



# Anion exchange membranes based on carbazole-containing polyolefin for direct methanol fuel cells



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## ABSTRACT

A series of anion exchange membranes was prepared from the copolymer of 1-vinyl imidazole and N-vinyl carbazole for direct methanol fuel cells (DMFCs). The structure of the membranes was studied using  $^1\text{H}$  NMR, scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and small angle X-ray scattering (SAXS). The thermal stability of the membranes was characterized by thermo-gravimetric analysis (TGA). The ion conductivity, methanol permeability, ionic exchange capacity (IEC), water uptake, swelling ratio, and alkaline stability of the membranes were investigated. It is found that the ion conductivity of the membranes varied from  $9.34 \times 10^{-2}$  to  $20.28 \times 10^{-2} \text{ S cm}^{-1}$  in deionized (DI) water and the methanol permeability varied from  $4.5 \times 10^{-8}$  to  $12.3 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  at  $30^\circ\text{C}$ . All the as-prepared membranes are stable in a 1.0 M KOH solution at  $60^\circ\text{C}$  for 1400 h due to the polyolefin backbone. A methanol/ $\text{O}_2$  single cell evaluation exhibited an open circuit voltage of 0.93 V and peak power density of  $125.8 \text{ mW cm}^{-2}$ . Therefore, the as-prepared membranes have great potential for application in alkaline fuel cells.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs), a kind of green efficient energy conversion device, have attracted great interests for stationary and mobile applications over the past two decades due to their high energy-conversion efficiency, high power density, and quiet operation [1–4]. As a key component of PEMFCs, proton exchange membranes (PEMs) can transport protons and serve as a barrier to separate the oxidant streams and fuels [5]. Unfortunately, a wide application of the commercial PEMs such as Nafion<sup>®</sup> from DuPont is impeded due to some obstacles, such as exclusive dependence on noble platinum-based electrocatalysts, slow oxygen reduction kinetics and complex water management [6–8]. Therefore, alkaline anion exchange membrane fuel cells (AEMFCs) with enhanced oxygen reduction kinetics and the potential use of non-noble metals as catalysts, in which the charge carriers are hydroxide ions instead of protons, are attracting growing interest [9].

Anion exchange membranes (AEMs), one of the key components of AEMFCs, play an important role in preventing electrolyte leakage and conducting anions. For this reason, significant

researches have been devoted to the fabrication of AEMs with excellent performance. One of the most effective methods for producing the AEMs is to introduce functional quaternary ammonium groups into a polymer matrix. The polymers including polysulfone [10], poly (ether sulfone) [11], poly (ether sulfone ketone) [12], poly (ether imide) [13], polybenzimidazole [14], cardo-polyetherketone [15] have been used to prepare AEMs by this method. However, most of the AEMs mentioned above were prepared by chloromethylation of the polymers with chloromethyl ether, a harmful process to the environment, followed by quaternization to form quaternary ammonium cation. Furthermore, the AEMs using alkyl quaternary ammonium groups as ion transport groups are generally unstable in a high pH aqueous solution, especially at elevated temperatures [16]. As a potential alternative, the AEMs containing imidazolium cation have been currently studied. The steric hindrance and the presence of the  $\pi$  conjugated structure of imidazolium cation make it have a high chemical stability [14,17–21]. Recently, Si and co-workers [17] reported a series of AEMs containing imidazolium cation with ion conductivity of  $1.6 \times 10^{-2} \text{ S cm}^{-1}$  at room temperature (RT). Morandi and co-workers synthesized imidazolium-functionalized AEMs with high chemical stability [19]. These studies inspired us to fabricate AEMs containing imidazolium cation with desirable performance for practical applications.

On the other hand, polyolefin AEMs, such as polystyrene and poly (ethylene-co-tetrafluoro ethylene)-based membranes have

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been synthesized recently due to their intensified fuel resistance, enhanced dimensional stability, and excellent alkaline stability [22,23]. However, most of the reported AEMs are not satisfactory. Therefore, the development of AEMs with high conductivity and excellent physicochemical properties is desirable. Moreover, carbazole is an important nitrogen-containing aromatic heterocyclic compound, and possesses large  $\pi$ -conjugated system with rigid fused rings leading to an excellent thermal stability and alkaline stability. The special structure of carbazole compounds makes them have wide potential application such as in photoelectrical materials, supramolecular recognition, dyes and medicinal agents. More importantly, the carbazole compounds can be modified so that various functional groups can be conveniently introduced into carbazole. The synthesis of carbazole derivatives and their potential applications were extensively studied in recent years [24]. Therefore, poly(*N*-vinyl carbazole) should have a potential application in AEMs by introducing the quaternary ammonium group into carbazole in a facile way.

In this paper, a series of quaternized poly(*N*-vinyl carbazole) (QPVK) membranes was prepared and characterized for alkaline direct methanol fuel cells (DMFCs). Although the ion conductivity of QPVK membranes is routine, the methanol resistance is excellent. To achieve high ion conductivity as well as low methanol permeability, a series of anion exchange membranes was successfully synthesized by quaternizing the copolymer of 1-vinyl imidazole and *N*-vinyl carbazole with imidazolium cation. This synthesis route can not only allow the easy design of different main chain structures, but also avoid the use of very toxic chloromethyl ether for chloromethylation. Moreover, both of the as-prepared AEMs exhibit acceptable performance.

