



Enhanced proton conductivity of Nafion composite membrane by incorporating phosphoric acid-loaded covalent organic framework



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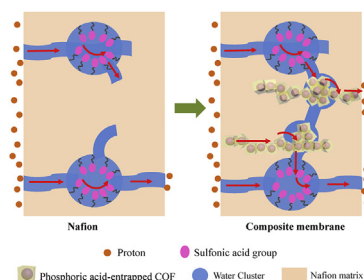
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HIGHLIGHTS

- Phosphoric acid is loaded into COFs with low guest leaching rate.
- $\text{H}_3\text{PO}_4@\text{S1}$ is introduced into Nafion to prepare COF-based PEMs for the first time.
- The $\text{H}_3\text{PO}_4@\text{S1}$ networks adjust the hydrophilic domains of membrane effectively.
- The membrane proton conductivity reaches 0.0604 S cm^{-1} at 51% RH and 80°C .

GRAPHICAL ABSTRACT



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ABSTRACT

Design and fabrication of efficient proton transport channels within solid electrolytes is crucial and challenging to new energy-relevant devices such as proton exchange membrane fuel cells (PEMFCs). In this study, the phosphoric acid (H_3PO_4) molecules are impregnated into SNW-1-type covalent organic frameworks (COFs) via vacuum assisted method. High loading of H_3PO_4 in SNW-1 and low guest leaching rate are achieved due to the similar diameter between H_3PO_4 and micropores in SNW-1. Then the COF-based composite membranes are fabricated for the first time with impregnated COFs ($\text{H}_3\text{PO}_4@\text{SNW-1}$) and Nafion matrix. For the composite membranes, the acid-base pairs formed between $\text{H}_3\text{PO}_4@\text{SNW-1}$ networks and Nafion optimize the interfacial interactions and hydrophilic domains. The acidic $-\text{PO}_3\text{H}_2$ groups in pores of $\text{H}_3\text{PO}_4@\text{SNW-1}$ provide abundant proton transfer sites. As a result, the continuous proton transfer channels with low energy barrier are created. At the filler content of 15 wt%, the composite membrane exhibits a superior proton conductivity of 0.0604 S cm^{-1} at 51% relative humidity and 80°C . At the same time, the maximum power density of single fuel cell is 60.3% higher than that of the recast Nafion membrane.

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1. Introduction

The growing requirements for environmentally benign applications with high power density have triggered great efforts to

develop proton exchange membrane fuel cells (PEMFCs) [1,2]. However, the large scale implementation of PEMFCs has been impeded due in part to the current challenges confronted by its performance-determining component, proton exchange membranes (PEMs) [3]. As a state-of-the-art PEM, the perfluorosulfonic acid Nafion® series membranes suffer from significant reduction in proton conductivity at temperature above 80 °C and relative humidity (RH) below 50% [4,5]. Improving the proton conduction of membrane materials, especially at high temperature and low RH, remains an important and challenging task.

Recently, a group of new porous materials such as metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have emerged showing tremendous potential as proton conducting materials [6–8]. The tailored functional groups (carboxyl groups, phosphonate groups, etc) on porous materials could enhance the proton transfer due partly to their hydrophilic character [9]. More importantly, the well-defined porous structure has offered the MOFs and COFs superior ability to accommodate guest molecules, which build multiple pathways for rapid proton transport [10,11]. The MOFs impregnated with sulfuric acid, imidazole and triazole have been used to fabricate hybrid membranes. The guest molecules inside the MOFs act as efficient proton transfer sites and render the hybrid membranes with high proton conductivity at high temperatures [12–14]. Unlike MOFs, the COFs with numerous pores are intrinsically constructed via strong covalent bonds [15,16]. The organic building units with low gravimetric weight endow COFs high thermal stability and outstanding compatibility with polymer. These features ensure their practicability in proton conducting processes. Banerjee et al. have found that Tp-Azo doped with phosphoric acid has a proton conductivity of $6.7 \times 10^{-5} \text{ S cm}^{-1}$ at 340 K under anhydrous conditions [17]. Nevertheless, the problem that guest molecules are prone to leach from the porous materials should be solved and the application of COF-based functional materials in proton conduction needs to be further investigated.

