



# Preparation and characterization of mono-sheet bipolar membranes by pre-irradiation grafting method for fuel cell applications



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## HIGHLIGHTS

- Novel mono-sheet bipolar membrane was prepared by pre-irradiation grafting method.
- The membranes showed good stability, ionic conductivity and ion exchange capacity.
- The thickness of anion/cation exchange layer of the membrane can be easily controlled.
- The properties of the membranes can be tuned by varying the degree of grafting.
- The membranes were successfully used in the fuel cells without humidification.

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## ABSTRACT

A new method for the preparation of the mono-sheet bipolar membrane applied to fuel cells was developed based on the pre-irradiation grafting technology. A series of bipolar membranes were successfully prepared by simultaneously grafting of styrene onto one side of the poly(ethylene-co-tetrafluoroethylene) base film and 1-vinylimidazole onto the opposite side, followed by the sulfonation and alkylation, respectively. The chemical structures and microstructures of the prepared membranes were investigated by ATR-FTIR and SEM-EDS. The TGA measurements demonstrated the prepared bipolar membranes have reasonable thermal stability. The ion exchange capacity, water uptake and ionic conductivity of the membranes were also characterized. The H<sub>2</sub>/O<sub>2</sub> single fuel cells using these membranes were evaluated and revealed a maximum power density of 107 mW cm<sup>-2</sup> at 35 °C with unhumidified hydrogen and oxygen. The preliminary performances suggested the great prospect of these membranes in application of bipolar membrane fuel cells.

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## 1. Introduction

Polymer electrolyte membrane fuel cells, including conventional proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs), have received considerable interest in recent decades. Although PEMFCs were identified as the prospective power sources for power generating stations, vehicular transportations, and portable power supply, there are still some obstacles to their commercialization such as sluggish oxygen reduction kinetics, complex water management and the high cost of the critical materials. AEMFCs may offer plenty of potential advantages, such as more facile electrokinetics, wider selection of catalyst, and lower fuel (e.g. alcohols) crossover. The most

encouraging aspect of AEMFCs is the cost of the fuel cell may be greatly reduced, because the non-noble metals, such as silver and nickel are allowed to be used as catalysts in the alkaline working condition. However, compared with PEMFCs, the poor ionic conductivity of the anion exchange membranes (AEMs) is a serious problem because it may lower the performance of the AEMFCs.

In an effort to use the proton exchange membrane which has high conductivity and still exploit the potential electrochemical advantages of the alkaline operating condition, recently, Kohl and his coworkers [1–6] described the use of the bipolar polymer electrolyte interfaces for H<sub>2</sub>/O<sub>2</sub> and direct methanol fuel cells. Although the power densities reported were relatively low, the bipolar membrane fuel cells are theoretically promising because they not only combine the advantages of PEMFCs and AEMFCs, but also have the function of self-humidification. The membrane electrode assembly (MEA) is the core component of the self-

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humidifying bipolar membrane fuel cell, which is composed of a bipolar membrane, an acidic anode and an alkaline cathode, with the cation exchange layer (CEL) facing the acidic anode while the anion exchange layer (AEL) facing the alkaline cathode [1,7]. The research team of Xiang and Djilali [7] recently reported that the bipolar membrane fuel cells (BMFCs) have achieved a maximum power density of  $327 \text{ mW cm}^{-2}$  at  $50 \text{ }^\circ\text{C}$  with dry feed gases. The BMFC showed good stability during 40 h of continuous operation. Ramani [8] reported that the direct borohydride fuel cells (DBFCs) using bipolar composite membranes as polymer electrolyte membranes and liquid hydrogen peroxide as the oxidant yielded a maximum power density of  $110 \text{ mW cm}^{-2}$ . Each of these bipolar membrane fuel cells used an acidic-alkaline composite membrane as the polymer electrolyte, including a commercial Nafion membrane and a homemade AEM (or using the anion exchange ionomer coating layer as the AEL). Nevertheless, the above-mentioned BMFCs still need to be improved further. One problem is that the costs of the BMFCs are still high because of the use of the expensive Nafion membrane. Another problem is the lifetime of the BMFCs. This kind of acidic-alkaline composite bipolar membrane may split at the junction of the CEL and AEL after long-term operation, owing to the difference of swelling ratio between the cation exchange resin and anion exchange resin. Accordingly, it is essential to prepare a more cost-efficient and integrated bipolar membrane for bipolar membrane fuel cells.

Radiation grafting method is known as one of the effective methods to prepare ion exchange membrane for polymer electrolyte membrane fuel cells [9–15]. Partially fluorinated poly(ethylene-co-tetrafluoroethylene) (ETFE) film exhibits superior radiation resistance [16], and has been used as base films for the preparation of ion exchange membranes by graft copolymerization and subsequent sulfonation or quaternarization [17–20]. These polymer electrolyte membranes showed very good mechanical property, chemical stability, thermal stability and fuel cell performance. However, there are few researches about mono-sheet bipolar membranes except one article reported by Fu et al. [21]. They prepared the mono-sheet bipolar membrane by simultaneous irradiation grafting of vinylbenzyl chloride and acrylic acid onto two sides of a porous polyethylene (PE) base membrane, respectively, and subsequent quaternarization. The resulting mono-sheet bipolar membranes were used in the field of electro dialysis and showed a voltage drop of 2.0 V at a current density of  $80 \text{ mA cm}^{-2}$  in  $1 \text{ mol L}^{-1}$  NaOH aqueous solution. To our best knowledge, no correlative literature about the mono-sheet bipolar membrane applied to fuel cells can be found.

