

# Nanostructured Organic-Inorganic Hybrid Membranes for Polymer Electrolyte Fuel Cells

Min-Kyu Song, Young-Teak Kim, Ji-Seok Hwang,  
James M. Fenton\*, H. Russel Kunz\* and Hee-Woo Rhee

Department of Chemical Engineering,  
Sogang University, Seoul 121-742, South Korea

\*Department of Chemical Engineering,  
University of Connecticut, Storrs, CT 06269, USA

## Introduction

Nafion<sup>®</sup> membrane must be well hydrated to obtain an optimal performance because its proton conduction mechanism relies on dissociation of protons from ion exchange group in the presence of water [1,2]. Above the boiling temperature of water, however, the increase in internal resistance of PEMFC is mainly related to dehydration of Nafion<sup>®</sup> membrane [3]. Thus, PEMFC is usually operating at temperatures below 100 °C despite various important advantages at high temperature operation including lower catalyst poisoning, higher system efficiency and better water management [4].

To obtain a high temperature membrane, Grot *et al.* proposed an in-situ doping method of zirconium hydrogen phosphate (ZHP) into Nafion based on ion exchange reaction of  $Zr^{4+}$  and  $H_3PO_4$  [5]. Costamagna *et al.* also obtained highly dispersed Nafion/ZHP composite membrane via impregnation of recast Nafion film with aqueous  $ZrOCl_2$  solution and 1 M phosphoric acid at 80 °C [6]. Inorganic filler particles were uniformly distributed and the composite membrane delivered about 1500 mA/cm<sup>2</sup> at 0.45 V at a cell temperature of 130 °C, whereas an unmodified commercial Nafion<sup>®</sup>117 membrane gave about 250 mA/cm<sup>2</sup> at the same conditions.

However, most ZHP particles might be formed in hydrophilic ion cluster region of Nafion<sup>®</sup> membrane because it was swollen with aqueous  $ZrOCl_2$  solution first. As a result, maximum ZHP content is usually less than 23 wt% with respect to dry polymer weight. In order to increase the weight fraction of ZHP, we prepared microporous Nafion membrane using nano-templating technique. As a hydrophobic plasticizer was mixed with Nafion<sup>®</sup> solution and phase-separated plasticizer domains are extracted from Nafion<sup>®</sup> membrane, the pores formed are expected to provide physical spaces with  $Zr^{4+}$  ion doping even in hydrophobic area. Hence, ZHP particles could be precipitated evenly in the entire polymer matrix. In this presentation, various physical properties of modified Nafion/ZHP composite ionomers were thoroughly characterized.

## Experimental

Nafion gels were precipitated from commercial 5 wt% Nafion<sup>®</sup>/H<sub>2</sub>O/propranol solution (Solution Technology, E.W.=1100) by evaporating alcoholic solvents at room temperature under vacuum. After they were dissolved in *N,N*-dimethylacetamide (DMA, Aldrich) at 80 °C, Nafion/DMA solution was mechanically mixed with 20 wt% plasticizer for 4 hours at 50 °C, and increased to 100 °C for 1 hour. Then, it was cast onto a glass plate above 100 °C in a convection oven.

As the recast membrane was stored in diethyl ether/methanol (1:1 vol.), the plasticizer component was gradually extracted from the polymer structure, which resulted in porous polymer membranes. Porous Nafion

membranes were swollen with 1 M  $ZrOCl_2 \cdot xH_2O$  aqueous solution for several hours at 80 °C, and then rinsed with distilled water to remove excess  $Zr^{4+}$  ion on membrane surface and finally placed in 1 M phosphoric acid for 24 hours at 80 °C. Consequently, ZHP was formed in-situ and entrapped in the nano-pores of the Nafion membrane. The membranes were then repeatedly rinsed with distilled water to remove excess acid.

Cross sectional morphology was observed by field emission scanning electron microscope (FESEM) (JEOL JSM 6330F). Fourier transform infrared spectroscopy (FT-IR) was employed to detect residual OH in the membrane at elevated temperature. The proton conductivity measurements (Zahner IM6 impedance analyzer) were conducted by a coaxial probe. Water content of the membrane was assumed to remain saturated during measurement over the frequency range 100 kHz to 10 MHz.

## References

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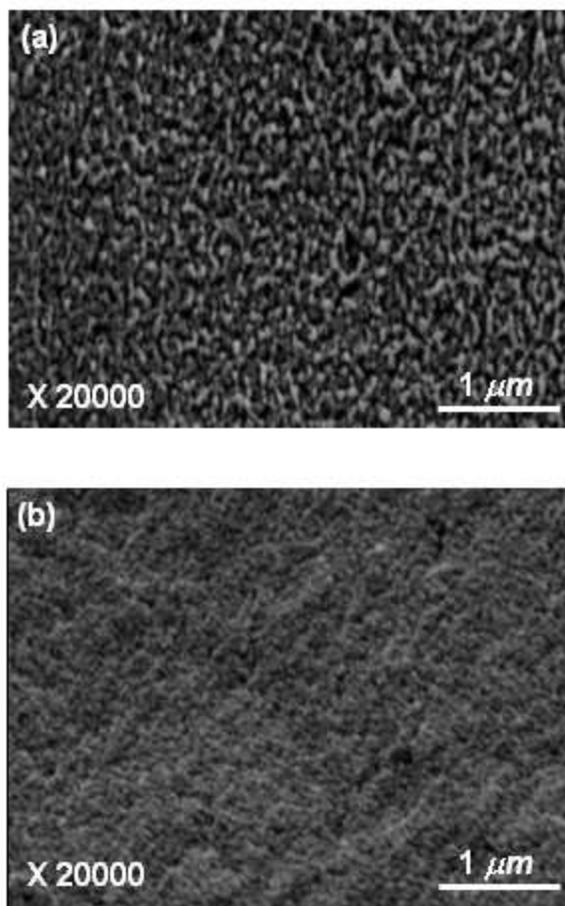


Fig. 1. Cross-sectional SEMicrographs for Membranes: (a) porous Nafion<sup>®</sup> membrane and (b) ZHP doped Nafion<sup>®</sup> membrane.