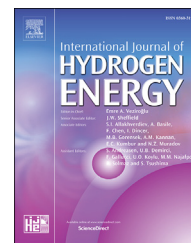


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# Imidazolium functionalized block copolymer anion exchange membrane with enhanced hydroxide conductivity and alkaline stability via tailoring side chains

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## ABSTRACT

To develop polymer electrolyte membrane with both high hydroxide conductivity and good alkaline stability, series of poly(arylene ether sulfone)s block copolymers bearing varied imidazolium functionalized aromatic pendants are synthesized, and the relationship between ionic pendants and the membrane properties are investigated and discussed. Atomic force microscopy (AFM) results suggest that, the well-controlled block copolymers and pendent aromatic chain structures are responsible for the formation of the well-defined microphase-separated morphology which is benefit to construct highly conductive ionic transport channels in membrane. The membranes tethering longer imidazolium functionalized aromatic pendants (Im-DFDM-bPES) exhibit large hydroxide conductivity than those bearing shorter ones (Im-DFDB-bPES) in spite of their comparable IEC values, this is in accordance with their sizes of hydrophilic domains in membrane. Among the membranes, Im-DFDM-bPES-x7y32 with IEC of 1.30 mequiv g<sup>-1</sup> gives the highest hydroxide conductivity (34.2 and 98.7 mS cm<sup>-1</sup> at 25 and 80 °C, respectively). Besides, both Im-DFDM-bPES and Im-DFDB-bPES membranes exhibit high alkaline stability after aging under severe conditions (4 M NaOH at 80 °C) for 144 h, where the aged Im-DFDM-bPES and Im-DFDB-bPES give hydroxide conductivity remaining by 74.8%–77.2% and 64.5%–66.4%, mechanical properties with maximum stress of 47.36–51.30 MPa and 60.03–62.28 MPa, respectively, indicating good chemical stability of both imidazolium moiety and block copolymer backbone.

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## Introduction

Polymer electrolyte fuel cells are one of promising clean power sources due to high efficiency and low pollution,

where proton exchange membrane (PEM) fuel cells (PEMFCs) have attracted extensive attention [1]. Although high performance can be arrived for PEMFCs, precious metal-based catalysts such as platinum used for acidic operating

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conditions impede their further commercial applications. Anion exchange membrane (AEM) fuel cells (AEMFCs) can allow nonprecious metal-based catalysts (e.g. silver, cobalt, nickel) instead of precious metal-based ones, and thus attract enormous attention in recent decades [2]. As a key component of AEMFC, AEM can transport hydroxide ions and prevent fuel crossover. For AEMFC applications, AEMs should possess high hydroxide conductivity and good alkaline stability. However, two challenges encumber the development of the AEMs, one is low ionic mobility of hydroxide ions (43% lower than that of protons), the other is poor stability of AEMs in alkaline condition [3,4]. To improve the performance, many kinds of copolymers are chosen for constructing AEMs because of their good chemical resistance, such as poly(phenylene oxide) [5–7], poly(arylene ether) [8–11], poly(phenylene) [12,13], meanwhile, several ionic functional moieties are utilized as anion groups, including quaternary ammonium [14,15], imidazolium [16,17], phosphonium [18] and guanidinium moieties [19].

So far, many strategies have been developed to achieve high hydroxide conductivity and acceptable good alkaline stability for the AEMs, such as semi-flexible copolymer ionomer [8], microporous copolymer ionomer [20], partially fluorinated copolymer ionomer [21], multiblock copolymer ionomer [22,23], and side-chain copolymer ionomer [24]. McKeown, Guiver and Xu et al. reported that microporous copolymer ionomer based AEM with a low ion exchange capacity (IEC) of  $0.82 \text{ mequiv g}^{-1}$  gave high hydroxide ion conductivity ( $164.4 \text{ mS cm}^{-1}$  at  $80^\circ\text{C}$ ), which suggests that the intrinsic microporosity of the charged copolymer matrix facilitates the ionic transportation [20]. Miyatake et al. reported that partially fluorinated and quaternized aromatic copolymer displayed hydroxide conductivity of  $152 \text{ mS cm}^{-1}$  in water at  $80^\circ\text{C}$  with enhanced alkaline stability, this is attributed to nanometer-scale phase-separated morphology based on the hydrophilic/hydrophobic differences in the copolymer components [21]. Yan et al. reported that semi-flexible poly(aryl ether sulfone) containing a flexible aliphatic chain in the polymer backbone with imidazolium cationic group showed high hydroxide conductivity ( $93 \text{ mS cm}^{-1}$  at  $60^\circ\text{C}$ ), this is considered that the introduction of the flexible aliphatic chain into the rigid aromatic polymer main-chain increases the mobility of polymer chain and thus contributes to a better hydrophilic/hydrophobic microphase separation structure [8]. Bae et al. reported that multiblock copolymer based AEM with a trifluoromethyl moiety exhibited chloride ion conductivity of  $60 \text{ mS cm}^{-1}$  at 100% RH and  $70^\circ\text{C}$ , this is ascribed to its clear hydrophilic/hydrophobic phase separation derived from block copolymer structures [22]. Generally, side-chain type or multiblock copolymer based AEMs display improved hydroxide conductivity, because they facilitate the construction of microphase separation and ion transport channel [23,24].

