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Phenolate anion-based branched/cross-linked poly (arylene ether sulfone) hydroxide exchange membranes

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ABSTRACT

Novel phenolate anion-based branched/cross-linked anion exchange membranes (AEMs) are synthesized via the quaternization reaction between poly (arylene ether sulfone) containing side-chain benzyl groups and 2,4,6-Tris(dimethylaminomethyl)phenol. The branched/cross-linked AEMs show much higher performance than the corresponding uncross-linked membrane (Q) because of branched/cross-linked structure and phenolate anion-based antioxidant structure in membrane. Among the branched/cross-linked AEMs, CQ15 with IEC of 1.25 mequiv.g⁻¹ shows a reasonably high hydroxide conductivity of 32 mS cm⁻¹ at 80 °C, low P_M of 0.41 × 10⁻⁷ cm² s⁻¹, large φ of 39 × 10⁴ Scm⁻³s, and display above three times of oxidative stability than Q. Meanwhile, CQ15 exhibits long-term stability against alkali treatment at 60 °C for 216 h with small reduction in hydroxide conductivity by only 16%, and also remains stable in 4 mol L⁻¹ NaOH solution at 80 °C for 132 h with low reduction in hydroxide conductivity by 20%, indicating high potential application for anion exchange membrane fuel cell.

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Introduction

Fuel cells are energy generation devices that can provide clean energy for transportation, stationary and portable power applications with high efficiency and low pollution, among kinds of fuel cells, polymer electrolyte membrane (PEM) fuel cells (PEMFCs) are one of the most promising technologies [1,2]. As

one of most widely used commercially PEMs, DuPont's Nafion membranes have high proton conductivity and excellent chemical stability, but they display large fuel crossover, high cost and environmental unfriendly [3]. Besides, PEMFCs require precious metal-based catalysts such as platinum to catalyze both the cathodic and the anodic reactions [4]. Compared with PEMFCs, anion exchange membrane (AEM) fuel cells (AEMFCs) are becoming a hot research field, because

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they have several potential advantages, such as allowing non-precious metals and exhibiting fast oxygen reduction kinetics [5–8].

In AEMFCs, AEM acts as an anion conductor for transporting hydroxide ions and prevents fuel crossover between anode and cathode. For AEMFC applications, AEMs require high hydroxide conductivity, low swelling degree, and high chemical stability [9–11]. Generally, high hydroxide conductivity can be obtained via increasing ion exchange capacity (IEC) of the membrane [12], as well as using block or side-chain type copolymer with better microphase separation [13,14]. The dimensional stability and chemical stability of AEMs can be effectively improved via favorable copolymer chain structures [15], stable cation structures [16], self-aggregation strategy [13,17–19], and kinds of cross-linking methods [20–22].

In recent years, many polymers are developed as AEMs, such as poly(phenylene oxide) (PPO) [16,23,24], polystyrene (PS) [25,26], and poly(arylene ether sulfone) (PAES) [27–29], whereas different polymer structures have sharply different long-term stability in hot alkali solution. Hickner's group has investigated the stability of quaternary ammonium-functionalized AEMs with different polymer backbone structures, the results show that PAES-based membrane displays the poorest long-term stability in 0.6 mol L⁻¹ KOD solution at 80 °C, which is attributed to the electron-withdrawing sulfone group in polymer backbone structure [30]. Further research show that imidazolium-functionalized poly(fluorenyl ether ketone sulfone)s (PFEKS) are comparable or even less stable than quaternary ammonium-functionalized PFEKS [31]. These results indicate that it is a great challenge for AEMs containing sulfone moiety in polymer backbone to achieve AEMFC applications. Recently, Li et al. [32] reported that side-chain type PAES-based AEM not only displayed high hydroxide conductivity, but also exhibited high long-term stability in hot alkali solution, which was attributed to the side-chain induced microphase separation and side-chain related electron effect. This gives the researchers an inspiration to further investigate PAES-based AEMs with cation groups in side-chain. Furthermore, several typical cross-linked AEMs bearing pendant tertiary ammonium groups have been developed, and most of them exhibit good stability and high hydroxide conductivity [33–42].

