



Self-crosslinking of comb-shaped polystyrene anion exchange membranes for alkaline fuel cell application



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ABSTRACT

A series of crosslinked, comb-shaped polystyrene (PS) anion exchange membranes (AEMs) having C-16 alkyl side chain were synthesized by a Cu(I)-catalyzed “click chemistry” reaction, and subsequently azide-assisted self-crosslinking for alkaline fuel cell application. The as-obtained crosslinked AEMs showed lower water uptake, and thus good dimensional stability as a result of crosslinking. The chemical stabilities of the AEMs were evaluated under severe conditions, and minor degradation was observed by measuring IEC and ion conductivity changes after stability testing. The crosslinked membranes retained their high ion conductivity even in 10 M NaOH at 80 °C for 400 h. Moreover, the PS-based AEMs shown higher hydroxide conductivity than that of the AEMs based on poly(2,6-dimethyl-phenylene oxide) (PPO) with similar architecture under the same testing condition probably due to the excellent compatibility between polystyrene backbone and alkyl side chain which may have helped to build a more efficient morphology for water uptake and thus the ion transport. These crosslinked cationic polymers were employed as membranes for alkaline fuel cells. The results indicated that the AEMs based on PPO having C-16 alkyl side chain had not initial performance, e.g. no open circuit voltage (OCV). In contrast, the initial fuel cell performance with the peak power density of 88 mW/cm² was observed for the alkaline fuel cell with xPS-65 membrane. It is assumed that the polystyrene polymer backbone may have helped to build a more efficient phase boundary between the catalyst layer and membrane probably resulted from the high water uptake though a more complete study would be needed to explain this phenomenon.

1. Introduction

Relative to acidic fuel cells, anion exchange membrane fuel cells (AEMFCs) have received significant interest in recent years due to the enhancement of electrode reaction kinetics, using of the non-noble metals or inexpensive metal oxides catalysts [1–3]. As a critical component of AEMFCs, the polymers with tethered organic cations generally have been demonstrated as anion exchange membranes (AEMs). The basic properties of ionic conductivity and chemical stability of AEMs control the performance and lifetime of AEMFCs. Various polymer backbone structures such as poly(olefins) [4,5], polystyrenes [6–8], poly(phenylene oxide)s [9,10], poly(phenylene)s [11], poly(arylene ether)s [12–17] have been chloroalkylated or bromoalkylated and subsequently quaternized by tertiary amine, pentamethylguanidine, or tertiary phosphine to obtain anion conductive copolymers having quaternary ammonium [10], guanidinium [16], or phosphonium groups [18].

The ionic conductivity of a AEM is related to a combination of the ion exchange capacity (IEC), its hydration level, and the micro-

phase separated morphology of the membrane [3]. Generally, high IEC values induce high ionic conductivity; however, increasing the IEC is always accompanied by consequent significant increase in water uptake which can lead to significant dimensional swelling, loss of mechanical properties [19,20], or even disintegration of the AEM, especially at elevated temperatures. Several approaches have been examined to improve anion conductivity, such as changes in the position of quaternary ammonium groups [21–23], control of membrane morphologies by block [24], grafting [25] or comb-shaped [10] copolymer architectures, and crosslinking of the high IEC membranes [26–30], displaying a wide range of conductivities. For example, AEMs aminated from bromoalkyl with long alkyl chains (six carbon atoms or more) have been proven to be highly hydroxide conductive, but higher water uptake was observed than AEMs based on benzyltrimethylamine [21]. Sequenced hydrophilic and hydrophobic groups as block and grafting copolymers were also claimed to be effective for this purpose by formation of nanochannel [23,24]. However, research on this class of copolymers is still in the initial stages, and the precise control of nanoscale morphology of multiblock or grafting copolymers is often

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restricted due to the polydispersity of each block. In addition to the morphology controlling, the covalent crosslinking has been reported as an effective method to stabilize high IEC AEMs against high water swelling. For example, the multifunctional groups of dithiol [27], dialdehyde [28], tri/tetraalkoxysilanes [29], and tetraepoxy [30] have been widely used for AEM crosslinking. Thermal self-crosslinking and simultaneous polymerization-crosslinking has also been developed to reduce swelling and to prepare high-performance AEMs due to their controllability [26,31].

Another critical challenge for practical application of AEMs in alkaline fuel cells is the chemical stability of AEMs under alkaline conditions [3,20]. Excellent alkaline resistance above 80 °C of AEMs has been believed to be highly required because of the possibility of diminishing the CO₂ solubility in water above 80 °C, which could prevent the formation of carbonate or bicarbonate in AEMs [3,20]. Moreover, the kinetics of electrochemical reactions will be enhanced when the fuel cell operated at elevated temperature. In general, the instability of AEMs resulted from the polymer backbone session and the degradation of organic cations. Fluorinated polymer backbone such as PVDF and its derivatives, which showed relatively high chemical and physical stabilities, have been reported to be easily degraded in a high-pH environment [20]. The poly (arylene ether sulfone)s backbone have also been confirmed to be degraded by the cleavage of C–O bonds [32]. Additionally, the well known degradation pathways of organic cation are beta-hydrogen (Hofmann or E2) elimination, direct nucleophilic substitution (SN2), and ylide formation at high pH conditions [3,20]. Thus, the stability of other organic cations under alkaline condition, such as benzimidazolium [33], morpholinium [34], pyridinium [35], pyrrolidinium [36], metal organic frameworks [37], ruthenium [38], tetrakis(dialkylamino)phosphonium [39], and N- or/and C2-substituted imidazoliums [40] have been investigated widely to overcome the disadvantages of using the ubiquitous benzyltrimethylammonium (BTMA). Marino and Kreuer [41] recently described a class of quaternary spiroammonium compounds that exhibited improved alkaline stability as compared to the acyclic counter. Coates and coworkers [40] found that the substituent identity at each position of the imidazolium ring has a dramatic enhancement of alkaline stability. Therefore, efficient anion transport combined with alkaline-resistant cationic groups and polymer backbones are critical criteria in the design of advanced AEM materials.

