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Synthesis and performance comparison of perfluorobenzoic acid and perfluorobenzenesulfonic acid membranes

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ABSTRACT

Perfluorobenzoic acid (PFBA) and perfluorobenzenesulfonic acid (PFBSA) membranes were synthesized from perfluorosulfonyl iodide via novel free-radical substitution reactions. Despite its lower ion-exchange capacity, the PFBA film has proton conductivities typically more than two times higher than PFBSA under various temperatures. For example, at 80 °C, PFBA has a proton conductivity of 109.6 mS/cm while the PFBSA membrane is only 44.1 mS/cm in water. The PFBA membrane also shows better performance than PFBSA in a 5 cm^2 PEMFC setting. The formation of unique dimerized/trimerized nanoclusters of $-CO_2H$ facilitates the hopping of protons across the membrane—leading to the higher ion-conductivities of PFBA. In addition, free-radical substitution reactions were found to be a general method for grafting aromatics or heteroaromatics to the terminals of fluoropolymer side chains via stable C–C bonds that can tolerate hydrolytic conditions. Such perfluoro-aromatic and perfluoro-heteroaromatic membranes may find applications in numerous fields like chemical, chlor-alkali, electric/electronic, optical, and construction industries.

1. Introduction

Nafion™ membranes (Fig.1) have been widely used in proton-exchange membrane fuel cells (PEMFCs), electrolyzers, flow batteries and many other electric devices [1,2]. In Nafion™, $-SO_3H$ serves as a cation-exchange group [2]. Nafion™ films are benchmark membranes produced by DuPont, which demonstrate chemical and thermal stability, as well as good proton conductivity at PEMFC operation temperatures around or below 80 °C [3].

Despite extensive R&D efforts, progress on the search of alternative cation-conductive fluoropolymer membranes has been limited. Fig. 1 lists some known proton-exchange membranes comprised of perfluorinated polymer backbones and side chains. Nafion™ CR contains a carboxylic acid functionality as the ion-exchange group. Nafion™ CR membranes are preferably employed in chlor-alkali cells as the carboxylate groups can severely hinder or eliminate the transport of hydroxyl anions—leading to the reduced alkali crossover and the enhanced performance of chlor-alkali cells. Perfluorosulfonamide-benzenesulfonic acid (**1**) [4] and perfluoroimide acid (**2**) [5] are the sulfonamide derivatives of PFSAs, many of which show good ionic conductivities. However, the presence of a sulfonamide group frequently renders these membranes too hygroscopic—leading to the lack of desired mechanic properties suitable for PEMFC operations [5]. In addition, the sulfonamide functionality is labile to acid or base-promoted hydrolysis—especially under high temperatures [6], which compromises the long-term chemical stability of sulfonamide-based Nafion™ derivatives—giving rise to the short durability of membranes. The DOE automobile fuel cell program has set up a goal of > 5,000 h for the membrane's life span [7].

In this paper, we report a novel approach for the synthesis of perfluorobenzoic acid (PFBA) and perfluorobenzenesulfonic acid (PFBSA) membranes via a free radical substitution reaction from perfluorosulfonyl iodide. Unlike perfluorosulfonamde-benzenesulfonic acid (**1**) and perfluoroimide acid (**2**) (Fig. 1), PFBA and PFBSA do not have a sulfonamide functionality. Instead, the benzoic acid and benzenesulfonic acid groups are grafted to the fluoropolymer side chains via covalent C–C bonds that are stable against hydrolytic degradations. The mechanic and electrochemical properties of PFBA and PFBSA membranes are examined and compared in this paper.

