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# Novel octopus shaped organic–inorganic composite membranes for PEMFCs

Qingting Liu <sup>a,b,c,\*</sup>, Quan Sun <sup>b</sup>, Na Ni <sup>b</sup>, Fang Luo <sup>b</sup>, Rong Zhang <sup>a,b</sup>, Shengfei Hu <sup>a,b</sup>, Xujin Bao <sup>c</sup>, Fan Zhang <sup>c</sup>, Feng Zhao <sup>d</sup>, Xiao Li <sup>d</sup>

<sup>a</sup> Hubei Province Key Laboratory of Green Materials for Light Industry, Wuhan, 430068, China

<sup>b</sup> School of Materials and Chemical Engineering, Hubei University of Technology, Wuhan, 430068, China

<sup>c</sup> Department of Materials, Loughborough University, Leicestershire, LE11 3NW, UK

<sup>d</sup> Wuhan Troowin Power System Technology Co. Ltd., Wuhan, 430056, China

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## ABSTRACT

Phosphoric acid doped polybenzimidazoles are among the most interesting proton exchange membrane materials for high temperature proton exchange membrane fuel cell applications. As a major challenge the proton conducting decline due to free phosphoric acid leaching during the long term fuel cell operation is addressed by fixing overmuch phosphoric acid in the polymer matrix. Novel organic-inorganic composite membranes are prepared via in situ synthesis of poly(2,5-benzimidazole) (ABPBI) and OctaAmmonium POSS (AM-POSS) hybrid composites (ABPBI/AM-POSS) following phosphoric acid doping and membrane casting procedures. Compared with the pristine ABPBI membrane, the introduction of AM-POSS into ABPBI polymer membrane caused water and phosphoric acid absorbilities increasing dramatically, resulting in the significant increase of proton conductivities at whether hydrous or anhydrous condition. ABPBI/3AM composite membranes with phosphoric acid uptake above 250% showed best proton conductivities from room temperature to 160 °C, indicating these composite membranes could be excellent candidates as a polymer electrolyte membrane for low and intermediate temperature applications.

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## Introduction

As an energy conversion device, fuel cells have many advantages such as high efficiency, high power density, no charging requirement, easy cleaning, etc. [1,2]. Among the family of fuel cells, polymer electrolyte membrane fuel cell (PEMFC) catalytically reacts with H<sub>2</sub> and O<sub>2</sub> to generate electricity with H<sub>2</sub>O as a byproduct and is regarded as the promising system as an environmentally friendly energy source [3,4]. In the PEMFC,

the polymer electrolyte membrane (PEM) acts as a crucial role because it has to provide the proton pathway whilst keeps good mechanical properties all along the fuel cell operating life. Perfluorosulfonic acid (PFSA) membranes such as Nafion<sup>®</sup> from DuPont Company have been extensively studied and predominantly commercially used as PEMs due to their high initial performances and their good chemical stabilities. However, these features are limited by the strict temperature requirement (less than 100 °C) [5,6]. Furthermore, PFSA membranes have been suffering aging phenomena during fuel

\* Corresponding author. Hubei Province Key Laboratory of Green Materials for Light Industry, Wuhan, 430068, China.

E-mail address: [liuqt@mail.hbut.edu.cn](mailto:liuqt@mail.hbut.edu.cn) (Q. Liu).

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cell working due to the irreversible loss of conductivity combined with membrane embrittlement and gas crossover [4,7,8], which pose limitations in the PEMFC application. Therefore, it is essential to develop membrane materials with good electrical conductivity as well as high thermal and chemical stabilities at a relatively high temperature (e.g. above 100 °C) that is not restricted by humid conditions.

Intermediate temperature proton exchange membrane fuel cells (IT-PEMFCs) which usually work between 100 and 200 °C get ever-increasing attention because of their many advantages, including faster electrochemical kinetics, improved and simplified water management, effective thermal management, improved CO tolerance etc. [9–11] However, the lack of suitable electrolyte materials that operate at the intermediate temperature range presents a great obstacle. Therefore, in the past few decades various systems have been developing to meet this challenge. Polybenzimidazoles (PBIs) have motivated extensive research activities with great progresses in recent years, because of their excellent chemical and thermal stabilities [12–15]. ABPBI [16] which is the simplest polybenzimidazole type polymer possessing comparable thermal and conducting properties as that of PBIs has also attracted the attention of many research groups in recent years [17–23]. However, the proton conductivities of polybenzimidazole membranes depend too much on the phosphoric acid (PA) doping percentages of membranes [24]. In addition, the mechanical properties and chemical stability of the acid-doped PBI membrane deteriorate rapidly due to seriously acid leaching under continuous usage [25]. To overcome the aforementioned drawbacks, the addition of modified inorganic/organic nanofillers to ABPBI matrix is regarded as an efficient approach [26–29].

