ether ketone) copolymers (SPEEK) with a range of sulfonate contents (SC 77–51%) were synthesized via nucleophilic substitution polycondensation from hydroquinone and sulfonated hydroquinone. Membranes obtained by solvent casting from dimethylacetamide onto glass surfaces were analyzed for surface behavior. The surfaces of a membrane were hydrophobic in air, but hydrophilic in water. This surface behavior was corroborated by water contact angle vs. time, using sessile drop measurements. Hydrophilic sulfonic group aggregates on SPEEK chain and various media contacting with the top or bottom surfaces of the membrane during the fabrication process caused differences in surface behavior. Angle-dependent XPS showed that there was a higher atomic S/C ratio of the bottom surface than on the corresponding top surface. The hydrophilic sulfonic groups were in higher concentration within the membrane, with the concentration gradually decreasing towards the surface for SPEEK-HQ-80 and SPEEK-HQ-70 membranes. Acidification with strong acid and higher temperature induced a more hydrophilic surface on a membrane than a milder acidification process. The depth profile at the membrane surface was examined by a combination of contact angle, XPS and ATR-FTIR.

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1. Introduction

Extensive efforts have been made to develop potential alternatives for Nafion[®] in PEM application [1]. Aromatic polymers with sulfonic acid groups and their sulfonated derivatives have attracted considerable interests due to their excellent thermal and chemical stability. Sulfonated derivatives of poly(ether sulfone) (SPES) [2], polyimide (SPI) [3], polyimidazole [4], polyphenylene [5], and polybenzimidazole [4] are among poly(aryl ether ketones) (PAEKs) being investigated as PEM materials.

PAEKs are of considerable interest due to the combination of their chemical stability, physical and mechanical properties. As a class of promising PAEK for PEM, aromatic sulfonated poly(ether ether ketone) (SPEEK) has been widely investigated. The two main approaches to introduce sulfonic acid groups into this type of polymer are (a) the post-sulfonation of existing polymers, or (b) the direct copolymerization of sulfonated monomers [1]. The sulfonation reaction of commercial Victrex PEEK, yielding sulfonated poly(ether ether ketone), has been thoroughly investigated by various groups [6–9]. The post-sulfonation process is advantageous due to the availability of inexpensive commercial polymers, such as PEEK, and because of a relatively simple sulfonation procedure that can be scaled up. Challenges, however, may be encountered in both

the precise control of the sulfonation sites location and the degree of sulfonation (DS), resulting in a random and less-defined distribution of sulfonic acid groups along the polymer chain. Moreover, harsh reaction conditions, i.e., elevated temperatures, extended reaction time and strongly-acidic sulfonation agents, may be required for the sulfonation process, which could lead to side reactions and polymer degradation [1].

Copolymers synthesized by direct copolymerization exhibit advantages in the controllability of the sulfonate content (SC) and sulfonation sites location, leading to more defined chain structures in comparison with the postsulfonation method [10]. Nevertheless, the compatibility between the solvent and reactants, such as potassium carbonate, monomers, intermediates, oligomers and growing polymer chains under the reaction conditions, is essential for a successful copolymerization. The solvent is chosen from the solubility of reactants, the solubility of high molecular weight polymer during polymerization process and the reactivity of the monomers. Moreover, the direct copolymerization process using sulfonated monomers is hampered by the limited availability or purity of sulfonated monomers.

The presence of a certain amount of water in sulfonated PEMs is vital for proton transport through the membrane. However, excessive water uptake in a PEM leads to unacceptable dimensional change [11] dimensional mismatch with the electrodes and delamination of catalyst layers from the PEM [12]. On the other hand, a loss of conductivity occurs at elevated temperatures (above

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80 °C) due to dehydration. These issues may result in a reduction of mechanical properties [13] or poor membrane electrode assembly (MEA) performance and durability [1].

The unique character of Nafion[®] originates from the combination of a highly hydrophobic perfluoropolymer backbone and flexible side chains bearing exceptionally hydrophilic and super acidic sulfonic acid groups. The surface of Nafion[®], however, transforms from a hydrophobic surface in the presence of air or water vapor atmosphere [14,15] into a hydrophilic surface when in contact with liquid water. This transformation is supported and elucidated by simulation models and experimental results. The highly incompatible hydrophobic backbone and hydrophilic side chain constituents separate the polymer matrix into micro-phases, which lead the sulfonic acid groups to cluster into hydrophilic domains and the polymer backbone to form hydrophobic domains [1]. In some polymer systems, the composition of the membrane surface differs, sometimes dramatically, from the composition within the bulk, resulting in a material with distinct surface properties, such as wettability and adhesion. Differences of the surface free energy of the components within a polymer may explain the overall surface morphology in which the lower surface energy component of polymer preferentially aggregates towards the polymer–air interface [16,17].