Abbreviations: PFBA, perfluorobenzoic acid; PFBSA, perfluorobenzenesulfonic acid; DMAc, N,N-dimethylacetamide; DMSO, dimethyl sulfoxide; TFA, trifluoroacetic acid; GC–MS, gas chromatography-mass spectrometry; TLC, thin layer chromatography

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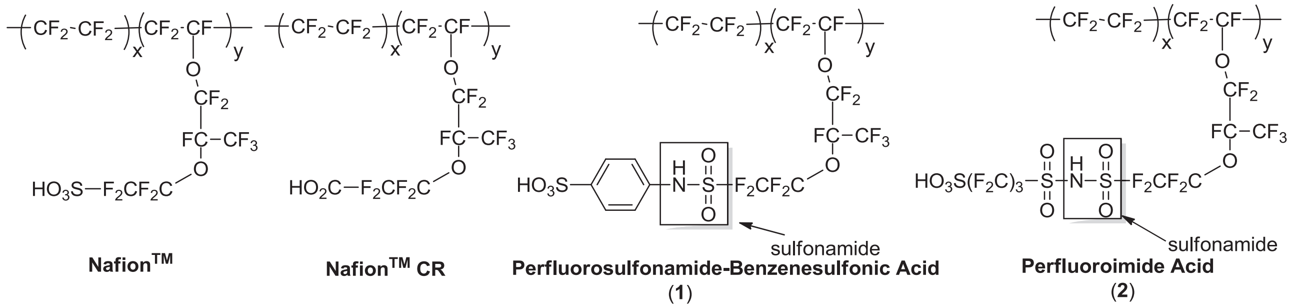

Fig. 1. The structures of known fluoropolymer-based cation-exchange membranes.

2. Experimental

2.1. Materials

Chemicals and organic solvents mentioned below were purchased from Sigma-Aldrich (Milwaukee, WI) or Acros Organics (Pittsburgh, PA) and used as received. Water was obtained from a Milli-Q water system purchased from Millipore Corporation (Milford, MA). The heavy metal and bacterial contaminant levels in Milli-Q water were below 10 parts per billion. The beads of Nafion™ were purchased from Ion Power, Sigma-Aldrich or Acros Organics. BT-112 Conductivity Cell from Scribner Associates (S. Pine, NC) was used for in-plane conductivity tests of membranes. CHI6112D Electrochemical Analyzer from CHI Instruments, Inc. (Austin, TX) and UBA5 Battery Analyzer from AA Battery Power Co. (Richmond, CA) were employed for analyzing the membrane and fuel cell performance. A 5 cm^2 fuel cell fixture was purchased from Scribner Associates. Elemental analysis of polymers was performed by Midwest Microlab, LLC (Indianapolis, IN).

2.2. Small molecule model reactions

To a mixture of pyridine (4 mmol), *t*-butyl hydroperoxide (2.4 mmol) and trifluoroacetic acid (2.4 mmol) in 8 mL acetone was added perfluorooctylsulfonyl halide (2.4 mmol). The reaction was carried out in a pressure bottle at 80 °C. After 12 h, the reaction was cooled down to ambient temperature and the solvent was removed *in vacuo*. Then, the product was isolated by flash chromatography (10% EtOAc/hexane) to obtain 2(4)-perfluorooctylpyridine. Sulfonyl fluoride led to ~45% yield while sulfonyl iodide gave rise to ~90% yield. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.80 (d, 1 H, H_d of the *ortho*-substituted pyridine), 8.60–8.45 (m, 2 H, H_X and $H_{X'}$ of the *para*-substituted), 7.75 (m, 1 H, H_b of the *ortho*-substituted), 7.67–7.57 (m, 2 H, H_a and H_c of the *ortho*-substituted), 7.15–7.05 (m, 2 H, H_Y and $H_{Y'}$ of the *para*-substituted). The molar ratio of the *para*- and *ortho*-substituted pyridine is 3.7:1. MALDI MS *m/z* 498.529 (100, $[M+1]^+$).

2.3. Membrane syntheses

2.3.1. Synthesis of the copolymer of tetrafluoroethylene and 4(2)-{1,1,2,2-tetrafluoro–2-[1,2,2-trifluoro–2-(1,2,2-trifluoroethenyloxy)–1-(trifluoromethyl)ethoxy]ethyl}-toluene (6)

