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Anionic quaternary ammonium fluorinated copolymers bearing thermo-responsive grafts for fuel cells

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ABSTRACT

Fluorinated copolymers are synthesized by grafting quaternary ammonium-functionalized 4-vinylbenzyl chloride (QVBC) and N-Isopropyl acrylamide (NIPAAM) from poly(vinylidene fluoride) (PVDF) via atom transfer radical polymerization (ATRP). Ionic QVBC and thermo-responsive PNIPAAM grafts are characterized by proton nuclear magnetic resonance (¹H NMR) spectroscopy. Polarity difference between flexible grafts and rigid fluorinated backbones allows convenient formation of ionic clusters, which impart resultant membranes excellent hydroxide conductivities in the range of 21–52 mS cm⁻¹ at 20 °C, and up to 98 mS cm⁻¹ at 70 °C. Moreover, amide–amide interactions between thermo-responsive grafts at high temperature can mitigate water swelling of hydrophilic clusters. This study suggests that the fluorinated copolymer bearing both ionic and thermo-responsive grafts holds a promising selectivity as novel materials for anion exchange membrane with enhanced hydroxide conductivity and controlled water swelling.

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Introduction

Polymer electrolyte fuel cells (PEFCs) have received great attention for decades due to the advantage of providing clean, renewable energy for stationary, automotive and mobile electronic devices [1,2]. Research on the development of alkaline polymer electrolyte fuel cells (APEFCs) containing alkaline anion exchange membranes (AAEMs) are currently increased to a significant level for efficient kinetic of oxygen

reduction and extensive options for cathode catalysts based on abundant transition metals [3,4].

As a critical component in APEFCs, AEM separates fuels, conducts hydroxide ions and maintains a high pH condition in the membrane electrode assembly (MEA). To date, most of studies on AEMs involve different functional anion-exchange head-groups. They usually were prepared by introducing quaternized ammonium [5–8], phosphonium [9–13], guanidinium [14–16] or heterocyclic ammonium groups [17–21] into halomethylated polymers by Menshutkin reaction. Although

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some of them demonstrate promising progress for AEMs in recent years, they still show much lower conductivity than perfluorosulfonated proton exchange membranes (PEMs), such as Nafion[®] (80 mS cm⁻¹, 20 °C), due to the inherently lower mobility of hydroxyl ions than protons and less ordered self-assembly morphologies. It is reported that Nafion[®] membranes consist of hydrophobic polytetrafluoroethylene (PTFE) backbones and hydrophilic pendent perfluoroether side-chains terminated with sulfonic acid groups. Ionic clusters derived from the aggregation of ionic side chains connect each other to form continuous ionic transport channels [22–24]. Inspired by the molecular architecture of Nafion[®], more efforts have been devoted to develop ionic side-chain type AEMs with distributed pendent functional groups. Guiver et al. reported similar pendent bis(phenyl-trimethylammonium) based AEMs, which exhibited hydroxide conductivities above 10 mS cm⁻¹ at room temperature [25]. To further improve their performance, grafting AEMs with highly ionized side chains are under development. Our previous work has grafted quaternary ammonium-functionalized 4-vinylbenzyl chloride onto PVDF backbones to prepare ionic grafting AEMs [26]. Experimental results suggest that increasing the ionic density of side chains can significantly enhance the polarity difference between hydrophobic backbones and hydrophilic side-chains, finally resulting in facial formation of ionic clusters. Their hydroxide conductivities reach up to 45 mS cm⁻¹ at 30 °C. However, a high ionic density generally results in excessive water uptake and dimensional swelling in water, which are drawbacks for fuel cell. Therefore, conductivity improvements and water swelling control are both required in the area of side-chain type AEMs.