Most recently, we have developed a series of comb-shaped poly(2,6-dimethylphenylene oxide) (PPO) AEMs which displayed improved anion conductivities, substantial alkaline stability, and advantageous properties for incorporation as catalyst ionomers in fuel cell devices [42]. The formed comb-shaped structures by introducing one long alkyl chain of up to 16 carbon atoms pendant to the cationic center induced microphase separation, and thus enhanced the ionic conductivities of these membranes. The long alkyl side chain has also been confirmed to be effective for improving the alkaline stability as a result of the reducing of nucleophilic attack by water or hydroxide at the quaternary ammonium (QA) moieties. However, poor mechanical properties of membranes were observed for high degree of functionalization (> 40%) probably owing to the poor compatibility between alkyl side chain and PPO backbone. Herein, we therefore employed the polystyrene backbone to develop a new system that would support high IEC values and thus high hydroxide conductivity, while retaining other good material properties, including hydroxide stability. It is believed that the polymer backbone of polyolefin would be more compatible with alkyl chains than the polyaromatics. Importantly, the polystyrene backbone has been proven to be favorable for alkaline resistance of benzyltrimethylamine (BTMA) groups in AEMs according to Hickner and coworkers' reports [43]. Combined with controllable Cu(I)-catalyzed “click chemistry” and azide-assisted self-crosslinking techniques, the crosslinked and comb-shaped polystyrene AEMs were prepared readily. A detailed investigation on the properties of these PS AEMs was performed. Their ionic conductivities, microphase-separated structure,

and alkaline stability and initial H₂/O₂ fuel cell performance are described and compared to those of crosslinked comb-shaped PPO AEMs.

2. Experimental section

2.1. Materials

4-Vinylbenzyl chloride (VBC, 90%) (Sigma-Aldrich) was washed with 5% NaOH solution for the removal of polymerization inhibitor. 2,2'-azobis-isobutyronitrile (AIBN), N,N-dimethylhexadecylamine, propargyl and other reagents were obtained from Energy and used as received. Alkyne-terminated quaternary ammonium having one alkyl side chain (16 carbon atoms) were synthesized according to our previous reports [44].

2.2. Synthesis of poly(4-vinylbenzyl chloride) (PVBC) homopolymer

Typically, a mixture of monomer VBC (5 mL, 35 mmol) and AIBN (0.029 g, 0.175 mmol) was added to a glass tube. After degassing with Ar gas, the reaction was carried out at 65 °C. After 4 h, the mixture was precipitated into excess methanol to yield a white solid. The polymer was purified by dissolving with THF and reprecipitating in methanol. The white product was dried under vacuum at 50 °C overnight with the yield of 73%.

2.3. The synthesis of crosslinkable cPS-x copolymers

The copolymers were synthesized by alkyne-azide “click chemistry” in NMP. A typical experiment of cPS-50 synthesis is as follows: To a 3-necked flask equipped with a magnetic stirring bar, PS-N₃ (4.7 g, 100 mmol), Alkyne-terminated quaternary ammonium having one alkyl side chain bromide salt (1.94 g, 50 mmol), ligand (PMDETA, 10 mmol), CuBr catalyst (5 mmol) were dissolved in 5 mL of NMP. The flask was degassed by three freeze-pump-thaw cycles, left under vacuum, and placed in a thermostated oil bath at 50 °C for 12 h. The reaction mixture was precipitated into water and then the product was washed with water three times. The crosslinkable comb-shaped copolymer cPS-50 (where the 50 refers to the degree of functionalization groups) was obtained after drying in vacuum at 80 °C for 24 h.

2.4. Membrane preparation, evaluation of crosslinking efficiency and ion exchange

The membranes (thickness ~70 μm) having crosslinkable azide groups were prepared by solution casting in NMP at 75 °C. Subsequently, the crosslinking of membranes was carried out in a vacuum oven at 135 °C for 18 h. The gel fraction was employed to determine the degree of crosslinking of the membranes, and was obtained by subjecting the membranes to NMP at 80 °C for 24 h under argon to effect removal of the soluble polymer fraction. The gel fraction value was calculated from the residual mass of the sample by the equation: gel fraction = (Wd/Wi)*100%, where Wi is the initial weight of dried membranes and Wd is the weight of the dried insoluble fraction of membranes after extraction. The crosslinked AEMs xPS-x in the hydroxide form (x Alkyne-terminated quaternary ammonium having one alkyl side chain, thus the degree of crosslinkable sites is 100-x) were obtained by ion exchange with 1 M NaOH solution at room temperature for 48 h.

2.5. Characterization and measurements

¹H NMR spectra were measured at 400 MHz on a Bruker AV 400 spectrometer using CDCl₃ or DMSO-*d*₆ as the solvent. The membranes in the bromide form were immersed in 100 mL of 0.1 M NaNO₃ standard for 24 h. The solutions were then titrated with a standardized

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