Journal of Membrane Science 325 (2008) 880–886

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Preparation of Nafion/PTFE/$Zr(HPO_4)_2$ composite membranes by direct impregnation method

Hsiu-Li Lin[a,b,*], Tsu-Jung Chang[a]

[a] Department of Chemical Engineering & Materials Science, Yuan Ze University, Chung-Li, Taoyuan 32003, Taiwan
[b] Fuel Cell Center, Yuan Ze University, Chung-Li, Taoyuan 32003, Taiwan

ARTICLE INFO

Article history:
Received 28 May 2008
Received in revised form 19 August 2008
Accepted 7 September 2008
Available online 24 September 2008

Keywords:
Nafion
Zirconium hydrogenphosphate
Solution viscosity
Poly(tetrafluoroethylene)
PEMFC

ABSTRACT

The viscosities of as received 5.1 wt.% Nafion solutions (EW = 1100, Du Pont Co) blended with various concentrations of $ZrOCl_2$ were studied. We show the solution viscosity decreases as the wt. ratio of [$ZrOCl_2$]/[Nafion] is increased from 0.0 to 0.03, then the viscosity does not change significantly as the wt. ratio of [$ZrOCl_2$]/[Nafion] is increased from 0.03 to 0.16, and then the viscosity increases dramatically as the wt. ratio of [$ZrOCl_2$]/[Nafion] is increased above 0.16. Four Nafion solutions consisting of 5.1 wt.% Nafion and $ZrOCl_2$ with [$ZrOCl_2$]/[Nafion] wt. ratios of 0.019–0.24 were used with porous poly(tetrafluoroethylene) (PTFE) film to prepare zirconium hydrogenphosphate (ZrP) hybridized Nafion/PTFE (NF–ZrP) composite membranes by direct impregnating porous PTFE in Nafion/$ZrOCl_2$ solutions. The influence of [$ZrOCl_2$]/[Nafion] wt. ratio of Nafion/$ZrOCl_2$ solution on the membrane morphology of NF–ZrP and polyelectrolyte membrane fuel cell (PEMFC) performance at temperatures of 110–130 °C with relative humidity of 51.7–28.8% RH was investigated.

1. Introduction

It is generally accepted that proton exchange membrane (PEM) fuel cells present an attractive alternative to traditional power sources, due to their high efficiency and non-pollution. One of the most successful PEMs used as proton-conducting separator in fuel cells is perfluorosulfonated ionomer (Nafion, a registered trademark of Du Pont Co). However, it is known that application of Nafion membranes to proton exchange membrane fuel cells (PEMFC) at temperatures above 90 °C has a problem of low proton conductivity, due to low moisture content of membrane at high temperature. Recent reports had shown that with a humidified H_2 fuel, Nafion-based PEMFC could work at high temperatures up to 130 °C [1]. It had been reported that hybridizing inorganic nano-particles, such as silicone oxide, diphenyl silicate, and zirconium hydrogenphosphate (ZrP), etc. could help Nafion membranes retain moisture at temperatures above 100 °C, and thus improve PEMFC performance when operating at temperatures of 90–130 °C [2–10]. Besides the applications to high temperature PEMFCs, it had also been shown that hybridizing inorganic nano-particles in Nafion membranes could reduce *methanol crossover* the membranes and improved direct methanol fuel cells (DMFC) performance [11–21].

One of the reasons retarding commercialization of PEMFC is the high cost of its components. Instead of using Nafion as a proton-conducting separator, recent research reports showed that low cost composite membranes could be prepared by impregnating a low cost sub-μm porous support material, such as polytetrafluoroethylene (PTFE) membranes, with a Nafion solution [22–30]. Owing to the high mechanical strength of PTFE, inserting porous PTFE film into Nafion membrane allows one to reduce membrane thickness (the thickness of composite membranes, prepared in our lab, is around 17–22 μm, the thicknesses of Nafion-117, Nafion-115, and Nafion-112 membrane are around 175, 125, and 50 μm, respectively). The lower thickness of Nafion/PTFE (NF) composite membranes leads them to have a lower proton resistance than Du Pont Nafion series membranes. Thus NF composite membranes have better PEMFC performance than Du Pont Nafion series membranes. It has been reported that NF composite membrane had a similar PEMFC performance to Du Pont Nafion-112 and a better PEMFC performance than Nafion-117 and Nafion-115 [25–29]. Besides low cost and low thickness, the NF composite membranes have other advantages such as good mechanical strength in both swollen and unswollen state, good thermo-stability, and low methanol permeability.

