# Nafion-microporous organic polymer networks composite membranes

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## ARTICLE INFO

## ABSTRACT

A series of new Nafion composite membranes have been prepared by the self-assembly of microporous organic polymer networks (MOPNs) and Nafion. X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) reveal that MOPNs and Nafion membranes have good miscibility affording homogeneous composite membranes Nafion-MOPN-x. Compared with the recast Nafion membrane, Nafion-MOPN-x composite membranes show excellent thermal and mechanical properties, good dimensional stability, low methanol permeability, and proper proton conductivity. Also, the passive direct methanol fuel cell (DMFC) of Nafion-MOPN-3 membrane presents a maximum power density of 21.5 mW cm$^{-2}$ at 25 °C. These results show the introduction of MOPNs can improve the interface compatibility and lessen the cavity problem between fillers and polymeric matrix during chemical blend. Therefore, it casts a new light on developing stable polymer electrolyte membranes (PEMs) for fuel cell application.

## 1. Introduction

In the last decade, intensive work has been focused on the research of a new class of energy conversion devices termed the direct methanol fuel cells (DMFCs) because renewable liquid methanol as fuel is safe for storage and transport [1–3]. With the progress in research on polymer electrolyte membranes (PEMs) for DMFCs, the perfluorosulfonic acid (PFSA) membrane (e.g. Nafion) especially attracts worldwide attention. It may be owing to its excellent stability in both chemical and thermal environments, as well as its high proton conductivity when containing enough water [4]. Nevertheless, PFSA membranes have high fuel (especially methanol) permeability, commonly referred to methanol crossover, resulting in a loss of fuel and the decrease of cathode voltage and cell performance. This represents one of the major problems in DMFC application [5,6]. Several methods for modifying PFSA membranes have been developed to reduce methanol crossover [7–15], such as bulk modification of Nafion [7,8], forming multilayer polymeric thin films on the surface of Nafion [9,10] and introducing inorganic–organic nanoparticles into the Nafion matrix [11–15]. However, Nafion composite membranes prepared by above methods usually face the problem of phase separation. It may arise from the differences in specific gravity and solvent concentration, which often leads to poor interface compatibility and cavities

between the two components [3,16]. Therefore, to achieve high-performance composites, homogeneous dispersion of reinforced component in the continuous organic matrix is significant. As well-known, ionic interactions can alleviate the problem of phase separation, although ionic cross-linking is considered to be weak and easily disappears above 80 °C [17]. Covalent cross-linking is strong enough, whereas covalent cross-linking membranes become brittle when they dry out. Thus, mixed cross-linking by ionic and covalent bonds has been proposed which is expected to combine the advantages and avoid the disadvantages of single cross-linking and represent a new trend [16–18].

Recently, Ji-Woong Park et al. have reported the synthesis of intrinsic microporosity of organic polymer networks (MOPNs) through an organic sol–gel process of tetra (p-aminophenyl) methane (TAPM) and hexamethylene diisocyanate (HDI) [19]. These organic polymer networks have a unique structure (rigid nodes, soft segments), consisting of covalent cross-linking three-dimensional organic frameworks and the internal amino groups. The covalent organic frameworks were built from tetrahedral building blocks providing open and interconnected pores with broad pore size distribution and large surface area. It is prone to capture efficiently a large amount of soft materials. Meanwhile, internal amino groups of TAPM/HDI networks are available for ionic cross-linking. Therefore, TAPM/HDI networks are an ideal candidate for mixed cross-linking.

The work presented here reports a new strategy for modifying Nafion membranes by the self-assembly of Nafion and TAPM/HDI

networks (Fig.1), which is based mostly on the following considerations: 1) Open covalent organic frameworks of TAPM/HDI can ensure the Nafion matrix is firmly confined to porous network to form tightly interweaving and interpenetrating first level nanocomposites. Then internal $-NH_2$ groups of TAPM/HDI and $-SO_3H$ groups of Nafion further form ionic cross-linking by strong electrostatic interactions affording the second level nanocomposites. It provides the possibility of decreasing expansion ratio and methanol permeation of the composite membranes. 2) There is no by-product in sol–gel polymerization of TAPM and HDI. TAPM/HDI networks and Nafion show good miscibility in sol state. Thus, the preparation process and technology of membrane are simple. This strategy can improve the interface compatibility and lessen the cavity problem between fillers and polymeric continuous matrix during chemical blend. To the best of our knowledge, this is the first reported example of Nafion composite membranes with MOPNs prepared by organic sol–gel processing method. Here, homogeneous dispersion of MOPNs in continuous Nafion matrix reduces the methanol permeability and increases the dimensional stability of Nafion-MOPN-x membranes with reasonable proton conductivity for fuel cell application.

## 2. Experimental section

### 2.1. Materials

Tetra (p-aminophenyl) methane (TAPM) was synthesized from triphenylmethylchloride and aniline according to previous reports [20]. Hexamethylene diisocyanate (HDI) (99%, Aldrich) was distilled under reduced pressure. Nafion solution (5 wt%) was obtained from DuPont Co. Ltd. N, N-dimethylformamide (DMF) was dried with $CaH_2$ and distilled under reduced pressure before use. All other chemicals were reagent grade and used as received.

