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## Recyclable cross-linked anion exchange membrane for alkaline fuel cell application

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### HIGHLIGHTS

- A recyclable cross-linked AEM was prepared by mild one-pot reaction.
- Exploiting disulfide chemistry, the cross-linked membrane can be reprocessed.
- The repeatedly recycled membrane exhibits acceptable conductivity.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Cross-linking can effectively solve the conductivity-swelling dilemma in anion exchange membranes (AEMs) but will generate solid wastes. To address this, we developed an AEM cross-linked via disulfide bonds, bearing quaternary ammonium groups, which can be easily recycled. The membrane (RC-QPPO) with IEC of 1.78 mmol g<sup>-1</sup>, when cross-linked, showed enhanced mechanical properties and good hydroxide conductivity (24.6 mS cm<sup>-1</sup> at 30 °C). Even at higher IEC value (2.13 mmol g<sup>-1</sup>), it still has low water uptake, low swelling ratio and delivers a peak power density of 150 mW cm<sup>-2</sup> at 65 °C. Exploiting the formation of disulfide bonds from -SH groups, the membrane can be readily cross-linked in alkaline condition and recycled by reversibly breaking disulfide bonds with dithiothreitol (DTT). The recycled membrane solution can be directly utilized to cast a brand-new AEM. By washing away the residual DTT with water and exposure to air, it can be cross-linked again and this process is repeatable. During the recycling and cross-linking processes, the membrane showed a slight IEC decrease of 5% due to functional group degradation. The strategy presented here is promising in enhancing AEM properties and reducing the impact of artificial polymers on the environment.

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## 1. Introduction

Fuel cell, which can directly convert chemical energy into electric energy without pollution, has attracted intensive research attention and is believed to be an effective approach in solving the

energy crisis [1]. However, high material cost has impeded the practical application of fuel cell, especially the proton exchange membrane fuel cell (PEMFC), which is operated in acidic electrolyte using noble metal catalyst and Nafion membrane [2]. By switching the acidic media to a basic one, the electrode reaction in anion exchange membrane fuel cell (AEMFC) can be catalyzed by inexpensive catalyst (such as Ag) and that will greatly reduce the cost of fuel cells [3]. Currently, the major challenge in AEMFC is developing stable (both chemically and mechanically), highly conductive and low-cost anion exchange membranes (AEMs). Most AEMs are not

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stable in alkaline media due to high water swelling, which facilitates the degradation of functional groups [4,5] and the breakdown of polymer backbones [6,7] by allowing easier access of  $\text{OH}^-$  to the membrane matrix.

Cross-linking, as an effective strategy, is commonly utilized and can be readily carried out by in-situ heat treatment [8] and/or by adding extra cross-linking agents [9] during the preparation of AEMs. Cross-linked AEMs generally deliver better mechanical properties, improved thermal and chemical stability, reduced water swelling and methanol permeability [10]. Typically, three types of interactions i.e. hydrogen bonding [11], ionic bonding [12] and covalent bonding [13] are involved in AEM cross-linking. Among them, cross-linking via covalent bonds is more stable and widely used in the preparation of AEMs [14]. However, AEMs cross-linked via covalent bonds cannot be dissolved anymore and that makes it difficult to recycle or reprocess the disposed AEMs, thus generating solid wastes, especially when fuel cell is widely implemented. In this case, recycling “retired” AEMs is of critical importance.

Inspired by the folding/unfolding of protein with the formation/break of disulfide bonds [15], we seek similar strategy to make recyclable AEMs in this contribution. Disulfide bond, with dissociation energies of 210–270  $\text{kJ mol}^{-1}$ , can be formed by oxidation of sulfhydryl groups ( $-\text{SH}$ ) with oxygen and broken by reduction with dithiothreitol (DTT) [16]. It has been utilized to design recyclable polymer network with improved mechanical properties. Otsuka et al. demonstrated the efficient reprocessing of cross-linked epoxy resins by breaking disulfide bonds. The disulfide bond cross-linked resin exhibited comparable tensile strength (24 MPa) to other permanently cross-linked resin (29 MPa) and can be completely broken into soluble fragments [17]. However, the  $-\text{SH}$  groups are too reactive to survive in the homogeneous membrane-casting solution when exposed to oxygen. Protection is therefore necessary to avoid forming insoluble gel. It is found that releasing  $-\text{SH}$  groups from thioacetate groups by alkaline hydrolysis and subsequently forming disulfide bonds by heating and/or exposing to oxygen is an effective approach in membrane self-crosslinking [18].

