



Short communication

Gradiently crosslinked polymer electrolyte membranes in fuel cells



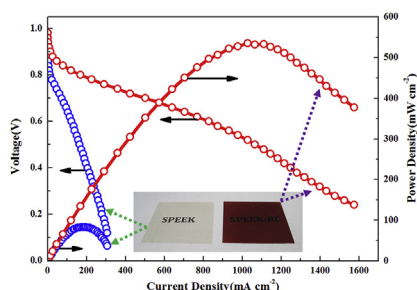
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HIGHLIGHTS

- A post treatment affords the SPEEK membrane with gradient crosslinking structure.
- Benzhydrol and sulfonic acid combine to form the crosslinks, evidenced by NMR, FTIR.
- Such structure restrains the membrane from over swelling, enhances tensile strength.
- The membrane shows high conductivity and low activation energy, comparable to Nafion.
- H₂/O₂ fuel cell with the post treated membrane shows good performance at 80 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Polymer electrolyte membranes in fuel cells should be high in both ionic conductivity and mechanical strength. However, the two are often exclusive to each other. To solve this conundrum, a novel strategy is proposed in this paper, with extensively researched sulfonated poly (ether ether ketone) (SPEEK) membrane as a paradigm. A SPEEK membrane of high sulfonation degree is simply post-treated with NaBH₄ and H₂SO₄ solution at ambient temperature for a certain time to afford the membrane with a gradient crosslinking structure. Measurements via ¹H NMR, ATR-FTIR and SEM-EDS are conducted to verify such structural changes. The gradient crosslinks make practically no damage to proton conductance, but effectively restrain the membrane from over swelling and greatly enhance its tensile strength. A H₂–O₂ fuel cell with the gradiently crosslinked SPEEK membrane shows a maximal power density of 533 mW cm⁻² at 80 °C, whereas the fuel cell with the pristine SPEEK membrane cannot be operated beyond 30 °C.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are known for their high fuel efficiency, high power density and zero/low-emission, and thus have attracted considerable attention for use

as mobile, portable and distributed stationary power [1]. Proton exchange membranes (PEMs) are a key component of PEMFCs, functioning both as a barrier to fuel crossover and the electrolyte for proton transport from anode to cathode. Perfluorosulfonic membranes developed by DuPont in 1960's under the trademark Nafion are the most widely adopted PEMs in fuel cells due to their superior proton conductivity and excellent long-time durability. However, Nafion membranes are far from ideal for problems like

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high expenses, alcohol crossover and high cost of waste disposal [2–4], which promote researches on new PEMs.

In recent years, much research effort is focused on alternative PEMs based on non-fluorinated aromatic ionomers [5–14]. Membranes of sulfonated polyarylether, especially sulfonated poly(ether ether ketone) (SPEEK), is among the most extensively researched [15–21]. Generally, these membranes would show high proton conductivity if they have high ion exchange capacity (IEC) or high degree of sulfonation (DS). However, a high IEC or DS usually leads to high water uptake, large dimensional variation and poor mechanical strength, rendering the membranes unsuitable for practical applications in PEMFCs.

To solve the above mentioned problem, a wide variety of methods were tried, e.g. polymer–polymer blending [22,23], inorganic–polymer hybridizing [24–26] and polymer crosslinking [27–30]. Among these methods, polymer crosslinking is the most straight forward solution to the problem, as it directly and effectively limits the excessive swelling of membrane. However, this method did not achieve much success so far, for crosslinked membranes can become brittle and the formation of proton channels inside the membrane can be disrupted [31,32]. In addition, some PEMs were crosslinked through sacrificing proton-bearing sulfonic acid groups in the ionomers [33], which usually resulted in decreased proton conductivity.

In this communication, we report a facile strategy to prepare gradiently crosslinked SPEEK membrane for PEM fuel cell. A pristine SPEEK membrane is post-treated by immersing in sodium borohydride and sulfuric acid solutions successively. As the sodium borohydride diffuses in the membrane, it reduces certain benzophenone moieties into benzhydrol groups, which is then allowed to react with sulfonic acid groups on SPEEK so that the reduced SPEEK ionomers are crosslinked. The simultaneous diffusion and reaction of sodium borohydride affords the membrane with a gradient crosslinking structure. The performance of the gradiently crosslinked SPEEK membrane will be presented and compared with that of pristine membrane.

