

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

# Enhancement of performance of pyridine modified polybenzimidazole fuel cell membranes using zirconium oxide nanoclusters and optimized phosphoric acid doping level

Mohamed Mahmoud Nasef<sup>a,b,\*</sup>, Tsuyohiko Fujigaya<sup>c,d</sup>,  
Ebrahim Abouzari-Lotf<sup>a,b</sup>, Naotoshi Nakashima<sup>c,d</sup>, Zehui Yang<sup>c</sup>

<sup>a</sup> Center for Hydrogen Energy, Institute of Future Energy, Univeristi Teknologi Malaysia, Kuala Lumpur, Malaysia

<sup>b</sup> Department of Environment and Green Technologies, Malaysia-Japan International Institute of Technology, Univeristi Teknologi Malaysia, Kuala Lumpur, Malaysia

<sup>c</sup> Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

<sup>d</sup> International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

## ARTICLE INFO

### Article history:

Received 30 October 2015

Received in revised form

26 February 2016

Accepted 3 March 2016

Available online 1 April 2016

### Keywords:

Nanocomposite proton conducting membranes

High temperature proton exchange membrane fuel cells

2,6-pyridine-polybenzimidazole

ZrO<sub>2</sub> nanoclusters

RSM optimization of phosphoric acid doping

## ABSTRACT

Nanocomposite proton conducting membranes incorporating zirconium oxide (ZrO<sub>2</sub>) nanoclusters into solution cast 2,6-pyridine polybenzimidazole (2,6-Py-PBI) films and doped with phosphoric acid (PA) were prepared. The content of ZrO<sub>2</sub> nanoclusters in the membrane matrix was varied from 0 to 10 wt%. The parameters of the acid doping reaction were optimized by the response surface method (RSM). The membrane properties were evaluated by Fourier transform infrared (FTIR), scanning transmission electron microscopy (STEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), universal mechanical tester and DC impedance. The incorporation of 5 wt% ZrO<sub>2</sub> nanoclusters increased the acid doping level and remarkably enhanced the proton conductivity of the membrane. A maximum proton conductivity of 60.0 mS/cm was recorded compared to 21.5 and 12.0 mS/cm for pristine and 10 wt% ZrO<sub>2</sub> containing membranes at 150 °C and dry condition, respectively. The membrane with 5 wt% ZrO<sub>2</sub> also showed the highest performance in a single cell at 120 °C under dry conditions. The results suggest that the composite membrane containing 5 wt% ZrO<sub>2</sub> nanoclusters has a potential for application in high temperature proton exchange membrane fuel cell application.

Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

\* Corresponding author. Center for Hydrogen Energy, Institute of Future Energy, Univeristi Teknologi Malaysia, Kuala Lumpur, Malaysia. Tel./fax: +60 3 2203 1229.

E-mail address: [mahmoudeithar@cheme.utm.my](mailto:mahmoudeithar@cheme.utm.my) (M.M. Nasef).

<http://dx.doi.org/10.1016/j.ijhydene.2016.03.022>

0360-3199/Copyright © 2016, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

High temperature (HT) operation of proton exchange membrane fuel cell (PEMFC) requires a new generation of less- or non-water dependent membranes to overcome the limitation of water solvated perfluorosulfonic acid membranes and simplify the balance of plant [1]. Composite membranes with basic matrix loaded with inorganic acids with high volatility such as phosphoric acid (PA) doped polybenzimidazole (PBI) membranes have been considered as important candidates for HT-PEMFC and therefore, they have been widely studied [2–5]. Particularly, two main PBI polymer systems that have been thoroughly investigated as acid-imbibed membranes are based on commercially available poly (2,2-m-phenylene-5,5-benzimidazole) (m-PBI) and poly (2,5-benzimidazole) (AB-PBI) having high molecular weights and good processability [6–8]. These membranes showed reasonable performances in temperature ranges close to 200 °C without humidification [9]. However, their stability is challenged by vulnerability to degradation through leaching of the loaded PA and reduction in the mechanical strength and chemical stability (above 150 °C) caused by excess PA doping [10] and dehydration of phosphoric acid together with other environmental issues [11].