Generally speaking, covalently cross-linking, which typically use small molecules with two or more cross-linking sites, has been widely employed to restrain water swelling. However, covalently cross-linked membranes, in which polymer backbones are tightly crosslinked, tend to be poor in conductivity due to the difficulty in ionic clusters formation. Herein, we are trying to control swelling without sacrificing conductivity by the H-bonding crosslinking of ionic clusters, other than the crosslinking of polymer backbones. To achieve this aim, we firstly graft poly(N-isopropylacrylamide) (PNIPAAm), which is a well-known thermo-responsive polymer with a low critical solution temperature (LCST) at about 32 °C in an aqueous solution, onto an ionic copolymer. Thermo-responsive PNIPAAm and ionic PQVBC are possible to aggregate together to form ionic clusters. At the temperature over LCST, water H-bonded to NIPAAm grafts will be extruded from ionic clusters due to newly formed hydrophobic amide–amide interactions. Hence, the unique phase transition of thermo-responsive PNIPAAm grafts are expected to mitigate water swelling of hydrophilic clusters, while the hydrophilic ionic grafts maintaining the conductivity.

Experimental

Materials

PVDF powder was purchased from Shanghai 3F New Materials Co., Ltd. 4-Vinylbenzyl chloride (98%) (VBC), which was

purchased from Changzhou Wujin Linchuan Chemical Co., Ltd., was purified by inhibitor remover. N-Isopropyl acrylamide (NIPAAm) was purchased from TCI. Copper(I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and washed with pure ethanol. N,N,N,N,N-Pentamethyldiethylenetriamine (PMDETA) was obtained from Energy Chemical Co., Ltd. N,N-dimethylformamide (DMF, AR), dimethylsulfoxide (DMSO, AR), ethanol (AR), acetone (AR), trimethylamine (TMA) aqueous solution (33.3%, AR) and sodium chloride (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received without further purification. Deionized water was used throughout.

Synthesis of quaternary ammonium-functionalized 4-vinylbenzyl chloride (QVBC)

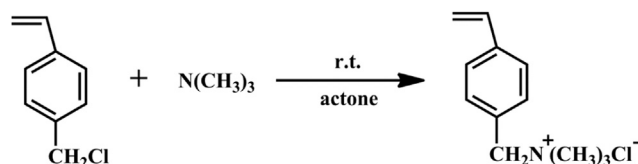
QVBC was synthesized according to our previous work [26]. The reaction is outlined in Scheme 1. The typical synthesis procedure is as follows; a solution of trimethylamine (0.620 mol) in acetone (123.9 ml) was added into a dried 250 ml three-neck round bottom flask equipped with a mechanical stirring device. VBC (30 ml, 0.211 mol) was then added dropwise while stirring at the ambient temperature. After stirring for 10 h to ensure complete reaction, the reaction mixture was filtrated. The obtained white precipitate powder was washed with acetone three times and dried under vacuum at 30 °C overnight.

Synthesis of PVDF-g-NIPAAm copolymers

Typical synthesis of PVDF-g-NIPAAm is shown in Scheme 2. PVDF powder (3 g) was added into a three-neck round bottom flask containing 24 ml DMF solution at 80 °C. After cooling down, NIPAAm (7.34 g) was added into the solution. The mixed solution was stirred at room temperature and degassed by N₂ bubbling for 1 h, then transferred into a sealed tube with 0.336 g CuBr and 480 μl PMDETA. Three freeze–pump–thaw cycles were carried out to remove oxygen. After being flame-sealed under vacuum, the tube was stirred in a preheated oil bath at 65 °C for 48 h. The polymerization was stopped by cooling and exposure to air. The product was obtained by depositing in a saturated sodium chloride solution and dried under vacuum at 30 °C for 24 h.

Synthesis of (PVDF-g-NIPAAm)-g-QVBC copolymers and membrane preparation

Typical synthesis of (PVDF-g-NIPAAm)-g-QVBC is shown in Scheme 2. PVDF-g-NIPAAm powder (0.3 g) and a controlled amount of QVBC were dissolved in DMF (12 ml) at 60 °C in a



Scheme 1 – Synthesis of QVBC.

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