In this contribution, we synthesized a PPO-based membrane (AcS-QPPO) bearing quaternary ammonium functional groups and thioacetate groups via mild one-pot reaction. Hydrolyzing the thioacetate groups in aqueous NaOH solution and exposing them to air lead to the formation of cross-linked, insoluble RC-QPPO membrane, which exhibited lower water uptake (37.4 wt% at 30 °C), lower water swelling ratio (13.4% at 30 °C), enhanced mechanical property, similar hydroxide conductivity (24.6  $\text{mS cm}^{-1}$  at 30 °C) and comparable alkaline stability in comparison with the traditional QPPO membrane. Moreover, RC-QPPO can be re-dissolved in DTT/DMF solution, and the resulting solution can be further utilized to cast a brand-new AEM. This membrane was then cross-linked again by washing off the residual DTT with water and exposure to oxygen. After two successive recycling and cross-linking processes, acceptable hydroxide conductivity (20.0  $\text{mS cm}^{-1}$  at 30 °C) was observed for membrane RC2-QPPO. The reversible cross-linking strategy demonstrated here can be widely adopted to prepare recyclable cross-linked AEMs.

## 2. Experimental

### 2.1. Materials

Brominated poly (2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) was kindly provided by Tianwei Membrane Corporation Ltd. (Shandong, P.R. China). It was purified by dissolving in 1-methyl-2-pyrrolidone (NMP), precipitating in deionized water, washing with ethanol and finally drying in vacuum oven at 30 °C for 48 h  $^1\text{H}$  NMR indicates 48 mol% benzyl bromide per repeating unit. Sodium

sulfate, sodium chloride, sodium hydroxide, sodium bicarbonate, 1-methyl-2-pyrrolidone (NMP), dimethyl formamide (DMF), ethanol and trimethylamine alcohol solution (TMA) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, P. R. China). Potassium thioacetate and dithiothreitol (DTT) were purchased from Energy Chemical (Shanghai, P. R. China). All reagents are of analytical grade and used as received.

### 2.2. QPPO membrane

BPPO (0.25 g) was dissolved in NMP (5 mL). Trimethylamine alcoholic solution (33 wt%) was then slowly added under vigorous stirring (the amount of trimethylamine might be varied to adjust the ion exchange capacity). The resulting solution was stirred at room temperature for 6 h and then cast in a 60 mm-diameter glass petri dish. After solvent evaporation, QPPO membrane in bromide form was obtained and transformed into  $\text{OH}^-$  form by immersing in aqueous NaOH solution (1  $\text{mol L}^{-1}$ ). Finally, the membrane samples (QPPO-n, n indicates the IEC value,  $\text{mmol g}^{-1}$ ) were thoroughly washed with deionized water to remove residual NaOH prior to characterization.

### 2.3. Reversibly cross-linked membrane (RC-QPPO)

BPPO (0.25 g) was dissolved in NMP (5 mL). Potassium thioacetate (7 mg, 0.1 equiv. to the benzyl bromide groups in BPPO) was added and stirred at room temperature for 2 h. Trimethylamine alcoholic solution (33 wt%) was then slowly added (the amount of trimethylamine might be varied to adjust the ion exchange capacity) and the resulting solution was stirred at room temperature for 6 h. Crude polymer, namely AcS-QPPO, was obtained by precipitation in acetone (40 mL) and centrifugation. It was then washed with aqueous HCl solution (pH = 3) three times and finally dried in vacuum oven at 30 °C overnight. The structure of AcS-QPPO was confirmed by  $^1\text{H}$  NMR spectroscopy. Similarly, dissolving AcS-QPPO polymer in DMF (10 wt%) and subsequent solution casting lead to AcS-QPPO membrane. Its cross-linking was conducted by immersion in aqueous NaOH solution (1  $\text{mol L}^{-1}$ ) and exposure to air. These disulfide bond cross-linked AEMs were designated as RC-QPPO-n (n indicates the IEC value,  $\text{mmol g}^{-1}$ ) and transformed into  $\text{Cl}^-$  or  $\text{HCO}_3^-$  form by immersing in aqueous NaCl or  $\text{NaHCO}_3$  solution (1  $\text{mol L}^{-1}$ ) before characterization.

### 2.4. RC-QPPO recycling and recasting

RC-QPPO membrane samples (25 mg) were cut into pieces and suspended in 5 mL DMF containing DTT (50 mg, 20 equiv. to the disulfide bonds in the membrane). The mixture was stirred at room temperature until the samples are completely dissolved. Similar solution casting procedure was used to prepare AEMs from the recycled membrane solution and the membranes were then cross-linked by washing off the residual DTT and exposing to air. These recycled membranes were designated as RCn-QPPO (n implies the recycling times).

### 2.5. Membrane characterization

#### 2.5.1. Nuclear magnetic resonance (NMR)

$^1\text{H}$  NMR spectra were conducted on a Bruker Avance III 400 MHz spectrometer, using  $\text{CDCl}_3$  or  $\text{DMSO}-d_6$  as solvent.

#### 2.5.2. Gel permeation chromatography (GPC)

Molecular weight ( $M_n$ ,  $M_w$ ) and polymer dispersity index ( $\text{PDI} = M_w/M_n$ ) of the original (RC-PPO) and recycled (RC1-PPO) polymer without being quaternised was investigated by gel

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