



# Novel anti-oxidative membranes based on sulfide-containing polybenzimidazole for high temperature proton exchange membrane fuel cells

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## ABSTRACT

The introduction of sulfide units is a potential strategy to improve solubility and processibility of polybenzimidazole (PBI) polymer, as well as to enhance antioxidant capacity of corresponding membrane. In this paper, the novel S-PBI- $x$  serial copolymers ( $x$  denotes the percentage of sulfide-containing monomer) were prepared by a microwave-assisted tetracopolymerization with 3,3',4,4'-tetraaminobiphenyl, 2,6-pyridinedicarboxylic acid, hexanedioic acid and the synthesized methyl 3-((2-methoxy-2-oxoethyl)thio)propanoate as copolymerized monomers in different proportion. The resultant copolymers were characterized by FT-IR, GPC and energy dispersive spectroscopy. These sulfide-containing copolymers exhibit much better solubility in aprotic solvents such as N,N-dimethylacetamide, N,N-dimethylformamide and dimethylsulfoxide than unmodified PBI. The oxidative stability of the membranes was studied by enhanced Fenton test (20% H<sub>2</sub>O<sub>2</sub> and 4 ppm Fe<sup>2+</sup>, 80 °C, refreshed every 3 h). Additionally, the oxidized membranes were further characterized by FT-IR, TGA, and tension test. The experimental results show that S-PBI-7% membrane suffers less than 5% weight loss after 24 h of treatment with enhanced Fenton reagent. Typically, after treated in enhanced Fenton reagent, the oxidized S-PBI-7% membrane still retains considerable thermal stability and mechanical strength. The anti-oxidative mechanism of the prepared membranes was discussed as well.

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## 1. Introduction

Polybenzimidazole (PBI) has attracted great interests for its applications in high temperature polymer electrolyte membrane fuel cells (HT-PEMFC) [1,2]. Compared with conventional membranes (e.g., commercial Nafion membrane), PBI membranes doped with acid (typically with phosphoric acid [3]) exhibit relatively high proton conductivity in the temperature range of 100–200 °C, at which temperature the CO catalyst poisoning and water reliance could be greatly reduced [4]. More and more efforts have been devoted to finding novel PBI structure with high acid content, good mechanical properties, excellent chemical and electro-chemical stabilities, and so forth.

However, high molecular weight PBI with some of the advantages mentioned above has poor solubility and processability for membrane casting, which makes it difficult for both research and practical use. Meanwhile, as a fully aromatic heterocyclic polymer, PBI contains multiple reactive sites, which are electron rich and easy to be attacked by oxidants. Up to

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now, a large number of measures has been carried out to overcome the shortcomings, including (1) structure modifications [5–7], (2) facile crosslinking methods [8–12], (3) copolymerization with other polymers [13–16], (4) blend with organic or inorganic compounds [17,18], (5) novel casting method [19,20] which allows for a single step polymerization/casting procedure to produce PBI polymers.

The fundamental interest in sulfide-containing monomers is shown because the sulfide unit possesses good flexibility and nucleophilicity. Moreover, the sulfide structure can be a powerful free radical scavenger against possible oxidation [21,22]. Among the various reports [23,24], sulfide-containing compounds are widely used for their antioxidant activity, especially in the field of cell biology and pharmacology [25–28]; however, the mechanism has not been frequently studied [29,30]. Some possible mechanisms [31] and theoretical models [32] were proposed based on experimental results, but many questions still remain to be clarified. Therefore, the application of sulfide in modifying the rigid matrix of PBI might be a beneficial trial as well as a great challenge for its uncertainty.