2. Experimental

2.1. Materials and chemicals

Poly (ether ether ketone) (PEEK) pellets (Victrex, Grade 450 P, MW = 38,300) were purchased from Nanjing Yuanbang Engineering Plastics. Sodium borohydride, dimethylformide, sodium hydroxide, hydrochloric acid and concentrated sulfuric acid (95–98%) were purchased from Tianjin Guangfu Fine Chemicals Research Institute and used as received. Deionized water (0.1 MΩ cm) was in-house prepared by means of reverse osmosis.

2.2. Preparation of SPEEK membrane

SPEEK resin of 80% sulfonation degree was prepared as reported in Ref. [5]. Typically, 28.6 g PEEK pellets were added into 200 mL concentrated sulfuric acid and vigorously stirred at 35 °C for 5 h to fully dissolve the polymer. The solution was then heated up to 70 °C to allow the sulfonation of PEEK for 1 h. Afterwards the solution was poured into ice cold water to terminate the sulfonation reaction and precipitate the sulfonated PEEK. The precipitated SPEEK was then rinsed thoroughly with deionized water and dried at 80 °C for 24 h. The sulfonation degree of the membrane was determined by back-titration method [5], in which 1–2 g weighted dry SPEEK was immersed in 0.5 M sodium hydroxide aqueous solution for 24 h and then back titrated with 1 M hydrochloric acid using phenolphthalein as the indicator.

To prepare SPEEK membrane, a 10 wt% SPEEK solution prepared

in dimethylformide (DMF) was cast on a clean glass plate and dried at 60 °C for 12 h. The resultant pristine membrane was immersed in deionized water, peeled off from the glass plate and dried again.

The post treatment of SPEEK membrane was carried out at ambient temperature and pressure. A pristine SPEEK membrane was immersed in a saturated sodium borohydride aqueous solution for 24 h to partially reduce the benzophenone moieties of SPEEK. The membrane was then washed with deionized water and transferred into 1 M sulfuric acid solution and immersed for 24 h to partially crosslink the membrane via reacting sulfuric acid with the benzhydrol moieties. Finally, the membrane was rinsed with deionized water to eliminate residual sulfuric acid and kept in deionized water. Hereafter, the pristine, sodium borohydride treated and sulfuric acid treated SPEEK membranes will be denoted as SPEEK, SPEEK-R and SPEEK-RC, respectively. The pristine SPEEK membrane equivalent in sulfonation degree to SPEEK-RC was also prepared for comparison and will be denoted as SPEEK-E.

2.3. Characterization

To characterize the molecular structures of SPEEK, SPEEK-R and SPEEK-RC membranes, proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a NMR spectrometer (Varian Inova 500 MHz, USA) with dimethyl sulfoxide-d₆ as solvent. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of membranes were also recorded on a FTIR spectrophotometer (FTS 6000, Bio-Rad, USA). The membranes were thoroughly washed with deionized water and dried in a vacuum oven for 24 h prior to ¹H NMR and ATR-FTIR measurements.

The profile of sulfonic acid groups along the membrane thickness direction was detected using a linear energy dispersive X-ray spectroscope (EDS) (Hitachi S4800, Japan). Prior to the EDS measurements, the membrane samples were submerged in 2 M sodium hydroxide solution for 24 h, washed thoroughly with deionized water and fractured in liquid nitrogen to expose the cross-section area.

Membrane samples of 40 mm × 40 mm in length at dry state were employed to determine their swelling degrees (SD). The samples were submerged in deionized water at a given temperature for 24 h to ensure swelling equilibrium. The swelling degree was calculated by:

$$SD = (L_{\text{wet}} - L_{\text{dry}}) / L_{\text{dry}} \quad (1)$$

where L_{wet} and L_{dry} are the length of swollen and dry membrane, respectively.

The through-plane proton conductivity of fully hydrated membranes was measured via a membrane test system (MTS-740, Scribner, USA) with a four electrode configuration [34]. The test system was connected to an electrochemical workstation (Parstat 2273, Princeton Applied Research, USA) which exerted an oscillating voltage of 10 mV at frequency from 100 Hz to 1 MHz. The through-plane proton conductivity σ of membrane was calculated using the relation:

$$\sigma = L / R \cdot S \quad (2)$$

where L is the thickness of membrane and S is the membrane area normal to the current flow. R is the membrane resistance obtained from the intercept of impedance curve with the $\text{Re}(Z)$ axis of the Nyquist plot at high frequency zone.

The tensile strength of membrane was measured using an electronic universal testing machine (WD-10D, Changchun 2nd Tester Factory, China). Dry membrane strips of 20 mm × 80 mm were fully hydrated by soaking in water overnight and gently wiped

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