However, some functional groups (such as bromomethyl groups, providing cationic sites) are consumed via convenient self-cross-linking method, which is harmful to improve hydroxide conductivity because of IEC decreasing. To avoid sacrificing bromomethyl groups during cross-linking reaction, cross-linkers such as diamine 1,4-diazabicyclo [2,2,2]octane (DABCO) and N,N,N',N'-Tetramethyl-1,6 -diaminohexane (TMHDA) have been used to construct the cross-linked structures, where every cross-link creates a hydroxide conductive group [43–48]. There are also other cross-linking methodologies for preparing AEMs without IEC decreasing, such as ring-opening metathesis polymerization [12,49,50].

Here, a novel cross-linker named as 2,4,6-Tris(dimethylaminomethyl)phenol (TAP), generally acting as curing catalyst for epoxy resin, possesses three dimethylamino methyl groups in phenol structure, is used to prepared cross-linked AEMs.

Where three dimethylamino methyl groups can act as effective cross-linking group with no sacrifice of hydroxide conductive group, meanwhile phenol structure can act as efficient radical scavenger to enhance the oxidative stability of the corresponding cross-linked AEMs. Series of AEMs containing branched/cross-linked structure, the aromatic side-chain quaternary ammonium groups and phenolic antioxidant structure are prepared via the quaterization reaction between PAES and TAP (Fig. 1). They are expected to have high performances according to the following considerations. The branched/cross-linked structure can suppress the membrane dimensional changes and enhance methanol resistance. The aromatic side-chain ion groups can help to enhance the hydroxide conductivity because of the side-chain induced microphase separation, as well as to improve chemical stability via avoiding Hofmann elimination of quaternary ammonium groups like the aliphatic side-chain. The phenolic antioxidant structure [51] can ensure the membrane excellent oxidative stability via consuming peroxide radical. The obtained branched/cross-linked membranes CQ10 and CQ15 show excellent dimensional stability, methanol resistance and oxidative stability, as well as outstanding long-term stability in hot alkali solution with keeping relative high hydroxide conductivity and mechanical properties, compared with the uncross-linked membrane Q.

Experimental part

Materials

4,4'-Biphenol (BP, Aladdin-reagent Co., China) and 4,4'-difluorodiphenyl sulfone (DFDPS, Zhejiang Shouferu Chemical Co., China) were used after vacuum sublimation. Dimethyl sulfoxide (DMSO) was dehydrated with 4 Å molecular sieve prior to use. The other reagents were purchased from Aladdin-reagent Co. or Sinopharm Chemical Reagent Co. and used as received. 5-(2,6-Difluorobenzyl)-1,3 -dimethylbenzene (DFDB) was prepared via the nucleophilic addition of 3,5-dimethylphenyl-magnesium bromide to 2, 6-difluorobenzonitrile.

Preparation of copolymer

PAES bearing two pendant methyl groups is synthesized by polycondensation in DMSO, where feed ratio of BP, DFDPS and DFDB is fixed to BP/DFDPS/DFDB of 5/1/4. Bromomethylated copolymer (PAES-Br) is obtained via bromomethylation of PAES using N-bromosuccinimide (NBS) as bromination reagent and 2,2'-azobis(2-Methylpropionitrile) (AIBN) as initiator. The synthetic process is described as follows: 2.0 g of PAES was dissolved in 40 mL of dichloroethane under nitrogen flow with stirring. Then 2.88 g of NBS (16.2 mmol) and 0.16 g of AIBN were added to the homogeneous solution, and the reaction mixture was heated to 60 °C and kept at this temperature for 24 h with stirring. After cooling to room temperature, the resulting solution was slowly poured into acetone. The obtained precipitate was dried below 40 °C in vacuum for 24 h after thoroughly washing with acetone.

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