Most early developed proton carrier sites focused on strong acidic $-\text{SO}_3\text{H}$ groups [18–21]. It has been found that each amphoteric $-\text{PO}_3\text{H}_2$ group possess two proton-donor sites and one proton-acceptor site [22], thus having a lower energy penalty (37.2 kJ mol^{-1}) when transferring protons compared with common used $-\text{SO}_3\text{H}$ groups (69.9 kJ mol^{-1}) [23]. In recent years, great efforts have been dedicated to developing PEMs based on $-\text{PO}_3\text{H}_2$ groups as alternative proton conductors [24–27]. Jiang et al. designed phosphoric acid-functionalized sintered mesoporous silica membrane, it achieved a high proton conductivity of $5 \times 10^{-3} \text{ S cm}^{-1}$ at 80 °C in the absence of external humidification [28]. We have previously prepared titania sol functionalized with $-\text{PO}_3\text{H}_2$ groups, and introduced it into sulfonated poly (ether ether ketone) matrix. The results showed that the proton conductivity of resultant hybrid membrane was 63.7% higher than that of sulfonated poly (ether ether ketone) membrane [29]. Construction of proton transfer sites with amphoteric $-\text{PO}_3\text{H}_2$ groups, where hydrogen bond networks can be formed dynamically, is anticipated to be a good choice in building efficient proton transport channels within polymer membranes.

In this study, we first synthesize Schiff base networks (SNW)-type COF networks with intrinsic amino groups and micropores. Then, the SNW-1 is impregnated with phosphoric acid via vacuum assisted method and introduced into Nafion matrix to prepare novel composite membranes. The interfacial interactions between SNW-1 networks and Nafion endow the composite membranes homogenous structure. Efficient proton transfer channels coupling efficient proton conductive groups and well-connected water clusters are constructed. The composite membranes are characterized by SEM, FTIR, TGA, SAXS, etc. The proton conductivity of the

as-prepared composite membranes is investigated, especially under low humidity conditions. This is the first report of COF-based PEMs up to date.

2. Experimental

2.1. Materials and chemicals

Melamine (>98%) and terephthalaldehyde (>98%) were purchased from Sigma-Aldrich. Nafion solution (5 wt%, DE520) was supplied by Dupont. Anhydrous dimethyl sulfoxide (DMSO) was received from Aladdin. Phosphoric acid (H_3PO_4 , 85%), *N,N*-dimethylformamide (DMF, >99.8%), tetrahydrofuran (THF, >99.8%), *N,N*-Dimethylacetamide (DMAC, >99.8%), dichloromethane (CH_2Cl_2 , >99.8%) and other reagents were provided by Guangfu Fine Chemical Research Institute (Tianjin, China) and used without further purification.

2.2. Synthesis of SNW-1

SNW-1 was synthesized as described in literature [30]. Typically, a dried three-necked flask fitted with a condenser was charged with melamine (0.94 g, 7.46 mmol), terephthalaldehyde (1.50 g, 11.18 mmol) and DMSO (50 ml). The mixture was heated at 180 °C for 72 h under argon atmosphere, after reaction, the reactor was cooled down to room temperature and the precipitated powder was isolated via filtration. The obtained SNW-1 was washed with excess DMF, THF and further purified by Soxhlet extraction with methanol, THF and methanol sequentially. Finally the powder was dried under vacuum at 120 °C overnight.

2.3. Impregnation of phosphoric acid into SNW-1

The H_3PO_4 was impregnated into the SNW-1 via vacuum assisted method (VAM). Firstly, the SNW-1 was treated by CH_2Cl_2 for 24 h under reflux to replace the high boiling point solvent by lower one. Secondly, the SNW-1 was treated in a Schlenk flask under vacuum at 120 °C for 24 h to remove residual CH_2Cl_2 and trapped air in pores. Thirdly, after the Schlenk flask was cooled to 80 °C, H_3PO_4 aqueous solution (25 wt%, 50 ml) was added into the Schlenk flask under vacuum for 12 h, then vacuum was removed and the mixture was stirred for another 12 h. The H_3PO_4 could be pressed into the cavities of SNW-1 by the pressure difference between the cavities and outside atmosphere. Finally, the as-treated SNW-1 was centrifuged, washed by water until pH of supernatant liquid reached neutral and dried at 60 °C under vacuum to obtain the H_3PO_4 impregnated SNW-1 (named as $\text{H}_3\text{PO}_4\text{@S1}$).

2.4. Preparation of composite membranes

The received Nafion solution was dried at 60 °C for 72 h. The obtained Nafion resin was re-dissolved in DMAC (0.05 g mL^{-1}). A preweighed amount of SNW-1 networks was mixed with the Nafion solution under vigorous stirring for 24 h. The resultant mixture was degassed and cast onto a glass plate, followed by heating at 80 °C for 12 h and annealing at 120 °C for 10 h. All the Nafion-based membranes were activated before use, i.e. soaking in 3 wt% H_2O_2 , water, 1 M sulfuric acid at 80 °C successively and each operation was carried out for 1 h. Finally each membrane was washed by water until the pH was neutral. The fabricated composite membranes were named as Nafion/ $\text{H}_3\text{PO}_4\text{@S1-X}$, where $\text{H}_3\text{PO}_4\text{@S1}$ stands for H_3PO_4 impregnated SNW-1, X is the weight percent of SNW-1 networks. The Nafion-based composite membrane containing 15 wt% SNW-1 without any H_3PO_4 (named as Nafion/S1-15) is also prepared for comparison. The thickness of all

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