



High durability and hydroxide ion conducting pore-filled anion exchange membranes for alkaline fuel cell applications



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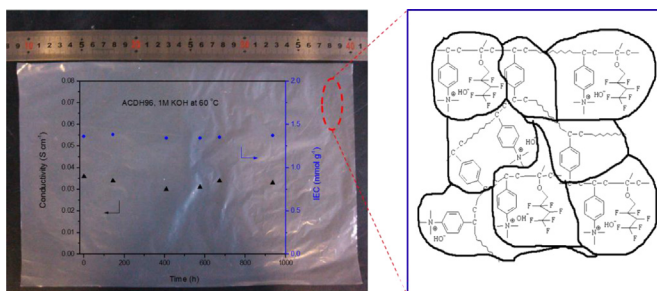
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HIGHLIGHTS

- The pore-filled anion exchange membranes are successfully prepared.
- The membranes exhibit high ionic conductivity and excellent alkaline durability.
- The fuel cell with the resulting membranes shows excellent high power out.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of composite anion exchange membranes are successfully synthesized by thermal polymerization of chloromethyl monomer in a porous polyethylene (PE) substrate followed by amination with trimethylamine for alkaline anion exchange membrane fuel cells (AAEMFCs) application. These membranes exhibit excellent alkaline durability and high ionic conductivity. The resulting alkaline anion exchange membranes (AAEMs) show a hydroxide conductivity up to 0.057 S cm^{-1} at 30°C in deionized water and do not exhibit significant changes in the ionic conductivity and the IEC in 1 M KOH solution at 60°C for around 1000 h. The maximum power density of 370 mW cm^{-2} is obtained at 50°C for H_2/O_2 AAEMFC.

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1. Introduction

There have been great demands for clean energy or renewable energy sources in the past decade. Fuel cells have attracted considerable attention due to their high energy efficiency and low pollution level. For the fuel cells operated in low temperatures, typically below 100°C , there are basically two types of fuel cells

distinguished by the different ions being transported in the electrolyte, proton exchange membrane fuel cells (PEMFCs) and AAEMFCs. In the past decades, most of the attention was focused on PEMFC due to the invention of the commercial Nafion which possesses a suitable combination of high ionic conductivity and excellent chemical stability [1,2]. Despite of the great success, there are still many challenging barriers which hinder their way of popularization and are difficult to overcome. Among the limitations, the dependence on noble metal catalyst is the critical one. AAEMFCs have begun to attract a lot of attention recently because of the significant advantages of AAEMFCs over PEMFCs in terms of

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high kinetic for oxygen reduction and fuel oxidation in alkaline environment, and the lower cost by using non-precious metal catalysts [3].

In an AAEMFC system, AAEM is a key component which is used to conduct anions and prevent gas crossover. Recently, many groups have devoted to producing AAEMs. Polymer such as poly-sulfone [4], poly (phthalazinon ether sulfone ketone) [5], poly (arylene ether sulfone) [6], poly (ether ketone) [7], poly (ether sulfone) cardo [8], and poly (ether ether ketone) [9] based AAEMs are investigated by successive chloromethylation and quaternization. The properties of AAEMs will have a significant impact on the performance and durability of AAEMFCs. In particular, high performance AAEMs are required to have high ionic conductivity, mechanical strength and dimensional stability simultaneously. To avoid dilemma between ionic conductivity and stability, some methods and techniques have been commonly utilized including chemical crosslinking technique, physical pore-filling and reinforcement techniques. Na's and Zhuang's group reported AAEMs by a simple self-crosslinking strategy respectively, the stability of the membranes are obviously enhanced by crosslinking technique [10,11]. Coates and co-workers reported the synthesis of a series of cross-linked AAEMs through the ring-opening metathesis polymerization of tetraalkylammonium-functionalized cyclic olefins [12,13]. Yamaguchi and co-workers prepared anion exchange pore-filling membrane by filling polyelectrolyte [14]. Another enhanced membrane method is reinforcement technique. Porous PTFE membrane has been adopted as supporting material due to its great mechanical strength, thermal and chemical stability, dimensional stability, lower cost and availability of thinner membranes. PTFE membrane reinforcement technique is considered as one of the most effective methods to increase membrane mechanical strength especially in fabricating reinforced proton exchange membranes [15,16]. In our previous study, we reported quaternary ammonia polysulfone/PTFE and crosslinked quaternary ammonia poly (vinylbenzyl)/PTFE composite membranes [17,18]. Although the membranes exhibited high ionic conductivity and good dimensional stability, our previous study encountered one problem: the membranes showed poor chemical stability especially in alkaline solution. Some reasons may be explained this problem: (1) quaternary ammonia group decomposition by OH⁻ attack [19], (2) material compatibility between porous membrane matrix and polymer. Because PTFE membrane is a hydrophobic and high porous material and the anionic exchange polymer is generally aromatic main chain unlike Nafion with C–F main chain, it has poor compatibility between matrix and polymer. So the polymer will be apt to fall apart from PTFE matrix in long-term alkaline solution. Moon's group reported AAEM from 4-vinylbenzyl chloride cross-linked by divinylbenzene via polymerization in PE matrix followed by quaternization, this membrane showed good stability in alkaline solution [20].

