



Quaternized triblock polymer anion exchange membranes with enhanced alkaline stability



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ABSTRACT

Alkaline stability is the critical issue for the practical application of anion exchange membranes (AEMs) in fuel cells. The benzyltrimethyl ammonium and backbone with C-O linkages of the traditional AEMs are susceptible to attack by hydroxide ions resulting in poor alkaline stability of the AEMs. Herein, we present the preparation of polystyrene-*b*-poly(ethylene-co-butylene)-*b*-polystyrene (SEBS) triblock copolymer via grafting, ketone reduction and quaternization for AEM fuel cell applications. The quaternary ammonium (QA) groups are attached to the SEBS backbone free of C-O linkages via long flexible alkyl spacers, which are responsible for the robust alkaline stability of the AEMs. Thus, the hydroxide conductivity of SEBS-CH₂-QA-1.5 was only decreased by 7.7% and 13.7% after immersing the membranes into a 1 M aqueous KOH solution at 60 and 90 °C for 360 h, respectively. Furthermore, SEBS-CH₂-QA-1.5 with IEC of 1.23 meq g⁻¹ exhibits a maximum hydroxide conductivity of 56.4 mS cm⁻¹ at 80 °C and a maximum power density of 94.6 mW cm⁻² under a current density of 300 mA cm⁻².

1. Introduction

The development of high-efficient electrochemical energy conversion/storage devices, such as fuel cells, redox flow batteries, reverse electrodialysis cells [1], has attracted considerable attention over the past decades. Of those, alkaline fuel cells (AFCs) are regarded to be more promising energy conversion devices for potential applications in mobile and stationary devices than proton exchange membranes (PEMs) fuel cells because of the faster oxygen reduction kinetic under alkaline condition. This permits the use of non-previous-metal electrocatalysts and reduces the cost of fuel cell devices [2,3]. Anion exchange membranes (AEMs), as one of the critical component of AFCs, are considered to be the ion conductor and separator between two electrodes. Desirable AEMs should possess high-efficient ion conducting channels, robust mechanical properties and good chemical stability under high pH condition. Although great efforts have been devoted to developing high performance AEMs, two major obstacles that severely hamper practical AFCs application are lower conductivity and alkaline stability of AEMs than those of PEMs.

The transport mechanism of OH⁻ in AEMs is similar to that of H⁺ conduction in PEMs [1]. There are three possible transport mechanisms in the membranes: Grotthuss mechanism, diffusion & migration and convection. The ionic conductivity of the AEMs is directly pertinent to

the ionic exchange capacity (IEC) and mobility of hydroxide ions [4,5]. In pursuit of AEMs with enhanced conductivity, increasing IEC is considered to be a common method for achieving sufficient ion conducting moieties, however, this often results in an excess of water uptake and significant swelling. Some works have been focused on improving ionic mobility by preparing block copolymer AEMs with microphase separated morphology because the ionic mobility can be enhanced remarkably by the formation of high-efficient ion conducting channels created by phase separation.

To date, AEMs based on various types of cationic groups, such as quaternary ammonium (QA) [6–8], imidazolium [9–11], guanidinium [12,13] and phosphonium [14,15], have been widely investigated. Of those cationic groups, QA group is the most commonly used cationic group. Recently, Akiyama et al. [16] reported a series of quaternized block copolymer AEMs that showed a high hydroxide conductivity of 130 mS cm⁻¹ at 80 °C (IEC = 2.47 meq g⁻¹) due to their well-developed hydrophilic/hydrophobic phase separated morphology. Nevertheless, about 28% of the QA groups lost after immersing in a 1 M aqueous KOH solution at 60 °C for 1000 h. This is attributed to the unstable benzyl-trimethyl ammonium (BTMA) that the QA groups are vulnerable to disintegrate under alkaline condition due to the displacement of the QA groups by hydroxide ions via direct nucleophilic substitution [2,17,18]. To solve this problem, methods including

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Nomenclature			
A	cross sectional area of the membranes, cm^2	R	the resistance of the membrane, $\text{k}\Omega$
IEC	ionic exchange capacity, meq g^{-1}	SR	swelling ratio, %
L_{wet}	length of wet membranes, cm	WU	water uptake, %
L_{dry}	length of dry membranes, cm		
m_{dry}	the weight of the dry membrane, g		
m_{wet}	the weight of the wet membrane, g		
		<i>Greek letter</i>	
		σ	ionic conductivity, mS cm^{-1}
		λ	hydration number

designing comb-shaped structure [17,19] or extending flexible spacers between the QA groups and backbone are proposed since the steric hindrance effect is effective at preventing nucleophilic attack from hydroxide ions [20,21]. For example, Li et al. [2,17] noted that the alkaline stability of comb-shaped quaternized poly(phenylene oxide) (PPO) AEMs was greatly enhanced by grafting long alkyl chains of 6–16 carbon atoms onto the QA groups. Dang et al. [20] reported quaternized PPO AEMs with cationic groups attached to the backbone via long flexible alkyl spacers. The conductivity and alkaline stability of the AEMs were greatly improved over the membranes bearing BTMA.

