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# Synthesis and properties of reprocessable sulfonated polyimides cross-linked via acid stimulation for use as proton exchange membranes

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## H I G H L I G H T S

- A series of cross-linked SPI membranes were successfully synthesized.
- The cross-linkable membranes can be reprocessed during film formation.
- The cross-linked membranes exhibit improved comprehensive performance.
- The resulting membranes show remarkable power density in the DMFC.

## A R T I C L E I N F O

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## A B S T R A C T

Cross-linked sulfonated polyimides are one of the most promising materials for proton exchange membrane (PEM) applications. However, these cross-linked membranes are difficult to reprocess because they are insoluble. In this study, a series of cross-linkable sulfonated polyimides with flexible pendant alkyl side chains containing trimethoxysilyl groups is successfully synthesized. The cross-linkable polymers are highly soluble in common solvents and can be used to prepare tough and smooth films. Before the cross-linking reaction is complete, the membranes can be reprocessed, and the recovery rate of the prepared films falls within an acceptable range. The cross-linked membranes are obtained rapidly when the cross-linkable membranes are immersed in an acid solution, yielding a cross-linking density of the gel fraction of greater than 90%. The cross-linked membranes exhibit high proton conductivities and tensile strengths under hydrous conditions. Compared with those of pristine membranes, the oxidative and hydrolytic stabilities of the cross-linked membranes are significantly higher. The CSPI-70 membrane shows considerable power density in a direct methanol fuel cell (DMFC) test. All of these results suggest that the prepared cross-linked membranes have great potential for applications in proton exchange membrane fuel cells.

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## 1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been identified as one of the most promising power sources because of

their high efficiencies and environmental friendliness. The PEM is one of the core constituents of a PEMFC system. An ideal PEM should possess good membrane stability and low resistance (high proton conductivity), which are closely related to high PEMFC performance [1,2]. Over the past few decades, perfluorosulfonic acid membranes (Nafion, Flemion, Aciplex) have been widely used as PEMs for PEMFCs because of their excellent chemical stabilities, good mechanical properties, and high proton conductivities. However, the commercial application of these materials has been limited by certain disadvantages, such as high methanol

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permeability, low proton conductivity at high temperatures (>80 °C), and, in particular, high cost [3,4]. To overcome these shortcomings, considerable efforts have focused on the development of novel PEMs based on sulfonated aromatic polymers [5–10]. Among these PEMs, sulfonated polyimides (SPIs) have attracted great interest as promising PEM materials for PEMFC devices because of their unique physical properties, excellent thermal stability and favorable durability [11–17].

SPI membranes should generally have high sulfonic acid levels to achieve high proton conductivity. However, high sulfonic acid levels often cause excessive swelling or degradation of SPI membranes in water, particularly at high temperatures [18,19]. To solve this problem, cross-linking methods have been applied to improve the properties of SPIs as PEMs. In recent years, many cross-linked SPI membranes with both suitable proton conductivity and excellent stability have been successfully developed [20–30]. The cross-linking is based on the reactions between acridine groups and dibromoalkane [22], carboxylic and alkane diols [27,29], and malimide and poly(ethylene glycol) diacrylates [30], among others.

However, one considerable obstacle limits the development of cross-linked SPIs for commercial membrane production. Once defects occur in the films, the cross-linked membranes are difficult to reprocess because of their insolubility. Triethoxysilyl can be used as a cross-linking agent to prepare cross-linked polymers when grafted onto polymer chains and subjected to a subsequent silylation-condensation reaction in the presence of an acid [31]. Theoretically, the polymers can dissolve in organic solvents after grafting triethoxysilyl and before the cross-linking reaction is completed by acid solution stimulation. In previous studies, many efforts have been made to develop Si hybrid PEMs based on silylation-condensation [32–34]. However, to date, few studies have focused on the reprocessing capabilities of cross-linked PEMs. Based on these observations, the aim of this study was to prepare reprocessable, covalently cross-linked SPI membranes by acid solution stimulation that can exhibit superior oxidative and hydrolytic stabilities, good mechanical strength and high proton conductivity for use as PEMs. The membranes can be reprocessed after film formation and before proton exchange and are easily cross-linked in acid solutions during the proton exchange process.

In this study, 3-glycidoxypropyltrimethoxysilane (KH-560), which contains an epoxy group that reacts with the H–N [21] of the imidazole group and a trimethoxysilyl group that is amenable to silane cross-linking [35], was grafted onto SPI, which contains an imidazole group in the main chain. When the membranes are immersed in an acid solution for proton exchange, the trimethoxysilyl groups hydrolyze and form a network within the membranes. The degree of cross-linking can be controlled by adjusting the concentrations of silane monomer and imidazole groups. The properties of these cross-linked membranes, including proton conductivity, mechanical properties, and oxidative and hydrolytic stabilities, were investigated. The performance of the cross-linked membrane in an actual single direct methanol fuel cell (DMFC) was also evaluated.