In this work, we first attempted to prepare the pore-filled anion exchange membranes refer to the method reported by Moon [20]. To further improve the performance of the membranes, we induced another fluoromonomer into the copolymer to construct "hydrophilic–hydrophobic micro-phase separation" structure. The fabricated membranes exhibited high conductivity and excellent durability in alkaline environment.

2. Experimental

2.1. Materials and composite membrane fabrication

Porous polyethylene used as a substrate was provide from Wide (porous PE, thickness: 20 μm and porosity: 40–50%). 4-vinylbenzyl chloride (VBC, Aldrich), 2, 2, 3, 4, 4, 4-hexafluorobutyl methacrylate

(HFM, Aldrich), divinylbenzene (DVB, Aldrich), and benzoylperoxide (BPO) were used as monomer, cross-linker, and thermal initiator, respectively.

Two monomer solution were prepared: (a) 96 mol% VBC, 4 mol% DVB and 0.12 mol% BPO, (b) 96(98) mol% VBC, 4(2) mol% DVB, 2 mol% HFM and 0.12 mol% BPO. Then, a porous PE substrate was immersed in the monomer solution for 10 min at room temperature to allow for complete impregnation of monomers into the porous substrate. After the monomer sorption process, the PE substrates were sandwiched between two pieces of glasses, and polymerized at 100 °C for 12 h. After the polymerization, it was aminated by soaking in trimethylamine (TMA) or a mixture of TMA and acetone (3:1 by vol.) for 48 h at room temperature. The quaternized membranes were washed with water. The membrane was subsequently soaked in 1 M KOH for 48 h. Finally, the resulting membranes were washed and stored in deionized water.

2.2. FTIR characterization

ATR-FTIR of membranes was obtained on a JASCO FT-IR 4100 spectrometer with an ATR accessory containing a Ge crystal with a wavenumber resolution of 4 cm⁻¹ and range of 500–4000 cm⁻¹.

2.3. Ion exchange capacity, water uptake, swelling behavior and mechanical strength

The ion exchange capacity (IEC) of the membranes was determined by titration method. The membrane with OH⁻ forms was soaked in 0.01 M HCl solution for 48 h at 30 °C. Subsequently, HCl was titrated against 0.01 M aqueous solution of NaOH with phenolphthalein as indicator. The IEC was calculated as follows

$$IEC = \frac{M_{o,HCl} - M_{e,HCl}}{m} \quad (1)$$

where $M_{o,HCl}$ and $M_{e,HCl}$ are moles of HCl before and after titration with NaOH, respectively, and m is the weight of the membrane.

Water uptake was measured by immersing the membrane into water at 30 °C for 24 h. Then the membranes were taken out, wiped with a tissue paper, and quickly weighed on a microbalance. The weights of the dry membranes were obtained after drying at 60 °C under vacuum for 24 h. The water uptake W_u (wt%) could be calculated as follows:

$$W_u(\text{wt}\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (2)$$

where W_{dry} and W_{wet} are the weights of dry and hydrated membranes, respectively.

The swelling ratio could be calculated as follows

$$\text{Swelling ratio (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100\% \quad (3)$$

The dimension (length, width and thickness) of sample was taken in the OH⁻ form when it was fully hydrated and dried, respectively. The drying of sample was carried out at 60 °C for 24 h.

The mechanical property of the membranes was measured with a WDW Electromechanical Universal Testing Machine at room temperature. The membrane specimens were of 10 mm width and tested using a programmed elongation rate of 50 mm min⁻¹. Before the measurements, the membrane samples were kept in DI water at room temperature overnight and water on the surface was absorbed with filter paper.

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