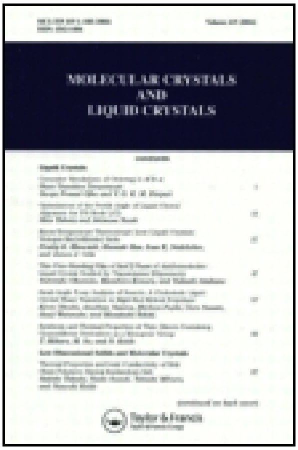

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CHARACTERIZATION OF NANOSTRUCTURED ORGANIC-INORGANIC HYBRID MEMBRANES

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CHARACTERIZATION OF NANOSTRUCTURED ORGANIC-INORGANIC HYBRID MEMBRANES

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We prepared structurally stable organic-inorganic hybrid ionomer membrane in which nano-sized solid proton conductors were uniformly dispersed in an ion exchange polymer matrix. Nafion membrane was in-situ doped with zirconium hydrogen phosphate (ZHP) after phase-separated hydrophobic porogen, dibutyphthalate, was leached out from Nafion membrane by diethyl ether and methanol co-solvent. FE-SEMicrographs showed that nanoporous structure in Nafion membrane was well developed by the solvent extraction process, and the pores were completely filled with in-situ doped ZHP particles. It was confirmed by FTIR study that hydrophilic ZHP fillers improved water retention of composite ionomer membrane at high temperature regions above 100°C. Consequently, the high temperature conductivity of Nafion/ZHP membranes was much higher than that of neat Nafion membrane.

Keywords: high temperature conductivity; Nafion®; nanocomposite; water retention; ziroconium phosphate

1. INTRODUCTION

Conventional polymer electrolyte membrane fuel cells (PEMFC) based on perfluorinated ionomers such as Nafion and Flemion are usually operating at moderate temperatures below 90°C [1] because their proton conductivity cannot be sustained above boiling temperature of water [2]. However, high

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temperature operation of PEMFC could offer much better anode kinetics in the presence of reformated hydrogen including CO impurities, and potentially eliminate complicated water management system [3]. In addition, simplified stack design including smaller heat exchanger and fuel processor is essential especially to practical fuel cell vehicles. It is, therefore, highly desirable to obtain high temperature conductivity of ionomer membranes at low levels of external humidification.

Various non-fluorinated ionomers such as arylene main chain polymers are under development by a number of research groups and industrial manufacturers, but their long-term reliability has not yet been reported [4]. On the other hand, the incorporation of proton conducting inorganic particles into fluorinated polymer matrix has shown significantly to improve the high temperature performance [5]. Polynetero acids, represented by phosphotungstic acid (PWA), suffered from solubility in water during cell operation, while structurally stable solid proton conductors have been received much attention as hygroscopic filler at high temperature [6]. Grot *et al.* first disclosed in-situ doping method of zirconium hydrogen phosphate (ZHP) into Nafion membrane by means of ion exchange reaction of Zr^{4+} and H_3PO_4 [7]. Yang *et al.* also obtained highly dispersed Nafion/ZHP composite membrane via impregnation of recast-Nafion film with aqueous $ZrOCl_2$ solution and 1 M H_3PO_4 [8]. The composite membrane delivered about 1500 mA/cm^2 at 0.45 V at a cell temperature of 130°C, compared with unmodified commercial Nafion 117 membrane of 250 mA/cm^2.

In previous attempts, most inorganic particles might be formed in hydrophilic cluster region of Nafion membrane because it was swollen with aqueous $ZrOCl_2$ solution first, thus maximum ZHP loading was less than 23 wt% with respect to dry polymer weight. In order to promote the ZHP loading and enhance water retention at elevated temperature, we prepared nanoporous Nafion membrane using solvent extraction process of a hydrophobic porogen component phase-separated in Nafion matrix. As low molecular organic compound, dibutylphthalate (DBP), was extracted from hydrophobic region in Nafion membrane, nano-sized pores remained behind are expected to provide physical voids with Zr^{4+} ion doping. Hence, more inorganic particles could be precipitated evenly in the entire Nafion membrane, which is supposed to facilitate high temperature proton conduction. This paper presents the preparation of characterization of modified Nafion/ZHP composite membranes.

2. EXPERIMENTAL

Nafion gels were precipitated from commercial 5 wt% Nafion/H_2O/prorpanol solution (Solution Technology, E. W. = 1100) by evaporating alcoholic solvents at room temperature under vacuum. After they dissolved in *N,N′*-dimethylacetamide (DMA, Aldrich) at 80°C, Nafion/DMA solution was ultrasonifically mixed with 20 wt% dibutylphthalate (DBP, Aldrich) for 4 hours at R.T., and increased to 100°C for 1 hour. Then, Nafion/DBP membranes were cast on a glass substrate above 100°C in a drying oven.

