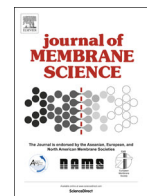Contents lists available at ScienceDirect

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High performance anion exchange membranes obtained through graft architecture and rational cross-linking

Jin Ran, Liang Wu, Qianqian Ge, Yaoyao Chen, Tongwen Xu *

CAS Key Laboratory of Soft Matter Chemistry, Lab of Functional Membranes, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

The graft copolymers poly(phenylene oxide)-g-quaternary 4-vinylbenzyl chloride (PPO-g-Q) with varied graft ratios ranging from 72% to 115% were synthesized according to the previous work. The resulting membranes displayed high hydroxide conductivity, while other fuel cell related properties are not so excellent. To enhance dimensional, thermal and alkaline stability of the PPO-g-Q anion exchange membranes (AEMs), brominated poly(phenylene oxide) (Br-PPO) possessing the identical compositions with the hydrophobic backbone of the graft copolymers, was used as a macromolecular cross-linker to form cross-linked networks in the hydrophobic domains. The simultaneous improvements of conductivity and stability were achieved with the combination of unique graft architecture and rationally designed cross-linking. Among these AEMs, Cr-PPO-g-Q115 presented a high hydroxide conductivity of 128 mS/cm at 90 $^\circ$C, a low dimensional swelling of 6.0%, and a dramatically improved thermal and alkaline stability compared with the uncross-linked membranes. The outstanding properties indicated the promising application of Cr-PPO-g-Q in fuel cells.

1. Introduction

Anion exchange membranes (AEMs) are a new class of materials which have been widely utilized in various electrochemical energy generation and storage devices [1–3]. Among them, fuel cells have attracted considerable attention due to their high efficiency, high energy density and quiet operation [4,5]. Nevertheless, the development of alkaline anion exchange membrane fuel cells (AEMFCs) has become a hot topic due to the enhanced kinetics for both the fuel oxidation and oxygen reduction in an alkaline environment [6]. Thus, as one of the key components of AEMFCs, AEMs have also become a hot area of research.

For AEMFCs applications, AEMs usually should possess high hydroxide conductivity, low swelling degree, and high chemical stability [7,8]. In general, AEMs require high ion exchange capacity (IEC) to attain high water uptake and considerable hydroxide conductivity [9]. However, the high water uptake leads to severe swelling, or even a disintegration of the AEM at elevated temperature. One of the promising approaches to overcome these drawbacks is to form cross-linked polymer networks, which not only suppresses excess

dimensional swelling and fuel crossover, but also enhances the mechanical and chemical stability [10–12].

As an effective method, cross-linking proton exchange membranes (PEMs) have been extensively investigated [13,14]. More recently, cross-linking technique has also been a proper strategy to improve the performances of AEMs [15,16]. Zhuang et al. have prepared the cross-linked quaternary ammonia polysulfone through replacing a part of quaternary ammonium groups with a tertiary amino group [17]. The resulting AEMs displayed extraordinary stability and durability in water particularly at high temperature. Na and co-workers have successfully introduced benzyl bromide groups onto poly(ether sulphone) and then employed these functional sites for producing cross-linked structure as well as quaternary ammonium hydroxide moieties [18]. However, research on the covalent cross-linked AEMs is still in the initial stage, and suffers from a crucial shortcoming of improving stability at the expense of sacrificing hydroxide ion conductivity. The reason is that some functional groups such as bromomethyl and chloromethyl groups, which originally can provide cationic sites, are consumed during the cross-linking reactions. Consequently, the final IEC values of these AEMs are low (usually below 1 mmol/g), which restricts the development of ion conduction domains and leads to low hydroxide conductivity [19]. On the other hand, firm cross-linked networks prevent the water molecules from entering into the interior of the membrane, thus

resulting in lack of sufficient medium for ion transport [20]. Undesirably, cross-linking might impede the formation of inter-connected ion conduction pathways, which are essential for guaranteeing the smooth passage of ions through the membrane [21]. Therefore, getting rid of the conductivity-stability dilemma remains a significant challenge.

Our previous study has reported a novel AEM derived from a graft copolymer with hydrophobic backbone and hydrophilic graft chains. The advanced architecture promotes the development of well-defined phase separation morphologies and thus high hydroxide conductivity [22,23]. However, excess water uptake and chemical instability are severe constraints for the practical applications of the graft copolymer AEMs. In an effort to disentangle the conductivity-stability dilemma for AEMs, we propose a unique strategy that the AEMs with graft structure will be endowed with cross-linked networks. The key point is that the main chain of the graft copolymer can be used as the macromolecular cross-linker. This cross-linking will not decrease the numbers of functional groups and thus high IEC can be expected. Another promising advantage of this strategy is that cross-linking will not alter the well-developed phase aggregation morphology, because the polymer cross-linkers tend to get into the hydrophobic regions. This point is attributed to the identical components between the cross-linker and the main chain of the graft copolymer. Consequently, high hydroxide conductivity and stability can be achieved, simultaneously.