### 2.2. Sol–gel polymerization

TAPM/HDI was prepared according to previous reports [19]. In a typical run with TAPM/HDI at a concentration of 0.04 g mL$^{-1}$, tetrakis(4-aminopheyl)methane (TAPM) (530.00 mg, 1.395 mmol) was dissolved in 10.0 mL of anhydrous DMF under a nitrogen atmosphere at room temperature. This solution was added, with stirring, to a solution of distilled hexamethylene diisocyanate (HDI) (468.72 mg, 2.790 mmol) in anhydrous DMF (2.5 mL) at room temperature. Then the mixture was stirred for 24 h at room temperature.

### 2.3. Preparation of the composite membranes

DMF solution of Nafion was prepared by evaporation of the Nafion raw solution in air at room temperature until solid resin was obtained, followed by re-dissolving in DMF (8 wt%). The TAPM/HDI solution was added drop by drop in a stirred Nafion solution. The amount of Nafion was adjusted to TAPM/HDI+Nafion=1.00 g, and DMF (12.5 mL) was constant, as listed in Table 1. Then two solutions were mixed to form a homogeneous polymer solution under stirring. After 1 h of vigorous stirring, the homogeneous solution was degassed and transferred to a preheated glass dish where the cross-linking reaction occurred. Followed by solvent evaporation at 60 °C under nitrogen flow for 4 h and desiccation at 80 °C under vacuum for 12 h, clear Nafion-MOPN-x membranes (40–60 μm) were obtained, where x referred to different concentrations of TAPM/HDI in the feed.

### 2.4. Measurements

$^1H$ NMR spectra were measured at 300 MHz on an AV 300 spectrometer. FT-IR spectra were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer. The wide-angle X-ray diffraction (WAXD) measurements were performed on a Rigaku Max 2500V PC X-ray diffractometer with Cu Kα radiation at a wavelength of 1.54 Å (40 kV, 200 mA) with a scanning rate of 5° min$^{-1}$ from 10° to 50°. SAXS experiments were performed using a NanoSTAR-U (BRUKER AXS INC.) with Cu Kα radiation. ($\lambda$=0.154 nm). The generator was operated at 40 kV and 650 μA. Two-dimensional SAXS patterns were obtained using a HI-STAR detector. The sample to detector distances were LSD = 1074 mm. The effective scattering vector q ($q = \frac{4\pi}{\lambda} \sin \theta$, where $2\theta$ is the scattering angle) at this distance ranges from 0.044 to 2.0 nm$^{-1}$. Thermogravimetric analysis (TGA) was performed in a nitrogen atmosphere on a TA instrument TGA Q500 thermogravimetric analyzer from 50 to 800 °C with the heating rate of 10 °C min$^{-1}$. Tensile measurements were conducted with an Instron-1211 at a speed of 1 mm min$^{-1}$ at room temperature and ambient
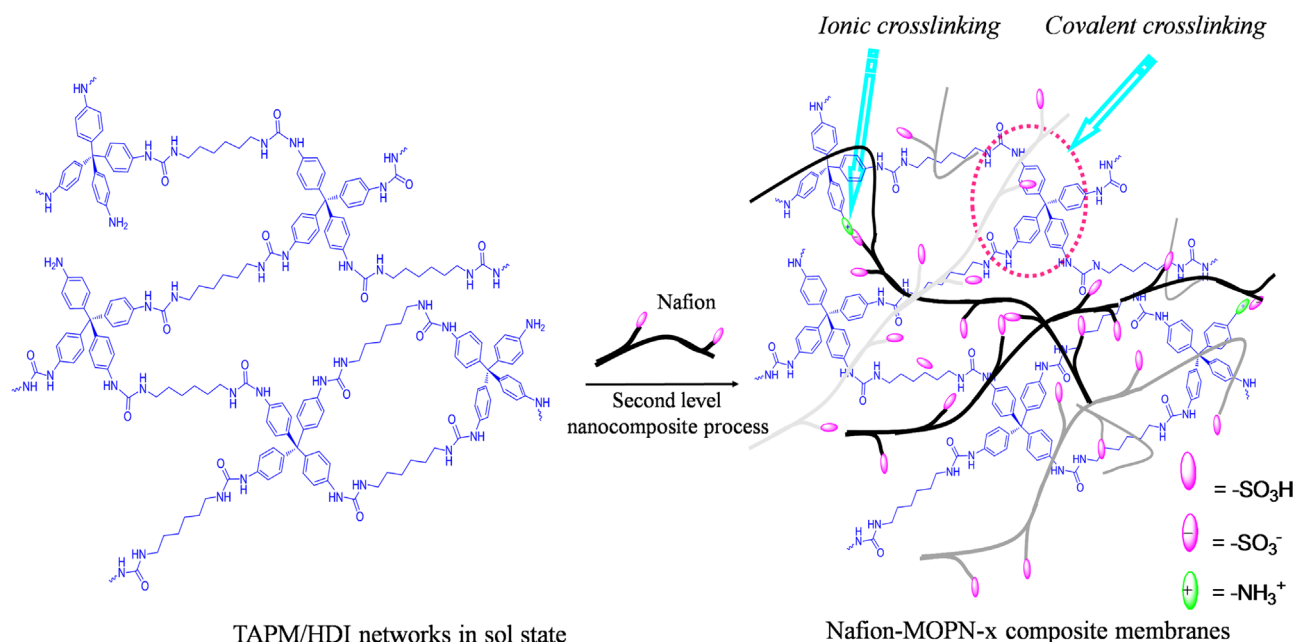


**Fig. 1.** A conceptual view of Nafion-MOPN-x composite membranes prepared from microporous organic polymer networks in sol state.