As the Nafion/DBP membranes were stored in diethyl ether/methanol (1:1 vol.), DBP was extracted from the polymer structure, which made nanoporous polymer membranes. The resultant Nafion membranes were swollen with 1 M $ZrOCl_2 \cdot xH_2O$ aqueous solution for 2 hours at 80°C under vacuum, and thoroughly rinsed with distilled water to remove excess Zr^{4+} ion on membrane surfaces and finally placed in 1 M phosphoric acid for 24 hours at 80°C. Thereafter, zirconium phosphate particles were formed in-situ and entrapped in the nanopores 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 (FE-SEM) (JEOL JSM 633OF). FTIR (Midac Prospect 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 method. The polymer membranes were stored in distilled water for adsorbing water, and then wiped quickly and insert into an in-house cell that allowed the coaxial probe to be pressed against one side membrane. Water content of the membrane was assumed to remain saturated during measurement over the frequency range 100 kHz to 10 MHz.

3. RESULTS AND DISCUSSION

Figure 1 show the cross-sectional SEMicrographs of composite membrane before and after in-situ ZHP precipitation. As seen in Figure 1(a), Nafion membrane revealed nano-sized dark spots indicative of additional nanopores, as the low molecular weight plasticizer was extracted from polymer matrix by ether/methanol co-solvent. This process is quite analogous to the preparation of microporous polyvinylidene fluoride matrix for PLiON technology developed by Telecordia [9] but in this work, methanol plays an inportant role in swelling Nafion membrane and facilitating DBP extraction. It is found from Figure 1(b) that nanopores did not exist anymore because they were completely occluded by in-situ doped ZHP particles.

Figure 2 shows the weight loss of Nafion/DBP membrane as a function of extraction time. DBP is a low viscous liquid plasticizer, and it was easy to form homogeneous polymer solution with dilute Nafion/DMA solution. It was evident that phase-separated DBP components was extracted from

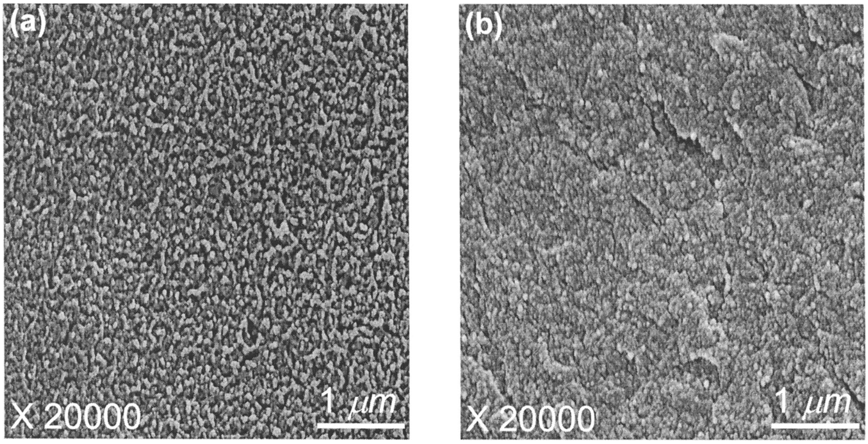

FIGURE 1 FE-SEM Cross sectional morphologies: (a) porous Nafion membrane and (b) Nafion/ZHP membrane.

polymer structure within several hours after Nafion/DBP membrane was exposed to diethyl ether or diethyl ether/methanol [10]. When 20 wt% DBP was added into polymer, it was not fully removed only by diethyl ether, but in diethyl ether/methanol (1/1 vol%) co-solvent, diethyl ether was likely to permeate into Nafion chains swollen with methanol and most plasticizers just left physical voids behind polymer membrane.

Both neat Nafion 117 and modified Nafion membranes were subjected to swelling with 1 M $ZrOCl_2$ aqueous solution and then ZHP particles were

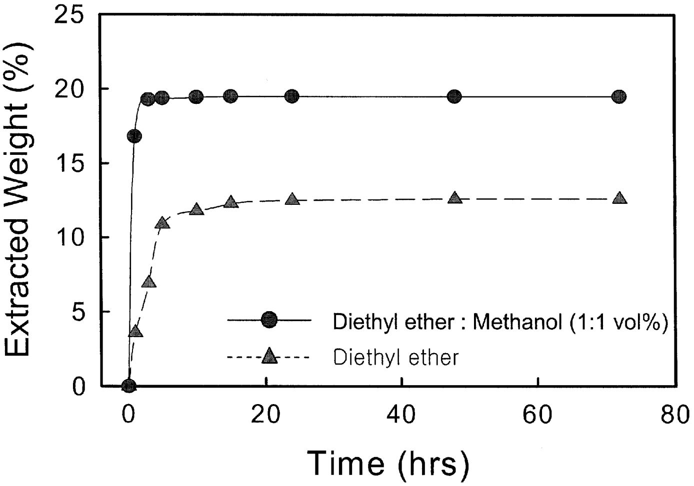

FIGURE 2 Weight change of Nafion/DBP membranes during solvent extraction.