Hybridizing pure Nafion membranes with ZrP had been reported by Grot and Rajendran [31], Yang et al. [4,6], and Costamagna et

---

* Corresponding author at: Department of Chemical Engineering & Materials Science, Yuan Ze University, Chung-Li, Taoyuan 32003, Taiwan.
Tel.: +886 3 4638800x2568; fax: +886 3 4559373.
E-mail address: sherry@saturn.yzu.edu.tw (H.-L. Lin).

0376-7388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2008.09.023

al. [5]. Si et al. [32] and Jiang et al. [33] prepared Nafion/PTFE/ZrP (NF–ZrP) composite membranes by impregnating sub-μm porous PTFE film in a as received 5 wt.% Nafion solution (Solution Technologies Inc, Mendenhall, PA) blended with $ZrOCl_2$. The $ZrOCl_2$ was then converted into $Zr(HPO_4)_2$ by treating the membrane with a phosphoric acid aqueous solution. Si et al showed the NF–ZrP composite membranes had an excellent fuel cell performance when operated at 120 °C with 31% relative humidity (RH). However, in their paper, Si et al. did not mention the concentration of $ZrOCl_2$ of Nafion/$ZrOCl_2$ solution used for preparing NF–ZrP composite membrane. Chen et al. [34] prepared NF–ZrP composite membranes using two processes. One was “direct impregnation” process which was same as that reported by Si et al. [32], i.e. impregnating the sub-μm porous PTFE film directly in a Nafion/2-propanol–water solution containing $ZrOCl_2$. The membrane was then annealed at a temperature above T_G of Nafion, and then converted $ZrOCl_2$ into $Zr(HPO_4)_2$ by treating the membrane with a H_3PO_4 aqueous solution. The other was *in situ* process, which was similar to the process of preparing Nafion/ZrP membranes reported by Grot and Rajendran [31]. In *in situ* process, NF composite membrane was prepared first by impregnating the sub-μm porous PTFE film in a Nafion solution and then annealed the membrane at a temperature above T_G of Nafion. The NF composite membrane was then immersed in a $ZrOCl_2$ solution, followed by treating the membrane with a H_3PO_4 aqueous solution to convert $ZrOCl_2$ into $Zr(HPO_4)_2$. Chen et al. [34] showed the composite membranes prepared by *in situ* method had a better DMFC performance than those prepared by “direct impregnation” method. They also showed rough surface of NF/ZrP membranes prepared by “direct impregnation” method. The reason for the rough surface of NF/ZrP composite membrane prepared by “direct impregnation” method was attributed to the aggregation of Nafion molecules in the solution via interaction of Nafion side chain $–SO_3H$ groups with $ZrOCl_2$ molecules. However “direct impregnation” process is simple and has the advantage of lower manufacture cost than *in situ* process. Thus from the industrial manufacture point of view, it is necessary to study the detail of “direct impregnation” process for preparing NF–ZrP composite membranes.

In present work, NF–ZrP composite membranes were prepared using “direct impregnation” process. The sub-μm porous PTFE films were impregnated directly in as received 5.1 wt.% Nafion solutions blended with various concentrations of $ZrOCl_2$ and then annealed at 120 °C. The $ZrOCl_2$ inserted in NF composites membranes was then reacted with phosphoric acid to form $Zr(HPO_4)_2$. It is known that Nafion is an ionomer with polyelectrolyte behaviour in dilute solutions [35–38]. $ZrOCl_2$ molecules dissociate into ZrO^{2+} and $2Cl^{2-}$ ions in Nafion solutions. The interaction of ZrO^{2+} ions with side chain $–SO_3^-$ groups of Nafion results in shielding of the negative charges of $–SO_3^-$ groups and reduces the electrostatic charge repulsions among the Nafion side chains $–SO_3^-$ groups. Thus blending $ZrOCl_2$ into a Nafion solution results in variations of Nafion molecules conformations and solution viscosity. The influence of blending $ZrOCl_2$ into as received 5.1 wt.% Nafion solution on the solution viscosity and the morphology of NF–ZrP composite membrane was studied. The PEMFC performances of membrane electrode assemblies (MEA) prepared from NF and NF–ZrP composite membranes were investigated at 110 °C with 51.7% RH, 120 °C with 38.2% RH, and 130 °C with 28.8% RH. The influence of the ZrP content in NF–ZrP composite membrane on the PEMFC performance was also investigated.