## 2. Experimental

### 2.1. Materials

1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA), m-cresol, triethylamine (Et<sub>3</sub>N), dimethyl sulfoxide (DMSO), and 3-glycidoxypropyltrimethoxysilane (KH-560) were purchased from Energy Chemical Co. 5-Amino-2-(4-aminophenyl) benzimidazole (APBIA) was purchased from Shanghai Longsheng Chemical Co. 4,4'-Diamino-2,2'-biphenyldisulfonic (DAPS, 75%) was purchased from Shanghai Dibo Chemical Reagent Co. and was purified

according to the procedure reported in the literature [11]. Other materials were purchased from Guangzhou Chemical Reagent Factory. APBIA and benzoic acid were dried at 80 °C, and NTDA was dried at 120 °C overnight before use. DMSO, m-cresol and Et<sub>3</sub>N were dried using 4 Å molecular sieves prior to use.

### 2.2. Synthesis of sulfonated polyimide (SPI-X)

Sulfonated polyimides SPI-X (where X refers to the mole percentage of DAPS groups) containing 50 mol% and 70 mol% DAPS groups were synthesized. A typical synthesis procedure is described using SPI-50 as an example. DAPS (1.5 mmol), m-cresol (15 ml) and Et<sub>3</sub>N (0.8 ml) were added to a dry 50-ml three-neck flask under nitrogen flow. The mixture was stirred until the DAPS was completely dissolved; then, APBIA (1.5 mmol) was added. After a clear solution was obtained, NTDA (3 mmol) and 0.52 g of benzoic acid were added to the flask while stirring. Following dissolution, the mixture was heated to 80 °C for 4 h and 180 °C for 20 h. After the reaction mixture was slowly cooled to 100 °C, additional m-cresol (15 ml) was added and stirred to obtain a homogeneous solution. The dark-brown solution was then poured into cold acetone, and the fiber-like precipitate was filtered and washed with acetone and methanol. The resultant brown-red polymer was dried under vacuum at 60 °C for 12 h.

### 2.3. Synthesis of sulfonated polyimide containing trimethoxysilane pendant groups (TSPI-X)

SPI-X with flexible pendant alkyl side chains containing trimethoxysilyl groups (TSPI-X) was synthesized from SPI-X and KH-560. The preparation of cross-linkable membranes (TSPI) is described below using TSPI-50 as an example. To a dry 50-ml three-necked flask, 0.6867 g (approximately 0.56 mmol N–H bonds) of SPI-50 was dissolved in DMSO to form 5 wt% solutions under nitrogen flow. The solution was heated to 120 °C, and 0.133 g KH-560 was then added. The solution was magnetically stirred at 120 °C for 40 min. The mixture was cast onto a 110 °C glass plate and dried under vacuum at 110 °C for 3 h. Then, the membrane was soaked in acetone for 6 h to remove any residual solvent.

### 2.4. Film formation, cross-linking and proton exchange

SPI-Xs (in triethylammonium salt form) were dissolved in DMSO to form 5 wt% solution mixtures at 80 °C. The solutions were cast onto clean glass plates and dried at 80 °C for 8 h under vacuum. The as-cast membranes were immersed in ethanol for 4 h to remove the residual solvent, and the membranes were then acidified with 1 M HCl for 12 h and washed with deionized water. For the TSPI-X, the membranes (in triethylammonium salt form) were directly immersed in 1 M HCl for 12 h. The membranes were cross-linked by trimethoxysilane pendant groups and acidified with HCl to simultaneously exchange (Et<sub>3</sub>N) with the acid. Finally, the cross-linked membranes (CSPI-X) were immersed in deionized water and thoroughly washed.

### 2.5. Membrane characterizations

#### 2.5.1. Measurements

<sup>1</sup>H NMR spectra, reported in ppm, were recorded using a Varian 400-Hz NMR instrument with tetramethylsilane (TMS) as the internal standard. FTIR spectra of the membranes were recorded using a Nicolet 6700 spectrometer. Reduced viscosity ([η]) was measured in DMSO at a polymer concentration of 0.5 g dL<sup>-1</sup>. The thermal stability of the polymers was investigated over a temperature range of 120 °C–600 °C at a heating rate of 10 °C min<sup>-1</sup> using

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