In this work, a new method for the preparation of the mono-sheet bipolar membrane was developed based on pre-irradiation graft copolymerization. Characterizations of the resulting bipolar membranes were carried out by ATR-FTIR, SEM-EDS and TGA, and the ion exchange capacity (IEC), ionic conductivity and water uptake (WU) of the membrane were measured. Besides, the preliminary  $\text{H}_2/\text{O}_2$  fuel cell tests based on these mono-sheet bipolar membranes were also presented.

## 2. Experimental

### 2.1. Materials

The original ETFE base film with the thickness of  $30 \text{ }\mu\text{m}$  was commercially provided by Asahi Glass Co., Ltd. 1-vinylimidazole (VI, CP, containing 100 ppm hydroquinone as inhibitor) and iodomethane (MeI, CP) were purchased from Beijing Source Fine Chemical Co., Ltd. Styrene (St, CP, containing 100–500 ppm hydroquinone as inhibitor) and iron (II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , AR) were obtained from Xilong Chemical Co., Ltd. 1-

vinylimidazole and styrene were distilled under reduced pressure before use. Chlorosulfonic acid was bought from China National Medicines Co., Ltd. The other chemicals were analytical grade and used as received. Deionized water was used throughout this work.

### 2.2. Membrane preparation

The process for the preparation of the mono-sheet bipolar membranes is shown in Scheme 1, in which four major steps are listed as follows: (1) Pre-irradiation of the ETFE base films, (2) Grafting reaction of the pre-irradiated ETFE base films, (3) Sulfonation of the styrene grafted side (St-Side) of the grafted membranes, followed by hydrolysis reaction, and (4) Alkylation of the 1-vinylimidazole grafted side (VI-Side) of the sulfonated membranes.

#### 2.2.1. Pre-irradiation of the ETFE base films

The ETFE base film samples were washed with acetone, then dried and weighed. After that, the samples were pre-irradiated with the  $^{60}\text{Co}$   $\gamma$ -ray source (Food Research Center of Wanheyuan, Xiamen, China) to the total dose of 100 kGy [17,22] at a dose rate of  $4 \text{ kGy h}^{-1}$  and ambient temperature under argon atmosphere. The irradiated membranes were stored at  $-38 \pm 2 \text{ }^\circ\text{C}$  for further use.

#### 2.2.2. Grafting reaction

The pre-irradiated ETFE base films, membrane A, B and C were grafted with the monomer solutions under the protection of nitrogen in a homemade reactor, as shown in Fig. 1. Membrane A was fixed between the Teflon frame ② and ③. Membrane B was fixed between the stainless steel plate ① and Teflon frame ② for measuring the grafting degree of styrene, while membrane C was fixed between the Teflon frame ③ and stainless steel plate ④ for measuring the grafting degree of 1-vinylimidazole. Eight holes in each stainless steel plate and Teflon frame were made and the homemade reactor could be fastened by eight bolts. The St solution (20 vol% or 30 vol% St in toluene) and VI solution (87.5 vol% VI aqueous solution containing a certain amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) [23] could be injected into the chambers from the inlet ⑤ and ⑥ and contacted with the membranes respectively. The grafting reaction was carried out at  $60 \text{ }^\circ\text{C}$  for 0.5–2 h. The monomers were grafted onto both side of the membrane A simultaneously, thus the St-g-ETFE-g-VI membrane was obtained. Only one side of the membrane B and C was grafted with St or VI monomer. After the reaction, the membranes were washed with organic solvents (methanol for VI-Side and toluene for St-Side, respectively) to remove the low molecular weight homopolymers. Finally, the obtained grafted membrane A, B and C were vacuum dried at  $60 \text{ }^\circ\text{C}$  for 24 h and weighed.

The degree of grafting (DOG) was calculated as follows:

$$\text{DOG} (\%) = (W_g - W_o) / W_o \times 100\% \quad (1)$$

where  $W_g$  and  $W_o$  are the weights of the membrane after and before the grafting reaction, respectively.

DOG-St-VI was determined from membrane A, which was grafted with St and VI onto both side of the membrane. DOG-St or DOG-VI was determined from membrane B or C, which was grafted with St or VI onto one side of the membrane.

#### 2.2.3. Sulfonation reaction

The grafted membranes were fixed in the homemade reactor with the St-Side facing the chlorosulfonic acid solution. In order to reduce the side reaction during the sulfonation, a relatively lower concentration of chlorosulfonic acid solution (2 vol% chlorosulfonic acid in dichloromethane) was used [9]. The membranes were sulfonated at room temperature for 1 h, hydrolyzed in  $0.1 \text{ mol L}^{-1}$

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