Recently, our group has developed series of side-chain type poly(arylene ether sulfone) ionomer based AEMs, the membranes showed reasonably high hydroxide conductivity of  $61.5 \text{ mS cm}^{-1}$  at  $80^\circ\text{C}$  and good alkaline stability [25]. The possible reason is that the large hydrophilic side-chain facilitates the formation of hydrophobic/hydrophilic phase separation, and thus enhances the transport of the hydrated hydroxide ions. To further improve the performance of

AEMs, the combination of block and side-chain structure is an attractive method to achieve high hydroxide conductivity and good alkaline stability because of possible distinct microphase separation. Some side-chain block copolymers have been developed, including multiblock copoly(arylene ether)s with long alkyl tethers for ionic head-groups [10], poly(phenylene-co-arylene ether ketone) bearing aromatic pendent ionic groups [13], side-chain block poly(styrene) caring pendent quaternary ammonium [15], whereas the reported methods generally adopt a alkyl or short aromatic pendent ionic groups.

Based on above consideration, two series of block poly(arylene ether sulfone) copolymers were prepared, where imidazolium groups were tethered to the aromatic side chains with different lengths. The corresponding membranes were obtained, and their properties including hydroxide conductivity, water absorption, membrane swelling, methanol permeability, and alkaline stability were studied. Compared to the AEMs bearing short imidazolium functionalized aromatic side chains, the membranes carrying longer ones are expected to give higher hydroxide conductivity and membrane stability.

## Experimental

### Materials

5-(2,6-Difluorobenzyl)-1,3-dimethylbenzene (DFDB) and 2,6-difluorophenyl [3-[(3,5-dimethyl phenyl) methyl]-5-methylphenyl] methanone (DFDM) were synthesized according to our reported method [25,26]. 4,4'-Difluorodiphenyl sulfone (DFDPS) was obtained from Zhejiang Shouerfu Chemical Co. Ltd. 4,4'-Biphenol (BP) was purchased from Aladdin Reagent and sublimated for purification before use. *N,N*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) was used after dehydration with  $4 \text{ \AA}$  molecular sieve. Other solvents and reagents were obtained from Sinopharm Chemical Reagent and used as received.

### Synthesis of DFDB-PE-OHy and DFDM-PE-OHy

The hydroxyl-terminated poly(arylene ether) hydrophilic oligomers DFDB-PE-OHy and DFDM-PE-OHy was synthesized according to the procedure shown in Fig. s1a in the supplementary information. As an example, DFDB-PE-OHy with theoretical oligomer length ( $y$ ) of 20 was described as follows. BP (0.5580 g, 2.997 mmol), DFDB (0.7028 g, 2.854 mmol), anhydrous potassium carbonate (0.4969 g, 3.596 mmol), 6.3 mL of DMSO and 6.3 mL of toluene were added to a dried 100 mL three-necked flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet. The mixture was stirred and heated to  $140^\circ\text{C}$  for 4 h under nitrogen flow, and then slowly heated to  $170^\circ\text{C}$  to remove the azeotrope of toluene and the produced water, and kept for another 4 h. After reaction, the resulting oligomer solution was poured into water to obtain crude product. The precipitate (DFDB-PE-OH20) was washed several times with water and methanol, respectively, and then dried at  $100^\circ\text{C}$  in vacuum for 24 h.

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