



## Semi-interpenetrating polymer network proton exchange membranes with narrow and well-connected hydrophilic channels

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### HIGHLIGHTS

- ▶ Proton exchange membranes for the direct methanol fuel cells (DMFCs).
- ▶ A semi-interpenetrating polymer network (SIPN) based on poly(phenylene oxide).
- ▶ Use of cross-linker structure to modify membrane morphology and properties.
- ▶ Narrow and well-connected hydrophilic channels are useful for DMFC applications.
- ▶ Demonstration of membranes which surpassed Nafion<sup>®</sup> 117 in single cell tests.

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### ABSTRACT

Four series of semi-interpenetrating polymer network (SIPN) membranes are fabricated by thermally cross-linking aminated BPPO (brominated poly(2,6-dimethyl-1,4-phenylene oxide)) with different epoxide cross-linkers in the presence of sulfonated PPO (SPPO). The cross-link structure and hydrophobicity are found to impact the membrane morphology strongly — smaller and more hydrophobic cross-links form narrow and well-connected hydrophilic channels whereas bulky and less hydrophobic cross-links form wide but less-connected hydrophilic channels. The membranes of the former can support facile proton transport and suppress methanol crossover to result in higher proton conductivity and lower methanol permeability than the membranes of the latter. The membranes are also fabricated into membrane electrode assemblies (MEAs) and tested in single-stack direct methanol fuel cells (DMFCs). It is found that some of these SIPN membranes can surpass Nafion<sup>®</sup> 117 in maximum power density, demonstrating their potential as a proton exchange membrane (PEM) for the DMFCs.

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### 1. Introduction

The main function of a proton exchange membrane (PEM) in the direct methanol fuel cell (DMFC) is to shuttle protons from the anode to the cathode and inhibit the diffusion of methanol at the same time [1]. A PEM typically comprises both hydrophilic and hydrophobic components. The former is used to support proton transport and usually contains sulfonic acid groups. The hydrophobic component, on the other hand, furnishes the mechanical strength and dimensional stability of the membrane [2]. In the

presence of water, microphase separation occurs between the hydrophilic and hydrophobic components — the sulfonic acid groups associate to form sulfonic acid clusters which, upon connection, form the “hydrophilic channels” [3]. Protons are transported through the hydrophilic channels with the assistance of water, thus the connectedness of the channels determines the proton conductivity of any given membrane.

A continuous networks of hydrophilic channels is clearly favorable to proton transport [4,5]. Such a network may however allow the unhindered diffusion of methanol molecules, leading to significant methanol crossover and the degradation of DMFC performance. One solution to reduce methanol crossover is to narrow the hydrophilic channels to increase the resistance selectively for the larger methanol molecules. Hence PEMs for DMFCs should be designed to provide narrow and well-connected hydrophilic channels. Currently block/graft copolymers specifically designed to promote self-assembly are used to prepare these PEMs

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[6–10]. The synthesis of the block/graft copolymers is often complex and has not been designed for scalable production [11].

The semi-interpenetrating polymer network (SIPN) can be an alternative approach to deliver the desired PEM morphology of narrow and well-connected hydrophilic channels. SIPN is a special class of polymer composites where a linear or branched polymer penetrates extensively into a network of other polymers [12–14]. It offers ease of preparation and more tailorability of the PEM morphology compared with the graft/block copolymers. This is because the hydrophilic and hydrophobic components can be very intimately mixed (approaching molecular level) in an SIPN structure. The uniform dispersion of the hydrophilic component in a hydrophobic polymer network can greatly increase the connectivity of the hydrophilic channels [15–17]. Hydrophilic sulfonic acid clusters with relatively small size are also formed at the same time. The hydrophilic channels can then be made narrower to inhibit the methanol passage more effectively.

A specific methodology of using the SIPN structure for PEM fabrication is presented here. Specifically, PEMs with well-connected hydrophilic channels are produced by thermally cross-linking aminated BPPO (brominated poly(2,6-dimethyl-1,4-phenylene oxide)) with an epoxide cross-linker in the presence of sulfonated PPO (SPPO). The PPO polymer is selected as the base material because of its good mechanical properties and excellent hydrolytic stability [18]. In the SIPN structure fabricated as such, the epoxide cross-linked aminated BPPO is the polymer network host providing the mechanical properties of the PEM while SPPO is the penetrant and the proton source. In order to optimize the selectivity of proton transport over methanol permeation, four epoxides with different sizes and solubility parameters, namely 1,4-butanediol diglycidyl ether (BDE), resorcinol diglycidyl ether (RDE), bisphenol A diglycidyl ether (BADE) and poly(bisphenol A-co-epichlorohydrin) (PBAE), are used as cross-linkers. Microstructural characterizations and electrochemical measurements reveal significant differences in the PEM morphology and proton transport properties due to the use of different cross-linkers. Changes in the cross-linker structure capped by two epoxide groups are used to provide a better understanding of the impact of the molecular segment between the two epoxide end groups on the proton and methanol transport properties of SIPNs. This is helpful to the development of some rudimentary composition–morphology–property relationships for the PEM design.