Polyhedral oligosilsesquioxane (POSS) are silsesquioxanes with a well-defined cube-octameric siloxane skeleton with eight organic vertex groups. These particular octahedral structural features render POSS to be a versatile additive for acquiring enhanced thermo-mechanical properties, better thermal stability, oxidative resistance and abrasion resistance [30,31]. Recently, the properties of Nafion/POSS composite membranes [32,33] and sulfonated poly(ether ether ketone)/POSS [30] have been reported. Due to the hygroscopic POSS cores and the functional groups from sulfonated POSS, the proton conductivity and mechanical properties have been greatly improved. Alli et al. [28] prepared composite membranes based on PBI and sulfonated POSS by solution casting as base materials for high temperature PEMFCs. After doping with PA, the composite membranes showed considerably improved ex situ proton conductivity under anhydrous as well as under fully humidified conditions in the 120–180 °C range which also benefit from functionalized POSS. Pan et al. [34] reported a new series of organic-inorganic cross-linked PEMs using sulfonated polyimides containing benzimidazole (SPI-BIs) and glycidyl ether of POSS and achieved the proton conductivity up to  $10^{-2}$  S  $\text{cm}^{-1}$  depending on the degree of sulfonation of the SPIBI.

We'd like to mention that, above development largely met PEMFCs' by requirement of working either at low temperature with fully hydrous or intermediate temperature with anhydrous and not for both low and intermediate temperature simultaneously. In this work, we selected OctaAmmonium

POSS nanofillers [35] to modified ABPBI membrane through an in situ synthesis method as they have a large number of hydrophilic silicon–oxygen–silicon groups and base amino groups to severally stabilize  $\text{H}_2\text{O}$  and  $\text{H}_3\text{PO}_4$  molecules, which are very important for PEMFC to work from low temperature to intermediate temperature with hydrous and anhydrous conditions through different proton transfer mechanisms (so called “vehicle” mechanism under hydrous condition and “hopping” mechanism under anhydrous condition, respectively).

## Experimental

### Polymer synthesis

ABPBI monomer 3,4-diaminobenzoic acid (DABA, 97%) was purchased from Beijing J&K Technology CO., Ltd. OctaAmmonium POSS (AM-POSS, trade name AM0285) was obtained from Hybrid Plastics Inc. Phosphorus pentoxide ( $\text{P}_2\text{O}_5$ ) and methane sulfonic acid (MSA, 99%) were obtained from Sinopharm Chemical Reagent CO., Ltd. and Aladdin Industrial Corporation, respectively. All chemicals and solvents were used as received without any further purification steps.

### Synthesis of ABPBI/AM-POSS composites

0.03 g of AM-POSS and 10 mL of MSA were added into a 100 mL three-neck flask and ultrasonicated at atmosphere for 30 min to obtain a milky white homogeneous solution. Then 1.0 g of DABA and 1.5 g of  $\text{P}_2\text{O}_5$  were added following another 30 min of ultrasonication treatment. Subsequently, the mixtures were heated under  $\text{N}_2$  atmosphere with a magnetic stirrer up to 100 °C and kept for 30 min, then continuously heated up to 150 °C and kept for about 2 h. The hot polymer solution was slowly poured into the deionized water (500 mL) to get very thin fibers. The obtained fibers were boiled in a beaker with 500 mL 10% NaOH solution at 100 °C for 2 h to remove phosphoric acid and the solvent, subsequently boiled in 500 mL deionized water for 1 h to remove NaOH. After that, the fibers were washed with deionized water for several times to remove residual NaOH. Finally, the fibers were dried in a vacuum oven at 110 °C for 24 h. The obtained dark brown fibers were placed in a sealed flask.

### Synthesis of ABPBI

ABPBI polymer as a reference was synthesized in MSA/ $\text{P}_2\text{O}_5$  media according to Kim et al.'s report [17]. The purification and dryness procedures were same as these of above ABPBI/AM-POSS composites.

### Membrane preparation

#### ABPBI/AM-POSS composite membranes

0.4 g of ABPBI/AM-POSS powder was dissolved in 6.0 mL of MSA with magnetic stirring overnight at room temperature to obtain a homogeneous solution. Then the viscous solution was cast onto a flat bottom Petri dish and solvent was removed by step by step heating in a ventilated oven up to 200 °C to avoid pin holes caused by rapid evaporation of MSA.

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