Until now, there has been no comparative investigation of partially sulfonated SPEEK prepared by the direct copolymerization process with the same composition as that originating from a post-sulfonation process of commercial Victrex PEEK. In this study, a series of SPEEK copolymers based on hydroquinone bearing various sulfonate contents were first synthesized by copolymerization using hydroquinone as an alternative to post-sulfonated SPEEK. Flexible, transparent and tough membranes were prepared by the solution casting. To better understand the effects of water on SPEEK membranes and the swelling of PEM, we investigated the differences in hydrophilicity between two surfaces of a membrane, and, between the surface and the bulk of these membranes. Furthermore, the change in membrane hydrophilicity upon contacting with water vapor and liquid water was investigated. The depth profiles of membrane surfaces were examined by contact angle, XPS, ATR-FTIR and FTIR, providing the surface information from 0.5 nm to 1 μm to the surface. It was observed that sulfonic groups aggregated within the membrane. The hydrophilicity of the membrane surface in contact with liquid water may be of practical importance in PEM fuel cells because liquid water is produced in traditional fuel cells application. Attempts were first initiated to interpret the composition difference between the glass–polymer surface and air–polymer surface of the same membrane.

2. Experimental section

2.1. Chemicals and materials

All chemicals were purchased from Sigma–Aldrich or Fluka. Hydroquinone (HQ) ReagentPlus™, ≥99% was purified by sublimation under vacuum. 4,4'-Difluorobenzophenone (DFK) 99% was used as obtained. 2,5-Dihydroxybenzenesulfonic acid potassium salt (SHQ), technical grade, was purified by recrystallization using ethanol/water (1/1,v/v). Potassium carbonate (anhydrous) was dried at 100 °C in a vacuum oven for 12 h. Anhydrous dimethyl sulfoxide (DMSO) 99.9%, 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc), 2-propanol (also designated as isopropanol (IPA)) and toluene were used without further purification.

2.2. SPEEK synthesis

2.2.1. Synthesis of copolymer SPEEK

The copolymers of SPEEK in potassium form were synthesized using DFK and HQ, with various stoichiometric amounts of SHQ.

The copolymer of SPEEK was denoted as SPEEK-HQ-XX, where XX refers to the molar ratio of SHQ to DFK (in percentage). In a typical copolymerization represented by SPEEK-HQ-70, SHQ (21 mmol, 4.7935 g), HQ (9 mmol, 0.9910 g), DFK (30 mmol, 6.5460 g) and potassium carbonate (34.5 mmol, 4.7682 g) were precisely weighed and transferred into a 250 mL three-neck flask equipped with a mechanical stirrer, Dean–Stark trap and an argon gas inlet. 80 mL of DMSO and 40 mL of toluene were added. The mixture was refluxed at 150 °C for 4 h, following which the toluene was removed, allowing the temperature to slowly increase to 175 °C. After a polymerization time of 24 h, the viscous mixture was vacuum filtered overnight, and then, the collected transparent dark red solution was poured into excess cold IPA under strong mechanical stirring to obtain a string-like polymer product. The resulting polymer fibers were washed thoroughly a few times using fresh IPA and cold water successively. The copolymer SPEEK-HQ-70 in potassium form was dried in a vacuum oven at 120 °C for 24 h.

2.3.2. Synthesis of post-SPEEK

The post-sulfonation of PEEK (Victrex PLC) was run using concentrated sulfuric acid according to the procedure described elsewhere [9,18]. The process was detailed in supporting information.

2.3. Membrane fabrication

SPEEK copolymer (4 g) was dissolved in DMAc (20 mL) under stirring overnight. A uniform and transparent polymer solution without bubbles was obtained, which was then filtered through a stainless steel pressure filter (Millipore) and cast using a doctor blade onto a clean glass plate (21 cm × 29.7 cm). The cast membrane solution was placed flat in a covered container at 60 °C with a slow argon purge for ~20 h. The resulting membrane was removed from the glass plate by immersing it in cold water. The membrane was stored in water at room temperature for 24 h, with the water being changed several times to remove residual solvent. The SPEEK membrane in the potassium form was converted to the acid form by placing it into 1 M H₂SO₄. Two acidification processes were used. One was acidification by 1 M H₂SO₄ at room temperature for 24 h. Another one was acidification by 1 M H₂SO₄ at room temperature for 21 h, followed by acidification at 84–90 °C for 2 h. After acidification, the membrane was immersed in water at room temperature for 24 h, with several changes of fresh water, until the wash water was at pH 7. Membranes in either the potassium or acid form were dried in ambient air in a fume hood overnight, and then laid flat in a vacuum oven at 60 °C for 12 h. The temperature was slowly increased to 120 °C and maintained at that temperature for 24 h. Finally, the membranes were stored in a desiccator prior to characterization.

2.4. Characterization and tests

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and Fourier transform infrared spectroscopy (FTIR) spectra of homogenous membranes were recorded at 45° of incidence angle from 4000–500 cm⁻¹ using a Thermo Nicolet Magna-850 (Thermo Scientific, Madison, WI) and a Thermo-Nicolet 760 FTIR, respectively. The Golden-Gate (diamond IRE) ATR accessories (Specac Ltd., London, U.K.) were used for ATR-FTIR measurement. ATR correction was applied for all resulting ATR-FTIR spectra using Thermo Nicolet Omnic software to illustrate the different penetration depths of the various wavelength. A liquid-nitrogen-cooled narrow-band Mercury Cadmium Telluride (MCT) detector was used for all spectra measurements. The sample chamber of Thermo-Nicolet 760 FTIR was purged with CO₂- and H₂O-free air before measurement. A thin film (0.01 mm) was used for FTIR measurements. All membrane samples were dried in vacuum-oven at

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