## 2. Experimental section

### 2.1. Materials

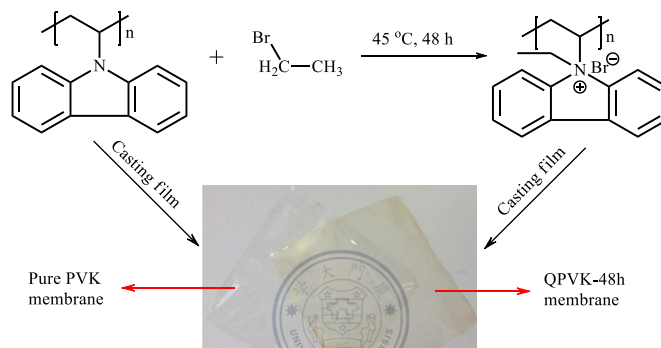
Poly(*N*-vinyl carbazole) (PVK) (99.0%), *N*-vinyl carbazole (99.0%), 1-vinyl imidazole (99.0%), 1,6-dibromohexane (98.0%), 1-methylimidazole (98.0%), 1,4-dibromobutane (98.0%) and bromoethane (99.0%) were purchased from Aladdin company. 1-methyl-2-pyrrolidinone (NMP) (98.0%) and *N,N*-dimethylformamide (DMF) (98.0%) were stirred over  $\text{CaH}_2$  for 24 h, then distilled under reduced pressure and stored over 4 Å molecular sieves. Azobisisobutyronitrile (AIBN) (99.0%) was purchased from Tianjin Guangfu Fine Chemical Research Institute (China) and recrystallized from methanol before use. All other reagents were supplied from Sinopharm Chemical Reagent Co., Ltd. (China).

### 2.2. Membrane preparation

#### 2.2.1. Preparation of quaternized poly(*N*-vinyl carbazole) (QPVK) membrane

PVK was dissolved in NMP under stirring at 25 °C in a stand-up flask. Bromoethane was then added to take a reaction with the PVK under stirring for different time (12, 24, 36, 48 and 60 h) at 35 °C, yielding a raw product. The product was precipitated and purified triple with acetone, and dried at 60 °C in vacuum for 24 h to obtain white (or sometimes yellowish) solid quaternized PVK (QPVK). The synthesis of QPVK membranes is shown in Scheme 1.

The QPVK was dissolved in NMP to make a 5 wt% solution, which was further cast onto a glass plate and dried at 50 °C for 24 h to form a QPVK film. The film was peeled off the glass plate, dried at 80 °C for 5 h. The QPVK membrane was treated with a 1 M NaOH solution at RT for 24 h to fully exchange  $\text{Br}^-$  for  $\text{OH}^-$ , then washed with deionized (DI) water several times and immersed in DI water for 48 h before testing.



**Scheme 1.** The procedure for the synthesis of the QPVK membranes (with photograph).

#### 2.2.2. Preparation of polyolefin membranes

The 1-(1-bromine hexyl)-3-methylimidazolium bromine (HmimBr) ionic liquid was synthesized by a method reported in the literature [25]. 1, 6-Dibromohexane (25 mL, 39.5 g, 0.16 mol) was added to a solution of 1-methylimidazole (5 mL, 5.15 g, 0.625 mol) in acetone (50 mL). The mixture was stirred at 40 °C for 24 h, and then filtered to remove the white solid (by-product). The filtrate was washed with acetone several times and rotor-evaporated to remove the acetone, yielding a yellow oil product. The synthesis of HmimBr is shown in Scheme 2.

The polyolefin was synthesized via free radical polymerization using AIBN as the initiator. Two monomers were fed with various proportions in the polymerization as shown in Table 1. The copolymerization was performed in a three-necked flask with magnetic stirring at 75 °C for 24 h under a nitrogen atmosphere. The copolymer was precipitated and Soxhlet extracted with acetone for 12 h, then dried at 60 °C in vacuum for 24 h to obtain a yellowish solid. The copolymer is termed Pxy, where x and y denote 1-vinyl imidazole and *N*-vinyl carbazole, respectively. The synthesis of Pxy is shown in Scheme 2.

The quaternized copolymer was synthesized using HmimBr as the quaternizing agent. A typical procedure was as follows: 2.87 g (10 mmol) of  $\text{Px}_x\text{y}_y$  (1-vinyl imidazole/*N*-vinyl carbazole = 1/1), 1.23 g (5 mmol) of HmimBr and 15 mL of DMF were introduced into a 50 mL three-necked round-bottomed flask equipped with magnetic stirrer to take a reaction at 40 °C for 3 h under a nitrogen atmosphere. Then, the mixture was poured into 100 mL of acetone, collected by filtration, Soxhlet extracted with acetone for 12 h, then dried at 80 °C in vacuum for 24 h to obtain a yellow solid (3.96 g, 96% yield) that is termed  $\text{QPx}_x\text{y}_y$ . The procedure for the synthesis of QPxy is shown in Scheme 2.

The as-synthesized  $\text{QPx}_x\text{y}_y$  (1 g) was dissolved in DMF to make a 5 wt% solution. 1, 4-Dibromobutane (0.05 g) was first made into a 5 wt% solution in DMF as the crosslinking agent and then added into the  $\text{QPx}_x\text{y}_y$  solution. Then, the solution was cast onto a glass plate and dried at 50 °C for 24 h to form a membrane. The membrane was peeled off the glass plate, dried at 80 °C for 5 h. The three possible crosslinking reactions are shown in Scheme 2 (dotted line in the graph). The crosslinked  $\text{QPx}_x\text{y}_y$  membrane was treated with a 1 M NaOH solution at RT for 24 h to fully exchange  $\text{Br}^-$  for  $\text{OH}^-$ , washed with DI water several times and immersed in DI water for 48 h before testing. The obtained crosslinked QPxy membranes are termed C-QPxy, where C denotes the crosslinking reaction.

### 2.3. Structure characterizations

$^1\text{H}$  NMR spectra of the as-synthesized monomer and copolymer were recorded by Avancell 500 MHz (Bruker, Switzerland) using dimethyl sulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ) or deuterated chloroform

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