In this study, sulfide-containing diester methyl 3-((2-methoxy-2-oxoethyl)thio)propanoate (MTMA for short), of which the structure is similar to hexanedioic acid, has been synthesized through facile Michael addition and acts as a promising monomer in the PBI polycondensation. One of the PBI copolymers in our previous work [33], which did not show satisfying performance as PEM, was used as the basic structure to be modified for comparison. In our present work, the sulfide-containing polybenzimidazole series of S-PBI-*x* (*x* refers to the molar feed percent of MTMA in total diacid monomers) have been prepared by microwave-assisted polycondensation. Through introducing the flexible antioxidant structure, the anticipated advantages of these sulfide-containing materials are as follows: The sulfide units could terminate radical chain reactions occurred in the fuel cell working process by removing free radical intermediates so that inhibit oxidative damage to the membrane [34]. Besides, the aliphatic structure offers more flexibility to the rigid matrix of the polymer than aromatic structure. Further, the sulfide units can act as potential proton acceptor [35,36] to help PA doping and proton transport. Among all the possible benefits brought by sulfide units, the antioxidant capacity, on which we mainly focused in this work, was estimated by the degradation of S-PBI-*x* in Fenton reagent. Accordingly, the effects of sulfide on solubility, mechanical properties, thermal stability, and proton conductivity were tested and discussed to better understand the influence of sulfide group in PBI applications.

## 2. Experimental

### 2.1. Materials

2,6-Pyridinedicarboxylic acid and 3,3',4,4'-tetraaminobiphenyl (DAB) were purchased from J&K Scientific Ltd., Beijing, China. Hexanedioic acid was purchased from Aladdin Industrial Corporation, Shanghai, China. Methyl thioglycolate (98%) was obtained from Energy Chemical, Shanghai, China. Methyl acrylate, Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and polyphosphoric acid (PPA, >84% P<sub>2</sub>O<sub>5</sub>) were purchased from Tianjin Guangfu Technology Development Co., Ltd., Tianjin, China. N,N-dimethylacetamide (DMAc), sodium bicarbonate (NaHCO<sub>3</sub>), N,N-dimethylformamide (DMF), potassium permanganate, phosphoric acid (PA, 85%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%) and other common reagents were purchased from Beijing Chemical Reagent Co., Ltd., China. All reagents mentioned above were used without further purification. The microwave reactor was purchased from Sineo Microwave Chemistry technology Co., Ltd, Shanghai, China.

### 2.2. Synthesis of methyl 3-((2-methoxy-2-oxoethyl)thio)propanoate (MTMA)

In a flask (stirrer, thermometer, dropping funnel), 1.06 g (10 mmol) methyl thioglycolate and 10 mL THF were presented. The mixture was cooled to 10 °C and then 1.00 g triethylamine was added. Under vigorous stirring, 0.86 g (10 mmol) of methyl acrylate was added dropwise within 30 min. After completion of dropping, the bright yellow solution was elevated to room temperature and stirred overnight. The resulting solution was acidified with 2 mol L<sup>-1</sup> hydrochloric acid and extracted with diethyl ether (3 × 20 ml). The combined organic phases were dried over sodium sulfate and the solvent was evaporated under reduced pressure to obtain yellow liquids with a specific odor. Yield: 1.75 g, 94.09%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 3.73 (d, *J* = 16.6 Hz, 6H), 3.27 (s, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.2 Hz, 2H). <sup>13</sup>C NMR (100.61 MHz, CDCl<sub>3</sub>) δ: 172.10, 170.75, 52.45, 51.86, 34.09, 33.47, 27.56.

### 2.3. Synthesis of copolymer containing sulfide structure (S-PBI-*x*)

The polybenzimidazole containing aliphatic sulfide structure (S-PBI-*x*) was prepared by a microwave-assisted solution polycondensation method, according to our previous work [33]. A typical synthetic route of S-PBI-5%, where 5% denotes to the molar feed percent of MTMA in total diacid monomers, was as follows. 45 g polyphosphoric acid (PPA) was deaerated under microwave irradiation in nitrogen atmosphere for 30 min. After the deaeration completed, 1.0714 g 3,3',4,4'-tetraaminobiphenyl (DAB), 0.4017 g hexanedioic acid, 0.3342 g 2,6-pyridinedicarboxylic acid and 0.0480 g MTMA were added into PPA. The mixture was vigorously stirred under microwave heating at 200 W under the following temperature conditions: 80 °C for 20 min, 100 °C for 20 min, 140 °C for 60 min, 170 °C for 20 min, 200 °C for 180 min. After the polycondensation completed, the resultant polymer solution was poured into deionized water, filtered and washed with deionized water

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