## 2. Experimental section

### 2.1. Preparation of SIPN membranes

Sulfonated PPO (SPPO) was synthesized by a published procedure using chlorosulfonic acid as the sulfonation reagent [19]. Specifically, a calculated amount of chlorosulfonic acid (99.0–99.4%, Sigma–Aldrich) was added to a PPO (Sigma–Aldrich) solution in chloroform (99%, Merck) at room temperature over a period of 30 min under vigorous stirring. The reaction was allowed to continue for 30 more min after the addition. The precipitate from the reaction was filtered off and dissolved in NMP (*N*-methyl-2-pyrrolidone), and dried in an oven at 80 °C for solvent removal. The oven-dried solid was washed with deionized water until the rinse water was pH 6–7, and then vacuum-dried. The ion exchange capacity (IEC) of the SPPO synthesized as such was determined to be 2.07 mmol g<sup>-1</sup>, or 29.8% degree of sulfonation according to the relation given in the literature [20].

The PPO-based SIPN membranes were prepared by a thermal cross-linking method. The preparation of BDE0.25 where the figure ‘0.25’ refers to the ratio of epoxide groups to bromomethyl groups (1.0 for complete cross-linking) is given below as an example. BPPO

(59.1% benzyl bromide and 40.9% aryl bromide as analyzed by <sup>1</sup>H NMR (Nuclear Magnetic Resonance) spectrometry, Tianwei Membrane Corporation Ltd. of Shandong) and SPPO were dissolved separately in NMP to a concentration of 30 mg mL<sup>-1</sup> each. Excess ammonia (32%, Merck) was added to the solutions to neutralize SPPO and to aminate BPPO, respectively. A measured amount of BDE (Sigma–Aldrich) cross-linker was also added to the BPPO solution. After stirring for 1 h, the two solutions were mixed. The mixture was cast onto a glass petri dish, cured at 80 °C for 48 h and then at 100 °C for 2 h in vacuum. The membrane formed as such was acidified in 1.0 M HCl for 24 h, washed several times with distilled water and then air-dried. A polymer blend membrane was also prepared from neutralized SPPO and aminated BPPO without any cross-linker, and used as the control. All the membranes examined in this study were prepared with a –SO<sub>3</sub>H/–CH<sub>2</sub>Br molar ratio of 5/1, which was found by screening experiments to represent a good balance between various membrane properties such as dimensional swelling and proton conductivity.

### 2.2. Characterizations

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2010 TEM operating at 200 kV accelerating voltage. Membranes for TEM examination were first treated with a saturated solution of Pb(NO<sub>3</sub>)<sub>2</sub> for 24 h to enhance the image contrast between ionic and non-ionic clusters. They were then rinsed with distilled water and dried under vacuum. The TEM samples were prepared by epoxy embedding (Sigma–Aldrich) and sectioned to 50 nm thin slices by an ultramicrotome (Leica). The slices were then placed on 100 mesh copper grids for TEM analysis. Scanning transmission electron microscopy (STEM) and elemental mapping by energy dispersive X-ray (EDX) spectroscopy were performed on a JEOL 2101F TEM. X-ray photoelectron spectroscopy (XPS) were collected by a Kratos Axis Ultra DLD spectrometer. All binding energies were referenced to the C1s carbon peak at 284.6 eV. The thermal properties of the membranes were evaluated by differential scanning calorimetry (DSC) on a Mettler-Toledo DSC 822e in N<sub>2</sub> atmosphere. Typically the membrane samples were heated from 25 to 270 °C at the rate of 10 °C min<sup>-1</sup>. A Bruker DRX-400 MHz NMR spectrometer operating at 500 MHz was used for <sup>13</sup>C NMR measurements. The tensile strengths and strains of the membranes were measured by an Instron 5544 universal tester at room temperature. For the measurements, a membrane was cut into a (3 × 1 cm) rectangle which was held in flat-faced grips and pulled apart at the crosshead speed of 1 mm min<sup>-1</sup>.

Water uptake (WU) by the membranes was measured by the difference in weights between the dry ( $W_{\text{dry}}$ , g) and water-saturated states ( $W_{\text{wet}}$ , g) of a membrane. Water uptake was calculated as the wt.% of the dry sample:

$$\text{WU} = \left( \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100\% \quad (1)$$

Membrane dimensional changes were estimated by equilibrating a sample strip in water at a fixed temperature for 24 h, and then measuring the changes in length:

$$\Delta l = \left( \frac{l_w - l_d}{l_d} \right) \times 100\% \quad (2)$$

where  $l_w$  and  $l_d$  are the lengths of the wet and dry membranes, respectively.

The membrane IEC was determined by acid–base titration. First, a membrane in its native H<sup>+</sup> form was equilibrated in 1.0 M NaCl for 24 h to fully exchange the protons with sodium cations. The acidity in the NaCl solution was then titrated with 0.01 M NaOH. The IEC (mmol g<sup>-1</sup>) was calculated as the moles of exchangeable protons

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