Herein, we chose brominated poly(phenylene oxide) (Br-PPO) as the starting material. The graft copolymers were synthesized using Br-PPO as the macro-initiator via atom transfer radical polymerization (ATRP) reaction. For this reaction, the desirable number of ionic groups, namely, the quaternary ammonium groups can be gained by easily adjusting the added monomer amounts. Then, Br-PPO served as a macromolecular cross-linker through a Friedel–Crafts reaction between the bromomethyl groups and aromatic rings without any catalysts [24]. The cross-linked AEMs' properties, such as hydroxide conductivity, swelling ratio, thermal and alkaline stability, were evaluated. The results showed that this method of cross-linking was effective for further research of AEMs.

2. Experimental

2.1. Materials

Brominated poly(phenylene oxide) (Br-PPO) was kindly provided by Tianwei Membrane Corporation Ltd. (Shandong, China). The commercial Br-PPO was purified by dissolving in NMP, precipitating in methanol, and drying at 40 °C. ^{1}H NMR indicates 57.8% bromobenzyl (¢-CH$_2$Br) and 42.2% aryl bromide (¢-Br) per repeat unit. 4-Vinylbenzyl chloride (98%) (VBC), which was purchased from Changzhou Wujin Linchuan Chemical Co., Ltd., was purified by inhibitor remover process.

Quaternary ammonium functionalized 4-vinylbenzyl chloride (QVBC) was prepared according to the prior literature [22]. Copper (II) bromide (CuBr$_2$, AR), ascorbic acid (AsAc, AR), 2,2′-bipyridyl (bpy, AR), N-methyl-2-pyrrolidolone (NMP, AR), dimethylsulphoxide (DMSO, AR), ethanol (AR), acetone (AR), diethyl ether anhydrous (AR), sodium chloride (AR), sodium hydroxide(NaOH, AR) and sodium sulphate (AR) were purchased from Sinopham Chemical Reagent Co., Ltd. All these reagents were used as received without further purification. Deionized water was used throughout.

2.2. Synthesis of PPO-g-Q copolymer via ATRP

Br-PPO (1.0 g) and a controlled amount of QVBC were dissolved in NMP (40 mL) at 60 °C in a dried 100 mL three-neck round bottom flask equipped with a magnetic stirring bar. After dissolving completely, the mixture was degassed by N$_2$ bubbling for an hour. In a dried sealed tube, CuBr$_2$ (0.0075 g) and bpy (0.0106 g), AsAc (0.0591 g) were added, and then the mixture solution was added into the sealed tube quickly. Three freeze-pump-thaw cycles were performed to remove oxygen. After the tube was flame-sealed under vacuum, it was stirred in a 120 °C pre-heated oil bath for 24 h. The polymerization reaction was stopped by cooling and exposure to air. The final PPO-g-Q copolymers were obtained by depositing into diethyl ether anhydrous. The QVBC monomers were removed by washing repeatedly with ethanol. The resulting copolymers were dried under vacuum at 60 °C for 24 h.

2.3. Preparation of cross-linked membranes and anion exchange

The PPO-g-Q copolymers were dissolved in DMSO to form a casting solution of about 10 wt% and then the cross-linker, Br-PPO (5 wt%) dissolved in NMP were added. The solution cast on a clean glass plate was dried at 60 °C for 1 day. For cross-linking the membranes, additional thermal treatment was performed in an oven at 100 °C for 2 h. The obtained membranes are termed as Cr-PPO-g-Q.

Then the OH$^-$ form membranes were obtained by treating the cross-linked membranes in 1 mol/L NaOH at room temperature for 24 h; they were washed thoroughly and immersed in deionized water for 48 h to remove residual NaOH. The resulting membranes were characterized immediately.

2.4. Characterization

2.4.1. Characterizations of polymers
The chemical structures of the materials used in this study and products were identified by ^{1}H NMR (DMX 300 NMR spectrometer operating at 300 MHZ). FT-IR spectra were recorded on thin membrane samples using a Thermo Scientific Nicolet IS10 spectrometer.

2.4.2. Differential scanning calorimetry (DSC)
Differential scanning calorimetry (DSC, TA Q2000, USA) was used for determining the cross-linking temperature and time of PPO-g-Q. DSC measurements were conducted three times in the temperature range from 25 °C to 160 °C with a heat flow rate of 10 °C/min. In addition, the degree of cross-linking at cross-linking temperatures of PPO-g-Q was observed by DSC. The cross-linking temperature of 100 °C was selected and the heat flow was observed by isothermal curing temperature for the cross-linking reaction. The degree of cross-linking (CL, given in %) was determined as $CL = (H_t/H_T) \times 100$, where H_t is the total heat flow of sample mass for a given cross-linking time t and H_T is the total heat flow of sample mass for a cross-linking time of 120 min.

2.4.3. Water uptake, swelling ratio, ion exchange capacity, and hydroxide conductivity
A sample of membrane (4 cm in length and 1 cm in width) was immersed in deionized water at a given temperature for 24 h. After this hydration step, the sample was removed from the water, the surfaces wiped with tissue paper (to remove excess surface water) and the mass and length were quickly measured. The water uptake (WU) of membranes was calculated as follows:

$$Wu = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \tag{1}$$

where W_{wet} is the hydrated mass and W_{dry} the mass of the sample when dehydrated (recorded after the membranes were dried until a constant weight at 60 °C).