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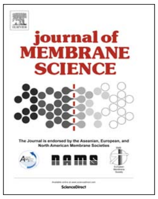

A novel strategy to construct highly conductive and stabilized anionic channels by fluorocarbon grafted polymers

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ABSTRACT

In contrast to typical grafted anion exchange membranes (AEMs), a novel graft type AEM owning flurocarbon side chains and quaternized ammonium aromatic backbone was developed by a controlled atom transfer radical polymerization (ATRP) reaction. The experimental results revealed this kind of structure facilitated the formation of robust and long connective ion transport channels. Thus, the resulting AEM (IEC = 1.35 mmol/g) exhibited a relatively high hydroxide conductivity of 44 mS/cm, although its water uptake was below 30% (at 30 °C). Simultaneously, this AEM also displayed fascinating mechanical strength and alkaline stability. A H_2/O_2 fuel cell test using incorporated fluorocarbon grafted AEMs yielded a peak power density of 85 mW/cm^2 at a current density of 150 mA/cm^2; this will be improved on development of a chemical compatible fluorine-based alkaline ionomer as ionic polymer binder in the electrodes' catalyst layers.

1. Introduction

Currently, there is increasing demands for developing clean energy technology worldwide to resolve the environment pollution issues caused by using conventional fossil fuels [1]. Fuel cells have emerged as environmentally benign energy generators that can extract the energy stored in chemical fuels [2]. Among them, proton exchange membrane fuel cells (PEMFC) were intensively investigated over the last decades, and great achievements on the power density and long-term stability issues have been made [2]. However, the widespread commercialization of PEMFCs is hindered by the lack of fuel flexibility and especially, by the exclusive dependence on noble and exhausted Pt catalysts [3]. Alkaline anion exchange membrane fuel cells (AAEMFC) are promising alternatives to PEMFCs, because AAEMFCs combine the significant advantages of much faster oxygen reduction kinetics operating under highly alkaline conditions, and the allowed usage of less expensive non-precious metal catalysts (e.g. Ni, Fe and Co metals). More importantly, the alkaline conditions enable more efficient water management and a broader choice of fuels [4].

Despite of such attractive features, the practical applications of AAEMFCs have far lagged because there are quite large gaps in terms of the conductivity and stability issues between proton exchange membranes (PEM) for PEMFCs and anion exchange membranes (AEM) for AAEMFCs. Typically, the mobility coefficient of OH^- ions is only half that of H^+ ions in infinitely dilute aqueous solutions at room temperature, resulting from the low hydroxide conductivity of AEMs [5]. Increasing the number of anion exchange groups (namely, ion exchange capacity (IEC)) for AEMs seems to be the most straightforward route to elevate hydroxide conductivity [6]. Nevertheless, the introduction of considerable ionic groups will bring about challenges in maintaining acceptable dimensional and alkaline stabilities for AEMs [7]. Hence, it is essential to search for other available strategies to promote OH^- mobility conductivity for AEMs, rather than solely relying on increasing ionic group concentration [8].

Clustering ionic groups to form connective ion transfer channels for ions transport is a well-established finding in pursing high ion conductivity [9]. With the rapid progresses in macromolecular nano-science and nano-technology, a variety of polymeric membranes with advanced architectures hold great potential in enhancing micro-phase separation between hydrophobic matrices and hydrophilic functional groups [10]. Particularly, AEMs composed of block and graft copolymers generally exhibit higher hydroxide conductivity compared to random copolymers, because well-defined hydrophobic/hydrophilic phase separation morphologies with perforative ionic channels are broadly observed in the formers [11].

Watanabe and co-workers reported that a multi-block poly(arylene ether) copolymer with alternatively sequenced hydrophobic and hydrophilic components gave considerably high hydroxide conductivity

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with 144 mS/cm at 80 °C (IEC = 1.93 mmol/g) [12]. Unfortunately, the water uptake (WU) of this membrane was extremely high (> 100% at room temperature), leading to mechanical failure in practical applications. In view of this, our group revealed that graft type AEMs having hydrophobic main chains and hydrophilic side chains could reach a comparable hydroxide conductivity with much lower WU [13,14]. This is mainly because hydrophilic grafted chains could aggregate with high efficiency to produce hydroxide ion transport channels. Even so, the channels dependence of aliphatic hydrophilic chains in grafted AEMs are subjected to water swelling and alkaline permeation. On the other hand, relatively short grafted chains in relation to main chains are unfavorable of establishing long connective channels, and thus the improvement of hydroxide conductivity is limited.

In this paper, alternative graft type AEMs owning flurocarbon side chains (hydrophobic grafted chains) and quaternized ammonium aromatic backbone (hydrophilic main chains) are developed through a reverse thinking. Strikingly enhanced phase separation can be expected from the high electronegativity fluorine moieties, similar to that in Nafion. The hydroxide transporting channels originate from aggregated rigid aromatic backbone rather than soft aliphatic grafted chains are likely to be more ordered in long-range for promoting conductivity and more robust in surpassing the excessive swelling as well as improving alkaline stability by limiting the permeation of water molecules.

