



Effects of non-planar hydrophobic cyclohexylidene moiety on the structure and stability of poly(arylene ether sulfone)s based anion exchange membranes



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ABSTRACT

Anion exchange membranes from cyclohexylidene moiety containing poly(arylene ether sulfone)s with N-methylimidazolium and 1,2-dimethylimidazolium pendant ionic groups were prepared. For comparison, bisphenol A moiety and biphenyl moiety containing AEMs with 1-methylimidazolium and 1,2-dimethylimidazolium pendant ionic groups were also prepared. The chemical structure of the polymers and corresponding AEMs obtained were characterized with ¹H NMR and FT-IR spectroscopies. The surface morphology and hydrophilic-hydrophobic phase separation of the AEMs were studied by SEM and AFM. The thermal and mechanical properties, ion exchange capacity, water uptake, swelling ratio, hydroxide conductivity as well as long-term alkaline stability of the AEMs were also intensively investigated. It was confirmed that AEMs having pendant ionic groups of 1,2-dimethylimidazolium were much stable than those having 1-methylimidazolium pendant ionic groups. Results also showed that the existence of the non-planar hydrophobic cyclohexylidene moiety in the AEMs backbone could not only create steric hindrance to facilitate dimensional and chemical stability, but also thwart the formation of large hydrophobic domains and provide additional free volume to facilitate water retention and ionic transportation. The hydroxide conductivity of cyclohexylidene moiety containing DIM-CHPAES AEM had a highest value of 90 mS cm⁻¹ at 80 °C, and degraded only 12.4% after soaked in 1 M NaOH solution for 35 days at 60 °C, bearing a high potential for practical applications in alkaline anion exchange membranes fuel cells.

1. Introduction

Recently, polymer electrolyte fuel cells (PEFCs) are recognized as one of the most promising energy conversion systems for stationary and automotive applications [1]. In the past decades, as one type of the PEFCs techniques, proton exchange membrane fuel cells (PEMFCs) have been greatly developed, however, their large-scale commercialization is still hampered by their high cost of production, mostly ascribing to the uses of expensive perfluorinated polymer-based proton exchange membranes (Nafion®) and noble metals (*Pt* catalyst) [2]. Alkaline anion exchange membrane fuel cells (AAEMFCs), which operated under alkaline media, had much faster electrode kinetics and in which costly noble metal catalysts could be replaced by earth-abundant transition metals (Ni, Co). This would significantly reduce the cost of fuel cell

devices [3,4].

As one of the core components of AAEMFCs, anion exchange membranes (AEMs) play a very important role. Currently, most AEM challenges are focused on improving their hydroxide conductivity and durability in alkaline environment [5,6]. Poly(arylene ether sulfone) (PAES)-based AEMs were among a great variety of AEMs materials reported previously [7–20]. Bulky cardo non-coplanar or asymmetric moieties, such as fluorene, phenolphthalein and phthalazinone [21–30], had been reported to create free volume inside PAES-based AEMs to facilitate the formation of ion transport channel [31]. We believed that cardo cyclohexylidene moiety may be a simpler candidate for providing fractional free volume in the membrane, however, the properties of the AEMs from polymer backbones containing cyclohexylidene moiety were not disclosed yet [32,33].

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Nomenclature

M_{wet}	mass of the dried membrane, g
M_{dry}	mass of the wet membrane, g
L_{wet}	length of the wet membrane, cm
W_{wet}	width of the wet membrane, cm
L_{dry}	length of the dry membrane, cm
W_{dry}	width of the dry membrane, cm
$M_{\text{H}_2\text{O}}$	molecular weight of water, g mol ⁻¹
V_{AgNO_3}	the volume of consumed AgNO ₃ solution, mL
C_{AgNO_3}	the concentration of AgNO ₃ solution, mol L ⁻¹

L	distance between the two electrodes, cm
A	the area of cross section, cm ²
R	membrane resistance, Ω
WU	water uptake, %
SR	swelling ratio, %

Greek letter

σ	ionic conductivity, S cm ⁻¹
λ	the average number of water molecules per ionic group

In this study, novel poly(arylene ether sulfone)s (PAES) AEMs containing non-planar cyclohexylidene moiety were prepared by copolymerization of 1,1-bis(4-hydroxyphenyl)-cyclohexane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl) propane and bis(4-fluorophenyl) sulfone. 1, 2-dimethylimidazolium (DIm⁻) and 1-methylimidazolium (Im⁻) pendant ionic groups were introduced by radical bromination and quaternization followed by hydroxide exchange process. Bisphenol A moiety and biphenyl moiety containing poly(arylene ether sulfone)s based AEMs were also prepared for comparisons. The characteristics of as-prepared membranes were intensively investigated and reported in this paper.