precipitated by boiling Nafion membrane doped with Zr^{4+} ions in 1 M H_3PO_4. The average weight change was obtained by weighing the polymer membrane before and after impregnation (Fig. 3). Maximum loading of ZHP was about 20 wt% for unmodified Nafion 117 and this is similar to the values reported in the literatures [8], while it was increased upto 40 wt% for modified Nafion/ZHP composite membrane. In case of unmodified Nafion membrane, the ion exchange reaction (1) was mainly occurred in hyrophilic region because most Zr^{4+} ion inserted into hydrophilic clusters of hydrated Nafion membrane.

$$ZrOCl_2 \cdot xH_2O + H_3PO_4 \rightarrow Zr(HPO_4) \qquad (1)$$

For modified Nafion membrane, porous structure created by DBP extraction offered a lot of sites for Zr^{4+} ion doping not only in hydrophilic region but also in hydrophobic region, because hydrophobic DBP might be extracted primarily from hydrophobic phase of Nafion.

Figure 4 shows the relative intensities of FTIR peak at 3250 cm^{-1} due to the hydroxyl stretching vibration at different temperature. Ionomer membranes were fully hydrated with distilled water before measurement and then the temperature was constantly elevated at a heating rate of 0.5°C/min without further humidification. The IR peak at 3250 cm^{-1} resulted from the presence of intermolecular bond of O–H, and the peak intensity was gradually decreased over time. Compared with the intensity at room temperature, that of unmodified Nafion membrane decreased down

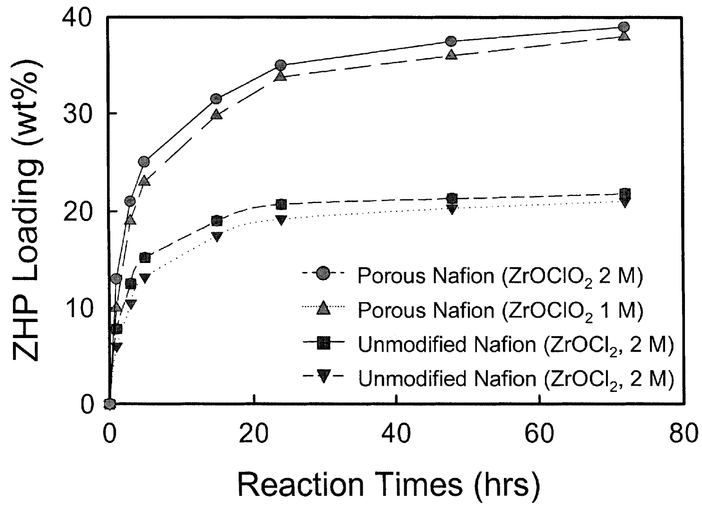

FIGURE 3 ZHP loading in Nafion matrix during in-situ doping reaction.

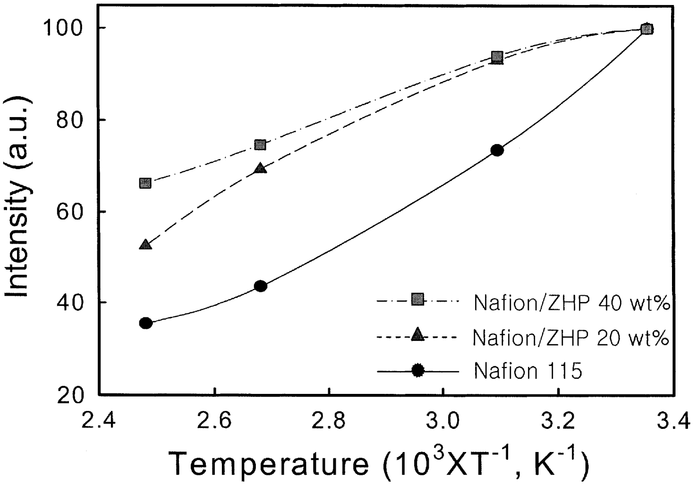

FIGURE 4 FTIR peak intensity ($3250\,\mathrm{cm}^{-1}$) of Nafion/ZHP nanocomposite membranes at elevated temperature.

to 35% at 130°C, but hygroscopic fillers prevented water molecules from evaporating even under dehydrating condition, and the peak intensity at 130°C reached around 52 and 65% for conventional Nafion/ZHP composite and modified Nafion/ZHP composite membrane, respectively. It seems that water molecules allowed to be adsorbed strongly on the additional ZHP nanoparticles within the membrane, and the presence of ZHP is likely to reduce the free space in intrinsic nanopores, promoting capillary condensation and thus water retention and proton conductivity [11].