2. Experimental section

2.1. Materials

Brominated poly(phenyleneoxide) (BPPO) was kindly provided by Tianwei Membrane Corporation Ltd. (Shandong, China). The commercial Br-PPO was purified by dissolving in NMP, precipitating in purified water, and drying at 40 °C. ^{1}H NMR (Fig. S1 in the Supporting information) indicates 63.5% bromobenzyl (¢-CH_2Br) per repeat unit. 4-fluorostyrene (95%) (FPS), which was purchased from Energy Chemical Co., Ltd., was purified by inhibitor remover. Copper(II) bromide ($CuBr_2$, AR), ascorbic acid (AsAc, AR), 2,2′-bipyridyl (bpy, AR), N-methyl-2-pyrrolidolone (NMP, AR), Dimethyl sulfoxide (DMSO, AR), trimethylamine (TMA) aqueous solution (33.3%, AR), potassium hydroxide (KOH , AR), sodium chloride (AR), sodium hydroxide (NaOH, AR), sodium sulfate (Na_2SO_4, AR), silver nitrate ($AgNO_3$), potassium iodide (KI), potassium chromate (K_2CrO_4) 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 BPPO-graft-FPS (B-g-F) copolymers

BPPO (1.0 g) and FPS (0.5 g or 1.5 g) were dissolved in 40 mL NMP at room temperature in a dried 100 mL three-neck round bottom flask equipped with a magnetic stirring stick. After dissolving completely, the mixture was degassed by N_2 bubbling for an hour. In a dried sealed tube, $CuBr_2$ (0.0112 g), bpy (0.0160 g), and AsAc (0.0886 g) were added in sequence, and then the mixture solution was added quickly into the sealed tube. Three freeze-pump-thaw cycles were carefully performed to remove soluble oxygen. After the tube was flame-sealed under vacuum, it was stirred in a 110 °C pre-heated oil bath for 24 h. The polymerization reaction was terminated by cooling and exposure to air. The final copolymers were obtained by deposition into water. The unreacted FPS monomers were removed by washing thoroughly with acetone. The resulting copolymers were dried under vacuum at 60 °C for 24 h. The resulting copolymer was denoted as 1.0 B-*g*-F0.5 and 1.0 B-*g*-F1.5. The 0.5 B-*g*-F0.2 and 0.5 B-*g*-F1.0 copolymers were synthesized by this identical process. Only changes lie in the added amounts of monomers and catalysts. For the 0.5 B-*g*-F0.2 and 0.5 B-*g*-F1.0 synthesis, FPS (0.2 g or 1.0 g), $CuBr_2$ (0.0056 g), bpy (0.0080 g), and AsAc (0.0443 g) were added.

2.3. Synthesis of quaternized BPPO-graft-FPS (QB-g-F)

The B-*g*-Q copolymers were dissolved in DMSO at 60 °C to form a solution of 5 wt%. Afterwards, the solution was filtered using non-woven fabrics to remove undissolved polymers. The homogeneous solution was further treated by dry TMA gases. Dry TMA gases were produced by dropwise added TMA solutions into KOH solids. For guaranteeing the complete conversion of -CH_2Br groups, the functionalization process was performed for 3 h. The membranes were denoted as m QB-*g*-Fn. The first number corresponds the amounts of catalysts, and the last number corresponds the amount of fluorocarbon monomers.

2.4. Membrane preparation and anion exchange

The above solutions were cast onto a leveled glass plate, and dried at 60 °C for 24 h to get the membranes. Then the OH^- form membranes were obtained by treating the 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.

Quaternary ammonium functionalized brominated poly(phenylene oxide) (QPPO) was prepared as follows: BPPO was immersed in excess aqueous TMA (1 mol/L) solution for 12 h at 25 °C to allow the partial conversion of -CH_2Br to quaternary ammonium groups.

2.5. Measurements

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). FTIR spectra of membranes were obtained on a ATR-IR spectrometer (Vector 22, Bruker) with a wave number resolution of 2 cm^{-1}.

2.5.1. Water uptake

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} is the mass of the sample when dehydrated (recorded after the membranes were dried at 60 °C until a constant weight was reached).

Dimensional swelling of the membranes in water was investigated by immersing samples (1 cm in width and 4 cm in length) into water at room temperature for 24 h, the changes were calculated from:

$$\Delta l = (L - L_s)/L_s \tag{2}$$

where L_s and L are the length of the membrane at dry state and wet state, respectively.

2.5.2. IEC

The ion exchange capacity (IEC) was measured using the Mohr method. Firstly, the membranes were converted into Cl^- form by immersing them into aqueous NaCl (1 mol/L) solution for 24 h. The membranes (in Cl^-) were washed with deionized water and dried at 80 °C under vacuum for 24 h before the masses were recorded. The membranes were then converted into the SO_4^{2-} form by immersion in aqueous Na_2SO_4 (0.5 mol/L) solution for 8 h. The Cl^- ions, released from the membranes, were then titrated with aqueous $AgNO_3$ (0.1 mol/L) aqueous solution using K_2CrO_4 as a colorimetric indicator. The IECs (expressed as mmol/g), were calculated from the amount of $AgNO_3$ (1:1