2. Experimental

2.1. Materials

Bis(4-fluorophenyl) sulfone (FPS) (99%, TCI, Japan), 1,1-bis(4-hydroxyphenyl)cyclohexane (HPCH) (98%, TCI, Japan), 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane (HDPP) (98%, Aladdin, China), anhydrous potassium carbonate (K₂CO₃) (99%, J & K, China), N-bromosuccinimide (NBS) (99%, Aldrich, American), benzoyl peroxide (BPO) (99%, J & K, China), tetramethylene sulfone (98%, J & K, China) and 1,2-dimethylimidazole (98%, Aladdin, China) were purchased and used without further purification. All of the other chemicals were purchased from Sinopharm Chemical Reagent Co. and also used without further purification.

2.2. Preparation of anion exchange membranes

2.2.1. Synthesis of cyclohexylidene moiety containing poly(arylene ether sulfone) (CHPAES)

The typical procedure for the synthesis of CHPAES as follows. Firstly, a 100 mL three-necked round bottom flask, equipped with a Dean-Stark trap, a mechanic stirrer, a condenser and a gas inlet and outlet, was charged with HPCH (2.1460 g, 8.0 mmol), FPS (4.0680 g, 16 mmol), HDPP (2.2751 g, 8.0 mmol) and potassium carbonate (5.528 g, 40 mmol). The polymerization reaction was carried out in 20 mL toluene and 16 mL tetramethylene sulfone. Then, heating the mixture to 150 °C and kept for 2 h under N₂ flow to remove the water in the system. Afterwards, the temperature was increased to 210 °C for another 2 h to yield a viscous brown mixture. Finally, the mixture was poured into 300 mL of methanol aqueous (methanol/deionized water=1/1) to produce an off-white crude product resin. The as-prepared copolymer CHPAES (which CH refers to cyclohexylidene moiety contained polymer) was washed by methanol and deionized water for several times, and then dried under vacuum oven at 80 °C for 24 h.

(The synthetic routes of bisphenol A containing PAES and biphenyl containing PSF copolymer were similar with CHPAES copolymer, respectively).

2.2.2. Bromination of CHPAES

A typical procedure for the radical substitution bromination reaction of CHPAES as follows. Firstly, 1.0 g CHPAES and 20 mL TCE were added into a dry 100 mL three-necked round bottomed flask and heated to 80 °C under N₂ flow. Then, 1.27 g (7.13 mmol) NBS and 0.086 g (0.36 mmol) BPO were added to the reaction solution after the polymer completely dissolved, in which NBS and benzoyl peroxide acted as the bromination agent and initiator, respectively. The reaction was kept at 80 °C for 6 h, then cooled to room temperature and poured it into a flask with 300 mL of methanol solution to get a white fibrous precipitate. The brominated product BCHPAES (which B refers to brominated polymer) was collected by filtration and dried in vacuum oven at 70 °C overnight.

2.2.3. Quaternization, membrane preparation and anion exchange process

The typical quaternization of BCHPAES was as follows. 1.0 g BCHPAES and 10.0 g DMAc were placed into a 100 mL of round bottom flask to form a 9 wt% solution. 200 mg of 1,2-dimethylimidazole was added to the solution after BCHPAES was completely dissolved. Heating the temperature to 50 °C and kept for 24 h. And then, we casted the mixture onto a clean and smooth glass plate at 60 °C for 24 h to produce the Br⁻ form AEMs. Finally, the membrane was soaked into 1 M NaOH aqueous at room temperature for 48 h to obtain the desired DIm-CHPAES membrane in OH⁻ form, in which DIm refers to 1,2-dimethylimidazolium functionalized membrane. The DIm-CHPAES membrane displayed tough and ductile yellow-colored transparent. The as-prepared membrane was washed with deionized water and kept in it before use. In addition, the procedure for the preparation of 1-methylimidazolium functionalized membrane was similar with DIm-CHPAES, and the membrane was named as Im-CHPAES, in which Im refers to 1-methylimidazolium functionalization. Similar routes to Im-CHPAES and DIm-CHPAES were taken for the synthesis and preparation of DIm-PAES, Im-PAES, Im-PSF and DIm-PSF.

2.3. Characterization of membranes

2.3.1. GPC measurement

The molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the prepared polymer resins were investigated by PL-GPC 220 equipped with refractive index (RI) detector and Agilent 1260 Infinity pump. CHCl₃ was used as the eluent with a flow rate of 1.0 mL min⁻¹ at 40 °C. Standard polystyrene samples were selected as calibration agent.

2.3.2. ¹H NMR and FT-IR spectroscopy

The chemical structure of the prepared resins, bromide products and membranes were confirmed using ¹H NMR spectra and FT-IR spectra. ¹H NMR spectra was tested on Bruker-400 spectrometer, using DMSO-d₆ or CDCl₃ as the deuterated solvent. FT-IR spectra of the samples were recorded on Thermo-Nicolet 6700 spectrometer in

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