Figure 5 shows the proton conductivities of neat Nafion 117 and Nafion/ZHP composite membrane at different temperatures. The proton conductivity was estimated by impedance spectra using coaxial probe method [12]. The coaxial probe is defined that when the thickness of membrane (*h*) is small compared to the gap size (*b-a*) as well as the skin depth (δ), the current distribution across the membrane can be considered to be uniform and the membrane characterized by a surface resistivity (R_S) is defined by $R_S = 1/\sigma h$. The value of R_s was determined from high frequency intercept on the real axis in complex impedance spectra. Then, the measured resistance, R_T, is obtained by carrying out the integration:

$$R_T = \int_a^b \frac{R_s}{2\pi r} dr = \frac{R_s}{2\pi} \ln(b/a)$$

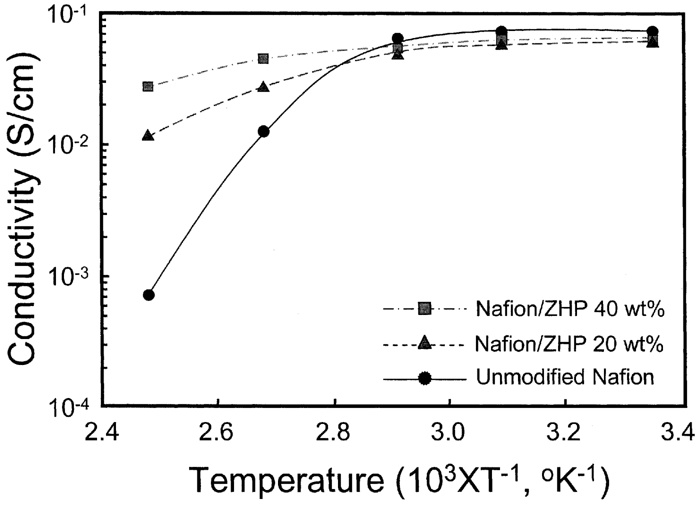

FIGURE 5 Proton conductivity of Nafion/ZHP nanocomposite membranes at different temperature.

The conductivity of the membrane is related to the measured resistance by the following expression:

$$\sigma = \frac{1}{2\pi R_T h}\ln(b/a)$$

Proton conductivity of unmodified Nafion 117 was approximately 0.08 S/cm at room temperature and it was slowly decreased until the temperature reached the boiling point of water, and then exponentially decreased after 100°C due to considerable evaporation of water. Water retention of the membrane is the most important parameter in determining the proton conductivity of these membranes. At high temperature, the vapor pressure is less than the saturation vapor pressure, so net evaporation from liquid phase in membrane to air might occur until chemical potentials are equal. This phenomenon caused dramatic decreasing of proton conductivity relied on water content. On the other hand, Nafion/ZHP composite membrane showed slightly lower conductivity that pure Nafion 117 because room temperature conductivity of ZHP is around 10^{-4} S/cm, but the initial conductivity was almost maintained upto 130°C, which implies that ZHP works as a hygroscopic agent and also proton conduction through ZHP particles may be possible at higher ZHP content around 40 wt%.

4. CONCLUSION

When unmodified commercial Nafion 117 membrane was impregnated with zirconium hydrogen phosphate (ZHP) via in-situ doping method, the maximum loading of proton conductng filler was less than 23 wt%. It was, however, found that ZHP loading could be increased upto 40 wt% while maintaining mechanical integrity, as the incorporation of inorganic nanoparticles took place in modified Nafion matrix that had additional nanopores produced by solvent extraction of phase-separated porogens.

SEMicrographs showed that nanoporous structure in Nafion membrane was well developed and the nanopores were completely occluded with in-situ doped ZHP particles. It was confirmed from FTIR study that hygroscopic ZHP fillers improved water retention of composite ionomer membrane above 100°C. As a result, high temperature conductivity of modified Nafion/ZHP membranes was higher than that of neat Nafion 117 membranes or conventional Naifion/ZHP composite. Consequently, modified Nafion/ZHP composite membrane appears to be highly suitable for high temperature operation of PEMFC.

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