Although the methods mentioned above are beneficial to improving the alkaline tolerance of QA groups, the alkaline stability of backbone is another important issue. So far, poly(ether sulfone)s [22,23], poly(ether ether ketone)s [24,25], PPO [26,27], poly(phenylene)s [28], etc. have been widely used for the preparation of AEMs via introducing ionic groups into the backbone. Unfortunately, the backbone bearing C-O linkages often undergoes cleavage via the attack of hydroxide ions when the cationic groups are adjacent to the backbone [29]. Arges et al. [30] used 2D NMR techniques to investigate the degradation of backbone and discovered that QA groups trigger the degradation of polysulfone backbone in alkaline condition via ether hydrolysis. Furthermore, Amel et al. [31] observed that the sulfone linkages had a profound negative influence on the stability of backbone for AEMs. More recently, we have also found that the backbone of poly(ether sulfone)s-based AEMs degraded slightly under alkaline condition [32] even though the electron-withdrawing QA groups were linked to the backbone via long flexible spacers. As noted by Choe et al. [33], who investigated the stability of the AEMs by computational modeling and experimental study, an ether-free backbone, such as poly(phenylene)s, remained stable while backbone bearing aryl-ether bonds degraded heavily under similar alkaline treatment. This provided design rules for AEMs with high-stability.

In order to combine the superiority of phase separation of a block copolymer structure and improved stability of cationic groups introduced by attaching QA groups to the backbone via flexible alkyl spacers, quaternized polystyrene-*b*-poly(ethylene-co-butylene)-*b*-polystyrene (SEBS) AEMs were prepared in this work. Triblock copolymer SEBS is chosen as the matrix for preparing AEMs since the polystyrene end blocks can aggregate into spherical domains [34] which seems to be critical for fabricating hydrophilic/hydrophobic phase separated morphology after quaternization modification in polystyrene segment. The cationic groups are linked to the backbone via a long flexible alkyl spacer. This is beneficial to improving the local mobility of ionic groups and weakening the electron-withdrawing effect of cationic groups on the backbone. Additionally, free of C-O linkages or sulfone linkages, SEBS has high alkaline tolerance. Herein, SEBS-based AEMs were prepared via Friedel-Crafts acylation, ketone reduction and quaternization. AEMs with different IECs were prepared by controlling the grafting degree of the polymers. Small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were used to investigate the phase separated morphology of the AEMs. The properties of the membranes, such as hydroxide conductivity, water uptake, swelling, mechanical properties, thermal stability and alkaline stability of the AEMs, were evaluated in detail.

2. Experimental section

2.1. Materials

SEBS powder (the molar content of styrene is 29%) with an average M_w of 118 kDa was bought from Sigma-Aldrich CO. Ltd. 6-Bromohexanoyl chloride (BHC) (97%) and triethylsilane (TES) (98%) were purchased from Tokyo Chemical Industry Co. Ltd and used without further purification. Aluminum chloride (AlCl_3) (AR) and trifluoroacetic acid (TFA) (99%) were obtained from Aladdin Chemistry Co. Ltd. Tin chloride (SnCl_4) (99%) and chloromethyl ethyl ether (95%) were bought from Shandong Xiya Chemical Industry Co. Ltd. (China). All other chemicals were supplied from Sinopharm Chemical Reagent Co. Ltd. and used without further treatment.

2.2. Preparation of anion exchange membranes

2.2.1. Synthesis of SEBS-CO-Br- x

The synthesis of SEBS-CO-Br- x ($x = 0.5, 0.75, 1.0$ and 1.5) is based on a slight modification of the method described by Hibbs [28], where x is the molar ratio of BHC to styrene. Taking SEBS-CO-1 as an example, SEBS (5 g) was dissolved in 200 mL of dichloromethane in a round bottom flask. Once the SEBS was completely dissolved, 2.1 mL of BHC and 1.85 g of AlCl_3 (Lewis acid catalyst) were added and the mixture was reacted at room temperature (RT) for 4 h. Subsequently, the mixture was poured into 1 L of methanol to precipitate the product. The products were washed with methanol for three times and dried under vacuum at 60°C for 24 h to obtain a white solid product.

2.2.2. Synthesis of SEBS- CH_2 -Br- x

The reduction of the ketone group in SEBS-CO-Br- x was carried out as follows. 2.0 g of SEBS-CO-Br-1.0 (0.40 mmol ketone group) was dissolved in 50 mL of 1,2-dichloroethane to form a solution in a round bottom flask equipped with a magnetic stirrer and a condenser at RT. 4.6 g of trifluoroacetic acid (40 mmol) and 0.46 g of triethylsilane (4 mmol) were added into the solution. The reaction mixture was heated to 100°C and kept reacting for 24 h, and then poured into a 0.01 M NaOH solution to precipitate the polymers. The resulting solid was filtered, washed with deionized (DI) water/methanol and then vacuum dried at 60°C for 24 h.

2.2.3. Membrane fabrication and quaternization

Membranes were prepared from the SEBS- CH_2 -Br- x solution (5 wt %) using chloroform as the solvent. The solution was filtered and poured into PTFE plates to evaporate the solvent slowly over a period of 48 h. The resulting membranes with a thickness of 50–60 μm were peeled off and immersed into a trimethylamine solution (30 wt%) at RT for 48 h to give quaternized membranes. The membranes were washed repeatedly with DI water to remove excess trimethylamine and soaked in a 1 M aqueous KOH solution for 48 h to make the OH^- form membranes. The membranes were washed with degassed DI water to remove residual KOH and immersed into DI water for 24 h before measurements.

Herein, quaternized SEBS bearing benzyltrimethylammonium group (SEBS-BTMA) was synthesized for comparison. The route for synthesis

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