Various strategies have been applied to improve the stability and conductivity of PBI membranes including optimization of membrane fabrication techniques [2,12], crosslinking of polymer backbone [13–16], blending with other polymers [17–20], and forming composite structure by incorporation of various inorganic acids [21–24]. However, the improvements brought by such modifications have been found rather limited and the PBI-based membranes remained demonstrating weakness in mechanical strength when highly loaded with acid and poor endurance when tested for a long term [25]. More details on various methods used for modification of PBI substrates and subsequent acid doping procedures were published in a number of review articles [12,26].

Ceramic nanoscale and mesoscale fillers such as Titania and Zirconia are attractive materials for designing composite PA doped PBI-based membranes with appealing properties [27,28]. Particularly, ZrO<sub>2</sub> fillers were recently tested for enhancing the conductivity and stability of PA doped PBI membranes [29,30]. However, the use of nanoscale ZrO<sub>2</sub> filler and the accompanied membrane casting is challenged by agglomeration and precipitation leading to drastic phase inhomogeneity despite the improvement in the hydro-mechanical properties by the reinforcement [31].

In another approach to impart significant improvements to the conductivity of PBI membranes, more nitrogen atoms were introduced to the polymer molecular structure to enhance the acid retention [27,32]. This was achieved by development of pyridine-polybenzimidazole (Py-PBI), which provides an additional pyridine ring capable of boosting the interaction with PA [3,27,33,34]. Few studies involving preparation of 2,4-, 2,5- and 2,6-Py-PBI and 3,5-Ppy-PBI based membranes doped with PA and their possible application in fuel cell were recently published [25,35]. However, 3,5-Py-PBI was not suitable for film formation because of

high solubility in PA, whereas, 2,6-Py-PBI membrane showed weak mechanical stability. To improve the stability and enhance the conductivity of 2,6-Py-PBI membranes, formation of composite matrices filled with nanosized ZrO<sub>2</sub> clusters loaded with an optimized acid doping level is an appealing approach that has not been reported in the literature.

The objective of the present study is to prepare composite 2,6-Py-PBI membranes with controlled acid doping level, improved mechanical strength and enhanced conductivity for HT-PEMFC application. This is carried out by introducing nanosized ZrO<sub>2</sub> filler (in a form clusters) to solution cast 2,6-Py-PBI films followed by PA acid doping under optimum conditions. The study involves optimization of acid doping parameters and content of ZrO<sub>2</sub> and their impacts on the properties of the composite 2,6-Py-PBI membranes. To avoid agglomeration and phase separation associated with the dispersion of inorganic nanoparticles, Zirconia nanoclusters prepared by electrospinning of suspension comprising PVP template loaded with ZrO<sub>2</sub> powder followed by calcination of the obtained PVP/ZrO<sub>2</sub> composite nanofibers and subsequent particle sizing were used. The various properties of the membranes were characterized by FTIR, XRD, XPS and universal mechanical tester. The proton conductivity of the membranes was also evaluated under different temperatures using DC impedance and the activation energy was estimated. The performance of the membranes was tested in a single cell at 120 °C under dry conditions.

## Experimental

### Materials and reagents

2,6-Py-PBI was prepared according to the method reported in Ref. [3]. Nanosized ZrO<sub>2</sub> clusters having an average particle size of 53 nm obtained following the procedure reported in the supporting document. 2-propanol, N,N-dimethylacetamide (DMAc), ethylene glycol (EG) and 85% phosphoric acid (PA) were purchased from Wako Pure Chemical Industries, Ltd. CB (Vulcan XC-72R). Carbon black (CB) powder was purchased from Cabot Chemical Co., Ltd. All the chemicals were used as received without any purification.

### Preparation ZrO<sub>2</sub> loaded 2,6-Py-PBI films

The composite membranes were prepared by adding 5 and 10 wt% of ZrO<sub>2</sub> nanoclusters to solutions of 2,6-Py-PBI made by dissolving 10 wt% of the polymer in DMAc under continuous stirring. The 2,6-Py-PBI/ZrO<sub>2</sub> mixtures were carefully cast on glass plates and heated to 50 °C for 1 h. Subsequently, the temperature was raised to 80 °C for 1 h and to 120 °C for another hour until DMAc was completely evaporated. The membrane was cooled to room temperature and peeled off from the glass plate. The thickness of the membranes was measured by Mitutoyo (Series 547) thickness gauge and found to be in the range 0.65–0.70 μm.

Download English Version:

<https://daneshyari.com/en/article/1270690>

Download Persian Version:

<https://daneshyari.com/article/1270690>

[Daneshyari.com](https://daneshyari.com)