2. Experimental

2.1. Materials

The Nafion solution (Du Pont Co) was 5.1 wt.% of 1100 EW Nafion diluted in a mixture solvent containing water, propanol, methanol, and unspecified ethers. The weight ratio, 5.1 wt.%, of Nafion in solution was determined by weighing method. The solvents of the solution were evaporated at 60 °C under vacuum for 8 h. The weights of the solution before evaporating solvents and the solid resin after evaporating solvents were determined and used to calculate the wt.% of Nafion in the as received solution. The sub-μm porous poly(tetrafluoroethylene) film (PTFE, a product of Yue-Ming-Tai Chemical Ind. Co., Taichung, Taiwan) with thickness of 18 ± 2 μm, pore sizes of 0.5 ± 0.1 μm, and porosity of 52 ± 5% was used as a supporting material of composite membranes. Zirconium oxychloride ($ZrOCl_2$, Aldrich Chemical Co.) with a purity of 98% was used without any purification.

2.2. Preparation of Nafion solutions blended with $ZrOCl_2$ and their viscosities measurements

Fourteen Nafion/$ZrOCl_2$ solutions were prepared by blending as received 5.1 wt.% Nafion solution with various concentrations of $ZrOCl_2$. The weight ratio of $[ZrOCl_2]/[Nafion]$ of Nafion/$ZrOCl_2$ solutions was ranged from 0.0117 to 0.3907. The viscosities measurements were carried out using an oscillatory flow rheometer (VE system, Vilastic Scientific Inc., Texas) with a cylindrical tube of length 6.115 cm and inner diameter 0.0513 cm. The viscosities of solutions were obtained at a frequency of $\omega = 1$ rad/s.

2.3. Preparation of NF composite membrane

A sub-μm porous PTFE film was mounted on a steel frame and boiled in acetone at 55 °C for 30 min. The pretreated PTFE film was impregnated in an as received 5.1 wt.% Nafion solution for 5 h. This impregnated membrane was then annealed at 130 °C for 1 h. After annealing, the membrane was swollen with distilled water at room temperature for 24 h, and then swollen with a 1.5N sulphuric acid solution at room temperature for another 6 h. The final compositions and thicknesses of NF composite membranes are listed in Table 1.

2.4. Preparation of Nafion/PTFE/zirconuim phosphate (NF–ZrP) composite membranes

Five Nafion/$ZrOCl_2$ solutions were prepared by blending $ZrOCl_2$ into as received 5.1 wt.% Nafion solution with $ZrOCl_2$/Nafion wt ratios of 0.0195, 0.0391, 0.1172, and 0.2344. The sub-μm PTFE porous film was boiled in acetone at 55 °C for 30 min and then impregnated in a Nafion/$ZrOCl_2$ solution at room temperature for 5 h, and then annealed at 130 °C for 1 h. The membrane was then

Table 1
Compositions and thickness of dried membranes without swollen with sulphuric acid solution.

Membrane	$ZrOCl_2$/Nafion blend ratio (g/g)	PTFE (g)	Nafion (g)	$Zr(HPO_4)_2$ (g)	Thickness (μm)
NF	0.0	51.30	48.62	–	20
NF–ZrP-19	0.0195	50.45	47.70	1.84	21
NF–ZrP-39	0.0391	49.53	46.83	3.64	22
NF–ZrP-117	0.1172	47.58	44.66	7.76	24
NF–ZrP-234	0.2344	49.02	47.29	3.69	22