To a mixture of polymer **3** (500 mg), *t*-butyl hydroperoxide (2.4 mmol) and trifluoroacetic acid (2.4 mmol) in 8 mL DMSO was added toluene (4 mmol). The reaction was carried out in a pressure bottle at 80 °C. After 12 h, the reaction was cooled down to ambient temperature and the solvent was removed *in vacuo*. Then, the polymer was washed by $CHCl_3$ (20 mL × 4). The polymer was further purified using a Soxhlet extractor with methanol for 48 h to remove non-bonded impurities to yield polymer **6** as a mixture of two isomers (472 mg): ^1H NMR (DMSO-d_6, 400 MHz) δ 8.20 (d, 2 H, H_X, $H_{X'}$ of the *para*-substituted, $J=10$ Hz), 8.00–7.90 (m, 1 H, H_a of the *ortho*-substituted), 7.80–7.68 (m, 1 H, H_b of the *ortho*-substituted), 7.68–7.60 (m, 1 H, H_d of the *ortho*-substituted), 7.45 (d, 2 H, H_A, $H_{A'}$ of the *para*-substituted), 7.29–7.14 (m, 1 H, H_c of the *ortho*-substituted), 2.71 (s, 3 H); IR (KBr pellet) 3098, 2819, 1639, 1475 cm^{-1}. Molar ratio of the *para*- and *ortho*-substituted is 6:4. Similar reactions employing water or acetic acid (8 mL) instead of DMSO as the solvent led to the reduced coupling yields (15–22%). Attempts to enhance the coupling efficiency by purging the reaction system with Ar gave rise to 478 mg of polymer **6** as a mixture of two isomers.

2.3.2. Synthesis of the copolymer of tetrafluoroethylene and 1,1,2,2-tetrafluoro–2-[1,2,2-trifluoro–2-(1,2,2-trifluoroethenyloxy)–1-(trifluoromethyl)ethoxy]ethyl-benzene (7)

The same procedure used for the synthesis of polymer **6** was adopted except that benzene (2.4 mmol) was employed instead of toluene. Polymer **7** was obtained as a solid (450 mg): ^1H NMR (DMSO-d_6, 400 MHz) δ 8.21–7.95 (br, 4 H, H_a, H_b), 7.64–7.55 (br, 1 H, H_c); IR (KBr pellet) 3090, 1652 cm^{-1}.

2.3.3. A general procedure for casting membranes

About 50–200 mg of a fluoropolymer was dissolved in DMAc 4 mL. The solution was poured to a 4.8 or 5.8 cm glass dish. The solvent was removed at 80 °C in a vacuum oven for 12 h followed by at 120 °C for two more hours. Water was added to help remove the membrane out of the dish.

2.3.4. Synthesis of the membrane of the copolymer of tetrafluoroethylene and 2(4)-{1,1,2,2-tetrafluoro–2-[1,2,2-trifluoro–2-(1,2,2-trifluoroethenyloxy)–1-(trifluoromethyl)ethoxy]ethyl}-benzoic acid (PFBA)

Membrane **6** (50 mg) was added to the mixture of cetyl trimethylammonium bromide (0.4 mmol) and KMnO4 (10 mmol) in 20 mL water. After 48 h at 50 °C, the membrane was removed and washed with 1 M HCl (20 mL × 3) and water (20 mL × 3). Then, the membrane was boiled in de-ionized water (20 mL) for 48 h to remove residues to yield membrane PFBA: ^1H NMR (DMSO-d_6, 400 MHz) δ 7.8–7.6 (br, 4 H, H_a, H_b); IR (KBr pellet) 3385, 1647, 1614, 1330, 1120, 984 cm^{-1}. UV–vis (1.6 wt% in CH_3CN): a major absorption peak at 265 nm. Caution: $KMnO_4$ is very corrosive. Care is needed when working with $KMnO_4$.

2.3.5. Synthesis of the membrane of the copolymer of tetrafluoroethylene and 2(4)-{1,1,2,2-tetrafluoro–2-[1,2,2-trifluoro–2-(1,2,2-trifluoroethenyloxy)–1-(trifluoromethyl)ethoxy]ethyl}-benzenesulfonic acid (PFBSA)

A membrane of **7** (~160 μm) was added to a solution of 30% $ClSO_3H$ and 70% fuming H_2SO_4. After at 120 °C for 48 h, the membrane was removed and washed with methanol and water until the water washing is neutral. Then, the membrane was boiled in de-ionized water for 1 h to remove the residual H_2SO_4. PFBSA